

Course notes for Solid State Physics II

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Preface

Condensed matter (solids and fluids) consist out of a large number of interacting particles. In contrast with gases, it is usually not possible to neglect the interactions between these particles, or to incorporate them in a way similar to kinetic gas theory. Rather, in order to derive the properties of matter from its microscopic building blocks, one has to turn to quantum many-body theory. The many-body theory of condensed matter rely on Green's function techniques and Feynman diagrams – mathematical tools that appear in nearly all disciplines of modern physics.

In the introductory chapter, the main concepts of the introductory course on solid state physics are summarized. The second quantization formalism, which most of you have seen in quantum mechanics courses, is presented in some detail in chapter 2. This brings us in chapter 3 to the description of the interacting electron gas and of electrons interacting with phonons, and we use standard techniques of quantum mechanics (perturbation theory and variational analysis) to explore the effects of these interactions. In order to go beyond a first exploration, and to systematically investigate interacting many-body systems, we introduce the Green's function formalism, leading us to Feynman diagrams, in chapter 4. The remaining two chapters focus on theoretical applications of these techniques: the response of the many-electron system to an external perturbation, and superconductivity.

Chapter 1

Introduction

A summary of basic solid state physics

In this chapter, we summarize the key concepts from introductory solid state physics courses. To do this, we follow more or less the historical development of solid state physics, which will bring us to the starting point of this course, modern field theoretical methods for solid state.

1.1 The Drude model of metals

In 1897 Thomson discovered the electron¹. The existence of a negatively charged particle as fundamental building block present in all solids made these electrons the perfect candidates to explain the electrical conductivity of metals. It rapidly became clear that a single electron has a small charge and a small mass, so that any theory of conductivity needs to deal with the fact that there is a huge number of electrons present in the metal. The only many-particle theory available at the end of the XIXth century was Boltzmann's kinetic gas theory. Inspired by this theory, Paul Drude² formulated a 'kinetic gas theory' for charged particles.

Metals are naturally neutral, so in addition to negatively charged building blocks of matter, we need also positive ones. Drude assumed that the neutralizing positive charge was associated with much heavier particles that are fixed and as such do not participate in the charge transport. Indeed, the small mass of the electron is not enough to account for the mass of the material. Later it became clear the large positive charges can be associated to the ions of the atoms (or molecules) that make up the material. When atoms come together to form a metal, the electrons from the outer atomic shell are delocalized - they no longer remain in the neighborhood of the atom but spread throughout the

¹<http://www.aip.org/history/electron/>

²Annalen der Physik **1**, 566, en **3**, 369 (1900).

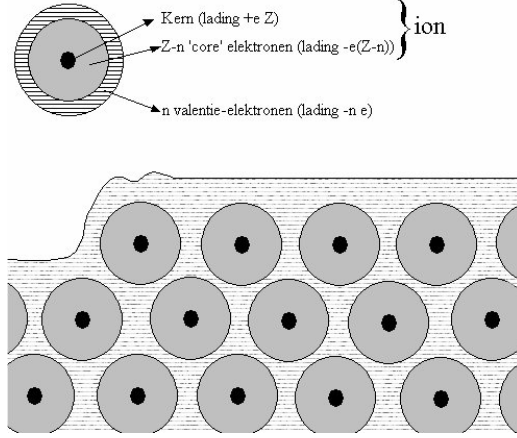


Figure 1.1: An isolated atom versus the atoms in a metal. In the metal the atoms keep the inner (valence band) electrons. The outer (conduction band) electrons delocalize. These conduction electrons are treated in the Drude model as classical, free particles. Note that for some elements, such as sodium, the isolated atom has a magnetic moment (an unpaired electron spin), but once these outer electrons end up in the conduction band, the material becomes diamagnetic.

metal. The ions are left behind on the lattice sites of the crystal, as illustrated in figure (1.1).

It is only recently that this microscopic model of metals has been observed directly. With scanning tunneling microscopy (STM) the surface of the electron sea of metals can be imaged with atomic resolution. Impurities, lattice defects, or steps at the surface lead to fluctuations in the sea of electrons that surround the ions. At the surface, these fluctuations show up as waves on the electron sea. These waves are visible in the STM image of the copper surface in figure (1.2). In this image, the height has been stretched out to reveal the electron waves – each step corresponds to the thickness of a single atomic layer. These amazing images reveal the quantum nature of electrons, in particular their wave function, modulus squared.

Back to the Drude model. Incapable of taking into account the interactions between the electrons, Drude assumes that the positive background of ions screens out the Coulomb repulsion between electrons completely. His basic description is that of electrons as free particles that lose momentum through occasional collisions (leading to damping) with atoms and gain momentum from the electric field:

$$\frac{d\mathbf{p}}{dt} = (-e)\mathbf{E} - \frac{\mathbf{p}}{\tau} \quad (1.1)$$

Here $(-e)\mathbf{E}$ is the electric force on the negatively charged electron, and τ is a

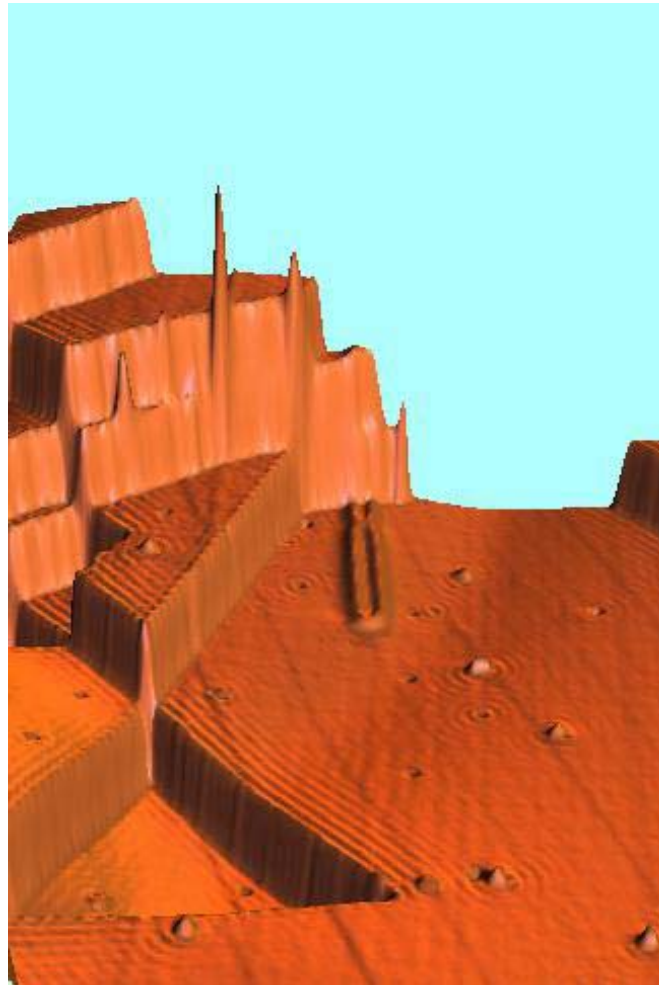


Figure 1.2: A copper surface, seen with atomic resolution, where one direction (the height) has been stretched out. Each step in the landscape corresponds to the height of a single atom. Some sharp peaks (about as high as a step) show individual atoms. The stretching allows to visualise the small waves on the electron sea surrounding the copper ions. Source: IBM Almaden Lab.

typical time needed for momentum to decay through ‘friction’. In the stationary state ($d\mathbf{p}/dt = 0$), the momentum must be $\mathbf{p} = -e\mathbf{E}\tau$, so that the electric current density is

$$\mathbf{j} = n(-e)\mathbf{p}/m = \frac{ne^2\tau}{m}\mathbf{E} \quad (1.2)$$

Here n is the density of electrons, and m their mass. This is a wonderful microscopic point of view on Ohm’s law $\mathbf{j} = \sigma\mathbf{E}$ that was already well-known in Drude’s time. It relates a phenomenological parameter, the conductivity σ , to microscopic parameters,

$$\sigma_{\text{Drude}} = \frac{ne^2\tau}{m}. \quad (1.3)$$

Moreover, the equation (1.1) can also be used for AC fields, by substituting $\mathbf{E} \rightarrow \mathbf{E}e^{-i\omega t}$ and $\mathbf{p} \rightarrow \mathbf{p}e^{-i\omega t}$ one gets

$$\begin{aligned} -i\omega\mathbf{p} &= (-e)\mathbf{E} - \frac{\mathbf{p}}{\tau} \\ \Rightarrow \mathbf{p} &= \frac{-e\tau}{1 - i\omega\tau}\mathbf{E} \\ \Rightarrow \sigma_{\text{Drude}}(\omega) &= \frac{ne^2\tau}{m} \frac{1}{1 - i\omega\tau} \end{aligned} \quad (1.4)$$

From the known values of the conductivity, we find that the momentum decay time scale should be $\tau \approx 10^{-14} - 10^{-15}$ s. If we follow Boltzmann’s kinetic gas theory, the typical velocity of an electron is given by $|\mathbf{v}| = \sqrt{3k_B T/m}$ with T the temperature and k_B Boltzmann’s constant. With this velocity computed at room temperature, the length that an electron can travel is indeed 0.1-1 nm, the typical distance between the ions. This was seen as a success of Drude’s model. Other successes were the calculation of the Hall coefficient (the ratio between transverse resistance and applied magnetic field), and the Wiedemann-Franz law. This law, dating from 1853, states that the ratio between heat conduction coefficient and conductivity is a constant for metals. If you assume that the electrons, unchained from their atoms, are responsible for both the electrical conductivity and the heat conductivity, this ratio can easily be calculated and is seen to provide a microscopic explanation for the Wiedemann-Franz law.

However, the Drude model from 1900 was incapable of explaining a number of other crucial phenomena such the thermoelectric effect, and gave very wrong results for the specific heat – the specific heat turns out to be much smaller than the value $3Nk_B/2$ expected for a gas of classical particles. You should already see the main error in the Drude model: electrons in a metal cannot be treated as a classical gas, but require quantum statistics.

1.2 Sommerfeld and the free electron gas

Around 1920-1930, Pauli’s discovery of the exclusion principle made it clear that no two electrons can be in the same state. This leads to the

unavoidable conclusion that a (cold, dense) gas of fermions does not satisfy the Maxwell-Boltzmann distribution

$$f_{\text{MB}}(\mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right) \exp \left(-\frac{m\mathbf{v}^2}{2k_B T} \right), \quad (1.5)$$

but needs a drastically different distribution, the Fermi-Dirac distribution:

$$f_{\text{FD}}(\mathbf{v}) = \frac{(m/\hbar)^3}{4\pi^2} \frac{1}{\exp \left[-\left(\frac{1}{2}m\mathbf{v}^2 - \mu \right) / (k_B T) \right] + 1}. \quad (1.6)$$

Here the chemical potential μ is fixed by the constraint $\int f_{\text{FD}}(\mathbf{v}) d\mathbf{v} = n$. Around 1925 Sommerfeld proposed to change Drude's theory of metals by replacing the Maxwell-Boltzmann distribution in his work by the Fermi-Dirac distribution. This simple improvement allowed to explain the specific heat of the electron gas.

The view on conduction in metals is also strongly affected by the improvement proposed by Sommerfeld. The Fermi energy and the Fermi sphere now determine the properties of metals. Scattering between two electrons can only take place when these two electrons scatter into unoccupied states. The electrons deep in the Fermi sea (i.e. with energies much below the Fermi energy) will therefore be less influenced by scattering and will not participate to a number of processes. For those of you who got their bachelor's degree at the Universiteit Antwerpen, I can refer to the course of statistical physics for a detailed derivation of the properties of a non-interacting Fermi gas, using the Fermi-Dirac distribution. For the others, I can actually also refer to any decent introductory statistical physics course.

1.3 Band structure

Up to the 1930's, we only have a decent microscopic theory of metals, but not of insulators and certainly not of semi-conductors. In order to understand these types of solids, we need to look at the effect of the atoms on the crystal lattice more carefully. In the free electron model, the state of an electron is a plane wave $\psi_{\mathbf{k}}(\mathbf{r}) = \exp\{i\mathbf{k}\cdot\mathbf{r}\}$ characterized by a wave vector \mathbf{k} and a dispersion relation $E(\mathbf{k}) = (\hbar\mathbf{k})^2/(2m)$. Bloch found a way to include the ions, and this turned out at the same time to explain why the Sommerfeld model was so successful to begin with:

“The main problem was to explain how the electrons could sneak past all the ions in a metal. ... By a straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation” [F. Bloch].

Put differently, the wave function of the electron is not really a plane wave but it is modulated by a set of functions $u_{\mathbf{k},n}(\mathbf{r})$ that have the same periodicity as the lattice:

$$\psi_{\mathbf{k},n}(\mathbf{r}) = u_{\mathbf{k},n}(\mathbf{r}) \exp\{i\mathbf{k}\cdot\mathbf{r}\}.$$

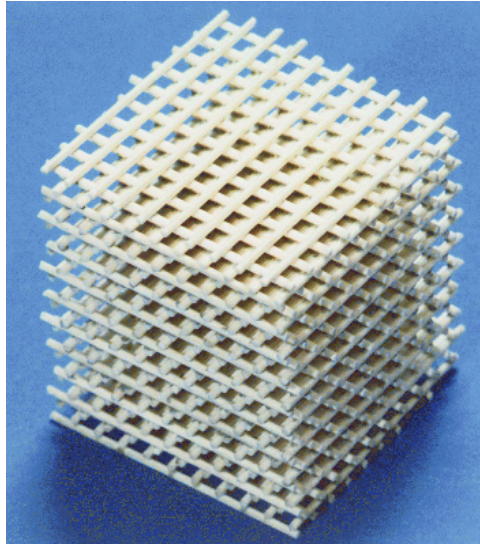


Figure 1.3: Optical bandgap material with a bandgap of 12-14 GHz, made from alumina sticks 3mm in diameter. These provide a periodic dielectric potential that does for photons what the periodic atomic potential does for electrons: it gives rise to a band structure. Source: Ames laboratory, condensed matter physics division.

These wavefunctions are still characterized by a wave number \mathbf{k} , and in addition there is a ‘band number’ n that labels the different suitable functions $u_{\mathbf{k},n}$ for each \mathbf{k} . Whereas without the ions, arbitrarily large values of \mathbf{k} can be accommodated, now only values of \mathbf{k} within the lattice’s Brillouin zone ($\mathbf{k} < 2\pi/a$) make sense. This corresponds to a distinction between length scales larger than the lattice distance a (so, again $\mathbf{k} < 2\pi/a$), where the plane-wave nature comes out, and length scales within one lattice distance, where we have a set of solutions $u_{\mathbf{k},n}(\mathbf{r})$ labeled by n that tell us how the electron charge distributes itself within a unit cell.

Substituting this wave function into the Schrödinger equation for electrons in a periodic potential, Bloch was able to prove that there are two effects on the dispersion relation $E(\mathbf{k})$ of the electrons:

- the electrons obtain an effective mass (the band mass) and
- for wave vectors near the edge of the lattice’s Brillouin zone, band gaps open up in the dispersion relation. So, these band gaps appear for electron wave lengths comparable to the lattice distance, which makes sense as we expect the effect of a periodic potential to be strongest for wave that wiggles with the same periodicity.

The existence of band gaps explains semiconductors and insulators: when electrons fill up an energy band completely, they need to bridge an energy gap in order to scatter to the next unoccupied level. If this requires much more energy than the thermal energy, they will never be able to participate in scattering or conduction. If this energy is comparable or smaller than the thermal energy, the electrons can participate but they will do so in a thermally activated process.

A recent application of Bloch's insightful idea are the so-called optical band-gap materials. What works for electrons, works for photons too. If these quanta of light are subjected to a periodic potential (for example a periodic stacking of dielectric sticks), again the dispersion $E(\mathbf{k}) = c\mathbf{k}$ will be modified and band gaps will appear. In these forbidden energy regions, photons cannot be present, so no light of a frequency in the gap can move through the optical band-gap material. This is used to trap and control light and has led to further developments such as metamaterials and invisibility cloaks.

1.4 Beyond the free electron gas

Even Bloch considers electrons to be (quasi) free particles: they are represented by plane waves, albeit modulated on sub-lattice length scales. The Coulomb interaction between the electrons, and more sophisticated dynamical effects of the lattice (such as lattice vibrations) are completely neglected. As a consequence, there are still many phenomena that escape Bloch's theory, such as a calculation of τ , a calculation of the dielectric function, and superconductivity.

Modern solid state physics was developed in interaction with and in symbiosis with quantum field theory. This allowed to overcome the shortcomings of the Sommerfeld/Bloch model, and led to many discoveries: the theory of conventional superconductivity, the quantum Hall effect, the development of modern electronics, solid-state lasers, new materials,...

Still the waxing tide of our understanding of solids has left a more than few questions that have resisted all attempts to answer them. A prime example of this is high-temperature superconductivity, both of cuprates and of the recently discovered superconducting pnictides. A microscopic understanding of these systems would result in a technological revolution. The questions that we did answer, on the other hand, have often led to new disciplines in their own right, such as nanophysics, that exploits our ability to tinker with materials on the nanometer scale in order to create new functionalities.

In this course the language of modern solid state physics will be explained and illustrated with a few key examples, such as conventional superconductivity. The purpose is not to review all the successes of solid state physics, but to enable you to follow the developments in the field and to contribute to them yourself.

Chapter 2

Second Quantization

In this chapter we introduce an operator formalism¹ that is generally applicable in quantum mechanics and in quantum field theory, and that is very well suited to describe not only harmonic oscillators but also systems with many identical particles. To illustrate this formalism, the second quantized description of electrons in a metal is set up explicitly (while keeping the ions as a neutralizing homogeneous charge density).

2.1 Basis kets for a many-particle system

Solids and condensed matter in general consists out of many interacting particles. As we have seen in the introductory chapter, we need a way to include the interactions of the particles in order to go beyond the simple Bloch model. In principle, the state of the many-body system can be completely described by a many-body wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t)$ that depends on the coordinates \mathbf{r}_j of the N particles in the system at time t . Just like in the case of a single-particle wave function $\Psi(\mathbf{r}, t)$, the modulus square has the meaning of a probability density. However, now it is the probability density to find the N -particle system in a configuration where particle 1 is on position \mathbf{r}_1 , particle 2 is on position \mathbf{r}_2 , etc. But wait – if all the particles are identical, then we cannot say which particle is at which position, and our description of the system should reflect this... Not just any $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t)$ will be a good wave function for many identical particles, we need to impose a *symmetry constraint*. But before we get to that we first need to take a closer look at how to build many-body wave functions without this symmetry constraint.

To discuss the many-body system, we have to construct the set of possible states. We start from the Hilbert space \mathcal{H}_1 of kets that describe the possible

¹This formalism is also discussed in depth in the course of advanced quantum mechanics (one of the mandatory courses for the master in physics degree).

quantum states of a single particle, and find a suitable basis for this Hilbert space:

- For a 3D system with translation invariance, this would be our friends the plane waves $\psi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \psi_{\mathbf{k}} \rangle = \exp\{i\mathbf{k} \cdot \mathbf{r}\} / \sqrt{2\pi}$ with $\mathbf{k} \in \mathbb{R}^3$ are often chosen basis functions.
- In a periodic crystal lattice, the Bloch waves $\psi_{\mathbf{k},n}(\mathbf{r})$ are suitable basis functions.
- A useful textbook example is a one-dimensional system of particles moving on a line segment $[0, 1]$. Here the suitable orthogonal basis functions are $\psi_k(x) = \langle x | \psi_k \rangle = \sin(k\pi x)$ with $k \in \mathbb{N}_0$.

In general, we denote the suitable basis kets of \mathcal{H}_1 as $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_k\rangle, \dots$. It's always a good idea to choose your basis kets $|\psi_k\rangle$ orthogonal – that makes life simple and formulas (slightly more) neat – but it is not required. We index the basis kets with “ k ”. This could be an arbitrary set of quantum numbers (such as wave number, band number, spin,...).

If $|\psi_k\rangle$ (with k a set of suitable quantum numbers) is an (orthonormal) basis for single-particle states, then outer products of N such basis kets $|\psi_{k_1}\rangle \times |\psi_{k_2}\rangle \times \dots \times |\psi_{k_N}\rangle$ form an (orthonormal) basis for N particles in the same system. This can be interpreted as a physical system where we have N single particles occupying each of the single-particle states $|\psi_{k_j}\rangle$ ($j = 1 \dots N$) appearing in the product.

Consider as an example a three-particle system in one dimension, confined to the line segment $[0, 1]$. The quantum mechanical state of this –possibly interacting– system is completely described by a three-particle wave function $\Psi(x_1, x_2, x_3; t)$. This can be decomposed in the three-particle basis

$$|\psi_{k_1}\rangle |\psi_{k_2}\rangle |\psi_{k_3}\rangle \text{ with } \{k_1, k_2, k_3\} \in \mathbb{N}_0 \quad (2.1)$$

If we use $\langle x | \psi_k \rangle = \sin(k\pi x)$ with $k \in \mathbb{N}_0$, then we get for the position representation of the three-particle basis ket:

$$\psi_{k_1}(x_1)\psi_{k_2}(x_2)\psi_{k_3}(x_3) = \sin(k_1\pi x_1)\sin(k_2\pi x_2)\sin(k_3\pi x_3) \quad (2.2)$$

We also note this as $\Phi_{k_1, k_2, k_3}^{(3)}(x_1, x_2, x_3)$. The decomposition in basis kets is given by

$$\begin{aligned} \Rightarrow \Psi(x_1, x_2, x_3; t) &= \sum_{k_1=1}^{\infty} \sum_{k_2=1}^{\infty} \sum_{k_3=1}^{\infty} C_{k_1, k_2, k_3}(t) \psi_{k_1}(x_1) \psi_{k_2}(x_2) \psi_{k_3}(x_3) \\ C_{k_1, k_2, k_3}(t) &= \int_{-1}^1 dx_1 \int_{-1}^1 dx_2 \int_{-1}^1 dx_3 \psi_{k_1}^*(x_1) \psi_{k_2}^*(x_2) \psi_{k_3}^*(x_3) \Psi(x_1, x_2, x_3; t) \end{aligned}$$

Each three-particle basis function $\Phi^{(3)}$ is characterized by 3 single-particle quantum numbers $\{k_1, k_2, k_3\}$. Analogously, the basis functions $\Phi^{(N)}$ for the N -particle problem are indexed by N single-particle quantum numbers $\{k_1, k_2, \dots, k_N\}$. The basis functions $\Phi^{(N)}$ form an orthonormal basis for the Hilbert space $\mathcal{H}^{(N)}$ that contains the N -particle wave functions. The product space $\mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \otimes \dots \otimes \mathcal{H}^{(N)} \otimes \dots$ is called the ‘Fock space’.

2.1.1 Bose and Fermi statistics

Now we are ready to discuss the *symmetry constraint*. The symmetry that we want to incorporate is the following: upon interchanging two particles, the physics of the system does not change. By this we mean that no expectation value changes. This, in turn, means that at most a global phase factor can appear in the many-body wave function when we swap two positions. When we swap the two positions again, the same global phase factor should appear again. But at the same time, we are back in the original configuration. The only phase factors that multiply to 1 when they appears twice as a factor are $+1$ and -1 . Hence, the symmetry constraint on the many-body wave function must state that for all $j, l \neq j$ we have:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_l, \dots, \mathbf{r}_N; t) = \pm \Psi(\mathbf{r}_1, \dots, \mathbf{r}_l, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N; t). \quad (2.3)$$

When spin is present, we must swap the spin and the position together (since interchange of particles not only swaps their positions but also their spin). The two possible phase factors, $+1$ and -1 , that multiply the wave function upon swapping two particles, lead to two possible classes of particles. The identical particles with a phase factor $+1$ are the *bosons*, and those with a phase factor -1 are the *fermions*.

The basis functions $|\psi_{k_1}\rangle \times |\psi_{k_2}\rangle \times \dots \times |\psi_{k_N}\rangle$ that we introduced in the previous section do not necessarily satisfy the symmetry constraint! They cannot represent physical states of many-boson or many-fermion systems. Naturally, we prefer basis kets that satisfy the symmetry constraint.

For this purpose we construct

$$|\psi_{k_1} \psi_{k_2} \dots \psi_{k_N}\rangle := \sqrt{\frac{1}{N!}} \sum_P \xi^P |\psi_{P[k_1]}\rangle |\psi_{P[k_2]}\rangle \dots |\psi_{P[k_N]}\rangle, \quad (2.4)$$

where the sum P runs over the $N!$ permutations of $\{k_1, k_2, \dots, k_N\}$, so that $P[k_j]$ is the j -th element of the permuted list of quantum numbers. For fermions $\xi = -1$ and for bosons $\xi = +1$, so that $\xi^P = -1$ for odd permutations of fermions and $+1$ in all other cases. These new basis kets satisfy the Bose or Fermi symmetry.

To have a unique phase for the fermionic basis kets, we have to adopt a convention and order the quantum numbers $k_1 < k_2 < \dots$, so that the

permutation with the ordered list has a factor $+1$. This is an ugly complication that we will get rid of by introducing the occupation number representation in a little while. But first a few examples to clarify the new ‘physical’ basis kets. Again we consider a system with three particles confined to the line segment $[0, 1]$, and the single-particle basis functions $\langle x | \psi_k \rangle = \sin(k\pi x)$. In that case, we find for the three-boson basis kets:

$$|\psi_{k_1} \psi_{k_2} \psi_{k_3}\rangle_{\text{boson}} = \frac{1}{\sqrt{6}} \begin{pmatrix} |\psi_{k_1}\rangle |\psi_{k_2}\rangle |\psi_{k_3}\rangle + |\psi_{k_2}\rangle |\psi_{k_1}\rangle |\psi_{k_3}\rangle \\ + |\psi_{k_2}\rangle |\psi_{k_3}\rangle |\psi_{k_1}\rangle + |\psi_{k_3}\rangle |\psi_{k_2}\rangle |\psi_{k_1}\rangle \\ + |\psi_{k_3}\rangle |\psi_{k_1}\rangle |\psi_{k_2}\rangle + |\psi_{k_1}\rangle |\psi_{k_3}\rangle |\psi_{k_2}\rangle \end{pmatrix}.$$

An example in position representation for a two-boson basis ket is:

$$\langle x_1 | \langle x_2 | \times |\psi_{k_1} \psi_{k_2}\rangle_{\text{boson}} = \frac{\sin(k_1\pi x_1) \sin(k_2\pi x_2) + \sin(k_2\pi x_1) \sin(k_1\pi x_2)}{\sqrt{2}}.$$

For the three-fermion system the basis kets are

$$|\psi_{k_1} \psi_{k_2} \psi_{k_3}\rangle_{\text{fermion}} = \frac{1}{\sqrt{6}} \begin{pmatrix} |\psi_{k_1}\rangle |\psi_{k_2}\rangle |\psi_{k_3}\rangle - |\psi_{k_2}\rangle |\psi_{k_1}\rangle |\psi_{k_3}\rangle \\ + |\psi_{k_2}\rangle |\psi_{k_3}\rangle |\psi_{k_1}\rangle - |\psi_{k_3}\rangle |\psi_{k_2}\rangle |\psi_{k_1}\rangle \\ + |\psi_{k_3}\rangle |\psi_{k_1}\rangle |\psi_{k_2}\rangle - |\psi_{k_1}\rangle |\psi_{k_3}\rangle |\psi_{k_2}\rangle \end{pmatrix}.$$

Finally, an example in position representation for a two-fermion system:

$$\langle x_1 | \langle x_2 | \times |\psi_{k_1} \psi_{k_2}\rangle_{\text{fermion}} = \frac{\sin(k_1\pi x_1) \sin(k_2\pi x_2) - \sin(k_2\pi x_1) \sin(k_1\pi x_2)}{\sqrt{2}}.$$

It is easy to check that the above examples satisfy the symmetry constraint (2.3). It is also trivial to see that *for fermions the same single-particle state never occurs twice* (otherwise (2.4) becomes zero!).

2.1.2 Product and Orthonormality

The product of two symmetrized many-body basis states can be written as a determinant or a permanent of the corresponding single-particle states.

Consider the product of an N -particle state (2.4) with another N -particle state

$$|\phi_{m_1} \phi_{m_2} \dots \phi_{m_N}\rangle := \sqrt{\frac{1}{N!}} \sum_P \xi^P |\phi_{P[m_1]}\rangle |\phi_{P[m_2]}\rangle \dots |\phi_{P[m_N]}\rangle.$$

The result of the multiplication is

$$\begin{aligned} & \langle \phi_{m_1} \phi_{m_2} \dots \phi_{m_N} | \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} \rangle \\ &= \frac{1}{N!} \sum_P \sum_{P'} \xi^{P+P'} \langle \phi_{P[m_1]} | \dots \langle \phi_{P[m_N]} | \times |\psi_{P'[k_1]}\rangle |\psi_{P'[k_2]}\rangle \dots |\psi_{P'[k_N]}\rangle \end{aligned}$$

This can be rewritten as

$$\langle \phi_{m_1} \dots \phi_{m_N} | \psi_{k_1} \dots \psi_{k_N} \rangle = \sum_{P''} \xi^{P''} \langle \phi_{m_1} | \psi_{P''[k_1]} \rangle \dots \langle \phi_{m_N} | \psi_{P''[k_N]} \rangle. \quad (2.5)$$

In its turn, this can be recast as

$$\langle \phi_{m_1} \dots \phi_{m_N} | \psi_{k_1} \dots \psi_{k_N} \rangle = \left| \begin{array}{cccc} \langle \phi_{m_1} | \psi_{k_1} \rangle & \langle \phi_{m_1} | \psi_{k_2} \rangle & \dots & \langle \phi_{m_1} | \psi_{k_N} \rangle \\ \langle \phi_{m_2} | \psi_{k_1} \rangle & \langle \phi_{m_2} | \psi_{k_2} \rangle & \dots & \langle \phi_{m_2} | \psi_{k_N} \rangle \\ \dots & \dots & \dots & \dots \\ \langle \phi_{m_N} | \psi_{k_1} \rangle & \langle \phi_{m_N} | \psi_{k_2} \rangle & \dots & \langle \phi_{m_N} | \psi_{k_N} \rangle \end{array} \right|_{\xi}, \quad (2.6)$$

where $|\dots|_{-1}$ represents the determinant (for fermions), and $|\dots|_{+1}$ represents the ‘permanent’, a sum of all the terms that also appear in the determinant without sign changes. In the case of fermions this determinant is sometimes called the ‘Slater determinant’.

Given the product as discussed in the previous paragraph we can check whether the basis kets (2.4) are orthonormal if we start from an orthonormal single-particle basis $|\psi_k\rangle$,

$$\begin{aligned} \text{orthonormality} & : \quad \forall k, k': \langle \psi_k | \psi_{k'} \rangle = \delta(k = k'), \\ \text{completeness} & : \quad \sum_k |\psi_k\rangle \langle \psi_k| = \hat{1}. \end{aligned}$$

The product of two basis states (2.4) is

$$\langle \psi_{k'_1} \dots \psi_{k'_N} | \psi_{k_1} \dots \psi_{k_N} \rangle = \left| \begin{array}{cccc} \langle \psi_{k'_1} | \psi_{k_1} \rangle & \langle \psi_{k'_1} | \psi_{k_2} \rangle & \dots & \langle \psi_{k'_1} | \psi_{k_N} \rangle \\ \langle \psi_{k'_2} | \psi_{k_1} \rangle & \langle \psi_{k'_2} | \psi_{k_2} \rangle & \dots & \langle \psi_{k'_2} | \psi_{k_N} \rangle \\ \dots & \dots & \dots & \dots \\ \langle \psi_{k'_N} | \psi_{k_1} \rangle & \langle \psi_{k'_N} | \psi_{k_2} \rangle & \dots & \langle \psi_{k'_N} | \psi_{k_N} \rangle \end{array} \right|_{\xi}$$

For fermions/bosons this determinant/permanent is zero unless

$$\exists P : \{k'_1, \dots, k'_N\} = P\{k_1, \dots, k_N\} \quad (2.7)$$

where P is some specific permutation. Indeed, if (2.7) is not satisfied, then there is an entire row of products that is zero, due to the orthogonality of the single-particle basis. In general, the number of terms in the determinant/permanent that differ from zero is equal to the number of permutations for which (2.7) can be satisfied. Only if a single-particle state k_j is present multiple times, there can be different permutations that satisfy (2.7). If $|\psi_{k_j}\rangle$ appears n_{k_j} times in the many-particle ket, then

$$\langle \psi_{k_1} \dots \psi_{k_N} | \psi_{k_1} \dots \psi_{k_N} \rangle = n_{k_1}! n_{k_2}! \dots n_{k_j}! \dots \quad (2.8)$$

Hence the normalized basis kets are defined by

$$|\psi_{k_1}\psi_{k_2}\dots\psi_{k_N}\rangle_{\text{normd.}} = \frac{|\psi_{k_1}\psi_{k_2}\dots\psi_{k_N}\rangle}{\prod_k \sqrt{n_k!}}. \quad (2.9)$$

Since for fermions all $n_k = 1$ or 0 , the many-body fermion basis kets $|\psi_{k_1}\psi_{k_2}\dots\psi_{k_N}\rangle_{\text{fermion}}$ are already normalized. Both for fermions and for bosons the completeness relation can be written as

$$\frac{1}{N!} \sum_{k_1} \sum_{k_2} \dots \sum_{k_N} |\psi_{k_1}\psi_{k_2}\dots\psi_{k_N}\rangle \langle \psi_{k_1}\psi_{k_2}\dots\psi_{k_N}| = \hat{1} \quad (2.10)$$

where the factor $N!$ takes into account the normalization, and each k_j sum runs over all possible values of the single-particle quantum numbers.

2.1.3 Occupation number representation

We've already encountered the unhappy fact that we label our many-body basis states with the list $\{k_1, k_2, \dots, k_N\}$ of single-particle quantum numbers, but that any permutation of that list actually represents the same basis state. One trick that we introduced is to order the list, but there is a better notation possible.

The basic difficulty is that, since the particles are all identical, it doesn't matter which of the N particles is in a given state. The only thing that matters to specify the many-body state is how many particles there are in each state, i.e. the *occupation number* of each single-particle state. Rather than using the list $\{k_1, k_2, \dots, k_N\}$ to label a many-body basis state, we better use the list $\{n_1, n_2, \dots, n_j, \dots\}$, where n_j is the number of times that the single-particle state $|\psi_j\rangle$ is present in the product $|\psi_{k_1}\dots\psi_{k_N}\rangle$.

As an illustration, in the table below I have listed a few examples of occupation numbers $\{n_1, n_2, \dots\}$ that correspond to three-particle basis functions $\Phi_{k_1, k_2, k_3}^{(3)}$:

$$\begin{array}{ll} \{k_1, k_2, k_3\} = & \{n_1, n_2, n_3, n_4, n_5, \dots\} = \\ \{1, 2, 1\} & \rightarrow \{2, 1, 0, 0, 0, \dots\} \\ \{3, 1, 4\} & \rightarrow \{1, 0, 1, 1, 0, \dots\} \\ \{2, 1, 1\} & \rightarrow \{2, 1, 0, 0, 0, \dots\}. \end{array}$$

Note that, as we mentioned, several $\{k_1, k_2, k_3\}$ lists result in the same list of occupation numbers. Each of these lists actually labels the same many-body basis ket – *two many-body basis kets are different if and only if their occupation numbers are different*. How many lists $\{k_1, \dots, k_N\}$ now with N single-particle quantum numbers, have exactly the same occupation numbers $\{n_1, n_2, \dots\}$? This is given by the repetition permutation number

$$\frac{N!}{n_1! \times n_2! \times \dots \times n_k! \times \dots}. \quad (2.11)$$

So, it is better to label the many-body basis functions by the occupation numbers – doing so we introduce the occupation number representation:

$$|n_1 n_2 \dots n_k \dots\rangle = |\psi_1 \dots \psi_1 \psi_2 \dots \psi_2 \dots\rangle_{\text{normd.}} = \frac{|\psi_1 \dots \psi_1 \psi_2 \dots \psi_2 \dots\rangle}{\prod_k \sqrt{n_k!}} \quad (2.12)$$

where ψ_j appears n_j times.

Alternatively, we can pick out one particular $\{k_1, k_2, k_3\}$ from all those that correspond to an individual many-body basis ket – from all the possible lists for that basis ket, we choose the one where the k_j 's are ordered. This is also what we have used to define the occupation representation, so both ways of uniquely labeling the many-body basis states are equivalent. Most of the time, we'll use the occupation representation. Only to derive the results in the next couple of sections it will be useful to keep track of the individual product and we'll stick to the ordered list of single-particle quantum numbers.

2.2 Creation- and annihilation operators

Now that we have defined a useful many-body basis, we want to find operators that transform the basis kets into one another. These are the creation and annihilation operators. They serve two purposes: firstly, we can now start with a vacuum state (the state with no particles, $|\emptyset\rangle$) and construct any other state by repeatedly applying these operators, and secondly, when rewriting other operators as a function of these creation and annihilation operators, their action becomes clear at the level of individual single-particle states.

2.2.1 Definitions

The formal definition of the creation operator \hat{a}_k^\dagger is

$$\boxed{\hat{a}_k^\dagger |\psi_{k_1} \psi_{k_2} \dots\rangle = |\psi_k \psi_{k_1} \psi_{k_2} \dots\rangle}, \quad (2.13)$$

where $\hat{a}_k^\dagger |\emptyset\rangle = |\psi_k\rangle$. Below, we derive several properties that follow from this definition. Firstly, \hat{a}_k^\dagger raises the occupation n_k of the single-particle state $|\psi_k\rangle$ by 1. Secondly, the hermitean conjugate of this operator, \hat{a}_k , decreases the occupation n_k of the single-particle state $|\psi_k\rangle$ by 1. For this reason, the operator \hat{a}_k is called the annihilation operator.

You have already encountered such operators in your basic quantum mechanics course: there are used to describe the harmonic oscillator. Here, their action should be interpreted more carefully.

2.2.2 Effect on the basis kets

Consider the transition matrix element

$$\mathcal{A} = \langle \phi_{m_1} \dots \phi_{m_{N-1}} | \hat{a}_k | \psi_{k_1} \dots \psi_{k_N} \rangle = \langle \psi_{k_1} \dots \psi_{k_N} | \hat{a}_k^\dagger | \phi_{m_1} \dots \phi_{m_{N-1}} \rangle^*.$$

This is equal to

$$\begin{aligned} \mathcal{A} &= \langle \psi_{k_1} \dots \psi_{k_N} | \psi_k \phi_{m_1} \dots \phi_{m_{N-1}} \rangle^* \\ &= \left| \begin{array}{cccc} \langle \psi_{k_1} | \psi_k \rangle & \langle \psi_{k_1} | \phi_{m_1} \rangle & \dots & \langle \psi_{k_1} | \phi_{m_{N-1}} \rangle \\ \dots & \dots & \dots & \dots \\ \langle \psi_{k_N} | \psi_k \rangle & \langle \psi_{k_N} | \phi_{m_1} \rangle & \dots & \langle \psi_{k_N} | \phi_{m_{N-1}} \rangle \end{array} \right|_\xi^* \end{aligned}$$

Developing this determinant/permanent along the first column, we find

$$\begin{aligned} \mathcal{A} &= \left(\sum_{j=1}^N \xi^{j-1} \langle \psi_{k_j} | \psi_k \rangle \left| \begin{array}{ccc} \langle \psi_{k_1} | \phi_{m_1} \rangle & \dots & \langle \psi_{k_1} | \phi_{m_{N-1}} \rangle \\ \dots & (\text{no } \psi_{k_j}) & \dots \\ \langle \psi_{k_N} | \phi_{m_1} \rangle & \dots & \langle \psi_{k_N} | \phi_{m_{N-1}} \rangle \end{array} \right|_\xi \right)^* \\ &= \sum_{j=1}^N \xi^{j-1} \langle \psi_k | \psi_{k_j} \rangle \langle \psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N} | \phi_{m_1} \dots \phi_{m_{N-1}} \rangle^*. \end{aligned}$$

Since this needs to hold for any $|\phi_{m_1} \dots \phi_{m_{N-1}}\rangle$, by necessity

$$\boxed{\hat{a}_k | \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} \rangle = \sum_{j=1}^N \xi^{j-1} \langle \psi_k | \psi_{k_j} \rangle | \psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N} \rangle.} \quad (2.14)$$

If ψ_k does not appear in the ket $|\psi_{k_1} \psi_{k_2} \dots \psi_{k_N}\rangle$, then all products $\langle \psi_k | \psi_{k_j} \rangle$ are zero, and we find $\hat{a}_k | \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} \rangle = 0$. If ψ_k appears n_k times, then there will be n_k terms in the sum (2.14).

A couple of examples to clarify this. Again we look at a three-boson case, and consider the basis ket

$$|\psi_3 \psi_5 \psi_5\rangle_{\text{boson}} = \frac{1}{\sqrt{3}} (|\psi_3\rangle |\psi_5\rangle |\psi_5\rangle + |\psi_5\rangle |\psi_3\rangle |\psi_5\rangle + |\psi_5\rangle |\psi_5\rangle |\psi_3\rangle).$$

In position representation with $\langle x | \psi_k \rangle = \sin(k\pi x)$ this becomes

$$\begin{aligned} \langle x_1 | \langle x_2 | \langle x_3 | \times |\psi_3 \psi_5 \psi_5\rangle_{\text{boson}} &= \frac{1}{\sqrt{3}} [\sin(3\pi x_1) \sin(5\pi x_2) \sin(5\pi x_3) \\ &+ \sin(5\pi x_1) \sin(3\pi x_2) \sin(5\pi x_3) + \sin(5\pi x_1) \sin(5\pi x_2) \sin(3\pi x_3)]. \end{aligned}$$

If the annihilation operator \hat{a}_3 acts on this state we find

$$\begin{aligned}\hat{a}_3 |\psi_3 \psi_5 \psi_5\rangle &= \langle \psi_3 | \psi_3 \rangle |\psi_5 \psi_5\rangle + \langle \psi_3 | \psi_5 \rangle |\psi_3 \psi_5\rangle + \langle \psi_3 | \psi_5 \rangle |\psi_3 \psi_5\rangle \\ &= |\psi_5 \psi_5\rangle,\end{aligned}$$

where the orthonormality of the single-particle states $|\psi_k\rangle$ has been used. Now let's see what the annihilation operator \hat{a}_5 does to the state $|\psi_3 \psi_5 \psi_5\rangle$:

$$\begin{aligned}\hat{a}_5 |\psi_3 \psi_5 \psi_5\rangle &= \langle \psi_5 | \psi_3 \rangle |\psi_5 \psi_5\rangle + \langle \psi_5 | \psi_5 \rangle |\psi_3 \psi_5\rangle + \langle \psi_5 | \psi_5 \rangle |\psi_3 \psi_5\rangle \\ &= 2 |\psi_3 \psi_5\rangle.\end{aligned}$$

In general, we find that when the single-particle state $|\psi_k\rangle$ appears n_k times in the many-body ket, then for bosons

$$\hat{a}_k |\psi_{k_1} \dots \psi_{k_N}\rangle = n_k |\psi_{k_1} \dots (\text{with 1 } \psi_k \text{ less}) \dots \psi_{k_N}\rangle$$

This can be written more neatly if we use the occupation number representation, by replacing the unnormalized many-body basis kets $|\psi_{k_1} \dots \psi_{k_N}\rangle$ by their normalized version (2.9):

$$\begin{aligned}& \hat{a}_k \left(\prod_{j \neq (k \neq k_j)} \sqrt{n_{k_j}!} \right) \sqrt{n_k!} |\psi_{k_1} \dots \psi_{k_N}\rangle_{\text{normd.}} \\ &= n_k \left(\prod_{j \neq (k \neq k_j)} \sqrt{n_{k_j}!} \right) \sqrt{(n_k - 1)!} |\psi_{k_1} \dots (\text{with 1 } \psi_k \text{ less}) \dots \psi_{k_N}\rangle_{\text{normd.}}\end{aligned}$$

Since we defined $|n_1 n_2 \dots n_k \dots\rangle = |\psi_{k_1} \dots \psi_{k_N}\rangle_{\text{normd.}}$ we can now write for bosons

$$\hat{a}_k |n_1, \dots, n_k, \dots\rangle = \sqrt{n_k} |n_1, \dots, n_k - 1, \dots\rangle. \quad (2.15)$$

If we replace in the definition (2.13) the many-body basis kets by normalized basis kets then we find

$$\hat{a}_k^\dagger |n_1, \dots, n_k, \dots\rangle = \sqrt{n_k + 1} |n_1, \dots, n_k + 1, \dots\rangle. \quad (2.16)$$

For fermions all the occupation numbers in many-body basis kets are either $n_k = 1$ or 0. However, there will be a phase factor since

$$\hat{a}_k |\psi_{k_1} \psi_{k_2} \dots \psi_{k_N}\rangle = \sum_j \xi^{j-1} \delta(k = k_j) |\psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N}\rangle. \quad (2.17)$$

hence the action of the fermionic annihilation operator is

$$\hat{a}_k |n_1, \dots, n_k, \dots\rangle = \begin{cases} (-1)^{n_1 + \dots + n_{k-1}} |n_1, \dots, n_k - 1, \dots\rangle & \text{if } n_k = 1 \\ 0 & \text{if } n_k = 0 \end{cases} \quad (2.18)$$

For fermions, also the creation operator introduces the same phase factor, that originates from pushing the ψ_k from the starting position $|\psi_k \psi_{k_1} \psi_{k_2} \dots\rangle$ down the list to its correct position in that list, so we get

$$\hat{a}_k^\dagger |n_1, \dots, n_k, \dots\rangle = \begin{cases} (-1)^{n_1 + \dots + n_{k-1}} |n_1, \dots, n_k + 1, \dots\rangle & \text{if } n_k = 0 \\ 0 & \text{if } n_k = 1 \end{cases} \quad (2.19)$$

The results (2.15), (2.16), (2.18), (2.19) summarize how the creation and annihilation operators link the different many-body basis kets of the occupation representation to each other.

2.2.3 Commutation relations

From the definition (2.13) we see that for arbitrary k and k' the following equality holds:

$$\hat{a}_k^\dagger \hat{a}_{k'}^\dagger = \xi \hat{a}_{k'}^\dagger \hat{a}_k^\dagger.$$

For bosons $\xi = 1$ and this can be written as

$$\text{bosons: } \xi = 1 \rightarrow [\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger] = 0, \quad (2.20)$$

$$\text{fermions: } \xi = -1 \rightarrow \{\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger\} = 0. \quad (2.21)$$

Here $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator and $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ is the anticommutator. We can write this compactly as

$$[\hat{A}, \hat{B}]_\xi = \hat{A}\hat{B} - \xi \hat{B}\hat{A}. \quad (2.22)$$

This allows us to write the above rule in one expression, valid for both bosons and fermions, $[\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger]_\xi = 0$. Taking the hermitean conjugate gives

$$[\hat{a}_k, \hat{a}_{k'}]_\xi = 0. \quad (2.23)$$

So, swapping two bosonic creation operators, or swapping two bosonic annihilation operators is allowed. But swapping two fermionic creation operators or two fermionic annihilation operators leads to a sign change. How about swapping a creation operator with an annihilation operator? Let's calculate $[\hat{a}_k, \hat{a}_{k'}^\dagger]_\xi$. The first term is

$$\begin{aligned} \hat{a}_k \hat{a}_{k'}^\dagger |\psi_{k_1} \dots \psi_{k_N}\rangle &= \hat{a}_k |\psi_{k'} \psi_{k_1} \dots \psi_{k_N}\rangle \\ &= \langle \psi_k | \psi_{k'} \rangle |\psi_{k_1} \dots \psi_{k_N}\rangle \\ &\quad + \sum_{j=1}^N \xi^{j-1} \langle \psi_k | \psi_{k_j} \rangle |\psi_{k'} \psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N}\rangle. \end{aligned}$$

The other term is

$$\begin{aligned} \hat{a}_{k'}^\dagger \hat{a}_k |\psi_{k_1} \dots \psi_{k_N}\rangle &= \hat{a}_{k'}^\dagger \sum_{j=1}^N \xi^{j-1} \langle \psi_k | \psi_{k_j} \rangle |\psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N}\rangle \\ &= \sum_{j=1}^N \xi^{j-1} \langle \psi_k | \psi_{k_j} \rangle |\psi_{k'} \psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N}\rangle. \end{aligned}$$

From this we find that

$$\left(\hat{a}_k \hat{a}_{k'}^\dagger - \xi \hat{a}_{k'}^\dagger \hat{a}_k\right) |\psi_{k_1} \dots \psi_{k_N}\rangle = \langle \psi_k | \psi_{k'} \rangle |\psi_{k_1} \dots \psi_{k_N}\rangle.$$

Thus, the (anti)commutation relation between creation and annihilation operators is

$$\boxed{\left[\hat{a}_k, \hat{a}_{k'}^\dagger\right]_\xi = \hat{a}_k \hat{a}_{k'}^\dagger - \xi \hat{a}_{k'}^\dagger \hat{a}_k = \langle \psi_k | \psi_{k'} \rangle} \quad (2.24)$$

This is one of the central results of the second quantization formalism. If we have an single-particle basis $|\psi_k\rangle$ for the Hilbert space \mathcal{H}_1 of the single-particle quantum states, then we can build an orthonormal many-body basis set for the N -body problem using a product of N creation operators $\hat{a}_{k_j}^\dagger$ ($j = 1 \dots N$). If we impose the (anti)commutation rules (2.24) then our many-body basis set, and all states in the Hilbert space generated by this basis, will **automatically** satisfy the symmetry constraint for Bose particles ($\xi = 1$) or Fermi particles ($\xi = -1$).

Note that if the single-particle basis kets $|\psi_k\rangle$ are orthonormal, then we have for bosons $[\hat{a}_k, \hat{a}_{k'}^\dagger] = \delta(k = k')$ and for fermions $\{\hat{a}_k, \hat{a}_{k'}^\dagger\} = \delta(k = k')$.

2.3 Second Quantized Hamiltonian

In the previous sections of this chapter, we have built a suitable many-body basis, that obeys the symmetry constraint and that is characterized by occupation numbers. We have also introduced creation and annihilation operators that connect the different many-body basis kets.

In this section we will start from a very general many-body Hamiltonian, and rewrite it in creation and annihilation operators. We start from the Hamiltonian in its usual form, with position and momentum operators:

$$\hat{H} = \sum_{j=1}^N \frac{\hat{\mathbf{p}}_j^2}{2m} + \sum_{j=1}^N V_1(\hat{\mathbf{r}}_j) + \frac{1}{2} \sum_{j=1}^N \sum_{j'(\neq j)=1}^N V_2(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_{j'}). \quad (2.25)$$

This is called the ‘first quantization’: start from the classical Hamiltonian and replace positions and momenta by operators $\hat{\mathbf{r}}_j$ and $\hat{\mathbf{p}}_j$ that satisfy particular commutation rules $[\mathbf{r}_j, \mathbf{p}_{j'}] = i\hbar\delta_{jj'}$. In the Hamiltonian, $V_1(\mathbf{r})$ is a one-body potential acting on each particle: this is usually an externally applied field, such as an electric field or gravity, and it can also include a periodic potential of a perfect lattice, for example. Next, $V_2(\mathbf{r}, \mathbf{r}')$ is the two-body interaction potential, such as the Coulomb interaction or the Van der Waals interaction. It depends on the positions \mathbf{r}, \mathbf{r}' of both particles that interact, and is summed over all possible pairs of interacting particles, taking care to avoid double-counting. The

many-body quantum state $|\Psi(t)\rangle$ of the system described by this Hamiltonian must satisfy

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = \hat{H} |\Psi(t)\rangle. \quad (2.26)$$

We can now multiply this many-body Schrödinger equation onto our many-body basis bra $\langle \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} |$, and insert the completeness relation:

$$\begin{aligned} & i\hbar \frac{d \langle \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} | \Psi(t) \rangle}{dt} \\ &= \frac{1}{N!} \sum_{k'_1} \sum_{k'_2} \dots \sum_{k'_N} \langle \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} | \hat{H} | \psi_{k'_1} \psi_{k'_2} \dots \psi_{k'_N} \rangle \langle \psi_{k'_1} \psi_{k'_2} \dots \psi_{k'_N} | \Psi(t) \rangle, \end{aligned} \quad (2.27)$$

2.3.1 One-body potentials

Consider first the one-body potential (or the kinetic energy) in the Hamiltonian \hat{H} . The corresponding term in the right hand side of (2.27) is

$$\begin{aligned} \mathcal{V}_1 &= \frac{1}{N!} \sum_{k'_1} \dots \sum_{k'_N} \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \sum_{j=1}^N V_1(\mathbf{r}_j) \right| \psi_{k'_1} \dots \psi_{k'_N} \right\rangle \\ &\quad \times \langle \psi_{k'_1} \dots \psi_{k'_N} | \Psi(t) \rangle. \end{aligned} \quad (2.28)$$

This matrix element can be written out in position representation as

$$\begin{aligned} & \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \sum_{j=1}^N V_1(\mathbf{r}_j) \right| \psi_{k'_1} \dots \psi_{k'_N} \right\rangle \\ &= \frac{1}{N!} \sum_{j=1}^N \sum_{P, P'} \xi^P \xi^{P'} \langle \psi_{P[k_1]} | \dots \langle \psi_{P[k_N]} | V_1(\mathbf{r}_j) | \psi_{P'[k'_1]} \rangle \dots | \psi_{P'[k'_N]} \rangle \\ &= \sum_{j=1}^N \sum_P \xi^P \langle \psi_{P[k_1]} | \dots \langle \psi_{P[k_N]} | V_1(\mathbf{r}_j) | \psi_{k'_1} \rangle \dots | \psi_{k'_N} \rangle \\ &= \sum_{j=1}^N \sum_P \xi^P \left(\int d\mathbf{r} \psi_{P[k_j]}^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{k'_j}(\mathbf{r}) \right) \left(\prod_{i \neq j} \int d\mathbf{r} \psi_{P[k_i]}^*(\mathbf{r}) \psi_{k'_i}(\mathbf{r}) \right). \end{aligned}$$

Now we can use

$$\prod_{i \neq j} \int d\mathbf{r} \psi_{P[k_i]}^*(\mathbf{r}) \psi_{k'_i}(\mathbf{r}) = \delta(k'_i = P[k_i]), \quad (2.29)$$

and introduce the following notation:

$$\int d\mathbf{r} \psi_{P[k_j]}^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{k'_j}(\mathbf{r}) = \langle \psi_{P[k_j]} | V_1 | \psi_{k'_j} \rangle. \quad (2.30)$$

If we substitute this back into (2.28) we find

$$\begin{aligned} \mathcal{V}_1 &= \frac{1}{N!} \sum_P \xi^P \sum_{j=1}^N \sum_{k'_1} \dots \sum_{k'_N} \left\langle \psi_{P[k_j]} | V_1 | \psi_{k'_j} \right\rangle \prod_{i \neq j} \delta(k'_i = P[k_i]) \\ &\quad \times \left\langle \psi_{k'_1} \dots \psi_{k'_N} | \Psi(t) \right\rangle. \end{aligned} \quad (2.31)$$

The delta functions allow us to trivially perform $N - 1$ summations. Only 1 summations remains, and we rename its summation index to k' . This yields:

$$\begin{aligned} \mathcal{V}_1 &= \frac{1}{N!} \sum_P \xi^P \sum_{k'} \sum_{j=1}^N \left\langle \psi_{P[k_j]} | V_1 | \psi_{k'} \right\rangle \\ &\quad \times \left\langle \psi_{P[k_1]} \dots \psi_{P[k_{j-1}]} \psi_{k'} \psi_{P[k_{j+1}]} \dots \psi_{P[k_N]} | \Psi(t) \right\rangle. \end{aligned} \quad (2.32)$$

The ket

$$\left| \psi_{P[k_1]} \dots \psi_{P[k_{j-1}]} \psi_{k'} \psi_{P[k_{j+1}]} \dots \psi_{P[k_N]} \right\rangle \quad (2.33)$$

contains all single-particle basis states that also appear in $|\psi_{k_1} \dots \psi_{k_N}\rangle$ except for 1: the single-particle state that has been replaced by $\psi_{k'}$. Since we will sum over all j and all permutations, we can write

$$\begin{aligned} \mathcal{V}_1 &= \frac{1}{(N-1)!} \sum_{\bar{P}} \sum_{k'} \sum_{j=1}^N \xi^{\bar{P}} \left\langle \psi_{k_j} | V_1 | \psi_{k'} \right\rangle \\ &\quad \times \left\langle \psi_{\bar{P}[k_1]} \dots \psi_{\bar{P}[k_{j-1}]} \psi_{k'} \psi_{\bar{P}[k_{j+1}]} \dots \psi_{\bar{P}[k_N]} | \Psi(t) \right\rangle. \end{aligned} \quad (2.34)$$

where \bar{P} are the permutations over $N - 1$ particles. Sorting the single-particle states in the many-body ket results in a phase factor:

$$\left| \psi_{\bar{P}[k_1]} \dots \psi_{\bar{P}[k_{j-1}]} \psi_{k'} \psi_{\bar{P}[k_{j+1}]} \dots \psi_{\bar{P}[k_N]} \right\rangle = \xi^{\bar{P}} \xi^{j-1} \left| \psi_{k'} \psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_N} \right\rangle. \quad (2.35)$$

With this, we find:

$$\begin{aligned} \mathcal{V}_1 &= \frac{1}{(N-1)!} \sum_{\bar{P}} \sum_{k'} \sum_{j=1}^N \xi^{j-1} \left\langle \psi_{k_j} | V_1 | \psi_{k'} \right\rangle \\ &\quad \times \left\langle \psi_{k'} \psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_N} | \Psi(t) \right\rangle. \end{aligned} \quad (2.36)$$

Each term in the sum over the permutations \bar{P} is exactly the same, so we get:

$$\mathcal{V}_1 = \sum_{k'} \sum_{j=1}^N \xi^{j-1} \left\langle \psi_{k_j} | V_1 | \psi_{k'} \right\rangle \left\langle \psi_{k'} \psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_N} | \Psi(t) \right\rangle. \quad (2.37)$$

Since

$$\begin{aligned} \sum_k \hat{a}_{k'}^\dagger \hat{a}_k |\psi_{k_1} \dots \psi_{k_N}\rangle &= \sum_k \hat{a}_{k'}^\dagger \sum_{j=1}^N \xi^{j-1} \delta(k - k_j) |\psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_N}\rangle \\ &= \sum_k \sum_{j=1}^N \xi^{j-1} \delta(k - k_j) |\psi_{k'} \psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_N}\rangle, \end{aligned}$$

we find that

$$\mathcal{V}_1 = \sum_{k'} \sum_k \langle \psi_k | V_1 | \psi_{k'} \rangle \langle \psi_{k_1} \dots \psi_{k_N} | \hat{a}_k^\dagger \hat{a}_{k'} | \Psi(t) \rangle \quad (2.38)$$

2.3.2 Two-body potentials

Keeping in mind the procedure for one-body potential, we turn to the more complicated case of the two-body potentials. The expression that we need to calculate is

$$\begin{aligned} \mathcal{V}_2 &= \frac{1}{N!} \sum_{k'_1} \dots \sum_{k'_N} \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \sum_{j=1}^N V_2(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_{j'}) \right| \psi_{k'_1} \dots \psi_{k'_N} \right\rangle \\ &\quad \times \langle \psi_{k'_1} \dots \psi_{k'_N} | \Psi(t) \rangle. \end{aligned} \quad (2.39)$$

The matrix element is again written in position representation:

$$\begin{aligned} &\left\langle \psi_{k_1} \dots \psi_{k_N} \left| \sum_{j=1}^N V_2(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_{j'}) \right| \psi_{k'_1} \dots \psi_{k'_N} \right\rangle \\ &= \sum_{j=1}^N \sum_{j'=1}^N \sum_P \xi^P \left\langle \psi_{P[k_1]} \right| \dots \left\langle \psi_{P[k_N]} \right| V_2(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_{j'}) \left| \psi_{k'_1} \right\rangle \dots \left| \psi_{k'_N} \right\rangle \\ &= \sum_{j=1}^N \sum_{j' \neq j=1}^N \sum_P \xi^P \left(\prod_{i \neq j} \int d\mathbf{r} \psi_{P[k_i]}^*(\mathbf{r}) \psi_{k'_i}(\mathbf{r}) \right) \\ &\quad \times \left(\int d\mathbf{r} \int d\mathbf{r}' \psi_{P[k_j]}^*(\mathbf{r}) \psi_{P[k_{j'}]}^*(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}') \psi_{k'_j}(\mathbf{r}) \psi_{k'_{j'}}(\mathbf{r}') \right). \end{aligned}$$

Using

$$\left(\int d\mathbf{r} \int d\mathbf{r}' \psi_{P[k_j]}^*(\mathbf{r}) \psi_{P[k_{j'}]}^*(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}') \psi_{k'_j}(\mathbf{r}) \psi_{k'_{j'}}(\mathbf{r}') \right) \quad (2.40)$$

$$= \langle \psi_{P[k_j]} \psi_{P[k_{j'}]} | V_2 | \psi_{k'_j} \psi_{k'_{j'}} \rangle, \quad (2.41)$$

and introducing the delta functions that arise from the orthonormality of the single-particle states, we obtain for (2.39) the following expression:

$$\begin{aligned} \mathcal{V}_2 &= \frac{1}{N!} \sum_P \xi^P \sum_{j=1}^N \sum_{j' \neq j=1}^N \sum_{k'_1} \dots \sum_{k'_N} \left\langle \psi_{P[k_j]} \psi_{P[k_{j'}]} | V_2 | \psi_{k'_j} \psi_{k'_{j'}} \right\rangle \\ &\quad \times \left\langle \psi_{k'_1} \dots \psi_{k'_N} | \Psi(t) \right\rangle \prod_{i \neq j, j'} \delta(k'_i = P[k_i]). \end{aligned} \quad (2.42)$$

The delta functions now allow to eliminate $N - 2$ summations. Two sums remain, and we rename their summation indices to k' and q' :

$$\begin{aligned} \mathcal{V}_2 &= \frac{1}{N!} \sum_P \xi^P \sum_{k', q'} \sum_{j=1}^N \sum_{j' \neq j=1}^N \left\langle \psi_{P[k_j]} \psi_{P[k_{j'}]} | V_2 | \psi_{k'} \psi_{q'} \right\rangle \\ &\quad \times \left\langle \dots \psi_{P[k_{j-1}]} \psi_{k'} \psi_{P[k_{j+1}]} \dots \psi_{P[k_{j'-1}]} \psi_{q'} \psi_{P[k_{j'+1}]} \dots | \Psi(t) \right\rangle. \end{aligned} \quad (2.43)$$

Since we sum over all j, j' pairs and over all permutations, this is:

$$\begin{aligned} \mathcal{V}_2 &= \frac{1}{(N-2)!} \sum_{\check{P}} \sum_{k', q'} \sum_{j=1}^N \sum_{j' \neq j=1}^N \xi^{\check{P}} \left\langle \psi_{k_j} \psi_{k_{j'}} | V_2 | \psi_{k'} \psi_{q'} \right\rangle \\ &\quad \times \left\langle \dots \psi_{\check{P}[k_{j-1}]} \psi_{k'} \psi_{\check{P}[k_{j+1}]} \dots \psi_{\check{P}[k_{j'-1}]} \psi_{q'} \psi_{\check{P}[k_{j'+1}]} \dots | \Psi(t) \right\rangle, \end{aligned} \quad (2.44)$$

where now \check{P} are the permutations over $N - 2$ particles. Now we get upon reordering of the single-particle states in the many-body ket:

$$\begin{aligned} &\left| \dots \psi_{\check{P}[k_{j-1}]} \psi_{k'} \psi_{\check{P}[k_{j+1}]} \dots \psi_{\check{P}[k_{j'-1}]} \psi_{q'} \psi_{\check{P}[k_{j'+1}]} \dots \right\rangle \\ &= \xi^{\check{P}} \xi^{j-1} \xi^{j'-2} \left| \psi_{k'} \psi_{q'} \psi_{k_1} \dots \psi_{k_{j-1}} \psi_{k_{j+1}} \dots \psi_{k_{j'-1}} \psi_{k_{j'+1}} \dots \psi_{k_N} \right\rangle. \end{aligned} \quad (2.45)$$

The phase factors appear in the case of fermions because of this reordering. We get

$$\begin{aligned} \mathcal{V}_2 &= \sum_{k', q'} \sum_{j=1}^N \sum_{j' \neq j=1}^N \xi^{j-1} \xi^{j'-2} \left\langle \psi_{k_j} \psi_{k_{j'}} | V_2 | \psi_{k'} \psi_{q'} \right\rangle \\ &\quad \times \left\langle \psi_{k'} \psi_{q'} \psi_{k_1} \dots (\text{no } \psi_{k_j}, \psi_{k_{j'}}) \dots \psi_{k_N} | \Psi(t) \right\rangle. \end{aligned} \quad (2.46)$$

Finally, since

$$\begin{aligned} & \sum_{k', q'} \hat{a}_{k'}^\dagger \hat{a}_{q'}^\dagger \hat{a}_k \hat{a}_q \left| \psi_{k_1} \dots \psi_{k_N} \right\rangle \\ &= \sum_{k', q'} \sum_k \sum_{j=1}^N \xi^{j-1} \delta(q - k_j) \hat{a}_{k'}^\dagger \hat{a}_{q'}^\dagger \hat{a}_k \left| \psi_{k_1} \dots (\text{no } \psi_{k_j}) \dots \psi_{k_N} \right\rangle \end{aligned} \quad (2.47)$$

$$\begin{aligned} &= \sum_{k', q'} \sum_{k, q} \sum_{j=1}^N \xi^{j-1} \delta(q - k_j) \sum_{j' \neq j=1}^N \xi^{j'-2} \delta(k - k_j) \\ & \quad \times \hat{a}_{k'}^\dagger \hat{a}_{q'}^\dagger \left| \psi_{k_1} \dots (\text{no } \psi_{k_j}, \psi_{k_{j'}}) \dots \psi_{k_N} \right\rangle, \end{aligned} \quad (2.48)$$

$$\begin{aligned} &= \sum_{k', q'} \sum_{k, q} \sum_{j=1}^N \xi^{j-1} \delta(q - k_j) \sum_{j' \neq j=1}^N \xi^{j'-2} \delta(k - k_j) \\ & \quad \times \left| \psi_{k'} \psi_{q'} \psi_{k_1} \dots (\text{no } \psi_{k_j}, \psi_{k_{j'}}) \dots \psi_{k_N} \right\rangle \end{aligned} \quad (2.49)$$

we find that

$$\mathcal{V}_2 = \sum_{k', q'} \sum_{k, q} \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \hat{a}_q^\dagger \hat{a}_k^\dagger \hat{a}_{q'} \hat{a}_{k'} \right| \Psi(t) \right\rangle. \quad (2.50)$$

Now we can combine the results (2.38) and (2.50) that we found for one-body and two-body operators and construct the full Hamiltonian.

2.3.3 Full Hamiltonian

The kinetic energy follows the same derivation as the one-body potential. We denote

$$\begin{aligned} \langle \psi_k | T | \psi_{k'} \rangle &= -\frac{\hbar^2}{2m} \int d\mathbf{r} \psi_k^*(\mathbf{r}) \Delta_{\mathbf{r}} \psi_{k'}(\mathbf{r}), \\ \langle \psi_k | V_1 | \psi_{k'} \rangle &= \int d\mathbf{r} \psi_k^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{k'}(\mathbf{r}), \\ \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle &= \int d\mathbf{r} \int d\mathbf{r}' \psi_q^*(\mathbf{r}) \psi_k^*(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}') \psi_{k'}(\mathbf{r}) \psi_{q'}(\mathbf{r}'). \end{aligned} \quad (2.51)$$

In the double integral it is important to place the correct integration variable in the correct single-particle wave function! If this is done wrongly, we get the wrong phase factors. Substituting the results (2.38) en (2.50) from the previous subsections in the Schrödinger equation (2.27) brings:

$$\begin{aligned} i\hbar \frac{d \langle \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} | \Psi(t) \rangle}{dt} &= \sum_{k'} \sum_k \langle \psi_k | T + V_1 | \psi_{k'} \rangle \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \hat{a}_k^\dagger \hat{a}_{k'} \right| \Psi(t) \right\rangle \\ &+ \frac{1}{2} \sum_{k', q'} \sum_{k, q} \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle \left\langle \psi_{k_1} \dots \psi_{k_N} \left| \hat{a}_q^\dagger \hat{a}_k^\dagger \hat{a}_{q'} \hat{a}_{k'} \right| \Psi(t) \right\rangle \end{aligned}$$

This result holds for all $\langle \psi_{k_1} \psi_{k_2} \dots \psi_{k_N} |$. The many body quantum state $|\Psi(t)\rangle$ satisfies $i\hbar d|\Psi(t)\rangle/dt = \hat{H}|\Psi(t)\rangle$. From this, we obtain one of the central results of this chapter:

The Hamiltonian in second quantization :

$$\hat{H} = \sum_{k'} \sum_k \langle \psi_k | T + V_1 | \psi_{k'} \rangle \hat{a}_k^\dagger \hat{a}_{k'} + \frac{1}{2} \sum_{k', q'} \sum_{k, q} \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle \hat{a}_q^\dagger \hat{a}_k^\dagger \hat{a}_{q'} \hat{a}_{k'} \quad (2.52)$$

The only operators still present are creation and annihilation operators: the other factors are expectation values, complex numbers and not operators. This recasting of an operator, such as the Hamiltonian, in a form that contains only creation and annihilation operators is ‘second quantisation’.

Note that this mathematical form of the Hamiltonian is exactly the same for bosons as for fermions. However, the creation and annihilation operators obey different commutation relations, and it is those commutation rules that enforce the correct Bose or Fermi statistics.

Finally, from the previous comment it should be clear that it is very important to write the operators in the correct order! In the last term the order of the annihilation operators $\hat{a}_{q'} \hat{a}_{k'}$ is the reverse of the order of the wave functions $\psi_{k'}(\mathbf{r}') \psi_{q'}(\mathbf{r})$ in the integration for the matrix element.

In general, single particle operators can be written in second quantization as

$$\begin{aligned} \hat{A} &= \sum_{j=1}^N A(\mathbf{r}_j) = \sum_{k'} \sum_k \langle \psi_k | A | \psi_{k'} \rangle \hat{a}_k^\dagger \hat{a}_{k'} \\ (&= \int d\mathbf{r} \psi_k^*(\mathbf{r}) A(\mathbf{r}) \psi_{k'}(\mathbf{r}) \hat{a}_k^\dagger \hat{a}_{k'}. \end{aligned} \quad (2.53)$$

An important and simple example is the counting operator \hat{N} that... counts how many particles are present. This becomes

$$\hat{N} = \sum_{j=1}^N \hat{1} = \sum_{k'} \sum_k \langle \psi_k | \hat{1} | \psi_{k'} \rangle \hat{a}_k^\dagger \hat{a}_{k'} = \sum_k \hat{a}_k^\dagger \hat{a}_k \quad (2.54)$$

2.4 Field operators

Modern field theory is generally written in the second quantisation formalism (the alternative is the path integral formalism). There, however, one often uses

so-called “field operators” rather than the creation and annihilation operators defined above. The field operators are defined by

$$\hat{\psi}(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) \hat{a}_k, \quad (2.55)$$

$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_k \psi_k^*(\mathbf{r}) \hat{a}_k^\dagger. \quad (2.56)$$

The sum runs over all possible values of the quantum numbers k , and adds up the products of the single-particle wave functions and their corresponding creation or annihilation operators. In this way, you create or annihilation a particle in a superposition of all single-particle wave functions at the same time. This comes down to creating or annihilating a particle that is fully localized in a specific location \mathbf{r} . The field operators satisfy the following (anti)commutation relations

$$\begin{aligned} \left[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}') \right]_\xi &= \sum_k \sum_{k'} \psi_k(\mathbf{r}) \psi_{k'}^*(\mathbf{r}') \left[\hat{a}_k, \hat{a}_{k'}^\dagger \right]_\xi \\ &= \sum_k \sum_{k'} \psi_k(\mathbf{r}) \psi_{k'}^*(\mathbf{r}') \delta_{kk'} \\ &= \sum_k \psi_k(\mathbf{r}) \psi_k^*(\mathbf{r}') \\ &= \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (2.57)$$

Here we used that the chosen single-particle basis functions $\psi_k(\mathbf{r})$ are orthonormal. The last equality comes from

$$\delta(\mathbf{r} - \mathbf{r}') = \langle \mathbf{r} | \mathbf{r}' \rangle = \langle \mathbf{r} | \hat{1} | \mathbf{r}' \rangle = \sum_k \langle \mathbf{r} | \psi_k \rangle \langle \psi_k | \mathbf{r}' \rangle = \sum_k \psi_k(\mathbf{r}) \psi_k^*(\mathbf{r}'). \quad (2.58)$$

The other (anti)commutators are zero,

$$\left[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}') \right]_\xi = 0 = \left[\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}') \right]_\xi$$

since the corresponding (anti)commutators for the creation and annihilations operators are zero.

The second quantization of operators can also be written in field operators rather than the usual creation and annihilation operators. For one-body potentials $\hat{V}_1 = V_1(\hat{\mathbf{r}})$ we get

$$\begin{aligned} \hat{V}_1 &= \sum_{k'} \sum_k \left[\int d\mathbf{r} \psi_k^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{k'}(\mathbf{r}) \right] \hat{a}_k^\dagger \hat{a}_{k'} \\ &= \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) V_1(\mathbf{r}) \hat{\psi}(\mathbf{r}) \end{aligned} \quad (2.59)$$

The expression for the two-body potential is analogous to that for the one-body potential. The Hamiltonian, written in field operators, becomes

$$\hat{H} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) [T(\mathbf{r}) + V_1(\mathbf{r})] \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}) \quad (2.60)$$

This version of second quantization is in a sense reciprocal to the one we wrote down with the usual creation and annihilation operators. *The creation operator \hat{a}_k^\dagger creates a particle in the single-particle state $\psi_k(\mathbf{r})$, whereas the field operator $\hat{\psi}^\dagger(\mathbf{r})$ creates a particle localized at position \mathbf{r} (i.e. in the single-particle state $|\mathbf{r}\rangle$).*

2.5 Summary

STEP 1 – Using an orthonormal single-particle basis, we can create a many-particle basis for the space \mathcal{H}_N of N -particle states. We do this by taking a product, and applying Bose or Fermi symmetrization to satisfy the identical-particle symmetry constraint:

$$|\psi_{k_1} \psi_{k_2} \dots \psi_{k_N}\rangle := \sqrt{\frac{1}{N!}} \sum_P \xi^P |\psi_{P[k_1]}\rangle |\psi_{P[k_2]}\rangle \dots |\psi_{P[k_N]}\rangle, .$$

Here $\xi^P = -1$ for odd permutations P of fermions, and $\xi^P = 1$ in all other cases. Since many lists $\{k_1, k_2, \dots, k_N, \dots\}$ correspond to the same many-body basis ket, we prefer to work with occupation numbers to obtain a one-on-one relation between the labels and the many-body basis kets. Thus, we define our occupation number basis for the space of many-particle states as:

$$|n_1 n_2 \dots n_k \dots\rangle = \frac{|\psi_1 \dots \psi_1 \psi_2 \dots \psi_2 \dots\rangle}{\prod_k \sqrt{n_k!}}$$

These form an orthonormal, complete basis set for the quantum many-body states of identical particles.

STEP 2 – Now that we have a good basis, we need to write down operators that connect the many-body basis kets. These will allow to rewrite any operator (such as the Hamiltonian) in a way that makes the basic processes and transitions clear, and that keep the symmetry constraint neatly satisfied. The fundamental operators that link the many-body basis kets are the creation

and annihilation operators, defined for bosons through:

BOSONS (2.61)

$$\begin{aligned} \hat{a}_k^\dagger |n_1 n_2 \dots n_k \dots\rangle &= \sqrt{n_k + 1} |n_1 n_2 \dots (n_k + 1) \dots\rangle \\ \hat{a}_k |n_1 n_2 \dots n_k \dots\rangle &= \sqrt{n_k} |n_1 n_2 \dots (n_k - 1) \dots\rangle \\ [\hat{a}_k, \hat{a}_{k'}^\dagger] &= \hat{a}_k^\dagger \hat{a}_{k'} - \hat{a}_{k'}^\dagger \hat{a}_k = \delta(k = k') \end{aligned}$$

and for fermions as:

FERMIONS (2.62)

$$\begin{aligned} \hat{a}_k^\dagger |n_1 n_2 \dots n_k \dots\rangle &= \begin{cases} (-1)^{n_1 + \dots + n_{k-1}} |n_1 n_2 \dots (n_k + 1) \dots\rangle & \text{if } n_k = 0 \\ 0 & \text{if } n_k = 1 \end{cases} \\ \hat{a}_k |n_1 n_2 \dots n_k \dots\rangle &= \begin{cases} (-1)^{n_1 + \dots + n_{k-1}} |n_1 n_2 \dots (n_k - 1) \dots\rangle & \text{if } n_k = 1 \\ 0 & \text{if } n_k = 0 \end{cases} \\ \{\hat{a}_k, \hat{a}_{k'}^\dagger\} &= \hat{a}_k \hat{a}_{k'}^\dagger + \hat{a}_{k'}^\dagger \hat{a}_k = \delta(k = k') \end{aligned}$$

The bosonic operators commute, the fermionic ones anticommute. We link these operators back to the many-body basis kets: both for fermions and for bosons we have

$$|n_1 n_2 \dots n_k \dots\rangle = \left(\prod_{j=1}^{\infty} \frac{(\hat{a}_j^\dagger)^{n_j}}{\sqrt{n_j!}} \right) |\emptyset\rangle. \quad (2.63)$$

Here the ket $|\emptyset\rangle$ represents the vacuum state, i.e. the state with no particles. When an annihilation operator acts in this state, the result is 0 by definition. The factors $(-1)^{n_1 + \dots + n_{k-1}}$ in the case of fermions result in the proper antisymmetry in (2.63) for fermions.

STEP 3 – Second quantization is the art of rewriting operators as products of creation and annihilation operators. The Hamiltonian of a many-body system with one-body potential $V_1(\mathbf{r})$ en two-body interaction $V_2(\mathbf{r}, \mathbf{r}')$ is given by

$$\begin{aligned} \hat{H} &= \sum_{k'} \sum_k \langle \psi_k | T + V_1 | \psi_{k'} \rangle \hat{a}_k^\dagger \hat{a}_{k'} \\ &\quad + \frac{1}{2} \sum_{k', q'} \sum_{k, q} \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle \hat{a}_q^\dagger \hat{a}_k^\dagger \hat{a}_{q'} \hat{a}_{k'} \end{aligned} \quad (2.64)$$

where

$$\begin{aligned} \langle \psi_k | T | \psi_{k'} \rangle &= -\frac{\hbar^2}{2m} \int d\mathbf{r} \psi_k^*(\mathbf{r}) \Delta_{\mathbf{r}} \psi_{k'}(\mathbf{r}), \\ \langle \psi_k | V_1 | \psi_{k'} \rangle &= \int d\mathbf{r} \psi_k^*(\mathbf{r}) V_1(\mathbf{r}) \psi_{k'}(\mathbf{r}), \\ \langle \psi_q \psi_k | V_2 | \psi_{k'} \psi_{q'} \rangle &= \int d\mathbf{r} \int d\mathbf{r}' \psi_q^*(\mathbf{r}) \psi_k^*(\mathbf{r}') V_2(\mathbf{r}, \mathbf{r}') \psi_{k'}(\mathbf{r}) \psi_{q'}(\mathbf{r}'). \end{aligned} \quad (2.65)$$

This formula is valid both for bosons and for fermions, the difference is encoded in the behavior of the creation and annihilation operators as you swap them around (commuting or anticommuting). Note furthermore that in the rest of our solid state course, for electrons we will choose a single-particle basis of Bloch waves. So our single-particle quantum numbers k include the wave vector \mathbf{k} , a band index n (usually omitted since we won't look at interband transitions), and a spin σ . But, in general, you can choose any single-particle basis that you want to build up a specific second-quantization formalism with it.

Chapter 3

Electrons and Phonons

The many-body system that we will deal with in the context of solid state physics and metals in particular, is the collection of free electrons in a material. Also the quantized lattice vibrations or phonons will play a role. In this chapter, we apply the language of second quantisation to describe the system of many electrons and phonons. Once we have obtained the Hamiltonian, we can estimate how ground-state properties are influenced by interactions – to do so we need to use perturbation theory or variational analysis.

3.1 Electrons in metals

We can now start refining Bloch’s theory of electrons in metals by including effects of the Coulomb interaction between the electrons. The starting point is a collection of N electrons, and a screened Coulomb interaction known as the Yukawa potential. We will also require a neutralizing background (the cores and valence band electrons): this will first be treated completely classically and statically.

3.1.1 The interacting electron gas

The Hamiltonian of the N conduction electrons is given in first quantization by

$$\hat{H}_{el} = \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} + \frac{1}{2} \sum_{j=1}^N \sum_{j' \neq j} \frac{e^2}{4\pi\epsilon_{\text{vac}}} \frac{e^{-\mu|\hat{\mathbf{r}}_j - \hat{\mathbf{r}}_{j'}|}}{|\hat{\mathbf{r}}_j - \hat{\mathbf{r}}_{j'}|}. \quad (3.1)$$

The factor $1/2$ avoids double counting of the electron pairs. This Hamiltonian describes N electrons in a crystal with volume V (at the end of the calculation we will take the thermodynamic limit, letting both N and V go to infinity in such a way that N/V is constant). We use SI units, so that $m = 9.109 \times 10^{-31}$ kg, $\epsilon_{\text{vac}} = 8.854 \times 10^{-12}$ F/m, $e = 1.602$ C. Note that to be more correct in describing the electrons, we should replace the vacuum electron mass by the conduction band mass.

We have multiplied the usual Coulomb interaction with a strange factor $e^{-\mu|\mathbf{r}_j - \mathbf{r}_{j'}|}$. This is essentially a convergence factor, needed to be able to calculate in some mathematical rigor integrals that will cancel out in the end. We need to assume that $1/\mu \ll L$ with L the length of the crystal for this factor not to have any physical influence. The real Coulomb interaction is retrieved if we put $\mu = 0$, and that is precisely the limit that we will take at the end of the calculations, when we have done the integrations and taken the thermodynamic limit.

Which single-particle basis shall we choose to construct our N -particle basis? If we work in a homogeneous material, we know that the wave number \mathbf{k} is a good quantum number. Indeed, the momentum is the generator of translations, and claiming translation invariance is the same as claiming that momentum commutes with the Hamiltonian so that these have a common eigenstate basis. Also the spin of the electrons should be taken into account. Electrons are spin-1/2 particles, so that the spin state is a two dimensional Hilbert space generated by two basis states, spin up $\sigma = +1$ and spin down $\sigma = -1$. Suitable single-particle states are therefore

$$\varphi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \eta_{\sigma}. \quad (3.2)$$

Here V is the volume of the crystal and η_{σ} is the spinor that corresponds to spin up or spin down,

$$\eta_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ en } \eta_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (3.3)$$

The allowed values of the wave numbers fitting in a cube with side $V^{1/3}$, and allowing for periodic boundary conditions are

$$\mathbf{k} = \frac{(2\pi)^3}{V} \mathbf{n} \text{ with} \quad (3.4)$$

$$\mathbf{n} = n_x \mathbf{e}_x + n_y \mathbf{e}_y + n_z \mathbf{e}_z \text{ where } n_x, n_y, n_z \in \mathbb{Z}. \quad (3.5)$$

The density of states in reciprocal space (wave number space) is $V/(2\pi)^3$. This allows to approximate the difficult-to-take sums over the allowed wave numbers by a much simpler integral:

$$\begin{aligned} \sum_{\mathbf{k}} f(\mathbf{k}) &= \sum_{n_x, n_y, n_z} f\left(\frac{(2\pi)^3}{V} \mathbf{n}\right) \\ &\xrightarrow{V \text{ large}} \int dn_x \int dn_y \int dn_z f\left(\frac{(2\pi)^3}{V} \mathbf{n}\right) \\ &= \frac{V}{(2\pi)^3} \int d\mathbf{k} f(\mathbf{k}). \end{aligned} \quad (3.6)$$

Note that there are different ways of setting up the chosen single-particle states. We can choose to normalize them by a factor $1/\sqrt{2\pi}$ rather than $1/\sqrt{V}$, and

we will switch to that normalization later on, after we have learnt what the role of the thermodynamic limit is. We can also use Dirichlet boundary conditions rather than periodic boundary conditions on the cube to obtain slightly different values of the allowed wave numbers. In the end, as discussed in C. Kittel's book (listed in the bibliography) in more detail, it doesn't matter. For example, we get the same results for ground state energy per volume. Now that we have chosen our single-particle basis states, we can associate with them creation and annihilation operators $\hat{a}_{\mathbf{k},\sigma}^\dagger$ and $\hat{a}_{\mathbf{k},\sigma}$, respectively. The general notation ' k ' that we have used in the previous chapter now becomes specific: $k = \{\mathbf{k}, \sigma\}$ contains four quantum numbers: three for the wave number in x, y, z directions and one for spin.

First, we rewrite the kinetic energy in second quantization, using the rules derived in the previous chapter. In order to find the second quantized version, we need to evaluate

$$\begin{aligned} \langle \psi_{\mathbf{k},\sigma} | T | \psi_{\mathbf{k}',\sigma'} \rangle &= -\frac{\hbar^2}{2m} \int d\mathbf{r} \varphi_{\mathbf{k},\sigma}^*(\mathbf{r}) \Delta_{\mathbf{r}} \varphi_{\mathbf{k}',\sigma'}(\mathbf{r}) \\ &= -\frac{\hbar^2}{2m} [\eta_{\sigma}^+ \eta_{\sigma'}] \times \left[-(k')^2 \frac{1}{V} \int d\mathbf{r} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} \right] \\ &= \frac{\hbar^2 (k')^2}{2m} \delta_{\sigma\sigma'} \delta(\mathbf{k} = \mathbf{k}'). \end{aligned} \quad (3.7)$$

Here we have used one of the many useful integral representations of the delta function:

$$\delta(\mathbf{q}) = \frac{1}{V} \int_V d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}}. \quad (3.8)$$

The second quantisation expression for the kinetic energy now becomes:

$$\begin{aligned} \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} &= \sum_{\mathbf{k}',\sigma'} \sum_{\mathbf{k},\sigma} \frac{\hbar^2 (k')^2}{2m} \delta_{\sigma\sigma'} \delta(\mathbf{k} = \mathbf{k}') \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k}',\sigma'} \\ &= \sum_{\mathbf{k},\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma}. \end{aligned} \quad (3.9)$$

Note the difference in approach between first and second quantisation. To calculate the total kinetic energy, *first quantisation sums over all the $j = 1, \dots, N$ particles* the kinetic energy contribution $\hat{p}_j^2/(2m)$ of each individual particle j separately. In contrast, *second quantisation sums over all the single-particle states $k = \{\mathbf{k}, \sigma\}$* the kinetic energy that a particle would have in that state, $(\hbar k)^2/(2m)$, multiplied by the number of particles in that state, $\hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma}$.

The second quantized form of the Coulomb interaction is

$$\hat{V}_C = \frac{1}{2} \sum_{\mathbf{k}',\sigma',\mathbf{q}',\zeta'} \sum_{\mathbf{k},\zeta,\mathbf{q},\sigma} \langle \varphi_{\mathbf{q},\sigma} \varphi_{\mathbf{k},\zeta} | V_2 | \varphi_{\mathbf{q}',\zeta'} \varphi_{\mathbf{k}',\sigma'} \rangle \hat{a}_{\mathbf{q},\sigma}^\dagger \hat{a}_{\mathbf{k},\zeta}^\dagger \hat{a}_{\mathbf{k}',\sigma'} \hat{a}_{\mathbf{q}',\zeta'}.$$

We need to calculate the matrix element

$$\begin{aligned} \langle \varphi_{\mathbf{q},\sigma} \varphi_{\mathbf{k},\zeta} | V_2 | \varphi_{\mathbf{q}',\zeta'} \varphi_{\mathbf{k}',\sigma'} \rangle &= \frac{e^2}{4\pi\epsilon_{\text{vac}}} \eta_{\zeta'}^+(1) \eta_{\sigma'}^+(2) \eta_{\sigma'}(2) \eta_{\zeta'}(1) \\ &\times \frac{1}{V^2} \int d\mathbf{r} \int d\mathbf{r}' \exp\{i(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{r} + i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}'\} \frac{e^{-\mu|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (3.10)$$

This integral can be performed by introducing new integration variables $\mathbf{u} = \mathbf{r} - \mathbf{r}'$ en $\mathbf{u}' = \mathbf{r}'$ (the Jacobian of this transformation is 1). We find

$$\begin{aligned} \langle \varphi_{\mathbf{q},\sigma} \varphi_{\mathbf{k},\zeta} | V_2 | \varphi_{\mathbf{q}',\zeta'} \varphi_{\mathbf{k}',\sigma'} \rangle &= \delta_{\zeta\zeta'} \delta_{\sigma\sigma'} \frac{1}{V} \int d\mathbf{u}' \exp\{i(\mathbf{q}' - \mathbf{q} + \mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}'\} \\ &\times \frac{e^2}{4\pi\epsilon_{\text{vac}}} \frac{1}{V} \int d\mathbf{u} \frac{e^{-\mu u}}{u} \exp\{i(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{u}\} \end{aligned}$$

The first integral is again a delta function:

$$\frac{1}{V} \int d\mathbf{u}' \exp\{i(\mathbf{q}' - \mathbf{q} + \mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}'\} = \delta[(\mathbf{q}' + \mathbf{k}') - (\mathbf{q} + \mathbf{k})]. \quad (3.11)$$

The delta function ensures that the total (incoming) momentum of the states that are being annihilated, $\hbar\mathbf{q}' + \hbar\mathbf{k}'$, equals the total (outgoing) momentum of the states are are created, $\hbar\mathbf{q} + \hbar\mathbf{k}$. This obviously is nothing but the conservation of momentum between the initial and final states of the two scattering electrons, and is linked to our assumption of homogeneity as stated before.

The remaining integral is

$$\begin{aligned} \int d\mathbf{u} \frac{e^{-\mu u}}{u} \exp\{i(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{u}\} &= 2\pi \int_0^\infty du \int_0^\pi d\theta u \sin \theta e^{-\mu u} \exp\{i|\mathbf{q}' - \mathbf{q}|u \cos \theta\} \\ &= 2\pi \int_0^\infty du u e^{-\mu u} \frac{e^{i|\mathbf{q}' - \mathbf{q}|u} - e^{-i|\mathbf{q}' - \mathbf{q}|u}}{i|\mathbf{q}' - \mathbf{q}|u} \\ &= \frac{4\pi}{(\mathbf{q}' - \mathbf{q})^2 + \mu^2}. \end{aligned}$$

With this result, we find

$$\langle \varphi_{\mathbf{q},\zeta} \varphi_{\mathbf{k},\sigma} | V_2 | \varphi_{\mathbf{q}',\zeta'} \varphi_{\mathbf{k}',\sigma'} \rangle = \frac{\delta_{\zeta\zeta'} \delta_{\sigma\sigma'}}{V} \delta[(\mathbf{q}' + \mathbf{k}') - (\mathbf{q} + \mathbf{k})] \frac{e^2/\epsilon_{\text{vac}}}{(\mathbf{q}' - \mathbf{q})^2 + \mu^2},$$

so that

$$\hat{V}_C = \frac{e^2}{2\epsilon_{\text{vac}} V} \sum_{\sigma,\zeta} \sum_{\mathbf{k}',\mathbf{q}'} \sum_{\mathbf{k},\mathbf{q}} \frac{\delta[(\mathbf{q}' + \mathbf{k}') - (\mathbf{q} + \mathbf{k})]}{(\mathbf{q}' - \mathbf{q})^2 + \mu^2} \hat{a}_{\mathbf{q},\sigma}^\dagger \hat{a}_{\mathbf{k},\zeta}^\dagger \hat{a}_{\mathbf{k}',\sigma} \hat{a}_{\mathbf{q}',\zeta}$$

Since the delta function expresses momentum conservation, we can rewrite the new wave numbers \mathbf{q}', \mathbf{k}' as the old wave numbers after exchange of a certain amount of momentum. Rename $\mathbf{k}_1 = \mathbf{k}'$ and $\mathbf{k}_2 = \mathbf{q}'$, and denote the exchange

amount of momentum by \mathbf{Q} , so that $\mathbf{k} = \mathbf{k}' + \mathbf{Q}$ and $\mathbf{q} = \mathbf{q}' - \mathbf{Q}$. Then we also have $\mathbf{q} - \mathbf{q}' = \mathbf{Q}$, and we find

$$\hat{V}_C = \frac{e^2}{2\varepsilon_{\text{vac}}V} \sum_{\sigma, \zeta} \sum_{\mathbf{k}_1, \mathbf{k}_2} \sum_{\mathbf{Q}} \frac{1}{Q^2 + \mu^2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma}.$$

The process described by the annihilation and creation operators is the following:

- Two electrons, like rugby players, are running with momenta $\hbar\mathbf{k}_1$ and $\hbar\mathbf{k}_2$.
- Then one of the electrons throws the rugby ball, with momentum $\hbar\mathbf{Q}$ to the other electron.
- The other electron catches it, and now has a momentum $\hbar(\mathbf{k}_2 + \mathbf{Q})$.
- The first electron, who threw the ball, experiences a recoil and ends up with momentum $\hbar(\mathbf{k}_1 - \mathbf{Q})$.

This is all described by the succession of annihilation and creation operators in \hat{V}_C . The annihilation operators remove the electrons from states $\{\mathbf{k}_1, \sigma\}$ and $\{\mathbf{k}_2, \zeta\}$ and the creation operators put them in states $\{\mathbf{k}_1 - \mathbf{Q}, \sigma\}$ and $\{\mathbf{k}_2 + \mathbf{Q}, \zeta\}$, respectively. The quantum mechanical amplitude (not probability!) for such a process (a ball-throw of momentum $\hbar\mathbf{Q}$ between the two electrons) is $e^2/(2\varepsilon_{\text{vac}}V) \times 1/(Q^2 + \mu^2)$. This turns out to be the Fourier transform of the Yukawa interaction potential! If you would use another potential, such as a Lennard-Jones potential to study a gas of fermionic atoms, you'd have the same expression for the second-quantized interaction, but with the Fourier transform of the Lennard-Jones potential in stead.

Note that we know from elementary particle physics that the rugby ball should be a force boson, here it is the photon. But an important and subtle distinction is that in solid state physics we focus on the non-relativistic case and look at an instantaneous Coulomb interaction linked to the longitudinal electric field, rather than the transverse photon that is used in particle physics.

The full Hamiltonian of the interacting electron gas becomes:

$$\boxed{\begin{aligned} \hat{H}_{el} = & \sum_{\mathbf{k}, \sigma} \frac{\hbar^2 k^2}{2m} \hat{a}_{\mathbf{k}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} \\ & + \frac{1}{2V} \sum_{\mathbf{Q}} \frac{e^2}{\varepsilon_{\text{vac}} Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1}. \end{aligned}} \quad (3.12)$$

Here we already attempt to put μ zero, but we need to look at this in more detail... We can take the limit $\mu \rightarrow 0$ for most terms in the sum, but not for

the terms that have $Q = 0$! If we separate these terms from the rest, we get

$$\begin{aligned}\hat{V}_C &= \frac{e^2}{2\varepsilon_{\text{vac}}V} \sum_{\mathbf{Q} \neq 0} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma} \sum_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma} \\ &\quad + \frac{e^2}{2\varepsilon_{\text{vac}}V\mu^2} \sum_{\mathbf{k}_1, \sigma} \sum_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_2, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma}.\end{aligned}\quad (3.13)$$

In the second term we reorder the operators, using the fermionic anticommutation relations:

$$\begin{aligned}\hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_2, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma} &= -\hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_2, \zeta}^\dagger \hat{a}_{\mathbf{k}_1, \sigma} \hat{a}_{\mathbf{k}_2, \zeta} \\ &= -\hat{a}_{\mathbf{k}_1, \sigma}^\dagger \left(\delta_{\sigma\zeta} \delta_{\mathbf{k}_1, \mathbf{k}_2} - \hat{a}_{\mathbf{k}_1, \sigma} \hat{a}_{\mathbf{k}_2, \zeta}^\dagger \right) \hat{a}_{\mathbf{k}_2, \zeta} \\ &= \hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_1, \sigma} \hat{a}_{\mathbf{k}_2, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} - \delta_{\sigma\zeta} \delta_{\mathbf{k}_1, \mathbf{k}_2} \hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_1, \sigma}.\end{aligned}$$

We recognize the counting operator $\hat{N}_{\mathbf{k}_1, \sigma} = \hat{a}_{\mathbf{k}_1, \sigma}^\dagger \hat{a}_{\mathbf{k}_1, \sigma}$ (cf. (2.54)) that counts the number of particles in the single-particle state $|\psi_{\mathbf{k}_1, \sigma}\rangle$ (the occupation number of that state):

$$\begin{aligned}\hat{V}_C &= \frac{e^2}{2\varepsilon_{\text{vac}}V} \sum_{\mathbf{Q} \neq 0} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma} \sum_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma} \\ &\quad + \frac{e^2}{2\varepsilon_{\text{vac}}V\mu^2} \sum_{\mathbf{k}_1, \sigma} \sum_{\mathbf{k}_2, \zeta} \left(\hat{N}_{\mathbf{k}_1, \sigma} \hat{N}_{\mathbf{k}_2, \zeta} - \delta_{\sigma\zeta} \delta_{\mathbf{k}_1, \mathbf{k}_2} \hat{N}_{\mathbf{k}_1, \sigma} \right).\end{aligned}\quad (3.14)$$

The sum over all occupation numbers equals the total number of particles, N , so that

$$\begin{aligned}\hat{V}_C &= \frac{e^2}{2\varepsilon_{\text{vac}}V} \sum_{\mathbf{Q} \neq 0} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma} \sum_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \zeta}^\dagger \hat{a}_{\mathbf{k}_2, \zeta} \hat{a}_{\mathbf{k}_1, \sigma} \\ &\quad + \hat{1} \frac{e^2}{2\varepsilon_{\text{vac}}V\mu^2} (N^2 - N).\end{aligned}\quad (3.15)$$

In the thermodynamic limit ($N \rightarrow \infty$ and $V \rightarrow \infty$ such that $N/V = \text{constant}$) the divergent term is

$$\hat{V}_C^{\text{divergent}} = \hat{1} \frac{e^2}{2\varepsilon_{\text{vac}}V\mu^2} (N^2 - N) \approx \hat{1} \frac{e^2}{2\varepsilon_{\text{vac}}V\mu^2} N^2.$$

This divergence comes from the fact that we have a collection of infinitely many negatively charged particles repelling each other, with no neutralizing background. Of course the Coulomb energy will diverge! If we want to make a more physical model, we need to include the neutralizing positively charged background of the ions on the lattice.

3.1.2 The Jellium-model for the background

The Hamiltonian of the atom core and valence electrons represents the positive background in which the conduction electrons can move. A full quantum mechanical picture is not only unsolvably complicated, it is also unnecessarily complicated to understand what is going on. In lowest approximation, we will assume that the background is static (we'll deal with the dynamics of the ions later on). This means there is no kinetic term – it is a reasonable assumption since the ions are much heavier than the electrons. We also neglect quantum fluctuations of the ions this way. Then we can describe the background as a classical charge density $en(\mathbf{x})$, and we can write down its electrostatic energy easily:

$$\hat{H}_n = \hat{1} \times \frac{1}{2} \frac{e^2}{4\pi\epsilon_{\text{vac}}} \int d\mathbf{x} \int d\mathbf{x}' n(\mathbf{x})n(\mathbf{x}') \frac{e^{-\mu|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|}. \quad (3.16)$$

In an additional simplification, we will smear out the positive charge homogeneously. Its periodic modulation will in first instance lead to a band mass, an effect that we can already take into account through m . The assumption of homogeneously smeared out classical positive charge for the background is called the **Jellium model**. We find for the Hamiltonian of the ions $\hat{H}_n = \hat{1} \times H_n$ with

$$\begin{aligned} H_n &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_{\text{vac}}} \int d\mathbf{x} \int d\mathbf{u} \frac{N^2 e^{-\mu|\mathbf{u}|}}{V^2 |\mathbf{u}|} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_{\text{vac}}} \frac{N^2}{V} 4\pi \int_0^\infty du u^2 \frac{e^{-\mu u}}{u} \\ &= \frac{e^2}{2\epsilon_{\text{vac}}} \frac{N^2}{V\mu^2}. \end{aligned} \quad (3.17)$$

Of course we also need to take into account the interactions between the background “jelly” and the nimble conduction electrons ploughing through it. This is the Hamiltonian of a quantum particle, with position operator $\hat{\mathbf{r}}_j$, interacting with a classical charge density:

$$\hat{H}_{el-n} = -\frac{e^2}{4\pi\epsilon_{\text{vac}}} \sum_{j=1}^N \int d\mathbf{x} n(\mathbf{x}) \frac{e^{-\mu|\mathbf{x}-\hat{\mathbf{r}}_j|}}{|\mathbf{x}-\hat{\mathbf{r}}_j|}. \quad (3.18)$$

As we assumed that the background charge is homogenous, we can choose the origin of the \mathbf{x} integration as we want and place it in $\langle \hat{\mathbf{r}}_j \rangle$ and obtain

$$\begin{aligned} \langle \hat{H}_{el-n} \rangle &= -\frac{e^2}{4\pi\epsilon_{\text{vac}}} \sum_{j=1}^N \hat{1} \times \int d\mathbf{x} \frac{N e^{-\mu|\mathbf{x}|}}{V |\mathbf{x}|} \\ &= \frac{-e^2}{\epsilon_{\text{vac}}} \frac{N^2}{V\mu^2}. \end{aligned} \quad (3.19)$$

The sum of the Hamiltonian of the background interacting with itself and with the electrons leads to another diverging energy contribution in the Jellium model:

$$\begin{aligned}\langle \hat{H}_n + \hat{H}_{el-n} \rangle &= \left(\frac{-e^2}{\varepsilon_{\text{vac}}} \frac{N^2}{V\mu^2} + \frac{e^2}{2\varepsilon_{\text{vac}}} \frac{N^2}{V\mu^2} \right) \\ &= \frac{-e^2}{2\varepsilon_{\text{vac}}} \frac{N^2}{V\mu^2}.\end{aligned}$$

Compare this with the divergent term in the Coulomb interaction between electrons, the term that collects the contributions from $Q = 0$ momentum transfers, and we find that all divergencies cancel out in the thermodynamic limit:

$$\langle \hat{V}_C^{\text{divergent}} + \hat{H}_n + \hat{H}_{el-n} \rangle = 0.$$

This illustrates the importance of taking the thermodynamic limit before $\mu \rightarrow 0$. We are only interested in terms of the order N^2/V in comparison to terms of order N/V .

So, in conclusion, what the jellium background does is in essence cancel out the $Q = 0$ terms in our electron Hamiltonian. The final form of the electron Hamiltonian in the Jellium model is:

$$\begin{aligned}\hat{H} &= \sum_{\mathbf{k},\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} \\ &+ \frac{1}{2V} \sum_{\mathbf{Q} \neq 0} \frac{e^2}{\varepsilon_{\text{vac}} Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1},\end{aligned}$$

3.2 Perturbation theory for electron-electron interactions

The electron-electron interaction term in the Hamiltonian is something that you have not yet studied in the introductory solid state course. What is its effect on the ground state energy? Whenever we cannot exactly diagonalize a Hamiltonian in quantum mechanics, we resort to either perturbation theory or variational analysis. In this section, we illustrate the use of perturbation theory on a many-body system. The goal is to perturbatively take the interaction part of the Hamiltonian into account. First, we need to remind ourselves of the solutions for the unperturbed case.

Without the Coulomb interactions, we have the unperturbed, free-electron Hamiltonian

$$\hat{H}_0 = \sum_{\mathbf{k},\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma}. \quad (3.20)$$

The eigenstates of this Hamiltonian are precisely our many-body basis states, built from the single-particle plane-wave states $|\varphi_{\mathbf{k},\sigma}\rangle$. Since we work with fermions, the occupation $N_{\mathbf{k},\sigma}$ of each single-particle state cannot be larger than 1. The many-body ground state is the lowest energy state by definition and so it should be built up from all the lowest energy single-particle states. This is similar to filling up the atomic orbitals from lowest energy to higher energies. Since the energy corresponding to a single particle state $|\varphi_{\mathbf{k},\sigma}\rangle$ equals $(\hbar k)^2/2m$, the ground state consists of single-particles states with $k \leq k_F$:

$$\begin{aligned} |\Psi_0\rangle &= \left| \dots \varphi_{\mathbf{k}_j,+} \varphi_{\mathbf{k}_j,-} \dots \right\rangle \text{ met all } |\mathbf{k}_j| \leq k_F \\ &= \left(\prod_{|\mathbf{k}| \leq k_F} \hat{a}_{\mathbf{k},+}^\dagger \hat{a}_{\mathbf{k},-}^\dagger \right) |\emptyset\rangle. \end{aligned}$$

Here spin up is denoted by "+" and spin down by "-". We have

$$N_{\mathbf{k},\sigma} = \langle \Psi_0 | \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} | \Psi_0 \rangle = \begin{cases} 1 & \text{for } k \leq k_F \\ 0 & \text{for } k > k_F \end{cases}. \quad (3.21)$$

In \mathbf{k} -space (reciprocal space, wave vector space) all single-particle states within a sphere with radius k_F are occupied. This sphere is called the Fermi sphere. The single-particle energy of highest occupied single particle state, $(\hbar k_F)^2/(2m)$, is called the Fermi level E_F . We can find it by first determining the Fermi wave number k_F , the radius of the Fermi sphere. We get

$$N = \sum_{\mathbf{k},\sigma} \langle \Psi_0 | \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} | \Psi_0 \rangle = \sum_{\sigma} \frac{V}{(2\pi)^3} \int_{k \leq k_F} d\mathbf{k}, \quad (3.22)$$

where the sums over allowed wave numbers, (3.4), have been replaced by a continuous integral of the density of states in \mathbf{k} -space, (3.6). The well-known result for the Fermi wave vector in 3D is easily retrieved:

$$\begin{aligned} N &= 2 \frac{V}{(2\pi)^3} \frac{4\pi}{3} k_F^3 \\ \Leftrightarrow k_F &= \sqrt[3]{3\pi^2(N/V)}. \end{aligned} \quad (3.23)$$

A commonly used quantity in the theory of metals is the Wigner-Seitz radius. This is a dimensionless parameter r_s , equal to the radius (expressed in Bohr radii $a_{\text{Bohr}} = 0.5292$) of a sphere that has the same volume as the average volume per electron. It is a measure for the distance between the electrons, and is given by

$$\begin{aligned} \frac{V}{N} &= \frac{4\pi}{3} (a_{\text{Bohr}} r_s)^3 \\ \Leftrightarrow r_s &= \frac{[3(V/N)/(4\pi)]^{1/3}}{a_{\text{Bohr}}}, \end{aligned} \quad (3.24)$$

so that its link to the Fermi wave number is

$$k_F = \frac{1}{a_{\text{Bohr}}} \sqrt[3]{\frac{9\pi}{4}} \frac{1}{r_s}. \quad (3.25)$$

When we switch on the Coulomb interactions, the many-body state $|\Psi_0\rangle$ is no longer an eigenstate of the Hamiltonian, so it can no longer be the ground state. We want to treat these Coulomb interactions in first order perturbation theory to find the correction to the ground state energy. Of course we first need the zeroth order (unperturbed) value of the ground state energy:

$$\begin{aligned} \langle \Psi_0 | \hat{H}_0 | \Psi_0 \rangle &= \sum_{\mathbf{k}, \sigma} \frac{\hbar^2 k^2}{2m_e} \langle \Psi_0 | \hat{a}_{\mathbf{k}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} | \Psi_0 \rangle \\ &= 2 \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| < k_F} d\mathbf{k} \frac{\hbar^2 k^2}{2m_e} \\ &= 2 \frac{\hbar^2}{2m_e} \frac{V}{(2\pi)^3} \frac{4\pi k_F^5}{5} \\ &= N \times \frac{3}{5} \frac{\hbar^2 k_F^2}{2m_e} = N \frac{\hbar^2}{2m_e a_{\text{Bohr}}^2} \times \frac{2.21}{r_s^2}. \end{aligned} \quad (3.26)$$

So, the zeroth order estimate for the energy per electron is $3/5$ of the Fermi-energy $(\hbar k_F)^2/(2m)$.

The first order perturbation theory correction to this energy is

$$\Delta E_1 = \frac{1}{2V} \sum_{\mathbf{Q} \neq 0} \frac{e^2}{\varepsilon_{\text{vac}} Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \langle \Psi_0 | \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1} | \Psi_0 \rangle \quad (3.27)$$

The expectation value is determined as follows:

- The single-particle states associated with quantum numbers \mathbf{k}_1, σ_1 and \mathbf{k}_2, σ_2 have to be occupied in $|\Psi_0\rangle$, otherwise the annihilation operators would give zero.
- Similarly, the states with $\mathbf{k}_1 - \mathbf{Q}, \sigma_1$ and $\mathbf{k}_2 + \mathbf{Q}, \sigma_2$ have to be unoccupied in $|\Psi_0\rangle$, otherwise the creation operators acting to the left on $\langle \Psi_0 |$ would give zero.
- We start from the Fermi sphere $|\Psi_0\rangle$, and the annihilation operators $\hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1}$ blow two holes in the poor Fermi sphere. If we are to finish at the end of the day with again an immaculate Fermi sphere for $\langle \Psi_0 |$, then the creation operators $\hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger$ must patch the holes drilled by the annihilation operators.

So, we have to pair up the damage-making annihilation operators and the patching creation operators, otherwise the expectation value is zero. This

pairing up can occur in two possible ways:

$$\begin{array}{c} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1} \\ \text{[-----]} \end{array} \quad \text{or} \quad \begin{array}{c} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1}, \\ \text{[-----]} \end{array}$$

this means

$$\left\{ \begin{array}{l} \mathbf{k}_2 + \mathbf{Q}, \sigma_2 = \mathbf{k}_1, \sigma_1 \\ \mathbf{k}_1 - \mathbf{Q}, \sigma_1 = \mathbf{k}_2, \sigma_2 \end{array} \right\} \quad \text{or} \quad \left\{ \begin{array}{l} \mathbf{k}_2 + \mathbf{Q}, \sigma_2 = \mathbf{k}_2, \sigma_2 \\ \mathbf{k}_1 - \mathbf{Q}, \sigma_1 = \mathbf{k}_1, \sigma_1 \end{array} \right\}.$$

The second set of conditions can only be satisfied if $\mathbf{Q} = \mathbf{0}$, and we have excluded these terms from the electron interaction Hamiltonian, as they are perfectly cancelled by the Jellium background. These terms correspond to the direct Coulomb interaction between the electrons (cancelled by the classical Coulomb interaction with the positive background).

But there are non-zero terms: the first condition can be satisfied if $\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$ and $\sigma_1 = \sigma_2$. This is a contribution that only occurs between electrons with the same spin, and we call this term the “exchange energy”, as we have exchanged the order of patchings for the Fermi sphere. Its origin is the Pauli exclusion principle: due to Pauli exclusion, an electron with spin-up keeps the other electrons with spin-up at bay, they cannot come to the same position. This leaves an “exchange hole” in the electron gas around an electron with a given spin. When we smear the classical positive jellium charge homogeneously over the volume, we have a small excess of positive charge in the exchange hole, lowering the energy. In general, exchange contributions in Fermi gases weaken the effects of interaction: same-spin fermions undergo a weaker interaction than opposite-spin fermions.

The expectation value becomes

$$\begin{aligned} \langle \Psi_0 | \hat{a}_{\mathbf{k}_2, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_1} \hat{a}_{\mathbf{k}_1, \sigma_1} | \Psi_0 \rangle &= \langle \Psi_0 | \hat{a}_{\mathbf{k}_2, \sigma_1}^\dagger \left(\delta_{\mathbf{k}_2, \mathbf{k}_1} - \hat{a}_{\mathbf{k}_2, \sigma_1} \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger \right) \hat{a}_{\mathbf{k}_1, \sigma_1} | \Psi_0 \rangle \\ &= n_{\mathbf{k}_1, \sigma_1} \delta_{\mathbf{k}_2, \mathbf{k}_1} - n_{\mathbf{k}_1, \sigma_1} n_{\mathbf{k}_2, \sigma_1} \end{aligned} \quad (3.28)$$

where the term with the delta function is again absent in the summation because it corresponds to. The first order energy correction becomes

$$\begin{aligned} \Delta E_1 &= -\frac{1}{2V} \sum_{\sigma} \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \frac{e^2}{\varepsilon_{\text{vac}} (\mathbf{k}_1 - \mathbf{k}_2)^2} n_{\mathbf{k}_1, \sigma} n_{\mathbf{k}_2, \sigma} \\ &= -\frac{1}{V} \sum_{\mathbf{k}_1 < k_F} \sum_{\mathbf{k}_2 < k_F, \mathbf{k}_2 \neq \mathbf{k}_1} \frac{e^2}{\varepsilon_{\text{vac}} (\mathbf{k}_1 - \mathbf{k}_2)^2}. \end{aligned} \quad (3.29)$$

where the terms with $k_2 = k_1$ are not present in the sum. This becomes

$$\begin{aligned} \Delta E_1 &= -\frac{Ve^2}{(2\pi)^6 \varepsilon_{\text{vac}}} \int_{\mathbf{k}_1 < k_F} d\mathbf{k}_1 \int_{\mathbf{k}_2 < k_F} d\mathbf{k}_2 \frac{1}{(\mathbf{k}_1 - \mathbf{k}_2)^2} \\ &= -\frac{Ve^2}{8\pi^4 \varepsilon_{\text{vac}}} k_F^4 \int_0^1 du_1 \int_0^1 du_2 \int_{-1}^1 dx \frac{u_1^2 u_2^2}{u_1^2 + u_2^2 - 2u_1 u_2 x} \end{aligned}$$

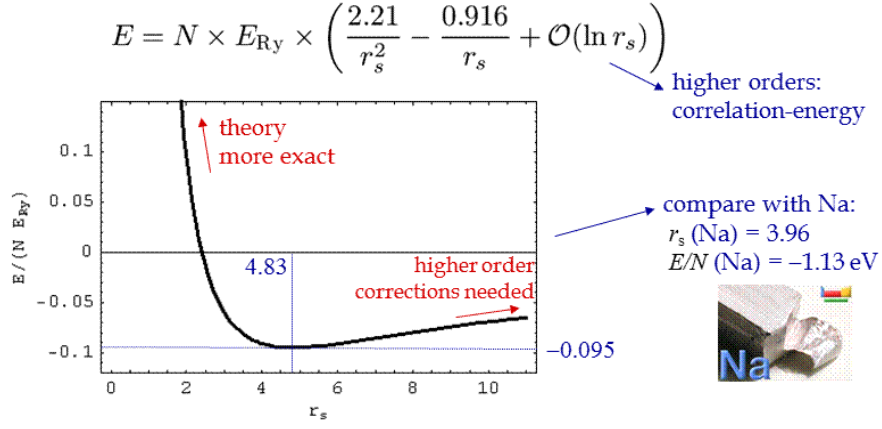


Figure 3.1: The result of the energy of the electron gas in a metal, up to first order perturbation in the electron-electron interactions.

The integral can be performed analytically, or on a computer, and we find

$$\Delta E_1 = -N \frac{e^2}{4\pi\epsilon_{\text{vac}}} \frac{3}{2\pi} k_F = -N \frac{e^2}{4\pi\epsilon_{\text{vac}} a_{\text{Bohr}}} \frac{0.916}{r_s} \quad (3.30)$$

Since for the Bohr radius we have by definition that

$$\frac{\hbar^2}{2m_e a_{\text{Bohr}}^2} = \frac{e^2}{4\pi\epsilon_{\text{vac}} a_{\text{Bohr}}} = E_{\text{Ry}},$$

with E_{Ry} the “Rydberg energy”, we can write the total energy of the interacting electron gas up to first order as:

$$E = N \times E_{\text{Ry}} \times \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \mathcal{O}(\ln r_s) \right) \quad (3.31)$$

This result is plotted in figure 3.1. The next term in the series is of order $\ln(r_s)$. A few remarks need to be made about this result for the binding energy of electrons in metals:

- This binding energy has a minimum, at $r_s = 4.83$ (there, the energy per electron is -0.095 Rydberg).
- At large values of r_s there is no doubt that we have to go beyond first-order perturbation theory. However, for sodium ($r_s = 3.86$) the result is still quite good: the experimental result of -1.13 eV agrees with the theoretical value of -1.21 eV . In general the results for the alkali metals work out well, for the other metals the result is less good. This is also due to the

fact that the other metals have Fermi surface that are not really spheres, due to their complicated band structure – it is however not too difficult to take that into account in the theory.

- The bulk modulus $B = -V(\partial^2 E / \partial V^2)_N$ can be computed using the relation between r_s and V . It becomes zero for $r_s = 6.03$, which points to an instability. In the limit of low density ($r_s \rightarrow \infty$) Eugene Wigner has shown that the Coulomb interaction dominates the kinetic energy term so that it becomes energetically advantageous for electrons to localize in a lattice. This is called the Wigner lattice.
- Before trying to take into account higher order corrections to the Coulomb energy, we need to have a better description of the background in order to get next order corrections.

3.3 Phonons

3.3.1 Phonon Hamiltonian

Phonons are quantized vibrations of the crystal lattice. In the introductory course on solid state physics (and in any course on waves and vibrations), the dispersion relation $\omega_{\mathbf{k},\lambda}$ of phonons with wave vector \mathbf{k} and mode λ ¹ is calculated. Often, one uses masses connected by springs as a model system to derive examples of dispersion relations. In practice, the phonon dispersion can be measured by for example Raman spectroscopy. For each wave number \mathbf{k} and mode λ we do not only have the frequency of the oscillation, but also its amplitude. This is quantized just as for harmonic oscillators, and leads to bosonic creation and annihilation operators $\hat{b}_{\mathbf{k},\lambda}^\dagger$ en $\hat{b}_{\mathbf{k},\lambda}$. The phonon Hamiltonian that we take from these earlier courses is

$$\hat{H}_{\text{fon}} = \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k},\lambda} \hat{b}_{\mathbf{k},\lambda}^\dagger \hat{b}_{\mathbf{k},\lambda}, \quad (3.32)$$

We've used the fact that the phonon dispersions that we study will often only depend on the size of the wave vector but not its direction. In actual materials this is not necessarily so. In our examples we will also only use a single phonon branch, so we do not need the label λ . The phonons in this model do not interact with each other, and this is yet another approximation, be it a very useful one.

¹Modes can be transverse or longitudinal, and acoustic or optical.

3.3.2 Electron-phonon interaction

The interactions between electrons and phonons is a very important topic in solid state physics. In metals it influence the transport properties of electrons and may lead to superconductivity. In semiconductors and polar crystals it influences mobility and optical response. To find the generic form of the interaction Hamiltonian, we start from the interaction potential between the ions and the electrons, and sum this over all ions and over all electrons:

$$\hat{H}_{\text{int}} = \sum_{i=1}^N V(\hat{\mathbf{r}}_i) \quad (3.33)$$

$$= \sum_{i=1}^N \left[\sum_{j=1}^{N_{\text{ion}}} V_{\text{e-i}}(\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_j) \right]. \quad (3.34)$$

Here $V_{\text{e-i}}$ obviously is the potential between electrons (at positions $\hat{\mathbf{r}}_i$) and lattice ions, atoms or molecules (at positions $\hat{\mathbf{R}}_j$). The position of ion or atom number j can be written as an equilibrium lattice position \mathbf{R}_j^0 plus a deviation out of equilibrium $\hat{\mathbf{Q}}_j$. These deviations are supposed to be small – indeed the Lindemann criterion states that if the atoms wander more than roughly 10% of a lattice distance away from their equilibrium position, the lattice melts. We then have a small parameter with which to expand the electron-ion potential:

$$\begin{aligned} V_{\text{e-i}}(\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_j) &= V_{\text{e-i}}(\hat{\mathbf{r}}_i - \mathbf{R}_j^0 - \hat{\mathbf{Q}}_j) \\ &= V_{\text{e-i}}(\hat{\mathbf{r}}_i - \mathbf{R}_j^0) - \hat{\mathbf{Q}}_j \cdot [\nabla V_{\text{e-i}}(\hat{\mathbf{r}}_i - \mathbf{R}_j^0)] + \mathcal{O}(\hat{\mathbf{Q}}_j^2) \end{aligned} \quad (3.35)$$

The higher-order terms describe the anharmonic oscillations and are not taken into account – they were already neglected in the phonon Hamiltonian (3.32) where they would lead to phonon-phonon scattering. The term $V_{\text{e-i}}(\hat{\mathbf{r}}_i - \mathbf{R}_j^0)$ does not depend on the deviations out of equilibrium and represents the effect of the perfect lattice. This is the periodic potential considered by Bloch, and we know its effect: it generates band mass and band gaps. In the jellium model this potential is even simpler: it is just a homogeneous constant. So, in the present approximation the quantum dynamics of the lattice is taken into account through the gradient term only. We can Fourier transform this particular term:

$$\begin{aligned} V(\hat{\mathbf{r}}_i) &= - \sum_{j=1}^{N_{\text{ion}}} \hat{\mathbf{Q}}_j \cdot [\nabla V_{\text{e-i}}(\hat{\mathbf{r}}_i - \mathbf{R}_j^0)] \\ &= - \sum_{j=1}^{N_{\text{ion}}} \sum_{\mathbf{q}} \left(\hat{\mathbf{Q}}_j \cdot \mathbf{q} \right) V_{\text{e-i}}(\mathbf{q}) \exp\{i\mathbf{q} \cdot (\hat{\mathbf{r}}_i - \mathbf{R}_j^0)\} \end{aligned} \quad (3.36)$$

In this expression we identify

$$\frac{1}{\sqrt{N_{\text{ion}}}} \sum_{j=1}^{N_{\text{ion}}} \hat{\mathbf{Q}}_j \exp\{-i\mathbf{q} \cdot \mathbf{R}_j^0\} = \hat{\mathbf{Q}}_{\mathbf{q}} = s_{\mathbf{q}} \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}}}} (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger). \quad (3.37)$$

This connection between the displacement operators $\hat{\mathbf{Q}}_j$ for the ions and the creation and annihilation operators for the phonons is the same as the connection between the position operator of a harmonic oscillator and its creation and annihilation operators. The student who wants more details will find it in the classic book of Ziman (cf. bibliography). There is one addition: the vector $\mathbf{s}_{\mathbf{q}}$ represents the polarisation vector of the phonon, i.e. the direction of the displacement $\hat{\mathbf{Q}}_j$. We have transversal phonons if $\mathbf{q} \cdot \mathbf{s}_{\mathbf{q}} = 0$, and longitudinal phonons for $\mathbf{q} \times \mathbf{s}_{\mathbf{q}} = 0$. We can now separate the parts of $V(\hat{\mathbf{r}}_i)$ that contain the operator character from the other parts, and group all factors that do not have operator character in a function $M(\mathbf{q})$:

$$V(\hat{\mathbf{r}}_i) = \sum_{\mathbf{q}} M(\mathbf{q})(\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger) \times e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_i}. \quad (3.38)$$

For now, we do not specify $M(\mathbf{q})$, just as we did not specify the electron-ion or electron-atom potential. It is an interaction amplitude.

Expression (3.38) is still given in first quantization as far as the electron operators are concerned. We can transform it to second quantization using the rules given in chapter 2:

$$\begin{aligned} \sum_{i=1}^N e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_i} &= \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \left[\int d\mathbf{r} \varphi_{\mathbf{k}', \sigma'}^*(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} \varphi_{\mathbf{k}, \sigma}(\mathbf{r}) \right] \hat{a}_{\mathbf{k}'}^\dagger \hat{a}_{\mathbf{k}} \\ &= \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \delta_{\sigma \sigma'} \left[\int d\mathbf{r} \frac{e^{-i\mathbf{k}' \cdot \mathbf{r}}}{\sqrt{V}} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{V}} \right] \hat{a}_{\mathbf{k}'}^\dagger \hat{a}_{\mathbf{k}} \\ &= \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \delta_{\sigma \sigma'} \delta(\mathbf{k} + \mathbf{q} - \mathbf{k}') \hat{a}_{\mathbf{k}'}^\dagger \hat{a}_{\mathbf{k}} \\ &= \sum_{\mathbf{k}, \sigma} \hat{a}_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} \end{aligned} \quad (3.39)$$

As a consequence, we find for the electron-phonon interaction Hamiltonian the following generic form:

$$\hat{H}_{\text{int}} = \sum_{\mathbf{q}} \sum_{\mathbf{k}, \sigma} M(\mathbf{q})(\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger) \hat{a}_{\mathbf{k}+\mathbf{q}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} \quad (3.40)$$

This form inspires the introduction of a short-hand notation, the phonon operator

$$\hat{B}_{\mathbf{q}} = \hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger = \hat{B}_{-\mathbf{q}}^\dagger \quad (3.41)$$

The reasoning behind introducing this operator is that creating a phonon with wave number $-\mathbf{q}$ is the same as removing a phonon with wave number \mathbf{q} , so we group both processes. Then $\hat{B}_{\mathbf{q}}$ is a more physical form for the phonon operator.

What story does the sequence of creation and annihilation operators in (3.40) tell? An electron comes by with momentum $\hbar \mathbf{k}$. It has a certain quantum

mechanical amplitude (not probability!) $M(\mathbf{q})$ to either absorb a phonon with momentum $\hbar\mathbf{q}$ or emit a phonon with momentum $-\hbar\mathbf{q}$. The effect is the same: the final momentum of the electron is $\hbar(\mathbf{k} + \mathbf{q})$.

3.3.3 Summary

The total Hamiltonian for the system of electrons and phonons is, in second quantization, given by:

$$\begin{aligned} \hat{H} = & \sum_{\mathbf{k},\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} + \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k},\lambda} \hat{b}_{\mathbf{k},\lambda}^\dagger \hat{b}_{\mathbf{k},\lambda} \\ & + \frac{1}{2V} \sum_{\mathbf{Q} \neq 0} \frac{e^2}{\epsilon_{\text{vac}} Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1} \\ & + \sum_{\mathbf{q}, \lambda} \sum_{\mathbf{k}, \sigma} M_\lambda(\mathbf{q}) (\hat{b}_{\mathbf{q}, \lambda} + \hat{b}_{-\mathbf{q}, \lambda}^\dagger) \hat{a}_{\mathbf{k} + \mathbf{q}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} \end{aligned} \quad (3.42)$$

The first line contains the Hamiltonian of the non-interacting electron gas and the non-interacting gas of phonons. The second line represents the Coulomb interaction between the electrons. The third line describes the interaction between phonons and electrons. Now we have finally obtained the full Hamiltonian that we want to study – we’ll search for the ground state and the ground state energy of this Hamiltonian, and try to understand also thermodynamical properties generated by it. This is a very complicated problem, and we will need the full force of many-body theories for it. This will be the object of the next chapter.

First, we’ll illustrate the use of perturbation theory and variational theory on a simpler problem: a single electron in an polar crystal. That will allow us not only to do some interesting solid state physics, but it will also show us the difficulties of perturbation theory as applied in its usual form. The Green’s function method explained in the next chapter will basically be a better way to systematically do perturbation theory and to select out those contributions that we think are important. But first, our starter: the polaron.

3.4 The Polaron problem

The calculation of the exact expression for $M(\mathbf{q})$ is not a trivial task and depends on the interaction potentials between the lattice of polarizable, displaceable atoms or ions. We have many possibilities: the same generic form of the Hamiltonian occurs for electrons interacting with longitudinal optical (LO) phonons or longitudinal acoustic phonons, or magnons, or librons, or vibrons,... The only thing that changes is what we plug in for the dispersion $\hbar\omega_{\mathbf{q}}$ and for the interaction amplitude $M(\mathbf{q})$.

We’ll look at a special case, polar crystals or ionic crystals where the positive and negative ions alternate, such as in salt, NaCl. If we place an electron in these

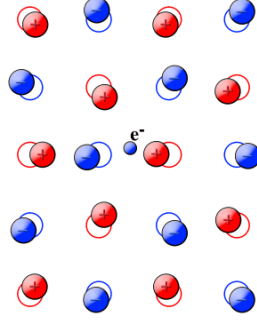


Figure 3.2: Illustration of a Fröhlich polaron: the electron deforms the polar lattice and drags this deformation along as it moves.

systems, it will attract the positive ions and repel the negative ions: in general, it will distort the lattice. The positive ions are pulled towards the electrons, the negative ones in the direction away from the electron, so it is clear that the crystal vibration mode with which the electron will interact most strongly is the longitudinal optical phonon in this case. That's nice, since optical phonons have a flat dispersion $\hbar\omega_{\mathbf{q}} = \hbar\omega_{LO}$ with $\hbar\omega_{LO}$ a constant of about 10-100 meV. *The electron, taken together with its lattice deformation, is called a polaron*, as illustrated in figure (3.2).

Fröhlich² derived the interaction amplitude for electrons to emit or absorb LO phonons. It is given by

$$M(\mathbf{q}) = -i \frac{\sqrt{\hbar\omega_{LO}}}{q} \frac{2\pi e^2}{\sqrt{V}} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right). \quad (3.43)$$

Here ε_{∞} is the high-frequency permittivity (the square of the index of refraction) and ε_0 is the static dielectric constant (the one that changes the electrostatic energy of a capacitor if you shove a piece of the material between the capacitor plates). In order to be completely accurate we should replace $1/q$ in this expression by

$$\frac{1}{q} \rightarrow \frac{\mathbf{s}_{LO} \cdot \mathbf{q}}{|q|^2} \quad (3.44)$$

where \mathbf{s}_{LO} is the direction of the displacements, and in the LO case these are parallel to \mathbf{q} .

In order to characterize the strength of the coupling between electrons and LO phonons, Fröhlich introduced the dimensionless parameter α , given by

$$\alpha = \frac{e^2}{\hbar} \sqrt{\frac{m}{2\hbar\omega_{LO}}} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \quad (3.45)$$

²H. Fröhlich, H. Pelzer and S. Zienau, Philos. Mag. 41, 221 (1950); J. T. Devreese, in Encyclopedia of Applied Physics, edited by G. L. Trigg (VCH, New York, 1996), Vol. 14.

and he re-writes the interaction amplitude as

$$M(q) = -i\sqrt{\frac{4\pi\alpha}{V}}\frac{1}{q}\hbar\omega_{LO}\sqrt{\frac{\hbar}{2m\omega_{LO}}} \quad (3.46)$$

The Hamiltonian for *a single electron* in a bath of LO phonons is then given by

$$\hat{H}_{\text{Fröhlich}} = \frac{\hat{p}^2}{2m} + \sum_{\mathbf{q}} \hbar\omega_{LO} \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} + \sum_{\mathbf{q}} M(q)(\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger)e^{i\mathbf{q}\cdot\hat{\mathbf{r}}} \quad (3.47)$$

Since we look at a single electron, there's no need for second quantization and we keep the first quantized position $\hat{\mathbf{r}}$ and momentum $\hat{\mathbf{p}}$ for the electron.

There's a final step to go in writing down the polaron Hamiltonian. We are going to use units in which $\hbar = 2m = \omega_{LO} = 1$. Thus, lengths are measured in units $\sqrt{\hbar/(2m\omega_{LO})}$ and any results we get for the energy are measured in units $\hbar\omega_{LO}$. We use these “polaronic” units to simplify the Fröhlich Hamiltonian to

$$\hat{H}_{\text{Fröhlich}} = \hat{p}^2 + \sum_{\mathbf{q}} \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} - i\sqrt{\frac{4\pi\alpha}{V}} \sum_{\mathbf{q}} \frac{1}{q}(\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^\dagger)e^{i\mathbf{q}\cdot\hat{\mathbf{r}}} \quad (3.48)$$

3.4.1 Perturbation theory for electron-phonon interactions

Just as we studied the effects of electron-electron interactions using first perturbation theory, we can investigate (3.48) with this theory. The unperturbed parts of the Hamiltonian,

$$\hat{H}_0 = \hat{p}^2 + \sum_{\mathbf{q}} \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}}, \quad (3.49)$$

have plane wave eigenfunctions for the single electron, $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ and occupation number many-body basis kets $|n_1, \dots, n_{\mathbf{q}}, \dots\rangle_{ph}$ as eigenfunctions of the phonon part. The eigenfunctions of \hat{H}_0 are

$$|\psi_{\mathbf{k}}\rangle |n_1, \dots, n_{\mathbf{q}}, \dots\rangle_{ph} \quad (3.50)$$

The energy of this state is given by

$$\begin{aligned} E_{\mathbf{k}, \{n_{\mathbf{q}}\}}^{(0)} &= \frac{(\hbar k)^2}{2m} + \hbar\omega_{LO} \sum_{\mathbf{q}} n_{\mathbf{q}} \\ &\rightarrow k^2 + \sum_{\mathbf{q}} n_{\mathbf{q}} \text{ in our units} \end{aligned} \quad (3.51)$$

The ground state is given by $\mathbf{k} = 0$ and the phonon vacuum $|\emptyset\rangle_{ph}$. We look at unperturbed states with a phonon vacuum $|\psi_{\mathbf{k}}\rangle |\emptyset\rangle_{ph}$ and ask: how does the

energy $E_{\mathbf{k}}^{(0)} = (\hbar k)^2/(2m)$ of the electron change due to the coupling with the bath of phonons? This is the central question of *the polaron problem*.

In first order perturbation theory we do not get any correction, since

$$\langle \emptyset | \langle \psi_{\mathbf{k}} | \hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^{\dagger} | \psi_{\mathbf{k}} \rangle | \emptyset \rangle_{ph} = 0. \quad (3.52)$$

We need to go to second order perturbation theory, and consider

$$\Delta E_{\mathbf{k}}^{(2)} = \sum_{|exc\rangle \neq |\psi_{\mathbf{k}}\rangle |\emptyset\rangle_{ph}} \frac{|\langle exc | \hat{H}_I | \psi_{\mathbf{k}} \rangle |\emptyset\rangle_{ph}|^2}{E_{\mathbf{k}}^{(0)} - E_{exc}^{(0)}}. \quad (3.53)$$

Here $|exc\rangle$ represents any state of the unperturbed Hamiltonian that is different from the original state $|\psi_{\mathbf{k}}\rangle |\emptyset\rangle_{ph}$. If the original state is the ground state then this is a summation over all excited states, hence then symbol $|exc\rangle$. The perturbation Hamiltonian is

$$\hat{H}_I = -i\sqrt{\frac{4\pi\alpha}{V}} \sum_{\mathbf{q}} \frac{1}{q} (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^{\dagger}) e^{i\mathbf{q}\cdot\mathbf{r}}. \quad (3.54)$$

For this perturbation, the only excited states that give an expectation value that is different from zero in (3.53) are those that contain a single phonon. If this phonon has wave number \mathbf{q} , the electron has lost momentum $\hbar\mathbf{q}$, so $|exc\rangle = |\psi_{\mathbf{k}-\mathbf{q}}\rangle |n_{\mathbf{q}} = 1\rangle_{ph}$. Then

$$\begin{aligned} \langle n_{\mathbf{q}} = 1 | \langle \psi_{\mathbf{k}-\mathbf{q}} | \hat{H}_I | \psi_{\mathbf{k}} \rangle | \emptyset \rangle_{ph} &= -i\sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} \langle \psi_{\mathbf{k}-\mathbf{q}} | e^{i\mathbf{q}\cdot\mathbf{r}} | \psi_{\mathbf{k}} \rangle \\ &= -i\sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} \end{aligned} \quad (3.55)$$

The unperturbed energy of this excited state is

$$\begin{aligned} E_{exc}^{(0)} &= \frac{\hbar^2(k-q)^2}{2m} + \hbar\omega_{LO} \\ \rightarrow E_{exc}^{(0)} &= (k-q)^2 + 1 \text{ in our units} \end{aligned} \quad (3.56)$$

Puzzling all this together, we get

$$\Delta E_{\mathbf{k}}^{(2)} = \sum_{\mathbf{q}} \frac{\left| -i\sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} \right|^2}{k^2 - (k-q)^2 - 1} \quad (3.57)$$

Replacing the summation over allowed wave number by an integral over reciprocal space we get

$$\Delta E_{\mathbf{k}}^{(2)} = \frac{V}{(2\pi)^3} \int d^3\mathbf{q} \left| -i\sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} \right|^2 \frac{1}{k^2 - (k-q)^2 - 1} \quad (3.58)$$

$$= -\frac{1}{2\pi^2} \alpha \int d^3\mathbf{q} \frac{1}{q^2} \frac{1}{q^2 - 2\mathbf{k}\cdot\mathbf{q} + 1} \quad (3.59)$$

This can be developed in powers of k , and we get

$$\begin{aligned}\Delta E_{\mathbf{k}}^{(2)} &= -\frac{2}{\pi}\alpha \int_0^\infty dq \frac{1}{q^2 + 1} \\ &\quad -\frac{1}{\pi}\alpha k^2 \int_0^\infty dq \int_0^\pi d\theta \sin \theta \frac{4q^2 \cos^2 \theta}{(q^2 + 1)^3}\end{aligned}\quad (3.60)$$

The integrals can be performed analytically and we get

$$\Delta E_{\mathbf{k}}^{(2)} = -\alpha - \frac{\alpha}{6}k^2 \quad (3.61)$$

Plugging our units back, we get that the electron dispersion is modified by the electron-phonon interaction up to first order in α to

$$E_{\mathbf{k}} = -\alpha\hbar\omega_{LO} + \frac{(\hbar k)^2}{2m}(1 - \alpha/6) \quad (3.62)$$

The result is plotted in the inset of figure 3.3. The first term is an overall energy shift: the energy of the electron is lowered by an amount $-\alpha\hbar\omega_{LO}$ by the potential that it digs for itself in the lattice. The second term can be interpreted as a change in mass, we can absorb the factor $1 - \alpha/6$ in the mass and use a $m_{pol} = m/(1 - \alpha/6)$ as increased mass. This is a very logical conclusion: the electron deforming the polar lattice is much like a person walking on the beach, deforming the soft sand on which he or she walks. The deformed sand makes a dimple under the person, lowering the (gravitational) energy, but it also makes it harder to walk, increasing the mass or inertia of the person.

3.4.2 Variational analysis of electron-phonon interactions

The perturbational analysis is valid at small coupling. For large coupling, we can turn to another paragon of quantum theory, variational analysis. When the coupling is large, we expect that the electron digs a deep potential hole in the polar lattice, and the electron wave function can get localized in that self-induced potential. Note that it is not the entire polaron that gets localized, since the total momentum commutes with the Hamiltonian. In this regime, Pekar³ expects the wave function of the system to be a product

$$|\psi_e\rangle |\phi\rangle_{ph} \quad (3.63)$$

of an unknown phonon part $|\phi\rangle_{ph}$ and a normalized Gaussian electron trial wave function

$$\psi_e(\mathbf{r}) = \frac{1}{(\pi r_p^2)^{3/4}} e^{-r^2/(2r_p^2)} \quad (3.64)$$

³Pekar SI (1951). "Issledovaniya po Ekelektronnoj Teorii Kristallov". Gostekhizdat, Moskva. Geschreven in volle koude oorlog maar ik heb geen cyrillisch geïnstalleerd op mijn computer.

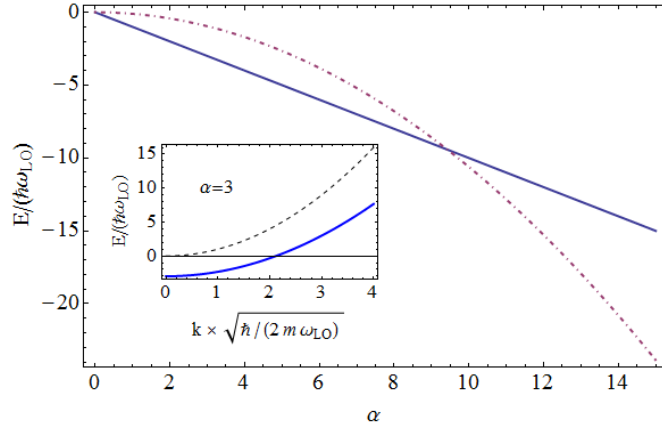


Figure 3.3: The main figure shows the result for the ground state energy of a polaron, from perturbation theory (blue line) and from variational analysis (purple dash-dotted line) – at low α the perturbation result is better than the variational value. The inset shows the dispersion relation (energy versus k) from perturbation theory (full line; the dashed line is $(\hbar k)^2/(2m)$). The dispersion shifts downwards and bends open (larger effective mass).

where r_p is the polaron radius (still using polaronic units), a variational parameter. We calculate the variational energy

$${}_{ph} \langle \phi | \langle \psi_e | \hat{H}_{\text{Fröhlich}} | \psi_e \rangle | \phi \rangle_{ph} \quad (3.65)$$

by first taking the expectation value with respect to the variational electron wave function. Using the electron kinetic energy

$$E_{kin}(r_p) = \left\langle \psi_e \left| \frac{\hat{p}^2}{2m} \right| \psi_e \right\rangle = \frac{3}{2r_p^2} \quad (3.66)$$

and electron density

$$\rho_{\mathbf{k}} = \langle \psi_e | e^{i\mathbf{k} \cdot \hat{\mathbf{r}}} | \psi_e \rangle = e^{-k^2 r_p^2 / 4} \quad (3.67)$$

we get

$$\begin{aligned} \langle \psi_e | \hat{H}_{\text{Fröhlich}} | \psi_e \rangle &= E_{kin} + \sum_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} \\ &+ \sum_{\mathbf{k}} \left[M(\mathbf{k}) \rho_{\mathbf{k}} \hat{b}_{\mathbf{k}} + M^*(\mathbf{k}) \rho_{\mathbf{k}}^* \hat{b}_{\mathbf{k}}^\dagger \right]. \end{aligned} \quad (3.68)$$

We can now complete the squares in the phonon operators, and write

$$\begin{aligned} \langle \psi_e | \hat{H}_{\text{Fröhlich}} | \psi_e \rangle &= E_{kin} + \sum_{\mathbf{k}} \left[\hat{b}_{\mathbf{k}}^\dagger + M(\mathbf{k})\rho_{\mathbf{k}} \right] \left[\hat{b}_{\mathbf{k}} + M^*(\mathbf{k})\rho_{\mathbf{k}}^* \right] \\ &\quad - \sum_{\mathbf{k}} |M(\mathbf{k})\rho_{\mathbf{k}}|^2 \end{aligned} \quad (3.69)$$

The second term represents a *displaced harmonic oscillator*. This means that in the ground state, the atoms are no longer in their original equilibrium positions, but in displaced positions due to the presence of the electron-phonon coupling. That is nothing but the deformed lattice! It is clear that the best variational phonon state is the state that forms the vacuum for the displaced phonon operator $\hat{d}_{\mathbf{k}} = \hat{b}_{\mathbf{k}} + M^*(\mathbf{k})\rho_{\mathbf{k}}^*/(\hbar\omega_{LO})$. In this state the variational energy is

$$E_{var} = E_{kin}(r_p) - \sum_{\mathbf{k}} \frac{|M(\mathbf{k})\rho_{\mathbf{k}}|^2}{\hbar\omega_{LO}} \quad (3.70)$$

$$= \frac{3}{2r_p^2} - \frac{\sqrt{2}}{\pi^{1/2}}\alpha\frac{1}{r_p} \quad (3.71)$$

Here we have performed the simple Gaussian integrals. The optimal value of r_p is

$$r_p = \frac{3\pi^{1/2}}{\sqrt{2}\alpha} \quad (3.72)$$

and the resulting variational energy is (in units $\hbar\omega_{LO}$)

$$E_{var} = -\frac{\alpha^2}{3\pi} \quad (3.73)$$

Now we find that the ground state energy goes down proportionally to $-\alpha^2$, rather than the perturbation result which is proportional to $-\alpha$. Both ground state energies as function of α are compared in figure 3.3. The variational result will be lower than the perturbation result for large α , which is the region of validity of the Pekar assumption.

What happens in between, for intermediate α ? How far away are we still from the exact result? What happens when there are multiple electrons, and we get an interacting polaron fluid? All these questions are beyond the scope of simple perturbational or variational analysis shown in this chapter. We need a more systematic approach, and setting up this approach is the goal pursued in the next chapter.

Chapter 4

Green's functions and Feynman diagrams

Green's functions and calculations with Feynman diagrams form the cornerstone of modern quantum physics, in particular in elementary particle physics and condensed matter physics. These methods allow to avoid the tangle of creation and annihilation operators that one encounters in the usual perturbation theory, by cleverly ordering and sorting them and making an intuitive graphical representation of what these products of operators actually mean. In this chapter, central to the whole course, we will explain these methods. In the next chapters they will be applied to calculate for example the response of electrons in metals.

4.1 Green's function: definition

The Green's function defined here is connected to the path integral propagator¹. The path integral propagator represents a quantum mechanical amplitude for a transition between fully specified initial and final states of the system. **The Green's function** is more specific: it **represents the amplitude that a single particle, added to the many-body system in a single-particle state $|\psi_k\rangle$ at time t' , will remain in the same single-particle state after a certain time $t - t'$** . Put in quantum mechanical notation, we define the Green's function by

$$G(k; t - t') := -i \left\langle \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') \right\rangle, \quad (4.1)$$

The creation and annihilation operators are given in the Heisenberg picture, and are time dependent. At temperature zero, the expectation value is

¹In the theory of distributions and partial differential equations one also uses a Green's function. That Green's function has close links to what is defined here, but in the context of many body theory it obtains a very specific meaning as discussed in the present chapter.

calculated in the many-body ground state $|\Psi_0\rangle$. For non-zero temperatures this becomes a quantum statistical expectation value, where in addition to the usual quantum expectation value we also average over a suitable statistical ensemble of many-body states. What else is in this formula? The symbol \mathcal{T} is the time ordering operator: it will order the operators that follow it in chronological order. The operator with the earliest time acts first, then the next, etc. So, in the above definition of the Green's function, the time ordering operator is a short-hand way to denote

$$G(k; t - t') = -i \begin{cases} \hat{a}_k(t) \hat{a}_k^\dagger(t') & \text{for } t' < t \\ \xi \hat{a}_k^\dagger(t') \hat{a}_k(t) & \text{for } t < t' \end{cases} \quad (4.2)$$

where for the fermions we obtain a minus sign when the two operators need to be swapped in order to get the chronological order. If the single-particle state $|\psi_k\rangle$ happens to be a single-particle eigenstate of the Hamiltonian with energy $\hbar\omega_k$, and the total energy of the many-body ground state $|\Psi_0\rangle$ is noted as $\hbar\omega_0$, then we have

$$\begin{aligned} \hat{a}_k^\dagger(t') |\Psi_0\rangle &= \exp\{i\omega_k t'\} |\Psi_0\rangle \\ \hat{a}_k(t) \hat{a}_k^\dagger(t') |\Psi_0\rangle &= \exp\{i\omega_k(t' - t)\} |\Psi_0\rangle \\ \Rightarrow G(k; t > t') &= -i \exp\{i\omega_k(t' - t)\}. \end{aligned} \quad (4.3)$$

In general, the single-particle states $|\psi_k\rangle$ that we choose for our second quantization formalism will lead to eigenstates of the system – if this were true we would have an exact solution to the problem. Bummer. But, usually, the Hamiltonian \hat{H} can be split up and written as a sum of a part \hat{H}_0 that does have known exact solutions, and a part that contains the other terms (usually the interaction contributions), \hat{H}_1 . Then the $|\psi_k\rangle$ are chosen to correspond to the single-particle eigenstates of \hat{H}_0 . The most useful representation to work in is then the Dirac picture (also known as interaction representation), rather than the Schrödinger or Heisenberg pictures. In the Dirac picture, both the wave functions and the operators depend on time – the wave functions follow a Schrödinger equation with \hat{H}_1 as Hamiltonian, and the operators follow a Heisenberg equation with \hat{H}_0 as Hamiltonian. If you've forgotten the Dirac picture, you'll find a summary of its main features in the addendum to this chapter.

Note that as $|\psi_k\rangle$ is not a single-particle eigenstate of the full Hamiltonian \hat{H} , the particle created by $\hat{a}_k^\dagger(t')$ at time t' , its amplitude will be spread over the true single-particle states by scattering and interactions. When we project the resulting state after some time $t - t'$ back onto the original state $|\psi_k\rangle$, we find how much amplitude is still left in that original state – this is the physical interpretation of Green's function in interacting systems. Taking the modulus squared tells us what the probability is to find the particle still in the original state, and this probability will go down the longer we wait since there is more chance for the particle to scatter into other states. This description closely matches what many solid-state experimental probes do: you shoot in a particle

beam (photons, electrons,...) and measure how much comes through in still the original beam, and how much is scattered. Our Green's functions seem perfectly suited to tell us the outcome of these experiment. If we can calculate them from the microscopic theories, this allows us to test these microscopic theories with experimental probes.

4.2 Non-interacting Green's functions

4.2.1 The filled Fermi sphere

Let's start our investigation of Green's functions with systems that have a known exact solutions. These will be non-interacting systems of electrons or phonons, and we will calculate their Green's functions first. For non-interacting electrons, we know that the ground state consists of a filled Fermi sphere $|\Psi_0^{\text{fb}}\rangle$. In a homogeneous medium, the single-particle states are plane waves, indexed by the wave vector \mathbf{k} and the spin quantum number σ . In the previous chapters we denoted these single-particle basis functions by $\varphi_{\mathbf{k},\sigma}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\eta_\sigma/\sqrt{V}$. The ground state energy for the filled Fermi sphere is (in 3D) given by $E_0 = (3/5)NE_F$.

Since all single-particle states with $k < k_F$ are filled, we find:

$$\langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma} \hat{a}_{\mathbf{k},\sigma}^\dagger | \Psi_0^{\text{fb}} \rangle = \theta(k > k_F). \quad (4.4)$$

It is only possible to create a particle in state $|\varphi_{\mathbf{k},\sigma}\rangle$ if this state is unoccupied ($k > k_F$). The annihilation operator brings the state with the extra particle back to the original ground state. Analogously we have

$$\langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} | \Psi_0^{\text{fb}} \rangle = \theta(k < k_F). \quad (4.5)$$

Note that these are the temperature zero results. At non-zero temperatures we need to use the Fermi-Dirac distribution rather than the filled Fermi sphere,

$$\theta(k < k_F) \rightarrow n_F(\mathbf{k}) = \frac{1}{\exp\{(E_k - \mu)/k_B T\} + 1}, \quad (4.6)$$

with $E_k = (\hbar k)^2/(2m)$ the energy corresponding to the single-particle state, and μ the chemical potential ($\mu \rightarrow E_F$ for $T \rightarrow 0$). The Green's function is

$$\begin{aligned} G(\mathbf{k}, \sigma; t - t') &= -i \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}(t) \hat{a}_{\mathbf{k},\sigma}^\dagger(t') | \Psi_0^{\text{fb}} \rangle \theta(t > t') \\ &\quad + i \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}^\dagger(t') \hat{a}_{\mathbf{k},\sigma}(t) | \Psi_0^{\text{fb}} \rangle \theta(t < t'). \end{aligned} \quad (4.7)$$

The expectation value evaluates to

$$\langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}(t) \hat{a}_{\mathbf{k},\sigma}^\dagger(t') | \Psi_0^{\text{fb}} \rangle = \langle \Psi_0^{\text{fb}} | e^{i\hat{H}t/\hbar} \hat{a}_{\mathbf{k},\sigma} e^{-i\hat{H}t/\hbar} e^{i\hat{H}t'/\hbar} \hat{a}_{\mathbf{k},\sigma}^\dagger e^{-i\hat{H}t'/\hbar} | \Psi_0^{\text{fb}} \rangle. \quad (4.8)$$

To calculate this, use

$$\begin{aligned}
 e^{i\hat{H}t'/\hbar} \hat{a}_{\mathbf{k},\sigma}^\dagger e^{-i\hat{H}t'/\hbar} |\Psi_0^{\text{fb}}\rangle &= e^{i\hat{H}t'/\hbar} \hat{a}_{\mathbf{k},\sigma}^\dagger |\Psi_0^{\text{fb}}\rangle \exp\{-iE_0 t'/\hbar\} \\
 &= \hat{a}_{\mathbf{k},\sigma}^\dagger |\Psi_0^{\text{fb}}\rangle \exp\{i(E_0 + E_k)t'/\hbar\} \exp\{-iE_0 t'/\hbar\} \\
 &= \hat{a}_{\mathbf{k},\sigma}^\dagger |\Psi_0^{\text{fb}}\rangle \exp\{iE_k t'/\hbar\}, \tag{4.9}
 \end{aligned}$$

where the second equality holds since $\hat{a}_{\mathbf{k},\sigma}^\dagger |\Psi_0^{\text{fb}}\rangle$ is also a many-body eigenstate of the non-interacting electron gas described by \hat{H}_0 . Moreover, it is a many-body eigenstate with total energy $E_0 + E_k$, since there is one additional electron in the single-particle state $|\varphi_{\mathbf{k},\sigma}\rangle$. Analogously we get

$$\begin{aligned}
 \langle \Psi_0^{\text{fb}} | e^{i\hat{H}t/\hbar} \hat{a}_{\mathbf{k},\sigma} e^{-i\hat{H}t/\hbar} &= \exp\{iE_0 t/\hbar\} \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma} e^{-i\hat{H}t/\hbar} \\
 &= \exp\{iE_0 t/\hbar\} \exp\{-i(E_0 + E_k)t/\hbar\} \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma} \\
 &= \exp\{-iE_k t/\hbar\} \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}, \tag{4.10}
 \end{aligned}$$

where the operators now act on the bra rather than the ket. Putting the previous results together we obtain

$$\begin{aligned}
 G(\mathbf{k}, \sigma; t - t') &= -i \exp\{-iE_k(t - t')/\hbar\} \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma} \hat{a}_{\mathbf{k},\sigma}^\dagger | \Psi_0^{\text{fb}} \rangle \theta(t > t') \\
 &\quad + i \exp\{-iE_k(t - t')/\hbar\} \langle \Psi_0^{\text{fb}} | \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma} | \Psi_0^{\text{fb}} \rangle \theta(t < t').
 \end{aligned}$$

Now we substitute (4.4) and (4.5) in this result:

$$\begin{aligned}
 G(\mathbf{k}, \sigma; t - t') &= -i \exp\{-iE_k(t - t')/\hbar\} \\
 &\quad \times [\theta(k > k_F) \theta(t > t') - \theta(k < k_F) \theta(t < t')]. \tag{4.11}
 \end{aligned}$$

That result is easy to interpret! The Heaviside functions make sure that you can create the electron (or hole) in the first place. But once it is created, it is also an eigenstate, nothing will happen to it. That is, the modulus of the amplitude (the probability) to remain in the same state must be 1. However, if we have a free particle with energy E_k and we leave it hanging in free space, what happens to the wave function is that the phase starts to rotate with frequency E_k/\hbar . So, the amplitude of a free particle in an energy eigenstate changes as $\exp\{-iE_k(t - t')/\hbar\}$ in time. And that is precisely the form of the Green's function.

The Fourier transform of the Green's function, from times $s = t - t'$ to frequencies, will be used with the following conventions for signs and 2π factors:

$$G(\mathbf{k}, \sigma; \omega) = \int_{-\infty}^{\infty} G(\mathbf{k}, \sigma; t) e^{i\omega t} dt, \tag{4.12}$$

$$G(\mathbf{k}, \sigma; t) = \int_{-\infty}^{\infty} G(\mathbf{k}, \sigma; \omega) e^{-i\omega t} \frac{d\omega}{2\pi}. \tag{4.13}$$

Note the location of the de factor 2π . Sometimes Fourier transforms are defined with a $\sqrt{2\pi}$ in the denominator for both dt and $d\omega$. A mnemonic to remember our convention is that *reciprocal space gets it all*, the full factor 2π . Frequencies moreover get the minus sign in $e^{-i\omega t}$ and wave number not $e^{i\mathbf{k}\cdot\mathbf{r}}$ so that we get for the space-time transform $\exp\{i(\mathbf{k}\cdot\mathbf{r} - \omega t)\}$.

We will use a very nice integral representation of the Heaviside step function $\theta(x)$:

$$\theta(x > 0) = - \int_{-\infty}^{\infty} \frac{du}{2\pi i} \frac{e^{-iux}}{u + i\delta}, \quad (4.14)$$

with δ an infinitesimal positive quantity. This formula can be proven by complex integration, where we complete the contour along the real axis with a large semi-circle. When $x > 0$ the contour need to be closed with a large semi-circle in the lower half plane, and this contains the simple pole $u = -i\delta$ with residue 1. When $x < 0$ then the contour has to be closed along the upper half plane, which does not contain poles, so that the integral evaluates to zero. With this integral representation we rewrite the heaviside functions in the Green's function and obtain

$$\begin{aligned} G(\mathbf{k}, \sigma; t - t') = & \int_{-\infty}^{\infty} \frac{d\nu}{2\pi} \left[\theta(k > k_F) e^{-iE_k(t-t')/\hbar} \frac{e^{-i\nu(t-t')}}{\nu + i\delta} \right. \\ & \left. - \theta(k < k_F) e^{-iE_k(t-t')/\hbar} \frac{e^{i\nu(t-t')}}{\nu + i\delta} \right]. \end{aligned} \quad (4.15)$$

Since the Fourier transform of the Green's function satisfies (4.13) and Fourier components are unique, we conclude by comparing the above result to (4.13) that

$$G(\mathbf{k}, \sigma; \omega) = \frac{\theta(k > k_F)}{\omega - E_k/\hbar + i\delta} + \frac{\theta(k < k_F)}{\omega - E_k/\hbar - i\delta}. \quad (4.16)$$

When we work in the grand canonical ensemble, setting the number of particles by fixing a chemical potential, it becomes useful to measure the energy from the chemical potential onwards. That is, we set $\omega \rightarrow (E - \mu)/\hbar$ and $E_k \rightarrow E_k - \mu$.

4.2.2 Green's function with field operators

Note that we can also define Green's functions with field operators:

$$G(\mathbf{r}, t; \mathbf{r}', t') := -i \left\langle \mathcal{T} \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right\rangle. \quad (4.17)$$

How this connects to our main definition can be seen by rewriting the field operators again as a function of the usual creation-and annihilation operators

according to definition (2.55) from the previous chapters and collecting the diagonal terms:

$$G(\mathbf{r}, t; \mathbf{r}', t') = \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) \psi_{\mathbf{k}}^*(\mathbf{r}') G(\mathbf{k}, t - t'). \quad (4.18)$$

For the special case of plane waves, both definitions of the Green's function are each other's Fourier transform. If the single-particle wave functions are $\varphi_{\mathbf{k},\sigma}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \eta_{\sigma} / \sqrt{V}$, then

$$G(\mathbf{r}, t; \mathbf{r}', t') = \delta_{\sigma,\sigma'} \int \frac{d\mathbf{k}}{(2\pi)^3} G(\mathbf{k}, t - t') e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \quad (4.19)$$

With this, we find for the filled Fermi sphere

$$\begin{aligned} G(\mathbf{r}, t; \mathbf{r}', t') &= \delta_{\sigma,\sigma'} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \int \frac{d\omega}{(2\pi)} e^{i\omega(t-t')} \\ &\quad \times \left(\frac{\theta(k > k_F)}{\omega - E_k/\hbar + i\delta} + \frac{\theta(k < k_F)}{\omega - E_k/\hbar - i\delta} \right), \end{aligned} \quad (4.20)$$

or

$$G(\mathbf{r}, t; \mathbf{r}', t') = \delta_{\sigma,\sigma'} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \int \frac{d\omega}{(2\pi)} e^{i\omega(t-t')} G(\mathbf{k}, t - t'). \quad (4.21)$$

We interpret this Green's function as the amplitude to find a particle at a position \mathbf{r} (and with spin σ) at a time t , given that it was created at time t' in at position \mathbf{r}' (and with spin σ'). Now the link with the Feynman propagator is very clear! Note that if the Hamiltonian does not contain terms that allow spin flips, then the particle created at space-time point $\{\mathbf{r}', t'\}$ should still have its original spin at space-time point $\{\mathbf{r}, t\}$, so we have a factor $\delta_{\sigma,\sigma'}$.

4.2.3 Phonon Green's function

Phonons are bosons, so that the creation and annihilation operators satisfy the commutation relation $[\hat{b}_{\mathbf{k},\lambda}, \hat{b}_{\mathbf{k}',\lambda'}^\dagger] = \delta(\mathbf{k} - \mathbf{k}') \delta_{\lambda\lambda'}$. Since creating a phonon with wave number \mathbf{k} is physically equivalent to destroying a phonon with wave number $-\mathbf{k}$, we introduce the following symmetrized operator:

$$\hat{B}_{\mathbf{k},\lambda} = \hat{b}_{\mathbf{k},\lambda} + \hat{b}_{-\mathbf{k},\lambda}^\dagger. \quad (4.22)$$

For phonon Green's functions we will use the symbol D rather than G , that we reserve for electrons. We define the phonon Green's function by

$$D(\mathbf{k}, \lambda; t - t') = -i \left\langle \mathcal{T} \hat{B}_{\mathbf{k},\lambda}(t) \hat{B}_{\mathbf{k},\lambda}^\dagger(t') \right\rangle. \quad (4.23)$$

The Hamiltonian for phonons is

$$\hat{H}^{\text{phonon}} = \sum_{\mathbf{k},\lambda} \hbar \omega_{\mathbf{k},\lambda} \hat{b}_{\mathbf{k},\lambda} \hat{b}_{\mathbf{k},\lambda}^\dagger. \quad (4.24)$$

The Heisenberg equation of motion for the phonon annihilation operators is

$$\begin{aligned}
 i\hbar \frac{d\hat{b}_{\mathbf{k},\lambda}}{dt} &= [\hat{b}_{\mathbf{k},\lambda}, \hat{H}^{\text{phonon}}] \\
 &= \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}',\lambda'} [\hat{b}_{\mathbf{k},\lambda}, \hat{b}_{\mathbf{k}',\lambda'} \hat{b}_{\mathbf{k}',\lambda'}^\dagger] \\
 &= \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}',\lambda'} \left(\hat{b}_{\mathbf{k}',\lambda'} [\hat{b}_{\mathbf{k},\lambda}, \hat{b}_{\mathbf{k}',\lambda'}^\dagger] + [\hat{b}_{\mathbf{k},\lambda}, \hat{b}_{\mathbf{k}',\lambda'}] \hat{b}_{\mathbf{k}',\lambda'}^\dagger \right) \\
 &= \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}',\lambda'} \hat{b}_{\mathbf{k}',\lambda'} \delta(\mathbf{k} - \mathbf{k}') \delta_{\lambda\lambda'} \\
 &= \hbar\omega_{\mathbf{k},\lambda} \hat{b}_{\mathbf{k},\lambda}
 \end{aligned} \tag{4.25}$$

This differential equation has a simple solution

$$\hat{b}_{\mathbf{k},\lambda}(t) = e^{i\omega_{\mathbf{k},\lambda}t} \hat{b}_{\mathbf{k},\lambda}. \tag{4.26}$$

With this result (and its hermitean conjugate) we can work out the phonon Green's function. We drop the mode index λ since it does not influence the result anyway:

$$\begin{aligned}
 D(\mathbf{k}; t - t') &= -i \left\langle [\hat{b}_{\mathbf{k}}(t) + \hat{b}_{-\mathbf{k}}^\dagger(t)] [\hat{b}_{\mathbf{k}}^\dagger(t') + \hat{b}_{-\mathbf{k}}(t')] \right\rangle \theta(t > t') \\
 &\quad -i \left\langle [\hat{b}_{\mathbf{k}}^\dagger(t') + \hat{b}_{-\mathbf{k}}(t')] [\hat{b}_{\mathbf{k}}(t) + \hat{b}_{-\mathbf{k}}^\dagger(t)] \right\rangle \theta(t < t').
 \end{aligned}$$

Note that now we *do not* get a minus sign upon swapping two operators due to the time ordering: these are bosonic operators so that $[\hat{b}_{\mathbf{k}}(t), \hat{b}_{\mathbf{k}}^\dagger(t')] = 0$ for $t \neq t'$ (cf. expression (4.2)). Only the terms that contain a creation operator and an annihilation operator remain:

$$\begin{aligned}
 D(\mathbf{k}; t - t') &= -i \left\langle \hat{b}_{\mathbf{k}}(t) \hat{b}_{\mathbf{k}}^\dagger(t') + \hat{b}_{-\mathbf{k}}^\dagger(t) \hat{b}_{-\mathbf{k}}(t') \right\rangle \theta(t > t') \\
 &\quad -i \left\langle \hat{b}_{\mathbf{k}}^\dagger(t') \hat{b}_{\mathbf{k}}(t) + \hat{b}_{-\mathbf{k}}(t') \hat{b}_{-\mathbf{k}}^\dagger(t) \right\rangle \theta(t < t').
 \end{aligned} \tag{4.27}$$

Now we use

$$\begin{aligned}
 \left\langle \hat{b}_{\mathbf{k}}(t) \hat{b}_{\mathbf{k}}^\dagger(t') \right\rangle &= e^{i\omega_{\mathbf{k}}(t-t')} \left\langle \hat{b}_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger \right\rangle = e^{i\omega_{\mathbf{k}}(t-t')} n_{\mathbf{k}}, \\
 \left\langle \hat{b}_{\mathbf{k}}^\dagger(t') \hat{b}_{\mathbf{k}}(t) \right\rangle &= e^{i\omega_{\mathbf{k}}(t-t')} \left\langle \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} \right\rangle = e^{i\omega_{\mathbf{k}}(t-t')} (n_{\mathbf{k}} + 1).
 \end{aligned}$$

where $n_{\mathbf{k}}$ is the number of phonons with wave number \mathbf{k} given by the Bose-Einstein distribution:

$$n_{\mathbf{k}} = \frac{1}{\exp[\hbar\omega_{\mathbf{k}}/(k_B T)] - 1}. \tag{4.28}$$

We also use that $\hat{b}_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger$ is the counting operator (and that $\hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} = \hat{b}_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger + 1$). For the phonon propagator we get

$$\begin{aligned}
 D(\mathbf{k}; t - t') &= -i \left\{ e^{i\omega_{\mathbf{k}}(t-t')} n_{\mathbf{k}} + e^{-i\omega_{\mathbf{k}}(t-t')} (n_{\mathbf{k}} + 1) \right\} \theta(t > t') \\
 &\quad + i \left\{ e^{i\omega_{\mathbf{k}}(t-t')} (n_{\mathbf{k}} + 1) + e^{-i\omega_{\mathbf{k}}(t-t')} n_{\mathbf{k}} \right\} \theta(t < t').
 \end{aligned} \tag{4.29}$$

This can be rewritten as

$$D(\mathbf{k}; t - t') = -i \left\{ e^{i\omega_k |t-t'|} n_{\mathbf{k}} + e^{-i\omega_k |t-t'|} (n_{\mathbf{k}} + 1) \right\}. \quad (4.30)$$

In the temperature zero limit we have the phonon vacuum and all $n_{\mathbf{k}} = 0$. We find:

$$T = 0 \rightarrow D(\mathbf{k}; t - t') = -ie^{-i\omega_k(t-t')}\theta(t > t') + ie^{i\omega_k(t-t')}\theta(t < t'). \quad (4.31)$$

Also for the phonon Green's function we need the Fourier transform to the frequencies:

$$\begin{aligned} D(\mathbf{k}, \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t - \delta|t|} D(\mathbf{k}; t) \\ &= -i \int_0^{\infty} dt e^{i(\omega - \omega_k + i\delta)t} + i \int_{-\infty}^0 dt e^{i(\omega_k + \omega - i\delta)t} \\ &= \frac{1}{\omega - \omega_k + i\delta} - \frac{1}{\omega + \omega_k - i\delta} \end{aligned} \quad (4.32)$$

In this expression we have introduced a convergence factor $e^{-\delta|t|}$ with δ an infinitesimal positive number. The derivation of this result is completely similar to our earlier derivation for the electron Green's function, using the integral representation (4.14) for the Heaviside function. We obtain

$$\boxed{D(\mathbf{k}, \omega) = \frac{2\omega_k}{\omega^2 - \omega_k^2 + i\delta}} \quad (4.33)$$

Here we have kept only the lowest order of the infinitesimal term, and renamed it ($2i\delta\omega_k \rightarrow i\delta$).

4.2.4 Summary

In this section we have defined the Green's functions

$$G(k; t - t') \quad : \quad = -i \left\langle \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') \right\rangle, \quad (4.34)$$

$$D(\mathbf{k}, \lambda; t - t') \quad = \quad -i \left\langle \mathcal{T} \hat{B}_{\mathbf{k}, \lambda}(t) \hat{B}_{\mathbf{k}, \lambda}^\dagger(t') \right\rangle, \quad (4.35)$$

and their frequency dependent counterparts

$$G(k, \omega) = \int_{-\infty}^{\infty} dt G(k; t) e^{i\omega t} \quad (4.36)$$

(similar for D). We calculated them for some important non-interacting systems. The result for the noninteracting-electron Green's function (at temperature zero) is

$$G_0(\mathbf{k}, \omega) = \frac{\theta(k > k_F)}{\omega - E_k/\hbar + i\delta} + \frac{\theta(k < k_F)}{\omega - E_k/\hbar - i\delta}, \quad (4.37)$$

and for the noninteracting-phonon Green's function we get

$$D_0(\mathbf{k}, \omega) = \frac{2\omega_k}{\omega^2 - \omega_k^2 + i\delta}. \quad (4.38)$$

Here we've added subscripts $_0$ so indicate that these are the Green's functions of the non-interacting systems. In the next sections of this chapter we will use these non-interacting solutions as the building blocks to construct the Green's functions of the more complicated case where interactions are present and no simple exact solution is available. Note that the electron Green's function G_0 has poles at $\hbar\omega = E_k/\hbar$, the eigen-energies of the system. This is a very general property of Green's functions and we are going to investigate this in the next section.

4.3 Interpreting Green's functions

Before tackling the central problem of calculating the Green's functions for the fully interacting system, we need to emphasize some properties of Green's functions which are linked to the way in which we interpret them, and which are useful for the chapter on optical response. To be very general, we again use the notation k for an arbitrary set of quantum numbers (keeping in mind our explicit example where it represents wave numbers and an occasional spin or phonon mode quantum number).

4.3.1 Advanced and retarded Green's functions

The Green's function that we used earlier was defined as

$$\begin{aligned} G(k; t - t') &= -i \left\langle \Psi_0 \left| \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') \right| \Psi_0 \right\rangle \\ &= \begin{cases} G^>(k; t - t') = -i \left\langle \Psi_0 \left| \hat{a}_k(t) \hat{a}_k^\dagger(t') \right| \Psi_0 \right\rangle & \text{for } t - t' > 0 \\ G^<(k; t - t') = -\xi i \left\langle \Psi_0 \left| \hat{a}_k^\dagger(t') \hat{a}_k(t) \right| \Psi_0 \right\rangle & \text{for } t - t' < 0 \end{cases}. \end{aligned} \quad (4.39) \quad (4.40)$$

Here \mathcal{T} is the time ordering operator that places the operator with the latest time to the left (and engenders a factor $\xi = -1$ for each swap of fermionic operators, but not for bosonic operators $\xi = 1$). We work at temperature zero and therefore calculate the expectation value with respect to the many body ground state $|\Psi_0\rangle$. If $t > t'$ then first a particle is created and later annihilated.

If, on the other hand $t < t'$, then first a particle is annihilated (=a hole is created) and then it is created (the hole is removed again). The retarded and advanced Green's function make this distinction between particles and holes more explicit. The **retarded Green's function** is defined as

$$G_R(k; t-t') = G - G^< = \begin{cases} -i \langle \Psi_0 | [\hat{a}_k(t), \hat{a}_k^\dagger(t')]_\xi | \Psi_0 \rangle & \text{for } t - t' > 0 \\ 0 & \text{for } t - t' < 0 \end{cases} \quad (4.41)$$

where $[\hat{a}_k(t), \hat{a}_k^\dagger(t')]_\xi = \hat{a}_k(t)\hat{a}_k^\dagger(t') + \xi\hat{a}_k^\dagger(t')\hat{a}_k(t)$ - for fermions this is the commutator, for bosons the anticommutator. This Green's function focuses on forward times and particle propagation, and is central to the discussion of causal phenomena, where the response (at time t) happens after the cause (at time t'). Analogously we define the **advanced Green's function** as

$$G_A(k; t-t') = G - G^> = \begin{cases} 0 & \text{for } t - t' > 0 \\ -\xi i \langle \Psi_0 | [\hat{a}_k(t), \hat{a}_k^\dagger(t')]_\xi | \Psi_0 \rangle & \text{for } t - t' < 0 \end{cases} \quad (4.42)$$

This focuses on backward time propagation, or forward time propagation of holes. This strange duality –holes moving forward in time are linked to particles moving backward in time– is an important insight of quantum field theory. Of course we could also introduce a retarded and advanced form for the phonon Green's function, but there the distinction is not so important since we have already symmetrized between annihilating a \mathbf{k} phonon and creating a $-\mathbf{k}$ phonon.

4.3.2 Spectral representation

The spectral representation of Green's function, also called “Lehmann representation”, brings to light some interesting properties of Green's function. This representation writes the operators in matrix form, using a complete set of many-particle eigenstates $|\Psi_n\rangle$ of the full Hamiltonian. You're right, we don't know what these many-body eigenstates are, but let's pretend that we do know them and see how far we get with that idea. Let's also pretend we know the ground state $|\Psi_0\rangle$, and use the completeness of the many-body basis in the Green's function:

$$\begin{aligned} G^>(k; t) &= -i \sum_n \langle \Psi_0 | \hat{a}_k(t) | \Psi_n \rangle \langle \Psi_n | \hat{a}_k^\dagger(0) | \Psi_0 \rangle \\ &= -i \sum_n \langle \Psi_0 | e^{iHt/\hbar} \hat{a}_k e^{-iHt/\hbar} | \Psi_n \rangle \langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle \\ &= -i \sum_n \langle \Psi_0 | \hat{a}_k | \Psi_n \rangle \langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle \exp\{-i(E_n - E_0)t/\hbar\}. \end{aligned}$$

Here we do some more bluffing: we note E_n as the eigen-energy belonging to the many-body eigenstate $|\Psi_n\rangle$. Then E_0 is the ground state energy (corresponding

to $|\Psi_0\rangle$). Analogously, we find

$$G^<(k; t) = -i\xi \sum_n \left\langle \Psi_0 \left| \hat{a}_k^\dagger \right| \Psi_n \right\rangle \langle \Psi_n | \hat{a}_k | \Psi_0 \rangle \exp\{+i(E_n - E_0)t/\hbar\}$$

Now let's once more look for the Fourier transform of these Green's functions as we have done before, using expression (4.12),

$$G(k; \omega) = \int_{-\infty}^{\infty} G(k; t) e^{i\omega t - \delta|t|} dt$$

The spectral decomposition allows us to write this as

$$\begin{aligned} G(k; \omega) &= \sum_n \frac{\langle \Psi_0 | \hat{a}_k | \Psi_n \rangle \langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle}{\omega - (E_n - E_0)/\hbar + i\delta} \\ &\quad - \xi \sum_n \frac{\langle \Psi_0 | \hat{a}_k^\dagger | \Psi_n \rangle \langle \Psi_n | \hat{a}_k | \Psi_0 \rangle}{\omega + (E_n - E_0)/\hbar - i\delta} \end{aligned} \quad (4.43)$$

Note that

$$\langle \Psi_0 | \hat{a}_k | \Psi_n \rangle \langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle = |\langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle|^2.$$

The retarded and advanced Green's functions are

$$\begin{aligned} G_R(k; \omega) &= \sum_n \frac{|\langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle|^2}{\omega - (E_n - E_0)/\hbar + i\delta} + \xi \sum_n \frac{|\langle \Psi_n | \hat{a}_k | \Psi_0 \rangle|^2}{\omega + (E_n - E_0)/\hbar + i\delta} \\ G_A(k; \omega) &= -\sum_n \frac{|\langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle|^2}{\omega - (E_n - E_0)/\hbar - i\delta} - \xi \sum_n \frac{|\langle \Psi_n | \hat{a}_k | \Psi_0 \rangle|^2}{\omega + (E_n - E_0)/\hbar - i\delta} \end{aligned}$$

In many-body systems there will typically be a very large number of eigenstates in any relevant energy interval $\hbar\Delta\omega$. We can therefore replace the sums by integrals, and introduce the **spectral functions**:

$$\mathcal{A}(k, \omega) = \sum_n \left| \langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle \right|^2 \delta[\omega - (E_n - E_0)/\hbar], \quad (4.44)$$

$$\mathcal{B}(k, \omega) = \sum_n |\langle \Psi_n | \hat{a}_k | \Psi_0 \rangle|^2 \delta[\omega - (E_n - E_0)/\hbar]. \quad (4.45)$$

With these, we find

$$G(k; \omega) = \int_0^\infty d\omega' \left[\frac{\mathcal{A}(k, \omega')}{\omega - \omega' + i\delta} - \xi \frac{\mathcal{B}(k, \omega')}{\omega + \omega' - i\delta} \right]. \quad (4.46)$$

This way of writing the Green's function in terms of the spectral functions $\mathcal{A}(k, \omega)$ and $\mathcal{B}(k, \omega)$ is called the Lehmann representation in quantum field

theory. It may seem that we just keep on finding new ways of writing the same old thing. But it is by doing this that Galitskii and Migdal² could study the analytic properties of Green's functions, derive dispersion relations, and relate the real and imaginary parts of these functions. The spectral representation also holds for interacting systems. Of course, then we do not know the many-body eigenfunctions $|\Psi_n\rangle$ that we formally use here, and we'll need the techniques developed further on to find the spectral functions. Only for non-interacting system can we readily write down the spectral functions, and generalizing the non-interacting result teaches us a new interpretation.

4.3.3 Green's function as quasiparticle propagator

Remember that the Green's function $G(k, t)$ represents a quantum mechanical amplitude to find a particle that was originally in state k at time $t = 0$ still in the same state k a time t later. In other words, $G(k, t)$ represents the propagator in time of a particle in state k . From (4.46) we know that this propagation (for $t > 0$) is determined by the spectral function $\mathcal{A}(k, \omega')$. For the non-interacting fermion system (the filled Fermi sphere) we can derive the spectral function directly from expressions (4.46) and (4.16) :

$$\mathcal{A}^{\text{fermibol}}(\mathbf{k}, \sigma, \omega) = \delta(\omega - E_k/\hbar)\theta(k > k_F). \quad (4.47)$$

So, for a free, non-interacting electron, the propagator is undamped and the Fourier transform of $G(\mathbf{k}, \sigma; t)$ has only one frequency component, at $\omega_k = E_k/\hbar = \hbar k^2/2m$. The spectral function contains a delta function at this frequency. In general, the spectral function will give the **frequency spectrum** corresponding to the possible energies with which a particle with momentum $\hbar\mathbf{k}$ and spin σ can propagate in the many-body system. In the absence of interaction, it can only have a momentum $\hbar\mathbf{k}$ if it has energy E_k/\hbar . When there are interactions between the particles, the spectral function for momentum $\hbar\mathbf{k}$ will no longer be a delta function at ω_k . The plane wave with wave number \mathbf{k} will overlap with many different many-body eigenstates, that may have different energies. All these energies appear in the spectral function, each energy weighed by how much overlap there is. The delta function will broaden, and possibly shift. This spectral function is typically what is measured in experiments: you shoot in a particle with a well defined momentum, and then measure how much energy was absorbed by the system – this will be proportional to the spectral function, and gives this function also its name.

This is an important concept. The behavior of \mathcal{A} , determined by the modulus of the matrix elements $\langle \Psi_n | \hat{a}_k^\dagger | \Psi_0 \rangle$ and the smearing of energies associated with the transitions represented by $\langle \Psi_n | \hat{a}_k^+ | \Psi_0 \rangle$ is more complicated. Injecting a particle with momentum $\hbar\mathbf{k}$, i.e. constructing $\hat{a}_\mathbf{k}^\dagger |\Psi_0\rangle$, gives a new state that is no longer a good eigenstate of the $(N + 1)$ -particle system. The new state

²V. Galitskii en A. Migdal, Soviet Phys. JETP **7**, 96 (1958).

will therefore have a finite lifetime so that the propagation will be damped – the modulus of the amplitude will decrease below 1.

Under which circumstances is it still possible to consider the additional state k as a separate particle that propagates in the system? The object consisting out of the originally injected particle and the disturbance in the many-body system is sometimes called a “quasiparticle³”. The polaron is a nice example: it is a quasiparticle consisting out of an electron together with the lattice deformation that it creates. The thing moves as a whole (as long as the electron’s velocity is small), the electron trailing its lattice deformation behind it like a little comet. The quasiparticle has a different effective mass and dispersion relation than the original electron (we’ve calculated those in the previous chapter), but it is still possible to treat the many-body deformation along with the particle as a single entity, a well-defined quasiparticle.

This is very useful: **it seems possible to replace the complicated strongly-interacting soup of electrons and phonons by a much simpler ideal gas of quasiparticles that gives the same physics!** The price we pay is that we have to find out the properties of the quasiparticles – and they will differ from that of the original particles. What we gain is that we end up with a gas of (almost) non-interacting particles. And you know from your introductory statistical mechanics course how to calculate all sorts of thermodynamic functions (specific heat, free energy,) for ideal gases, given the dispersion relation! So, if we have found the properties of quasiparticles, and if it is possible to use the concept, then we have in fact solved the many-body problem as far as equilibrium thermodynamics are concerned!

OK, so what is the link between Green’s functions and quasiparticles? First of all, in order for quasiparticles to exist and to be a useful concept, the Green’s function must behave as

$$G(k, t) = -iZ_k e^{-i\tilde{E}(k)t/\hbar} e^{-\Gamma_k t} \quad (4.48)$$

for some time. Then, the quasiparticle concept is valid. Indeed, the form (4.48) shows that, with overall amplitude Z_k , we have a particle with energy $\tilde{E}(k)$ because what happens to its amplitude as we wait is that the phase rotates with a frequency $\tilde{E}(k)/\hbar$, just like for a free electron in the previous section. In contrast to the free electron, the probability for it to remain in that state is less than one, and decays with time as $e^{-\Gamma_k t}$. The lifetime of the quasiparticles is $1/\Gamma_k$. In general, the concept of quasiparticles will be meaningful if we look at times $\tilde{E}(k)/\hbar < t < 1/\Gamma_k$, where the lower boundary is determined by the Heisenberg uncertainty. In order for the Green’s function as a function of time to have the form (4.48), it’s Fourier transform must have a pole at $\omega = \tilde{E}(k)/\hbar + i\Gamma_k$, and its spectral function must have a peak at $\omega = \tilde{E}(k)/\hbar$, with a width Γ_k .

Fourier transforming (4.48) from time to frequency space lets us conclude that a quasiparticle manifests itself as a pole in the frequency-dependent Green’s function $G(k, \omega)$. In other words, **if the Green’s function has a pole in**

³D. Pines, *The Many-Body Problem*, Addison-Wesley publ., Reading MA, USA (1997).

$\omega = E_k/\hbar - i\Gamma_k$, then an additional particle injected into the system can propagate as an approximate eigenstate (a quasiparticle) with energy E_k and lifetime $1/\Gamma_k$. If there are multiple poles, then there are multiple possible excitations, and the additional particle can propagate as different kinds of eigenstates, where the amplitude is given by the overlap of the eigenstate with the given initial state in which the particle was created⁴.

4.4 Tackling interactions adiabatically

4.4.1 Time evolution operator

In the Dirac picture (see the addendum to this chapter) the Hamiltonian is split in an exactly solvable part, \hat{H}_0 , and a part that is treated as a perturbation and that usually contains the interactions, \hat{H}_1 . Operators transform according to \hat{H}_0 , so that

$$\hat{H}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{H}_1 e^{-i\hat{H}_0 t/\hbar}, \quad (4.49)$$

and wave functions transform according to the perturbation part, according to

$$i\hbar \frac{d|\Psi(t)\rangle_I}{dt} = \hat{H}_I(t) |\Psi(t)\rangle_I. \quad (4.50)$$

This differential equation can be integrated, giving:

$$|\Psi(t)\rangle_I = |\Psi(t_0)\rangle_I + \frac{1}{i\hbar} \int_{t_0}^t dt_1 \hat{H}_I(t_1) |\Psi(t_1)\rangle_I. \quad (4.51)$$

We can substitute this equation into itself: for $|\Psi(t_1)\rangle_I$ in the right hand side of the equation we again use (4.51) and get

$$\begin{aligned} |\Psi(t)\rangle_I &= |\Psi(t_0)\rangle_I + \frac{1}{i\hbar} \int_{t_0}^t dt_1 \hat{H}_I(t_1) |\Psi(t_0)\rangle_I \\ &\quad + \frac{1}{i\hbar} \int_{t_0}^t dt_1 \hat{H}_I(t_1) \frac{1}{i\hbar} \int_{t_0}^{t_1} dt_2 \hat{H}_I(t_2) |\Psi(t_2)\rangle_I. \end{aligned} \quad (4.52)$$

Now we can do this again for $|\Psi(t_2)\rangle_I$, and continue to iterate the procedure. This results in:

$$\begin{aligned} |\Psi(t)\rangle_I &= \left\{ \hat{1} + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \right. \\ &\quad \left. \times \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n) \right\} |\Psi(t_0)\rangle_I. \end{aligned} \quad (4.53)$$

⁴Additional argumentation for the quasiparticle interpretation of Green's functions can be found in A. L. Fetter & J. D. Walecka's book "Quantum Theory of Many-Particle Systems" (McGraw-Hill, Inc., Boston USA, 1971), p. 72 onwards.

From this we define a time evolution operator

$$\hat{U}(t, t_0) |\Psi(t_0)\rangle_I = |\Psi(t)\rangle_I \quad (4.54)$$

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n) \quad (4.55)$$

The integration boundaries give rise to a difficult integration domain, but we can re-order them to simplify this. To see how this works, look at the case for $n = 2$. Start by swapping the two integrations,

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}_I(t_1) \hat{H}_I(t_2) &= \int_{t_0}^t dt_2 \int_{t_2}^t dt_1 \hat{H}_I(t_1) \hat{H}_I(t_2) \\ &= \int_{t_0}^t dt'_1 \int_{t_2}^t dt'_2 \hat{H}_I(t'_2) \hat{H}_I(t'_1) \end{aligned} \quad (4.56)$$

from which it follows that

$$\begin{aligned} &\Rightarrow \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}_I(t_1) \hat{H}_I(t_2) \\ &= \frac{1}{2} \int_{t_0}^t dt_1 \left[\int_{t_0}^{t_1} dt_2 \hat{H}_I(t_1) \hat{H}_I(t_2) + \int_{t_1}^t dt_2 \hat{H}_I(t_2) \hat{H}_I(t_1) \right] \\ &= \frac{1}{2} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \mathcal{T}[\hat{H}_I(t_1) \hat{H}_I(t_2)] \end{aligned} \quad (4.57)$$

where \mathcal{T} is again the time ordering operator. In general (for any n) we find

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{1}{(i\hbar)^n} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \mathcal{T}[\hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n)] \quad (4.58)$$

This series can also be seen as an expansion of an exponential function, so that we can write the result in a more compact form:

$$\hat{U}(t, t_0) = \mathcal{T} \left\{ \exp \left[\frac{1}{i\hbar} \int_{t_0}^t dt_1 \hat{H}_I(t_1) \right] \right\}. \quad (4.59)$$

This nicely agrees with the simple definition of the time evolution operator for time-independent Hamiltonians, in basic quantum mechanics: $\hat{U}(t, t_0) = \exp\{i(t - t_0)\hat{H}_I/\hbar\}$. Also for Hamiltonians that explicitly depend on time we have $\hat{U}^\dagger(t, t_0) = \hat{U}(t_0, t)$ and $\hat{U}(t, t_1)\hat{U}(t_1, t_0) = \hat{U}(t, t_0)$.

4.4.2 Adiabatic activation and the Gell-Mann Low theorem

The Green's function for the interacting system is

$$G(k; t - t') = -i \frac{\langle \Psi_G | \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}, \quad (4.60)$$

where $|\Psi_G\rangle$ is the unknown ground state of the interacting system described by the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$. The dominator $\langle \Psi_G | \Psi_G \rangle$ ensures that we have a normalized wave function and is kept explicitly. The operators are in the Heisenberg picture, as in our earlier definition. We want to relate this function to the known Green's function of the non-interacting system,

$$G_0(k, t - t') = -i \langle \Psi_0 | \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') | \Psi_0 \rangle, \quad (4.61)$$

where $|\Psi_0\rangle$ is the known ground state of the non-interacting system described by the unperturbed Hamiltonian \hat{H}_0 . The G_0 's were already calculated for several examples earlier in this chapter.

To make the connection between the two, we will *switch on the interactions adiabatically*: this means that we construct the following Hamiltonian (in the Dirac picture):

$$\hat{H}(t) = \hat{H}_0 + e^{-\epsilon|t|} \hat{H}_1(t). \quad (4.62)$$

At time $t = -\infty$ this represents the unperturbed system, with ground state $|\Psi_0\rangle$. The term with $\hat{H}_1(t)$ is not present then. At time $t = 0$ this represents the interacting system with ground state $|\Psi_G\rangle$. The parameter ϵ is taken to be infinitesimally small, so that the changes occur adiabatically slow – without changing the entropy or, in quantum mechanical words, as a unitary transformation. That means we can consider a time evolution operator corresponding to the Hamiltonian (4.62), the energy levels will shift and move continuously, but their occupation will not change. If a particle is in the ground state energy level, it will not transition to a higher level but follow the change of the wavefunction associated with the ground state. Moreover, as a unitary transformation does not change the degeneracy of quantum levels, the non-degenerate ground state cannot be crossed by any other level, so it remains the lowest level. So, we get

$$|\Psi_G\rangle = \hat{U}(0, -\infty) |\Psi_0\rangle. \quad (4.63)$$

This powerful assumption was proven to be correct also for degenerate ground states, and is known as the **theorem of Gell-Mann and Low**⁵. Inserting this result in the definition of the interacting system's Green's function gives

$$G(k; t - t') = -i \frac{\langle \Psi_0 | \hat{U}(\infty, 0) \left\{ \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') \right\} \hat{U}(0, -\infty) | \Psi_0 \rangle}{\langle \Psi_0 | \hat{U}(\infty, 0) \hat{U}(0, -\infty) | \Psi_0 \rangle}. \quad (4.64)$$

⁵M. Gell-Mann en F. Low, Phys. Rev. **84**, 350 (1951). For a proof of the theorem we again refer to A. L. Fetter & J. D. Walecka's "Quantum Theory of Many-Particle Systems" (McGraw-Hill, Inc., Boston USA, 1971), pp. 61-64.

Here we used the time reversal symmetry of the adiabatic activation, so that the hermitean conjugate of the time-evolution operator that evolves a state from $t = -\infty$ to $t = 0$ is equal to the time-evolution operator that evolves the state from time $t = 0$ to $t = \infty$. The link between the operators $[\hat{a}_k(t)]_I$ in the Dirac picture and their versions $[\hat{a}_k(t)]_H$ in the Heisenberg picture is given by

$$\begin{aligned} [\hat{a}_k(t)]_H &= e^{i\hat{H}_I(t-0)/\hbar} \hat{a}_k e^{-i\hat{H}_I(t-0)/\hbar} \\ &= \hat{U}(0, t) [\hat{a}_k(t)]_I \hat{U}(t, 0). \end{aligned} \quad (4.65)$$

For $t > t'$, the numerator can be rewritten with all operators in the Dirac picture as follows:

$$\begin{aligned} & \left\langle \Psi_0 \left| \hat{U}(\infty, 0) \left\{ \mathcal{T} \hat{a}_k(t) \hat{a}_k^\dagger(t') \right\} \hat{U}(0, -\infty) \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \hat{U}(\infty, 0) \hat{U}(0, t) \hat{a}_k(t) \hat{U}(t, 0) \hat{U}(0, t') \hat{a}_k^\dagger(t') \hat{U}(t', 0) \hat{U}(0, -\infty) \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \hat{U}(\infty, t) \hat{a}_k(t) \hat{U}(t, t') \hat{a}_k^\dagger(t') \hat{U}(t', -\infty) \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{a}_k^\dagger(t') \hat{U}(\infty, -\infty) \right] \right| \Psi_0 \right\rangle, \end{aligned} \quad (4.66)$$

so that

$$G(k; t - t') = -i \frac{\left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{a}_k^\dagger(t') \hat{U}(\infty, -\infty) \right] \right| \Psi_0 \right\rangle}{\left\langle \Psi_0 \left| \hat{U}(\infty, -\infty) \right| \Psi_0 \right\rangle}. \quad (4.67)$$

This expression now contains **only expectation values with respect to the known ground state of the non interacting system**. That is what we gain with the adiabatic activation: we no longer have expectation values with respect to the unknown ground state. The price we pay is that the expression now contains the time-evolution operator. If we substitute our earlier result for the time-evolution operator into the result for the Green's function we finally get

$$\boxed{G(k; t - t') = \frac{-i}{\left\langle \Psi_0 \left| \hat{U}(\infty, -\infty) \right| \Psi_0 \right\rangle} \sum_{n=0}^{\infty} \frac{1}{n!} \frac{1}{(i\hbar)^n} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \dots \int_{-\infty}^{\infty} dt_n} \\ \times e^{-\epsilon(|t_1| + \dots + |t_n|)} \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n) \hat{a}_k^\dagger(t') \right] \right| \Psi_0 \right\rangle.} \quad (4.68)$$

The exponential factor will usually be left out since we take the limit of ϵ going to zero. In the relevant domain of the integrand this factor will then be ≈ 1 .

If the interaction $\hat{H}_I(t_1)$ is weak, then the subsequent terms in the series (4.68) represent subsequent orders of perturbation. The zeroth order term from the numerator is

$$-i \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{a}_k^\dagger(t') \right] \right| \Psi_0 \right\rangle = G_0(k; t - t'). \quad (4.69)$$

This is indeed exactly the same as our earlier G_0 ! The next term in the numerator is denoted by G_1 :

$$G_1(k; t - t') = \frac{1}{i\hbar} \int_{-\infty}^{\infty} dt_1 \left(-i \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{H}_I(t_1) \hat{a}_k^\dagger(t') \right] \right| \Psi_0 \right\rangle \right) \quad (4.70)$$

and in general we have for the n^{th} order term

$$G_n(k; t - t') = \frac{-i}{n! (i\hbar)^n} \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{H}_I(t_1) \dots \hat{H}_I(t_n) \hat{a}_k^\dagger(t') \right] \right| \Psi_0 \right\rangle$$

So, the difficulty to be solved is that we need to take expectation values that look like

$$\left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_k(t) \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n) \hat{a}_k^\dagger(t') \right] \right| \Psi_0 \right\rangle \quad (4.71)$$

and relate them to our known building blocks $G_0(k; t - t')$. There's a neat trick to do this, and that is the subject of the next section.

4.5 Wick's theorem

*Wick's theorem*⁶ allows to write the expectation value of a long product of creation and annihilation operators as a product of expectation value of pairs of creation and annihilation operators.

Let's consider an example to see how this comes about, and go back to the electron gas in the metal, which we already treated to lowest order in perturbation in chapter 3. In this case, the electrons interact through a Coulomb potential and they are embedded in a neutralizing background of homogeneous positive charge. The second quantisation Hamiltonian that we wrote down in chapter 3 is given by (3.12) :

$$\begin{aligned} \hat{H}_{el} &= \hat{H}_0 + \hat{H}_1 \\ \hat{H}_0 &= \sum_{\mathbf{k}, \sigma} \frac{\hbar^2 k^2}{2m_e} \hat{a}_{\mathbf{k}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma} \\ \hat{H}_1 &= \frac{1}{2V} \sum_{\mathbf{Q} \neq 0} \frac{e^2}{\epsilon_{\text{vac}} Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1}. \end{aligned} \quad (4.72)$$

Now, in order to calculate G_1 to get a first order approximation, we need to look at horribly long products such as

$$\left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger(t_1) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \right] \right| \Psi_0 \right\rangle \quad (4.73)$$

⁶G. C. Wick, Phys. Rev. **80**, 268 (1950).

and then plug the result back in (4.68).

Wick noted that the effect of a creation/annihilation operator on the Fermi sphere consists in adding/removing an electron in state $|\varphi_{\mathbf{k},\sigma}\rangle$, thus going the ground state $|\Psi_0\rangle$ to basis state in the occupation representation. States with different occupation numbers are orthogonal to each other, as we know from chapter 2. So, after all the creation and annihilation operators have done their thing, the only way that the expectation value is nonzero, i.e. that the projection on $\langle\Psi_0|$ is nonzero, is that the creation and annihilation operators must undo each other's actions. We need to end up again with the original filled Fermi sphere after all the creation and annihilation operators acted on it. As we put it earlier: the annihilation operators drill holes in the Fermi sphere, and the creation operators should repair those holes in some order. That way,

$$\langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k},\sigma}(t)\hat{a}_{\mathbf{k}',\sigma'}^\dagger(t')|\Psi_0\rangle$$

is zero unless $\mathbf{k}, \sigma = \mathbf{k}', \sigma'$, and –as we had in chapter 3–

$$\langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_4,\sigma_4}(t)\hat{a}_{\mathbf{k}_3,\sigma_3}^\dagger(t_1)\hat{a}_{\mathbf{k}_2,\sigma_2}(t_2)\hat{a}_{\mathbf{k}_1,\sigma_1}^\dagger(t')|\Psi_0\rangle$$

is zero unless $(\mathbf{k}_1, \sigma_1 = \mathbf{k}_2, \sigma_2$ and $\mathbf{k}_3, \sigma_3 = \mathbf{k}_4, \sigma_4)$, the direct contribution, or unless $(\mathbf{k}_1, \sigma_1 = \mathbf{k}_4, \sigma_4$ and $\mathbf{k}_2, \sigma_2 = \mathbf{k}_3, \sigma_3)$, the exchange contribution. Wick found a clever way to catalogue the possible pairings and arrived at the following very useful conclusion:

In making all possible pairing of creation and annihilation operators, each pair needs to appear in a time-ordered product. The time ordering of each pair gives the correct time ordering of the entire product.

So, the expectation value of the time ordered product of creation and annihilation operators is equal to the sum, over all possible ways of pairing these operators, of the product of expectation values of the time ordered pairs. With each odd permutation of fermionic operators we need to include a factor -1.

For example, we get

$$\begin{aligned} & \langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_4,\sigma_4}(t)\hat{a}_{\mathbf{k}_3,\sigma_3}^\dagger(t_1)\hat{a}_{\mathbf{k}_2,\sigma_2}(t_2)\hat{a}_{\mathbf{k}_1,\sigma_1}^\dagger(t')|\Psi_0\rangle \\ &= \langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_4,\sigma_4}(t)\hat{a}_{\mathbf{k}_3,\sigma_3}^\dagger(t_1)|\Psi_0\rangle\langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_2,\sigma_2}(t_2)\hat{a}_{\mathbf{k}_1,\sigma_1}^\dagger(t')|\Psi_0\rangle \\ & \quad - \langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_4,\sigma_4}(t)\hat{a}_{\mathbf{k}_1,\sigma_1}^\dagger(t')|\Psi_0\rangle\langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_2,\sigma_2}(t_2)\hat{a}_{\mathbf{k}_3,\sigma_3}^\dagger(t_1)|\Psi_0\rangle \\ &= [\delta(\mathbf{k}_3 - \mathbf{k}_4)\delta(\mathbf{k}_2 - \mathbf{k}_1)\delta_{\sigma_3,\sigma_4}\delta_{\sigma_2,\sigma_1} - \delta(\mathbf{k}_1 - \mathbf{k}_4)\delta(\mathbf{k}_2 - \mathbf{k}_3)\delta_{\sigma_1,\sigma_4}\delta_{\sigma_2,\sigma_3}] \\ & \quad \times \langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_4,\sigma_4}(t)\hat{a}_{\mathbf{k}_4,\sigma_4}^\dagger(t_1)|\Psi_0\rangle\langle\Psi_0|\mathcal{T}\hat{a}_{\mathbf{k}_2,\sigma_2}(t_2)\hat{a}_{\mathbf{k}_2,\sigma_2}^\dagger(t')|\Psi_0\rangle. \end{aligned}$$

In constructing annihilation-creation pairs we need to take into account the following set of rules:

1. As mentioned, we get a minus sign if there is an odd number of swaps of fermionic operators. In our example, the second term has a minus sign because there are three swaps needed to re-order the product

$$\hat{a}_{\mathbf{k}_4, \sigma_4}(t) \hat{a}_{\mathbf{k}_3, \sigma_3}^\dagger(t_1) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger(t')$$

into

$$\hat{a}_{\mathbf{k}_4, \sigma_4}(t) \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger(t') \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_3, \sigma_3}^\dagger(t_1).$$

2. If there are different types of operators (i.e. for different types of particles), then these can be factorized from the start. For example, if we have also phonon operators $\hat{B}_{\mathbf{q}}$ in the product, you can collect all of them and immediately take them out as a separate expectation value factor, keeping the order of the phonon operators within the expectation value unchanged:

$$\begin{aligned} & \left\langle \Psi_0 \left| \mathcal{T} \hat{a}_{\mathbf{k}_4, \sigma_4}(t) \hat{a}_{\mathbf{k}_3, \sigma_3}^\dagger(t_1) \hat{B}_{\mathbf{q}_1}(t_1) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{B}_{\mathbf{q}_2}(t_2) \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger(t') \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \mathcal{T} \hat{a}_{\mathbf{k}_4, \sigma_4}(t) \hat{a}_{\mathbf{k}_3, \sigma_3}^\dagger(t_1) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_1, \sigma_1}^\dagger(t') \right| \Psi_0 \right\rangle \\ & \quad \times \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{q}_1}(t_1) \hat{B}_{\mathbf{q}_2}(t_2) \right| \Psi_0 \right\rangle. \end{aligned}$$

This factorization is always possible when two types of operators commute with each other.

3. Wick's theorem also works for phonon operators:

$$\begin{aligned} & \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_2}(t_2) \hat{B}_{\mathbf{k}_1}(t') \right| \Psi_0 \right\rangle \\ &= \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_3}(t_1) \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_2}(t_2) \hat{B}_{\mathbf{k}_1}(t') \right| \Psi_0 \right\rangle \\ & \quad + \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_2}(t_2) \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_1}(t') \right| \Psi_0 \right\rangle \\ & \quad + \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_1}(t') \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_2}(t_2) \right| \Psi_0 \right\rangle. \end{aligned}$$

Now we need all possible ways to make pairs of \hat{B} operators. With the electron operators, we need to make 'hetero' couples that contain a creation and an annihilation partner. But the phonon operators introduced previously have a double nature. Note also that there will be no more minus signs when we swap two bosonic operators. Now the expectation value of a pair will be zero unless the phonon wave numbers are equal and opposite. So we get for example:

$$\begin{aligned} & \left\langle \Psi_0 \left| \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_2}(t_2) \hat{B}_{\mathbf{k}_1}(t') \right| \Psi_0 \right\rangle \\ &= \delta(\mathbf{k}_4 + \mathbf{k}_3) \delta(\mathbf{k}_1 + \mathbf{k}_2) \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_4}(t_1) \right\rangle_0 \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_2}(t_2) \hat{B}_{\mathbf{k}_2}(t') \right\rangle_0 \\ & \quad + \delta(\mathbf{k}_4 + \mathbf{k}_2) \delta(\mathbf{k}_1 + \mathbf{k}_3) \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_2}(t_2) \right\rangle_0 \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_1}(t') \right\rangle_0 \\ & \quad + \delta(\mathbf{k}_4 + \mathbf{k}_1) \delta(\mathbf{k}_2 + \mathbf{k}_3) \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_4}(t) \hat{B}_{\mathbf{k}_1}(t') \right\rangle_0 \left\langle \mathcal{T} \hat{B}_{\mathbf{k}_3}(t_1) \hat{B}_{\mathbf{k}_2}(t_2) \right\rangle_0. \end{aligned}$$

4. What if two operators act at the same time? Again, if we need to do an odd number of swaps of fermionic operators, this results in a minus sign:

$$\begin{aligned}
 \langle \Psi_0 | \mathcal{T} \hat{a}_{\mathbf{k},\sigma}(t) \hat{a}_{\mathbf{k}',\sigma'}^\dagger(t) | \Psi_0 \rangle &= - \langle \Psi_0 | \hat{a}_{\mathbf{k}',\sigma'}^\dagger(t) \hat{a}_{\mathbf{k},\sigma}(t) | \Psi_0 \rangle \\
 &= -\delta(\mathbf{k} - \mathbf{k}') \delta_{\sigma\sigma'} \langle \Psi_0 | \hat{a}_{\mathbf{k},\sigma}^\dagger(t) \hat{a}_{\mathbf{k},\sigma}(t) | \Psi_0 \rangle \\
 &= -\delta(\mathbf{k} - \mathbf{k}') \delta_{\sigma\sigma'} n_{\mathbf{k},\sigma}(t).
 \end{aligned} \tag{4.74}$$

In this result, $n_{\mathbf{k},\sigma}(t)$ is the number of fermions in the single-particle state $|\varphi_{\mathbf{k},\sigma}\rangle$ at time t . Note that if the operators act at different times, the creation operator is written to the right in the product, so that

$$\langle \Psi_0 | \mathcal{T} \hat{a}_{\mathbf{k},\sigma}(t) \hat{a}_{\mathbf{k}',\sigma'}^\dagger(t') | \Psi_0 \rangle = iG_0(\mathbf{k}, \sigma; t - t') \delta(\mathbf{k} - \mathbf{k}') \delta_{\sigma\sigma'}. \tag{4.75}$$

We get back our building block! Alternatively we can write for the equal-time case:

$$\begin{aligned}
 \langle \Psi_0 | \mathcal{T} \hat{a}_{\mathbf{k},\sigma}(t) \hat{a}_{\mathbf{k}',\sigma'}^\dagger(t) | \Psi_0 \rangle &= \int dt' iG_0(\mathbf{k}, \sigma; t - t') \delta(t - t') \tag{4.76} \\
 &= iG_0(\mathbf{k}, \sigma; 0).
 \end{aligned} \tag{4.77}$$

Also, we have

$$\langle \Psi_0 | \mathcal{T} \hat{B}_{\mathbf{k}}(t) \hat{B}_{-\mathbf{k}}(t') | \Psi_0 \rangle = iD_0(\mathbf{k}, t - t')$$

Using Wick's theorem in conjunction with the adiabatic activation of the interactions we finally have a way to write down the Green's function of the interacting system in terms of the non-interacting Green's functions G_0 and D_0 . *The adiabatic activation results in a perturbation series, where each term contains a long product of creation and annihilation operators. Wick's theorem chops this up into neat little pieces that we can identify with G_0 and D_0 .* Will there be any systematics and physical interpretation of the resulting perturbation terms? Yes, and that is precisely what Feynman diagrams are about.

4.6 Feynman diagrams

We will again explain this using a concrete example, namely the electron-phonon interactions. The second quantized Hamiltonian describes free electrons (our unperturbed system) interacting with a bath of phonons:

$$\begin{aligned}
 \hat{H} &= \hat{H}_0 + \hat{H}_1, \\
 \hat{H}_0 &= \sum_{\mathbf{k},\sigma} \frac{\hbar^2 k^2}{2m_e} \hat{a}_{\mathbf{k},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma}, \\
 \hat{H}_1 &= \sum_{\mathbf{q}} \sum_{\mathbf{k},\sigma} M(\mathbf{q}) \hat{B}_{\mathbf{q}} \hat{a}_{\mathbf{k}+\mathbf{q},\sigma}^\dagger \hat{a}_{\mathbf{k},\sigma}.
 \end{aligned} \tag{4.78}$$

This is a generalization of the polaron problem where we considered only a single electron. The Green's function, up to second order in the interaction amplitude $M(\mathbf{q})$, is

$$G(\mathbf{k}, \sigma; t - t') = \frac{G_0(\mathbf{k}, \sigma; t - t') + G_1(\mathbf{k}, \sigma; t - t') + G_2(\mathbf{k}, \sigma; t - t')}{\langle \Psi_0 | \hat{U}(\infty, -\infty) | \Psi_0 \rangle}, \quad (4.79)$$

with

$$\begin{aligned} G_1(\mathbf{k}, \sigma; t - t') &= \frac{-1}{\hbar} \int_{-\infty}^{\infty} dt_1 \sum_{\mathbf{q}} \sum_{\mathbf{k}_1, \sigma_1} M(\mathbf{q}) \\ &\times \langle \Psi_0 | \mathcal{T} \left[\hat{a}_{\mathbf{k}, \sigma}(t) \hat{B}_{\mathbf{q}}(t_1) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \right] | \Psi_0 \rangle \\ &= 0. \end{aligned}$$

This becomes zero because we cannot pair up phonon operators, there being only one. The first nonzero correction term is

$$\begin{aligned} G_2(\mathbf{k}, \sigma; t - t') &= \frac{-i}{2(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} M(\mathbf{q}) M(\mathbf{q}') \\ &\times \langle \Psi_0 | \mathcal{T} \left[\begin{aligned} &\hat{a}_{\mathbf{k}, \sigma}(t) \hat{B}_{\mathbf{q}}(t_1) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \\ &\times \hat{B}_{\mathbf{q}'}(t_2) \hat{a}_{\mathbf{k}_2 + \mathbf{q}', \sigma_2}^\dagger(t_2) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \end{aligned} \right] | \Psi_0 \rangle, \end{aligned} \quad (4.80)$$

Here, according to the rules of Wick's theorem, we can factorize out the phonon operators, resulting in factor

$$\langle \Psi_0 | \mathcal{T} [\hat{B}_{\mathbf{q}}(t_1) \hat{B}_{\mathbf{q}'}(t_2)] | \Psi_0 \rangle = \delta(\mathbf{q} + \mathbf{q}') iD_0(\mathbf{q}; t_1 - t_2) \quad (4.81)$$

that contains the (unperturbed) phonon propagator (4.38), and fixes $\mathbf{q}' = -\mathbf{q}$. We still have an expectation value of the product of the electron operators, on which we let loose the Wick beast, that rips this expectation value in piece like a rabid hound:

$$\begin{aligned} &\langle \Psi_0 | \mathcal{T} [\hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t')] | \Psi_0 \rangle \\ &= \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \\ &\quad - \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \\ &\quad + \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \\ &\quad - \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \\ &\quad + \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \\ &\quad - \langle \mathcal{T} \hat{a}_{\mathbf{k}, \sigma}(t) \hat{a}_{\mathbf{k}, \sigma}^\dagger(t') \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_2 - \mathbf{q}, \sigma_2}^\dagger(t_2) \rangle_0 \langle \mathcal{T} \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \rangle_0 \end{aligned}$$

After the bloody slaughter six terms remain, as listed in the above expression. Let's denote these terms by $\mathcal{A}_1, \dots, \mathcal{A}_6$, starting at the top line (\mathcal{A}_1) until the sixth line (\mathcal{A}_6) of the right hand side. The first one can be rewritten as

$$\begin{aligned} \mathcal{A}_1 = & \delta_{\sigma\sigma_1}\delta_{\sigma_1\sigma_2}\delta_{\sigma_2\sigma} \times \delta(\mathbf{k} - (\mathbf{k}_1 + \mathbf{q}))\delta(\mathbf{k}_1 - (\mathbf{k}_2 + \mathbf{q}'))\delta(\mathbf{k}_2 - \mathbf{k}) \\ & \times iG_0(\mathbf{k}, \sigma; t - t_1)iG_0(\mathbf{k} - \mathbf{q}, \sigma; t_1 - t_2)iG_0(\mathbf{k}, \sigma; t_2 - t') \end{aligned}$$

All these delta functions allow to perform the summations in (4.80):

$$\begin{aligned} & \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \delta(\mathbf{q} + \mathbf{q}') iD_0(\mathbf{q}; t_1 - t_2) M(\mathbf{q}) M(\mathbf{q}') \mathcal{A}_1 \\ = & \sum_{\mathbf{q}} |M(\mathbf{q})|^2 D_0(\mathbf{q}; t_1 - t_2) G_0(\mathbf{k}, \sigma; t - t_1) G_0(\mathbf{k} - \mathbf{q}, \sigma; t_1 - t_2) G_0(\mathbf{k}, \sigma; t_2 - t') \end{aligned} \quad (4.82)$$

Let's now decorticate this form, peeling of the factors one by one. Remember that the Green's function $G_0(\mathbf{k}, \sigma; t_2 - t')$ describes a process whereby an electron, created with wave number \mathbf{k} and spin σ at time t' , propagates through the many-body system, and is destroyed or measured at a time t_2 . Feynman represents this electron-*propagator* by an line with an arrow, starting at time t' where the electron is created, and going to the time of doom t_2 where it is annihilated. If we let the time axis run from left to right his is

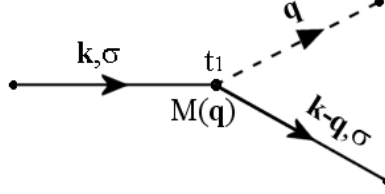
$$G_0(\mathbf{k}, \sigma; t_2 - t') = \begin{array}{c} \mathbf{k}, \sigma \\ \bullet \xrightarrow{\hspace{1cm}} \bullet \\ t' \hspace{1.5cm} t_2 \end{array}$$

In the same way, $D_0(\mathbf{q}; t_1 - t_2)$ is interpreted as a *propagator* for the phonon: the phonon is created at time t_2 with wave vector q and propagates merrily along its way until time t_1 where it is annihilated. This can also be represented by an arrow, but to make the distinction with propagating electrons we use a dashed line (sometimes one uses a wiggly line):

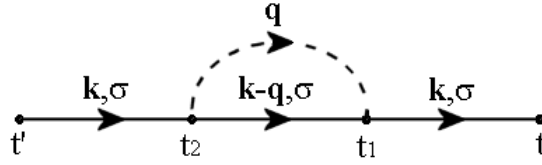
$$D_0(\mathbf{q}; t_2 - t_1) = \begin{array}{c} \mathbf{q} \\ \bullet \text{-----} \xrightarrow{\hspace{1cm}} \text{-----} \bullet \\ t_2 \hspace{1.5cm} t_1 \end{array}$$

The factors $M(\mathbf{q})$ belong with $\hat{B}_{\mathbf{q}}(t_1)\hat{a}_{\mathbf{k}_1+\mathbf{q},\sigma_1}^\dagger(t_1)\hat{a}_{\mathbf{k}_1,\sigma_1}(t_1)$ in the Hamiltonian. So they are connected to just one instant in time, here time t_1 . They lie on the point where the electron with $\mathbf{k}_1+\mathbf{q}, \sigma_1$ is created (so where an electron line begins), and where the phonon with wave vector \mathbf{q} is absorbed (so where the phonon line ends). There's another electron line, associated with $G_0(\mathbf{k} - \mathbf{q}, \sigma; t_1 - t_2)$, that begins in t_2 and also ends at t_1 . So, the point where $M(\mathbf{q})$ acts lies on a crossroads, a connection between three lines (namely two electron lines and one phonon line, always). Such a connecting point is called a *vertex*. The factor $M(\mathbf{q})$ is called the *vertex factor*. Momentum is conserved in a vertex: the sum of the momenta of incoming lines (arrow pointing to the vertex) is equal to the sum of the momenta of outgoing lines (arrow pointing

away from the vertex). The vertex is drawn as a little dot that connects the three lines:



Having identified all the building blocks and having proposed little drawings for each of them, we can make the drawing for the entire expression (4.82) by putting together lines at vertices. The drawing appearing in the calculation of a Green's function with given momentum and \mathbf{k} and spin σ must always start and end with \mathbf{k}, σ . The momenta of the lines in between start and end line can be anything, but we need to satisfy the momentum conservation in the vertices. Thus, we get:



Self-interaction diagram

Such a cartoon, telling us the chronology of the creation and annihilation of particles, is called a *Feynman diagram*. The story told by this specific Feynman diagram goes as follows: an electron, created at time t' in the single-particle state $|\varphi_{\mathbf{k},\sigma}\rangle$, propagates through the system undisturbed until the fatal moment t_2 , when it emits a phonon with wave number \mathbf{q} , and continues on its walk with wave vector $\mathbf{k} - \mathbf{q}$, reduced by the recoil of throwing out a phonon. It's spin σ is unchanged. Lo and behold, at time t_1 the darn phonon boomerangs right back into its face, and gets absorbed. The smack restores the original wave number \mathbf{k} of the electron, and slightly dazzled, it continues its journey up till the final time t . It's done all this to itself, so we could call this a self-interacting diagram.

The term in (4.80) that belongs to this specific Feynman diagram is precisely the quantum mechanical amplitude for this process to take place. If we'd take its modulus square we would know the probability that this story unfolds. But wait! We know from the double-slit experiment that we must first add the amplitudes of all possible alternatives before taking modulus square. In the double slit experiment, there are just two possible stories: the particle goes through slit number one or the particle goes through slit number two. Here there are zillions of alternative stories for a day in the life of an electron. It could have thrown the boomeranging phonon at any time. It could have thrown

a second phonon! That phonon could have interacted with another electron before flying back! Ah, the possibilities. The higher we go in perturbation order, the more complicated our scenario's are allowed to become. In the lowest nonzero order, there can be only one phonon involved. In the next nonzero order we are allowed to make all possible stories that involve our protagonist, the electron, and two phonons.

The total Greens function of the interacting system is the sum of the amplitudes of all possible adventures that the electron can experience in its journey from time t' to time t . There are only a few constraints in the possible scenario's: the start and the end of the script are fixed. The electron starts alone, at time t' in state $\{\mathbf{k}, \sigma\}$ and ends alone at time t again in state $\{\mathbf{k}, \sigma\}$. Also, we cannot connect 3 electron lines or any other combination except precisely two electron lines and one phonon line. No more, no less. Finally, there is momentum (and spin) conservation at the vertices. The Feynman diagrams are drawings, cartoons, that depict all the possible stories within these constraints. Now we still need the rules to translate each drawing into an amplitude.

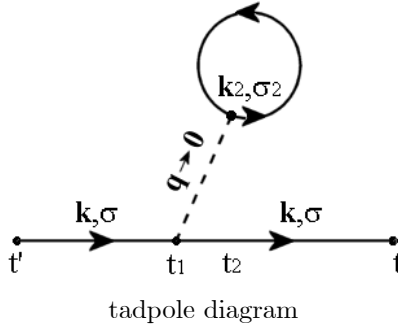
To find the rules, let's continue working out our example, the second order correction to the electron Green's function in an interacting electron-phonon system. We have for the second term:

$$\begin{aligned} \mathcal{A}_2 = & -\delta_{\sigma\sigma_1}\delta_{\sigma_2\sigma_2}\delta_{\sigma_1\sigma} \times \delta(\mathbf{k} - (\mathbf{k}_1 + \mathbf{q}))\delta(\mathbf{k}_2 - (\mathbf{k}_2 - \mathbf{q}))\delta(\mathbf{k}_1 - \mathbf{k}) \\ & iG_0(\mathbf{k}, \sigma; t - t_1)iG_0(\mathbf{k}_2, \sigma_2; t_2 - t_2)iG_0(\mathbf{k}, \sigma; t_1 - t'). \end{aligned} \quad (4.83)$$

This results in the following contribution to (4.68):

$$\begin{aligned} & \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \delta(\mathbf{q} + \mathbf{q}') iD_0(\mathbf{q}; t_1 - t_2) M(\mathbf{q}) M(\mathbf{q}') \mathcal{A}_2 \\ = & - \sum_{\mathbf{k}_2, \sigma_2} |M(\mathbf{q} \rightarrow \mathbf{0})|^2 D_0(\mathbf{q} \rightarrow \mathbf{0}; t_1 - t_2) G_0(\mathbf{k}, \sigma; t - t_1) \\ & \times G_0(\mathbf{k}_2, \sigma_2; t_2 - t_2) G_0(\mathbf{k}, \sigma; t_1 - t'). \end{aligned} \quad (4.84)$$

We can again look at this expression piece by piece and reconstruct the story behind it:



Somebody with a weird imagination once called this diagram the tadpole

diagram, and the name has stuck. Note that the little loop represents $G_0(\mathbf{k}_2, \sigma_2; t_2 - t_2)$, which is equal to $n_{\mathbf{k}_2, \sigma_2}$, the number of electrons that are in the single-particle state $|\varphi_{\mathbf{k}_2, \sigma_2}\rangle$ in our many body system. In this result there is still a summation over \mathbf{k}_2, σ_2 left. A loop like this is called a “*closed fermion loop*”. It gives all sort of divergence trouble in elementary particle physics, but we’re safe in solid state physics since the integrations over \mathbf{k}_2 don’t go from zero to infinity, but from the smallest value of k_2 , namely π/L with L the size of the crystal, to the largest value, namely π/a with a the size of the lattice constant. So, we have natural cutoffs to the wave number integrals. These sometimes matter: it should come as no surprise that some material properties indeed depend on the size of the system or the crystal lattice size. The tadpole diagram tells the story of an electron that sends out a phonon at time t_1 , but the phonon doesn’t boomerang back. Rather, it is absorbed by the other electrons present in the many-body system. Momentum conservation tells us that this should be a $\mathbf{q} = 0$ phonon. Do such phonons exist? For the acoustic modes the long wavelength limit $q \rightarrow 0$ corresponds to a uniform translation of the entire crystal, this is not really a physical quantity since it corresponds to a Galilean transformation of reference frame. But for the optical phonons, the $\mathbf{q} = 0$ phonons do matter: they are a uniform displacement of negative ions versus positive ions, and have a nonzero frequency. The physics of the tadpole diagram corresponds to the lattice taking the recoil of the electron.

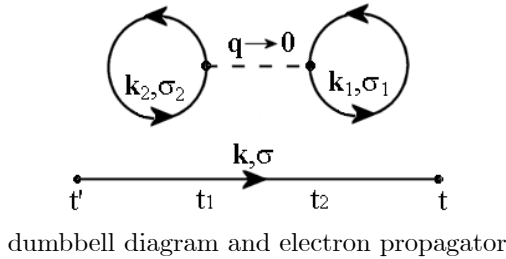
Next, we note that contributions \mathcal{A}_3 and \mathcal{A}_4 are identical to \mathcal{A}_1 and \mathcal{A}_2 , respectively. The next new diagram is \mathcal{A}_5 , and it looks weird. We get

$$\mathcal{A}_5 = \delta(\mathbf{q}) iG_0(\mathbf{k}, \sigma, t - t') iG_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) iG_0(\mathbf{k}_2, \sigma_2, t_2 - t_2)$$

from which

$$\begin{aligned}
 & \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \delta(\mathbf{q} + \mathbf{q}') iD_0(\mathbf{q}; t_1 - t_2) M(\mathbf{q}) M(\mathbf{q}') \mathcal{A}_5 \\
 = & G_0(\mathbf{k}, \sigma, t - t') \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} |M(\mathbf{q} \rightarrow \mathbf{0})| D_0(\mathbf{q} \rightarrow \mathbf{0}; t_1 - t_2) \\
 & \times G_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) G_0(\mathbf{k}_2, \sigma_2, t_2 - t_2)
 \end{aligned}$$

with corresponding Feynman diagram



The strange thing about this diagram is that the dumbbell part is not connected

to the electron propagator. The electron propagator tells the storyline of the protagonist: our created electron. What happens to it? Absolutely nothing. The most boring day. No phonons emitted or absorbed. But meanwhile, somewhere completely different, the many-body system through which it travels gets all riled up and does all sorts of things, it fluctuates around, emits and reabsorbs phonon. Sure, there can be all sorts of electrons and holes popping in and out of existence in the many-body ground state that acts as a background to the main plotline, but as long as they don't interact with our main character of the story, we feel intuitively that this shouldn't change the outcome of the summing up of amplitudes in the end... We look more closely at this point when we study the vacuum polarization.

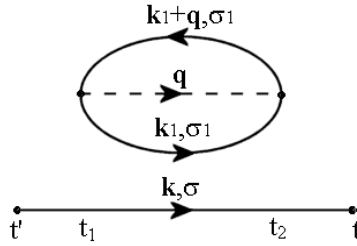
This type of diagram, where not all parts of the picture are connected to each other, is called a *disconnected diagram*. Those that have no loose pieces are called *connected diagrams* (no kidding). Also \mathcal{A}_6 leads to a disconnected diagram:

$$\begin{aligned} \mathcal{A}_6 = & -\delta_{\sigma_1\sigma_2}\delta(\mathbf{k}_2 - (\mathbf{k}_1 + \mathbf{q}))iG_0(\mathbf{k}, \sigma, t - t') \\ & \times iG_0(\mathbf{k}_1, \sigma_1, t_1 - t_2)iG_0(\mathbf{k}_2, \sigma_2, t_2 - t_1). \end{aligned}$$

From this we find

$$\begin{aligned} & \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \delta(\mathbf{q} + \mathbf{q}') iD_0(\mathbf{q}; t_1 - t_2) M(\mathbf{q}) M(\mathbf{q}') \mathcal{A}_6 \\ = & G_0(\mathbf{k}, \sigma, t - t') \sum_{\mathbf{q}} \sum_{\mathbf{k}_1, \sigma_1} |M(\mathbf{q})|^2 D_0(\mathbf{q}; t_1 - t_2) \\ & \times G_0(\mathbf{k}_1, \sigma_1, t_1 - t_2) G_0(\mathbf{k}_1 + \mathbf{q}, \sigma_2, t_2 - t_1) \end{aligned} \quad (4.85)$$

with corresponding diagram



Oyster diagram and electron propagator

This completes our survey of the diagrams (and the possible stories) that appear in the calculation of the electron Green's function up to second order in the electron-phonon interaction. All these diagrams contain 1 phonon propagator and three electron propagators and two vertices. These numbers are fixed since the number of electron and phonon operators is fixed as soon as

we specify that we want to look in second order. Each order contributes a \hat{H}_I with one phonon and two electron operators. Can you see that the fourth order will have two phonon lines, five electron lines, and four vertices? Let's conclude this section by putting together all contributions that make up G_2 :

$$G_2(\mathbf{k}, \sigma; t - t') = \frac{-i}{2(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}} |M(\mathbf{q})|^2 D_0(\mathbf{q}; t_1 - t_2) \times \left\{ \begin{aligned} &+2G_0(\mathbf{k}, \sigma; t - t_1)G_0(\mathbf{k} - \mathbf{q}, \sigma; t_1 - t_2)G_0(\mathbf{k}, \sigma; t_2 - t') \\ &-2\delta(\mathbf{q})G_0(\mathbf{k}, \sigma; t - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2; t_2 - t_2)G_0(\mathbf{k}, \sigma; t_1 - t') \\ &+\delta(\mathbf{q})G_0(\mathbf{k}, \sigma, t - t') \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2, t_2 - t_2) \\ &-G_0(\mathbf{k}, \sigma, t - t') \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_2)G_0(\mathbf{k}_1 + \mathbf{q}, \sigma_2, t_2 - t_1) \end{aligned} \right\}. \quad (4.86)$$

The first line comes from \mathcal{A}_1 and \mathcal{A}_3 . The second line corresponds to the contributions of \mathcal{A}_2 and \mathcal{A}_4 . The third lines comes from \mathcal{A}_5 , and the fourth line from \mathcal{A}_6 . Note that the connected diagrams appear twice: the contributions of \mathcal{A}_1 and \mathcal{A}_3 are the same and differ only by the order of the intermediate times t_1 and t_2 over which we need to integrate – and we integrate over all times anyway. This integrating over all times is a summation over a bunch of possible histories of the electron: we sum up all the stories where the script only differs by the possible times at which the phonon emission and absorption occur. In the n -th order term G_n we'll find that the intermediate times t_1, \dots, t_n appear in $n!$ different orderings. This will cancel out the factor $n!$ in the series expansion (4.68).

4.7 Vacuum polarisation

We worked out the numerator in the Green's function, but not yet the denominator $S_0 = \langle \Psi_0 | \hat{U}(\infty, -\infty) | \Psi_0 \rangle$. Also here, we can expand $\hat{U}(\infty, -\infty)$ in successive orders of the interaction Hamiltonian:

$$S_0 = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{1}{(i\hbar)^n} \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \langle \Psi_0 | \mathcal{T} \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_n) | \Psi_0 \rangle.$$

The term with $n = 1$ again becomes zero, as was the case for the numerator, so that the expansion can be written as $S_0 = 1 + S_0^{(2)} + \dots$ where the second order contribution is given by

$$S_0^{(2)} = \frac{-i}{(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} M(\mathbf{q}) M(\mathbf{q}') \times \left\langle \Psi_0 \left| \mathcal{T} \left[\begin{aligned} &\hat{B}_{\mathbf{q}}(t_1) \hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \\ &\times \hat{B}_{\mathbf{q}'}(t_2) \hat{a}_{\mathbf{k}_2 + \mathbf{q}', \sigma_2}^\dagger(t_2) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \end{aligned} \right] \right| \Psi_0 \right\rangle. \quad (4.87)$$

The phonon operators factorize to

$$\left\langle \Psi_0 \left| \mathcal{T} \left[\hat{B}_{\mathbf{q}}(t_1) \hat{B}_{\mathbf{q}'}(t_2) \right] \right| \Psi_0 \right\rangle = \delta(\mathbf{q} + \mathbf{q}') i D_0(\mathbf{q}, t_1 - t_2), \quad (4.88)$$

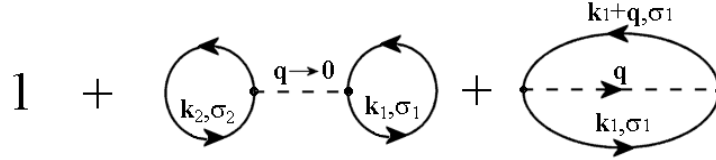
and the remaining electron operators evaluate to

$$\begin{aligned} & \left\langle \Psi_0 \left| \mathcal{T} \left[\hat{a}_{\mathbf{k}_1 + \mathbf{q}, \sigma_1}^\dagger(t_1) \hat{a}_{\mathbf{k}_1, \sigma_1}(t_1) \hat{a}_{\mathbf{k}_2 + \mathbf{q}', \sigma_2}^\dagger(t_2) \hat{a}_{\mathbf{k}_2, \sigma_2}(t_2) \right] \right| \Psi_0 \right\rangle \\ &= \delta(\mathbf{q}) \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2, t_2 - t_2) \\ & \quad - \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_2) G_0(\mathbf{k}_1 + \mathbf{q}, \sigma_2, t_2 - t_1). \end{aligned} \quad (4.89)$$

The result for S_0 up to second order then becomes:

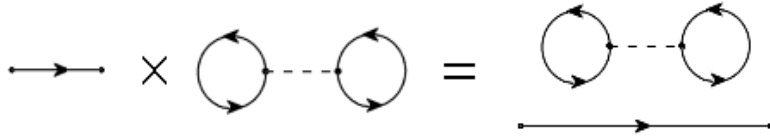
$$\begin{aligned} S_0 &= 1 + \frac{-1}{(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}} |M(\mathbf{q})|^2 D_0(\mathbf{q}, t_1 - t_2) \\ & \quad \times \left\{ \delta(\mathbf{q}) \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2, t_2 - t_2) \right. \\ & \quad \left. - \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_2) G_0(\mathbf{k}_1 + \mathbf{q}, \sigma_2, t_2 - t_1) \right\} + \dots \end{aligned} \quad (4.90)$$

Depicted as Feynman diagrams this becomes



Vacuum polarization up to second order

The diagrams that appear here (the dumbbell diagram and the oyster diagram) are part of the set of vacuum polarization terms. Symbolically we can represent a multiplication of two diagrams as a new, disconnected diagram, that contains both pieces. The amplitude of this new disconnected diagram is just a multiplication of the amplitudes of the two loose pieces:



Multiplication of diagrams

This particular multiplication corresponds to

$$[G_0(\mathbf{k}, \sigma, t - t')] \times \left[D_0(\mathbf{q}, t_1 - t_2) \sum_{\mathbf{k}_1, \sigma_1} G_0(\mathbf{k}_1, \sigma_1, t_1 - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2, t_2 - t_2) \right],$$

and we've seen it before, namely in the expression for \mathcal{A}_5 . The big collection of all possible stories of the electron (in the numerator) can be seen as combined stories represented by a connected diagram for the electron, together with any loose piece(s) from the vacuum polarization that mean that something else is going on somewhere. This means we can factorize the numerator as

Factorization of the numerator in (4.68).

In our example of the second order correction we only took terms up to second order (so with at most two vertices and one phonon line). The first factor in this decomposition is the sum over all connected diagrams – let's indicate this by $G_c(\mathbf{k}, \sigma; t - t')$. The second factor corresponds precisely to the vacuum polarization terms $S_0 = \langle \Psi_0 | \hat{U}(\infty, -\infty) | \Psi_0 \rangle$. This factor appears both in the numerator and in the denominator, and cancels out, so that

$$G(\mathbf{k}, \sigma; t - t') = \frac{G_c(\mathbf{k}, \sigma; t - t') \langle \Psi_0 | \hat{U}(\infty, -\infty) | \Psi_0 \rangle}{\langle \Psi_0 | \hat{U}(\infty, -\infty) | \Psi_0 \rangle} = G_c(\mathbf{k}, \sigma; t - t') \quad (4.91)$$

We won't prove this theorem, but note that it confirms our earlier intuitive remark that whatever goes on elsewhere unconnected to the story of the protagonist shouldn't influence the final amplitude. Another way to come to this result is to see that if we indeed would use the properly normalized true ground state $|\Psi_G\rangle = \hat{U}(0, -\infty) |\Psi_0\rangle$, then the denominator should be 1. But, since we approximate $\hat{U}(0, -\infty) |\Psi_0\rangle$, we have to explicitly correct for a wrong normalization – and this correction comes down to simply dropping all disconnected diagrams from our calculation.

4.8 Green's function in reciprocal space

If there is no preferred moment in time (i.e. homogeneity in time), it is useful to work the Green's function in frequency space. We've already defined

$$G(\mathbf{k}, \sigma; t) = \int_{-\infty}^{\infty} G(\mathbf{k}, \sigma; \omega) e^{-i\omega t} \frac{d\omega}{2\pi} \quad (4.92)$$

The connected second order diagrams from (4.86) are:

$$G_v(\mathbf{k}, \sigma; t - t') = \frac{-i}{2(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}} |M(\mathbf{q})|^2 D_0(\mathbf{q}; t_1 - t_2) \\ \times \left\{ \begin{aligned} &+2G_0(\mathbf{k}, \sigma; t - t_1)G_0(\mathbf{k} - \mathbf{q}, \sigma; t_1 - t_2)G_0(\mathbf{k}, \sigma; t_2 - t') \\ &-2\delta(\mathbf{q})G_0(\mathbf{k}, \sigma; t - t_1) \sum_{\mathbf{k}_2, \sigma_2} G_0(\mathbf{k}_2, \sigma_2; t_2 - t_2)G_0(\mathbf{k}, \sigma; t_1 - t') \end{aligned} \right\}.$$

The right-hand side is

$$\text{RHS} = \frac{-i}{(i\hbar)^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sum_{\mathbf{q}} |M(\mathbf{q})|^2 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} e^{-i\omega_1(t_1 - t_2)} D_0(\mathbf{q}; \omega_1) \\ \times \left\{ \begin{aligned} &\int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} e^{-i\omega_2(t - t_1)} G_0(\mathbf{k}, \sigma; \omega_2) \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi} e^{-i\omega_3(t_1 - t_2)} G_0(\mathbf{k} - \mathbf{q}, \sigma; \omega_3) \\ &\times \int_{-\infty}^{\infty} \frac{d\omega_4}{2\pi} e^{-i\omega_4(t_2 - t')} G_0(\mathbf{k}, \sigma; \omega_4) - \delta(\mathbf{q}) \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} e^{-i\omega_2(t - t_1)} G_0(\mathbf{k}, \sigma; \omega_2) \\ &\times \sum_{\mathbf{k}_2, \sigma_2} \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi} e^{-i\omega_3(t_2 - t_2)} G_0(\mathbf{k}_2, \sigma_2; \omega_3) \int_{-\infty}^{\infty} \frac{d\omega_4}{2\pi} e^{-i\omega_4(t_1 - t')} G_0(\mathbf{k}, \sigma; \omega_4) \end{aligned} \right\}$$

The integrations over t_1 and t_2 yield two delta functions, simplifying the expression

$$\text{RHS} = \frac{-i}{(i\hbar)^2} \int \frac{d\omega}{2\pi} e^{-i\omega(t - t')} \\ \times \left\{ \begin{aligned} &\sum_{\mathbf{k}_1} |M(\mathbf{k}_1)|^2 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \left[D_0(\mathbf{k}_1; \omega_1) G_0(\mathbf{k}, \sigma; \omega) \right. \\ &\quad \left. \times G_0(\mathbf{k} - \mathbf{k}_1, \sigma; \omega - \omega_1) G_0(\mathbf{k}, \sigma; \omega) \right] \\ &- |M(0)|^2 \sum_{\mathbf{k}_2, \sigma_2} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \left[D_0(0, 0) G_0(\mathbf{k}_2, \sigma_2; \omega_2) \right. \\ &\quad \left. \times G_0(\mathbf{k}, \sigma; \omega) G_0(\mathbf{k}, \sigma; \omega) \right] \end{aligned} \right\} \quad (4.93)$$

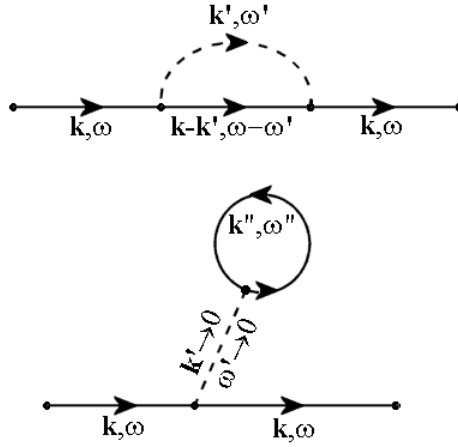
The left-hand side is

$$\text{LHS} = \int \frac{d\omega}{2\pi} e^{-i\omega(t - t')} G_v(\mathbf{k}, \sigma; \omega)$$

From this we find:

$$\begin{aligned}
 & G_V(\mathbf{k}, \sigma; \omega) \\
 = & i \sum_{\mathbf{k}'} \frac{|M(\mathbf{k}')|^2}{\hbar^2} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \left\{ \begin{aligned} & D_0(\mathbf{k}'; \omega') G_0(\mathbf{k}, \sigma; \omega) \\ & \times G_0(\mathbf{k} - \mathbf{k}', \sigma; \omega - \omega') G_0(\mathbf{k}, \sigma; \omega) \end{aligned} \right\} \\
 & - i \frac{|M(\mathbf{0})|^2}{\hbar^2} \sum_{\mathbf{k}'', \sigma''} \int_{-\infty}^{\infty} \frac{d\omega''}{2\pi} \left\{ \begin{aligned} & D_0(0, 0) G_0(\mathbf{k}'', \sigma''; \omega'') \\ & \times G_0(\mathbf{k}, \sigma; \omega) G_0(\mathbf{k}, \sigma; \omega) \end{aligned} \right\}. \quad (4.94)
 \end{aligned}$$

The Feynman diagrams that correspond to these two contributions are



Self-energy and tadpole diagrams in reciprocal space

Here we've omitted the spin index in the electron propagators. We see now that in each vertex not only the momentum is conserved but also the energy $\hbar\omega$! The sum of incoming energy (from lines pointing to the vertex) and outgoing energy (from lines pointing away from the vertex) is conserved.

4.9 Diagrammatics

4.9.1 Feynman rules

He indeed does. But here we mean to list the set rules that translate Feynman diagrams into amplitude, expressions that we can get some numbers out. Working out the second order term took a lot of effort, especially since we performed the Wick decomposition in all its splendor and then finished off with a Fourier transform. We are now in a position to simplify the whole complicated procedure of the previous sections by formulating a set of rules, the Feynman rules, to draw and translate all relevant diagrams.

We'll also include the electron-electron interactions as *instantaneous Coulomb interactions*. These are mediated by photons, that we can write as wiggly lines that, just as the phonon lines, can be emitted or absorbed by the electrons. We won't derive these rules, but we could do that by going through the same procedure as before.

The rules, for the electron-phonon system with both Coulomb interactions (mediated by photons) and electron-phonon interactions, are:

1. To calculate a transition amplitude between an initial and final state, draw all the connected diagrams that begin and end with these initial and final states (for our example of the electron Green's function the initial and final states were one electron in the state $\{\mathbf{k}, \sigma\}$). Use the correct number of lines (determined by the order of perturbation you want) and connect them correctly to vertices (e.g. an electron-phonon/photon vertex needs two electron lines and one phonon/photon line)

2. PROPAGATORS:

- (a) For each electron propagator (full lines), introduce the following Green's function:

$$G_0(\mathbf{k}, \sigma; \omega) = \frac{\theta(k > k_F)}{\omega - E_k/\hbar + i\delta} + \frac{\theta(k < k_F)}{\omega - E_k/\hbar - i\delta}, \quad (4.95)$$

where $E_k = (\hbar k)^2/(2m)$ is the energy corresponding to the single particle state $|\varphi_{\mathbf{k}, \sigma}\rangle$.

- (b) For each phonon propagator (dashed line), introduce the following Green's function:

$$D_0(\mathbf{k}, \omega) = \frac{1}{\omega - \omega_{\mathbf{k}} + i\delta} - \frac{1}{\omega + \omega_{\mathbf{k}} - i\delta}, \quad (4.96)$$

where $\hbar\omega_{\mathbf{k}}$ is the energy of a free phonon with wave number \mathbf{k} .

- (c) For each photon propagator (wiggly line), introduce the following Green's function: $1/q^2$, where \mathbf{q} is the wave number of the photon.

3. VERTICES:

- (a) Conserve momentum and energy in each vertex.
- (b) For an electron-phonon vertex, include a factor $M(\mathbf{q})/\hbar$ (or $M^*(\mathbf{q})/\hbar$), where \mathbf{q} is the wave vector of the absorbed (or emitted, respectively) phonon.
- (c) For an electron-photon vertex, include a factor $\sqrt{e^2/(\hbar\epsilon_{vac})}$.

4. Sum over all momenta and energy that still can be chosen freely, given the initial and final states are fixed and the conservation rule is satisfied. These freely chosen energy-momenta are called internal degrees of freedom and the sums can be written as integrals

$$\int \frac{d\omega'}{2\pi} \int \frac{d\mathbf{k}'}{(2\pi)^3}. \quad (4.97)$$

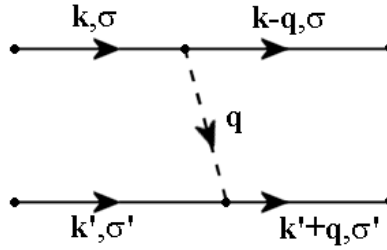
5. Multiply the result with a phase factor

$$i^m (-1)^F (2S + 1)^F \quad (4.98)$$

where F is the number of closed fermion loops, S is the spin ($=1/2$), and m is the order of perturbation (=the number of internal phonon and photon lines when calculating electron Green's functions, or half the number of vertices when calculating phonon Green's functions).

4.9.2 Generalization

The Green's function is an amplitude to guide an electron with given wave number, spin and energy through the many body system. The power of the Feynman rules is that we can apply them to more complicated questions. For example, we could ask ourselves what the amplitude is that two electrons with initial wave number and spin $\{\mathbf{k}, \sigma\}$ and $\{\mathbf{k}', \sigma'\}$ scatter and exchange momentum $\hbar\mathbf{q}$ to end up in final states with wave number and spin $\{\mathbf{k} - \mathbf{q}, \sigma\}$ and $\{\mathbf{k} + \mathbf{q}, \sigma'\}$. This is sometimes called the two-particle Green's function. Again, we need to add up all possible ways for this to happen, but surely the simplest way is just by exchanging a single phonon:



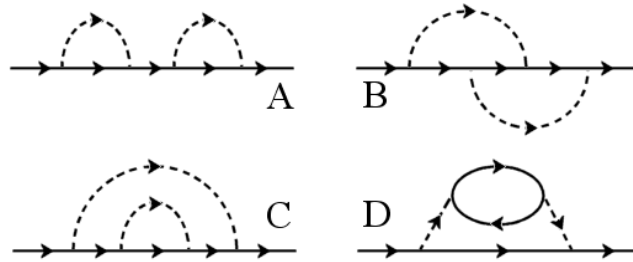
Scattering of two electrons by phonon exchange

The Feynman rules allow you to calculate also this amplitude: just translate all the separate pieces, plug in the numbers, and you get out a complex number representing the amplitude of this process. You can then start by refining your answer by drawing other connected Feynman diagrams for the same initial and final states, calculating their amplitudes as well and adding up all amplitudes. Maybe you don't have to take into account very many diagrams and the sum converges really quickly...

There are more Feynman rules. Also in elementary particle physics Feynman diagrams are used to calculate the amplitude of specific processes such as scattering, decay, absorption,... Each type of particle (quark, gluons, photons,...) has its own propagator, its own line. Each type of interaction (color, electromagnetic, ...) has its own vertices and vertex factors. The Feynman rules relevant to the different branches of physics (solid state physics, elementary particle physics, nuclear physics, quantum gravity) have been collected in a book that is aptly titled 'Diagrammatics'⁷. With this book, and your imagination for story-drawing you can calculate the quantum mechanical amplitudes corresponding to any process you want.

4.10 Dyson equation

We have obtained the lowest order non-zero correction to the Green's function of the electron-phonon system (4.78). We can then look for the Feynman diagrams of the next order non-zero contribution. This will be of fourth order in $M(\mathbf{q})$, and consist of the connected diagrams containing two phonon and five fermion lines. Let's for clarity leave out the tadpole diagrams, removing the $q = 0$ phonons or setting $M(0) = 0$. You can check that the remaining connected diagrams are:

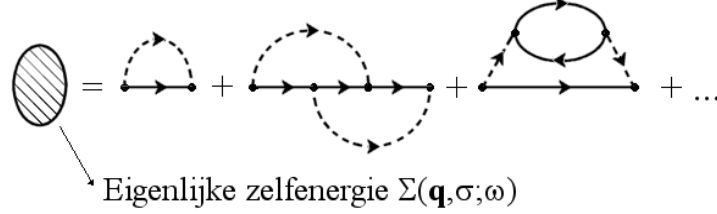


Connected diagrams of fourth order

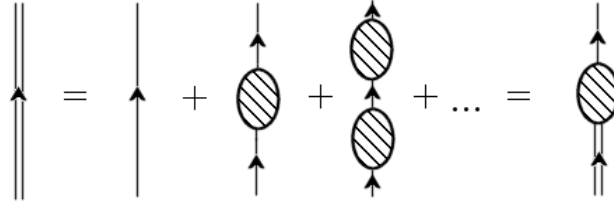
The only diagram without $q = 0$ phonons up to second order in $M(\mathbf{q})$ was the self-energy diagram. From all four diagrams shown above for fourth order, diagram A will be easy to calculate. It is the only diagram that can fall in two pieces by just cutting a single internal line (i.e. not the starting or final line). Try it, if you cut an internal line in any of the others, the whole thing is still tethered together. Cutting the middle line in diagram A just results in two pieces that we obtained in lower order. Such diagrams that can be cut up in lower order parts are called *improper diagrams*. The others are called *proper diagrams*.

⁷M. Veltman, "Diagrammatics: the path to Feynman diagrams" (Cambridge University Press, Cambridge, 1994). Verscheen eerst als G. 't Hooft en M. Veltman, Diagrammar, CERN Yellow Report, 73-9. Is ook op het CERNweb te downloaden: http://preprints.cern.ch/cgi-bin/setlink?base=cernrep&categ=Yellow_Report&id=73-09

We define the *proper self-energy* $\Sigma(\mathbf{k}, \sigma; \omega)$ as the following pieces of diagram:



(It is called “eigenlijke zelfenergie” in Dutch – improper would be “oneigenlijk”. For the non-native speaker, don’t hurt your tongue trying to pronounce all this). Note that these pieces all begin and end in a vertex with one ‘loose bond’, an open connector in which to plug in an electron line. The contributions to the Green’s function, also these of higher orders, all begin and end with $G_0(\mathbf{k}, \sigma; \omega)$. For the part in between we can write all improper diagrams by stringing together pieces of proper self-energy with electron lines! Diagram A above is found by stringing together two copies of lowest order piece in the proper self energy. So, the collection of all connected diagrams can be written as the collection of all proper diagrams, and all ways to string together two or more pieces of proper self-energy diagrams. Let’s put this conclusion into drawing. If we denote the Green’s function of the complete interacting system with a double line (rather than a single line, reserved for G_0), then the Green’s function is given by



Graphical representation of the Dyson equation

Let’s drop the $(\mathbf{k}, \sigma; \omega)$ from $G(\mathbf{k}, \sigma; \omega)$ for ease of notation in the next expression. The first equality is

$$\begin{aligned} G &= G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots \\ &= G_0 + G_0 \Sigma \underbrace{(G_0 + G_0 \Sigma G_0 + \dots)}_G \end{aligned}$$

This is called the Dyson series. From it we get

$$G(\mathbf{k}, \sigma; \omega) = G_0(\mathbf{k}, \sigma; \omega) + G_0(\mathbf{k}, \sigma; \omega) \Sigma(\mathbf{k}, \sigma; \omega) G(\mathbf{k}, \sigma; \omega). \quad (4.99)$$

This is called the Dyson equation. We can solve it with respect to G :

$$\boxed{G(\mathbf{k}, \sigma; \omega) = \frac{G_0(\mathbf{k}, \sigma; \omega)}{1 - G_0(\mathbf{k}, \sigma; \omega) \Sigma(\mathbf{k}, \sigma; \omega)}} \quad (4.100)$$

If we now plug in our result for G_0 for a single electron, we find

$$G(\mathbf{k}, \sigma; \omega) = \frac{1}{\omega - E_{\mathbf{k}}/\hbar + i\delta - \Sigma(\mathbf{k}, \sigma; \omega)} \quad (4.101)$$

Great! We've just summed infinitely many diagrams!

But there is more. Remember from the Lehmann representation (section 4.3) that we can interpret poles of Green's functions and relate them to quasiparticles. The Green's function shown here has a pole satisfying $\omega = E_{\mathbf{k}}/\hbar + \Sigma(\mathbf{k}, \sigma; \omega)$. As long as Σ is not too big with respect to $E_{\mathbf{k}}$, then we can approximate the pole's location by $\omega \approx E_{\mathbf{k}}/\hbar + \Sigma(\mathbf{k}, \sigma; E_{\mathbf{k}}/\hbar)$. This result is interpreted as follows: if the eigen-energies of the unperturbed system were given by $E_{\mathbf{k}}$, then the effect of interactions consists in shifting these energies by an amount

$$\Delta E_{\mathbf{k}} = \hbar \operatorname{Re}[\Sigma(\mathbf{k}, \sigma; E_{\mathbf{k}}/\hbar)] \quad (4.102)$$

related to the real part of the self-energy, and giving these states a life time

$$\tau = \hbar / \operatorname{Im}[\Sigma(\mathbf{k}, \sigma; \omega)] \quad (4.103)$$

related to the inverse of the imaginary part of the self energy. Well, no wonder we call this Σ the “self-energy” of the interacting electrons. And now that we have the quasiparticle dispersion relation, we have access to the thermodynamics of the system using our good old statistical mechanics for weakly interacting (quasi)particles.

The power of the Dyson equation lies in the fact that it performs resummations of an infinite amount of diagrams. Suppose that we limit ourselves to the lowest order non-zero perturbation result for our electron-phonon problem: $G(\mathbf{k}, \sigma; \omega) = G_0(\mathbf{k}, \sigma; \omega) + G_2(\mathbf{k}, \sigma; \omega)$. Having done this calculation, we immediately have Σ_2 since it is just a part of G_2 , namely

$$\Sigma_2(\mathbf{k}, \sigma; \omega) = i \sum_{\mathbf{k}'} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{|M(\mathbf{k}')|^2}{\hbar^2} D_0(\mathbf{k}'; \omega') G_0(\mathbf{k} - \mathbf{k}', \sigma; \omega - \omega') \quad (4.104)$$

This is the lowest order non-zero diagram in Σ . If we now refuse to do any more integrals, we can use this Σ_2 in stead of Σ in the Dyson equation. Doing so, we have in fact also included part of the higher order contributions, for example $G_0 \Sigma_2 G_0 \Sigma_2 G_0$ and $G_0 \Sigma_2 G_0 \Sigma_2 G_0 \Sigma_2 G_0$. Thus, we calculate one diagram and we get a sum over infinitely many at no extra cost. It's not yet all diagram, so it is a partial resummation, but nevertheless this is a result beyond simple perturbation theory. It will be particularly useful in the next chapter to figure out how photons propagate through the solid.

Addendum: Dirac or interaction picture

The Schrödinger and Heisenberg picture should be known from your quantum mechanics classes. The Dirac picture is not much more complicated. Consider a Hamiltonian given by the sum of a part \hat{H}_0 that can be diagonalised and a perturbation \hat{H}_1 . The properties of the three pictures of quantum mechanics, and their links, are summarized in the table below:

Schrödinger picture $i\hbar \frac{d}{dt} \Psi(t)\rangle_S = \hat{H} \Psi(t)\rangle_S$ \hat{A}_S time independent.	\longleftrightarrow	$ \Psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar} \Psi(t)\rangle_S$ $\hat{A}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{A}_S e^{-i\hat{H}_0 t/\hbar}$	(4.105)
\uparrow $ \Psi(t)\rangle_S = e^{-i\hat{H} t/\hbar} \Psi\rangle_H$ $\hat{A}_H(t) = e^{i\hat{H} t/\hbar} \hat{A}_S e^{-i\hat{H} t/\hbar}$	\downarrow	Interaction picture $i\hbar \frac{d}{dt} \Psi(t)\rangle_I = \hat{H}'_1 \Psi(t)\rangle_I$ $i\hbar \frac{d}{dt} \hat{A}_I(t) = [\hat{A}_I(t), \hat{H}_0]$	
\downarrow Heisenberg picture $ \Psi\rangle_H$ time independent $i\hbar \frac{d}{dt} \hat{A}_H(t) = [\hat{A}_H(t), \hat{H}]$	\longleftrightarrow	\uparrow $ \Psi(t)\rangle_I = e^{-i\hat{H}_1 t/\hbar} \Psi\rangle_H$ $\hat{A}_I(t) = e^{-i\hat{H}_1 t/\hbar} \hat{A}_H e^{i\hat{H}_1 t/\hbar}$	

Here $\hat{H}'_1 = e^{i\hat{H}_0 t/\hbar} \hat{H}_1 e^{-i\hat{H}_0 t/\hbar}$. We also assume that we can write

$$\exp\{i\hat{H}_0 t/\hbar\} \exp\{-i\hat{H} t/\hbar\} = \exp\{i\hat{H}_1 t/\hbar\}.$$

Furthermore, we have to choose (arbitrarily) an initial time $t = 0$ where $\hat{A}_S = \hat{A}_I(0) = \hat{A}_H(0)$ and $|\Psi\rangle_H = |\Psi(0)\rangle_S = |\Psi(0)\rangle_I$ holds; at that time all three pictures coincide. From that time onwards, the dynamics is described differently: in the Heisenberg picture the operators change, in the Schrödinger picture the wave functions change, and in the interaction or Dirac picture both change – the wave functions according to the perturbation part, and operators via the unperturbed Hamiltonian.

Chapter 5

Dielectric function and linear response

In the previous chapter we set up and investigated the diagrammatic technique to calculate the properties of the electron gas. Here we are going to apply this technique to find how the electron gas responds to an external perturbation. This makes the link to experiments that probe material properties. In these experiments, the response of the material to an external probe such as an electric field for conductance, an electromagnetic wave for optical properties, a polarized neutron beam for spin waves. We're going to focus on the case of light shining on a material, and therefore we need to begin by reviewing how Maxwell's theory of electromagnetism is adapted to include the presence of a medium, a material background.

5.1 Remembering Maxwell in a medium

It is worthwhile to remind ourselves of some basic electromagnetism before we proceed. Start from the Maxwell equations,

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_v, \quad (5.1)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (5.2)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (5.3)$$

$$\nabla \times \mathbf{B} = \mu_v \mathbf{J} + \mu_v \epsilon_v \frac{\partial \mathbf{E}}{\partial t}, \quad (5.4)$$

and the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (5.5)$$

Here, I work in SI units, so the electric field \mathbf{E} is in volt/m, the magnetic induction \mathbf{B} is in tesla, the charge density ρ is in coulomb/m³, the current

density is in amps/m², the vacuum permittivity is $\epsilon_v = 8.85 \dots \times 10^{-12}$ farad/m, and the vacuum permeability $\mu_v = 4\pi \times 10^{-7}$ henry/m.

In a material there are already a lot of charges and currents present. Most charges and currents are compensated, so the net charge and current is zero. But sometimes we can pull the charges in the material a bit apart, creating dipoles, or redistribute the charges in the material, which also creates a nonzero net charge distribution. And sometimes little current loops prefer to run clockwise rather than anticlockwise and the two directions don't add up to zero. These kind of changes in charge or currents will be induced in the material when we apply an external perturbation. Therefore we'll call these uncompensated charges and currents running around in the material the *induced charge density* ρ_{ind} and the *induced current* J_{ind} .

On the other hand, we can take some external charge (such as an ion) and shoot it in the material, or we can drive an external current through the material by hooking it up to an electric circuit. We want distinguish these external charges and currents from the induced ones, and denote them by ρ_{ext} and J_{ext} . In total we have

$$\rho = \rho_{ind} + \rho_{ext}, \quad (5.6)$$

$$\mathbf{J} = \mathbf{J}_{ind} + \mathbf{J}_{ext}. \quad (5.7)$$

With this distinction, the first and fourth Maxwell equations (those with source terms) are now written as

$$\nabla \cdot \mathbf{E} = (\rho_{ind} + \rho_{ext}) / \epsilon_v, \quad (5.8)$$

$$\nabla \times \mathbf{B} = \mu_v (\mathbf{J}_{ind} + \mathbf{J}_{ext}) + \mu_v \epsilon_v \frac{\partial \mathbf{E}}{\partial t}. \quad (5.9)$$

We'd like to be able to ignore the presence of the complicated material and the complication of all those induced charge and current redistributions in the material. We'd like to work with effective fields that look like obeying Maxwell's equations as if there were no material:

$$\nabla \cdot \mathbf{D} = \rho_{ext}, \quad (5.10)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_{ext} + \frac{\partial \mathbf{D}}{\partial t} \quad (5.11)$$

The fields defined by these equations are the displacement field \mathbf{D} and the magnetic field \mathbf{H} (what's in a name). Note that by (stupid) definition the units are different, \mathbf{D} is in coulomb per meter and \mathbf{H} is in amps per meter. Now, together with the second and third Maxwell equations (those that didn't contain any source terms), we have again a set of equations as if no material is present. Of course, all we've really done is swept the effects of the medium under the rug. How do we deal with the induced charges and currents? This requires a hard many-body calculations, but there are two easy ways to approximate this.

5.1.1 Polarization and magnetisation

The first way is to give ρ_{ind} and \mathbf{J}_{ind} their own field, by defining

$$-\nabla \cdot \mathbf{P} = \rho_{ind} \quad (5.12)$$

$$\nabla \times \mathbf{M} = \mathbf{J}_{ext} - \frac{\partial \mathbf{P}}{\partial t} \quad (5.13)$$

Again, more silliness with conventions: a changed sign for the polarization field \mathbf{P} (again in coulomb per meter) and this also trickles down in the equation for the magnetization \mathbf{M} (in amps per meter). These new fields can be interpreted as the induced polarization field from all the little induced charge displacements or dipoles, and the induced magnetic field from all the uncompensated induced current loops and the changing polarization field. Now we can relate \mathbf{E} , \mathbf{D} and \mathbf{P} through

$$\nabla \cdot \mathbf{E} = \frac{1}{\varepsilon_v} (\rho_{ind} + \rho_{ext}) = \frac{1}{\varepsilon_v} (\nabla \cdot \mathbf{D} - \nabla \cdot \mathbf{P}) \quad (5.14)$$

$$\Rightarrow \varepsilon_v \mathbf{E} = \mathbf{D} - \mathbf{P} \quad (5.15)$$

$$\Leftrightarrow \mathbf{D} = \varepsilon_v \mathbf{E} + \mathbf{P}. \quad (5.16)$$

Note that the vacuum permittivity is just a constant to get the units right. We can also relate \mathbf{B} , \mathbf{H} and \mathbf{M} in the same way

$$\nabla \times \mathbf{B} = \mu_v (\mathbf{J}_{ind} + \mathbf{J}_{ext}) + \mu_v \varepsilon_v \frac{\partial \mathbf{E}}{\partial t} \quad (5.17)$$

$$\Leftrightarrow \nabla \times \mathbf{B} = \mu_v \left(\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} \right) + \mu_v \left(\nabla \times \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t} \right) + \mu_v \varepsilon_v \frac{\partial \mathbf{E}}{\partial t}$$

$$\Leftrightarrow \frac{1}{\mu_v} \nabla \times \mathbf{B} = \nabla \times \mathbf{H} + \nabla \times \mathbf{M}$$

from which

$$\mathbf{H} = \mathbf{B}/\mu_v - \mathbf{M} \quad (5.18)$$

Now it is clear what we want from a microscopic theory: it should give us the polarization \mathbf{P} and the magnetisation \mathbf{M} that are the material's response to a field \mathbf{B} and \mathbf{E} . In its simplest form (first order perturbation) one could guess that the induced polarization will just be proportional to the electric field, $\mathbf{P} = \chi_e \varepsilon_v \mathbf{E}$, and that the magnetization will just be proportional to the magnetic induction, $\mathbf{M} = \chi_m \mathbf{B}/\mu_v$. The theory can be made more precise by looking at nonlinear terms, and by taking into account that polarization may be induced in a direction different from that of the electric field,...

5.1.2 Dielectric function and permeability

The second way to include the effects of the material is not to use \mathbf{P} and \mathbf{M} , but to include the influence of the medium into the permittivity and the permeability, and change the vacuum values to new values. That is, we change

$$\mathbf{D} = \varepsilon_v \mathbf{E} + \mathbf{P} \rightarrow \mathbf{D} = \varepsilon \mathbf{E}, \quad (5.19)$$

and

$$\mathbf{H} = \mathbf{B}/\mu_v - \mathbf{M} \rightarrow \mathbf{H} = \mathbf{B}/\mu. \quad (5.20)$$

You immediately see that this won't always work with a scalar for ε and $1/\mu$. Indeed, when the electric field for example results in an induced polarization that is in a different direction, then ε should be a tensor. Also, if the response is nonlinear, then ε still depends on \mathbf{E} , and the whole concept becomes very messy indeed. But, in the simple world of homogeneous, isotropic materials and linear response, all still works well. Another side-remark is that we define the ε and $1/\mu$ strictly speaking in reciprocal space, i.e. through the relations

$$\mathbf{D}(\mathbf{k}, \omega) = \varepsilon(\mathbf{k}, \omega) \mathbf{E}(\mathbf{k}, \omega) \quad (5.21)$$

$$\mathbf{H}(\mathbf{k}, \omega) = \mathbf{B}(\mathbf{k}, \omega)/\mu(\mathbf{k}, \omega) \quad (5.22)$$

As you certainly remember, products in reciprocal space become, after inverse Fourier transform, convolutions in real space. So if the dielectric function depends from point to point, be aware that $\mathbf{D}(\mathbf{r}, \omega) \neq \varepsilon(\mathbf{r}, \omega) \mathbf{E}(\mathbf{r}, \omega)$, where the NOT EQUAL sign is to be emphasized. The equality is in reciprocal space, by definition. In our simple world of homogeneous materials, ε doesn't depend on position and we only have a frequency dependence, $\varepsilon(\omega)$, and the above caveat is often omitted and forgotten.

Another thing often forgotten is the distinction between longitudinal and transversal dielectric function – a subtlety that we discuss in the next section. But first, let's see what becomes of the Maxwell equations when ε is just a constant, not even depending on ω . Then we can combine (5.10) and (5.11) with $\mathbf{D} = \varepsilon \mathbf{E}$ and $\mathbf{H} = \mathbf{B}/\mu$ and get

$$\nabla \cdot \mathbf{E} = \rho_{ext}/\varepsilon, \quad (5.23)$$

$$\nabla \times \mathbf{B} = \mu \mathbf{J}_{ext} + \mu \varepsilon \frac{\partial \mathbf{E}}{\partial t}. \quad (5.24)$$

to be solved with the equations without source terms,

$$\nabla \cdot \mathbf{B} = 0, \quad (5.25)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (5.26)$$

and the continuity equation for the external charges

$$\frac{\partial \rho_{ext}}{\partial t} + \nabla \cdot \mathbf{J}_{ext} = 0. \quad (5.27)$$

That looks again like the Maxwell equations without the presence of the material! The changes are in the value of the permittivity, now ε rather than ε_v and the permeability μ rather than μ_v .

What are the consequences? One of them is a different strength of the Coulomb potential – If we have a point charge $\rho(\mathbf{r}) = q\delta(\mathbf{r})$ we get

$$\begin{aligned} \nabla \cdot \varepsilon \mathbf{E} &= q\delta(\mathbf{r}) \\ \Rightarrow \mathbf{E} &= \frac{1}{4\pi\varepsilon} \frac{q}{r} \mathbf{e}_r \end{aligned} \quad (5.28)$$

The coulomb potential now has ε in stead of ε_v . Remember that the photon propagator $1/k^2$ in the electron gas description from the previous chapter is related to the Fourier transform of the Coulomb interaction. The photon propagator in the medium is changed by a factor $\varepsilon/\varepsilon_v$. This also means that another consequence will be that electromagnetic waves propagate differently.

5.1.3 Drude dielectric function

OK, let's take a step back and calculate our first dielectric function, to see how this second way works. Let's take *no external charges* and suppose that *all fields oscillate in time with a frequency ω* . That is, we can write all functions $F(\mathbf{r}, t)$ as $F(\mathbf{r})e^{-i\omega t}$. Then the time derivatives in the (original) Maxwell equations simplify and we get:

$$\nabla \cdot \varepsilon_v \mathbf{E} = \rho_{ind}, \quad (5.29)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (5.30)$$

$$\nabla \times \mathbf{E} = i\omega \mathbf{B}, \quad (5.31)$$

$$\nabla \times \mathbf{B} = \mu_v \mathbf{J}_{ind} - i\mu \varepsilon_v \omega_v \mathbf{E}. \quad (5.32)$$

and

$$-i\omega \rho_{ind} + \mathbf{J}_{ind} = 0. \quad (5.33)$$

The continuity equation can be used to replace the charge density by the (longitudinal, see next section) current, and the first equation becomes

$$\nabla \cdot (\varepsilon_v \mathbf{E}) = \frac{\mathbf{J}_{ind}}{i\omega}. \quad (5.34)$$

Now, we still need to eliminate \mathbf{J} . Suppose that we don't have any external current, then we are left only with the induced currents. Let's take our simplest theory for the induced current, that is Ohm's law:

$$\mathbf{J}_{ind} = \sigma(\omega) \mathbf{E}. \quad (5.35)$$

That's all we need to get rid of the induced current in the first and fourth Maxwell equations:

$$\nabla \cdot (\varepsilon_v \mathbf{E}) = \frac{\sigma}{i\omega} \mathbf{E}, \quad (5.36)$$

$$\nabla \times \mathbf{B} = \mu_v \sigma \mathbf{E} - i\mu \varepsilon_v \omega_v \mathbf{E}. \quad (5.37)$$

This is

$$\nabla \cdot \left[\left(\varepsilon_v - \frac{\sigma}{i\omega} \right) \mathbf{E} \right] = 0, \quad (5.38)$$

$$\nabla \times \mathbf{B} = -i\mu \left(\varepsilon_v - \frac{\sigma}{i\omega} \right) \omega_v \mathbf{E}. \quad (5.39)$$

Now you see that it is indeed possible to write the Maxwell equations as if the material is not present, provided we use a dielectric function for the metal ε_m , given by

$$\varepsilon_m(\omega) = \varepsilon_v - \frac{\sigma(\omega)}{i\omega}. \quad (5.40)$$

We then get

$$\nabla \cdot \varepsilon_m \mathbf{E} = 0, \quad (5.41)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (5.42)$$

$$\nabla \times \mathbf{E} = i\omega \mathbf{B}, \quad (5.43)$$

$$\nabla \times \mathbf{B} = -i\mu\varepsilon_m\omega_v \mathbf{E}. \quad (5.44)$$

This is the same as (5.29)–(5.32), without the induced fields and with changed ε . We can now use the Drude conductivity (1.4) to get

$$\varepsilon_m(\omega) = \varepsilon_v - \frac{1}{i\omega} \frac{ne^2\tau}{m} \frac{1}{1 - i\omega\tau} \quad (5.45)$$

If we assume $\omega\tau \gg 1$ (valid for optical frequencies and most metals), and introduce the short-hand notation

$$\omega_{pl} = \frac{ne^2}{m\varepsilon_v} \quad (5.46)$$

called the *plasma frequency*, we get the *Drude dielectric function for metals*:

$$\frac{\varepsilon_m(\omega)}{\varepsilon_v} = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i/\tau)} \approx 1 - \frac{\omega_{pl}^2}{\omega^2} \quad (5.47)$$

Furthermore, we know that the solution of the Maxwell equations in vacuum is a wave, $F(\mathbf{r}) = Fe^{i\mathbf{k}\mathbf{r}}$ with wave length

$$k = \omega/c = \varepsilon_v\mu_v\omega \quad (5.48)$$

All we need to do now to find the solutions is the metal with our simplest dielectric function is to replace ε_v by ε_m , and obtain

$$k = \varepsilon_m\mu_v\omega = \varepsilon_v\mu_v\sqrt{\omega^2 - \omega_{pl}^2} \quad (5.49)$$

For frequencies much higher than the plasma frequency $\omega \gg \omega_{pl}$ the waves propagate nearly with vacuum light speed. But, for $\omega < \omega_{pl}$, the situation is quite different: k becomes imaginary, instead of waves we have an exponentially decaying amplitude (the decay length is roughly ω_{pl}/c). This means electromagnetic waves with frequencies smaller than the plasma frequency cannot penetrate the metal and will be reflected. Since ω_{pl} usually is in the far-UV, this means that seen in optical frequencies, metals are shiny. Reducing n , the density of electrons, brings down the plasma frequency.

For insulators, the plasma frequency goes to zero, so insulating crystals are transparent (unless there are some other light-absorbing molecules embedded in them of course).

The goal of this chapter is to show how better approximations to ε can be calculated using our diagrammatic formalism. But first, as announced, some words on the distinction between longitudinal and transversal fields.

5.2 Longitudinal and transversal fields

There is a subtle difference between EM fields generated by transversal currents, such as light, and EM fields generated by charges. This is not generally appreciated, and I add it to these course notes just for those of you who are interested in the fine print of electromagnetism. All other may skip this chapter with advanced material.

5.2.1 Helmholtz decomposition

First, it is useful to be reminded of the fact that any vector field $\mathbf{V}(\mathbf{r})$ for which a Fourier transform exists can be decomposed in longitudinal and transversal fields, $\mathbf{V}(\mathbf{r}) = \mathbf{V}_\ell(\mathbf{r}) + \mathbf{V}_{tr}(\mathbf{r})$. A vector field is called *longitudinal* or *curl-free* or *irrotational* if and only if

$$\nabla \times \mathbf{V}_\ell(\mathbf{r}) = \mathbf{0}. \quad (5.50)$$

A vector field is called *transversal* or *divergence-free* if and only if

$$\nabla \cdot \mathbf{V}_{tr}(\mathbf{r}) = 0. \quad (5.51)$$

The decomposition is performed in reciprocal space (i.e. via the Fourier transform). This changes the curl and div into

$$i\mathbf{k} \times \mathbf{V}_\ell(\mathbf{k}) = \mathbf{0}, \quad (5.52)$$

$$i\mathbf{k} \cdot \mathbf{V}_{tr}(\mathbf{k}) = 0. \quad (5.53)$$

Splitting the field in longitudinal and transversal components is called the Helmholtz decomposition, and it requires the introduction of the unit vector along the \mathbf{k} direction:

$$\boldsymbol{\kappa} = \frac{\mathbf{k}}{k}. \quad (5.54)$$

With this unit vector, the components can be found through

$$\mathbf{V}_\ell(\mathbf{k}) = \boldsymbol{\kappa} [\boldsymbol{\kappa} \cdot \mathbf{V}(\mathbf{k})], \quad (5.55)$$

$$\mathbf{V}_{tr}(\mathbf{k}) = \mathbf{V}(\mathbf{k}) - \mathbf{V}_\ell(\mathbf{k}). \quad (5.56)$$

Note that if we go back to real space, the multiplication $\boldsymbol{\kappa} \cdot \mathbf{V}(\mathbf{k})$ becomes a convolution, which means that the value of \mathbf{V}_ℓ or $\mathbf{V}_{tr}(\mathbf{r})$ in the point \mathbf{r} depends

non-locally on the values of $\mathbf{V}(\mathbf{r}')$ in all locations \mathbf{r}' . Typically, the main contribution will come from locations within a wavelength's distance from \mathbf{r} . In reciprocal space however, the connection between the vector field $\mathbf{V}(\mathbf{k})$ and its longitudinal and transverse components remains local, and we need to know $\mathbf{V}(\mathbf{k})$ only in a single \mathbf{k} -value to find the longitudinal and transversal field in this same value. Note that there is no Helmholtz decomposition for $\mathbf{V}(\mathbf{0})$. Furthermore, it is clear that the decomposition is not relativistically (Lorentz) invariant, meaning that the Helmholtz decomposition of four-vectors depends on the frame of reference. Finally, note that $\mathbf{V}_{tr}(\mathbf{k}) \cdot \mathbf{V}_\ell(\mathbf{k}) = 0$.

5.2.2 Longitudinal from charges, transverse from current

The Maxwell equations in reciprocal space are well-suited to rewrite in longitudinal and transversal components. Via the calculation rules $\mathbf{k} \times \mathbf{V} = \mathbf{k} \times \mathbf{V}_{tr}$ and $\mathbf{k} \cdot \mathbf{V} = \mathbf{k} \cdot \mathbf{V}_\ell$ it is easy to find

$$\mathbf{E}_\ell(\mathbf{k}, t) = \frac{-i\mathbf{k}}{k^2} \frac{1}{\varepsilon_v} \rho(\mathbf{k}, t), \quad (5.57)$$

$$\mathbf{B}_\ell(\mathbf{k}, t) = 0, \quad (5.58)$$

$$\dot{\mathbf{B}}_{tr}(\mathbf{k}, t) = -i\mathbf{k} \times \mathbf{E}_{tr}(\mathbf{k}, t), \quad (5.59)$$

$$\dot{\mathbf{E}}_{tr}(\mathbf{k}, t) = ic^2 \mathbf{k} \times \mathbf{B}_{tr}(\mathbf{k}, t) - \frac{1}{\varepsilon_v} \mathbf{J}_{tr}(\mathbf{k}, t). \quad (5.60)$$

There are two independent source terms, $\rho(\mathbf{k}, t)$ for the longitudinal fields and $\mathbf{J}_{tr}(\mathbf{k}, t)$ for the transversal fields. The longitudinal current is not independent from the charge, as it is given by the continuity equation $\dot{\rho}(\mathbf{k}, t) = -i\mathbf{k} \cdot \mathbf{J}_\ell(\mathbf{k}, t)$.

We can also formulate the Maxwell equations slightly differently, using the vector potential and scalar potential. We can use the gauge freedom to choose the vector potential completely transversal, $\mathbf{A}(\mathbf{k}, t) = \mathbf{A}_{tr}(\mathbf{k}, t)$. This is the Coulomb gauge. Then, the Maxwell equations become

$$k^2 \phi(\mathbf{k}, t) = \frac{1}{\varepsilon_v} \rho(\mathbf{k}, t), \quad (5.61)$$

$$\ddot{\mathbf{A}}_{tr}(\mathbf{k}, t) + c^2 k^2 \mathbf{A}_{tr}(\mathbf{k}, t) = \frac{1}{\varepsilon_v} \mathbf{J}_{tr}(\mathbf{k}, t). \quad (5.62)$$

from which we get again the longitudinal and transversal electromagnetic fields:

$$\mathbf{E}_\ell(\mathbf{k}, t) = -i\mathbf{k}\phi(\mathbf{k}, t), \quad (5.63)$$

$$\mathbf{B}_\ell(\mathbf{k}, t) = \mathbf{0}, \quad (5.64)$$

$$\mathbf{B}_{tr}(\mathbf{k}, t) = i\mathbf{k} \times \mathbf{A}_{tr}(\mathbf{k}, t), \quad (5.65)$$

$$\mathbf{E}_{tr}(\mathbf{k}, t) = -\dot{\mathbf{A}}_{tr}(\mathbf{k}, t). \quad (5.66)$$

where again $\dot{\rho}(\mathbf{k}, t) = -i\mathbf{k} \cdot \mathbf{J}_\ell(\mathbf{k}, t)$ must be satisfied. The solutions are given

by

$$\phi(\mathbf{k}, t) = \frac{1}{\varepsilon_v} \rho(\mathbf{k}, t) \frac{1}{k^2} \quad (5.67)$$

$$\Rightarrow \frac{1}{4\pi\varepsilon_v} \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.68)$$

and

$$\begin{aligned} \mathbf{A}_{tr}(\mathbf{k}, \omega) &= \frac{\mathbf{J}_{tr}(\mathbf{k}, \omega)/\varepsilon_v}{c^2 k^2 - \omega^2} \\ \Rightarrow \mathbf{A}_{tr}(\mathbf{r}, t) &= \frac{\mu_v}{4\pi} \int d\mathbf{r}' \frac{\mathbf{J}_{tr}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|/c)}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (5.69)$$

The solution for the scalar potential is not retarded, that for the vector potential is. That is a consequence of choosing the Coulomb gauge in stead of the Lorentz gauge.

5.2.3 A distinction to keep in mind

It is of crucial importance to note that the source terms for the transverse fields in both formulations is given by \mathbf{J}_{tr} *AND NOT BY \mathbf{J}* ! This means that in real space the time derivative of the transversal field $\mathbf{E}_{tr}(\mathbf{r}, t)$ will depend on the values of the current $\mathbf{J}(\mathbf{r}')$ in all points \mathbf{r}' (but mainly those points within a wave length from \mathbf{r}). This is very often overlooked, and \mathbf{J} , \mathbf{J}_ℓ and \mathbf{J}_{tr} are not distinguished in most texts, and assumed equal, which is mathematical nonsense.

When we eliminate currents and charges from the medium by introducing the dielectric function or conductivities as we did in the first section of this chapter, we should be introducing *two* distinct conductivities: the longitudinal and the transversal,

$$\mathbf{J}_{\ell, tr}(\mathbf{k}, \omega) = \sigma_{\ell, tr}(\mathbf{k}, \omega) \mathbf{E}_{\ell, tr}(\mathbf{k}, \omega) = i\omega (\varepsilon_{\ell, tr} - \varepsilon_v) \mathbf{E}_{\ell, tr}(\mathbf{k}, \omega). \quad (5.70)$$

These need not be equal, $\varepsilon_{tr} \neq \varepsilon_\ell$. Indeed, Lindhard has extended the long-wavelength Drude result (5.47) to

$$\frac{\varepsilon_{tr}(\omega)}{\varepsilon_v} = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i/\tau)} \quad \text{and} \quad \frac{\varepsilon_\ell(\omega)}{\varepsilon_v} = 1 - \frac{\omega_{pl}^2}{(\omega + i/\tau)^2}. \quad (5.71)$$

As it happens, for simple materials, at optical wavelengths and frequencies where $\omega\tau \gg 1$, the difference does not matter. We will therefore continue to work with just a single σ and a single ε , but keep in mind that the better physicist will make a distinction between longitudinal response (relating to redistributing charges) and transversal response (related to transversal currents).

5.3 Kubo Response formalism

A cornerstone of modern quantum many-body physics is no doubt Kubo's formalism for linear response. It teaches us how to compute the change in various observables, resulting from an external pump or perturbation coupling to the system. It only works for small changes, in the linear regime. Here 'linear' means that if you double the strength of the perturbation, the change in the observable that you monitor will also double.

Let's start from the Hamiltonian \hat{H}_0 of the system without the external perturbation. Now this is the Hamiltonian of the full system with electron-electron and electron-phonon interactions, and with the generally unknown ground state $|\Psi_G\rangle$, it is only the externally applied disturbance that is not in it! This doesn't mean that we don't know anything about the interacting system. For example, we can safely assume that without any external disturbance, the density of electrons in the metal will be homogeneous, so the charge is compensated everywhere. What we want to know, is of course the net charge density that will be induced by an external probe field. We can describe the system with the many-body ground state wavefunction $|\Psi_G\rangle$ as we did before, but here we switch to the many-body density matrix. At temperature zero, it is given by $\hat{\rho}_0 = |\Psi_G\rangle\langle\Psi_G|$, but the advantage is that we can also compute it at nonzero temperature,

$$\hat{\rho}_0 = \frac{1}{\mathcal{Z}} e^{-\hat{H}_0/(k_B T)} = \frac{1}{\mathcal{Z}} e^{-\beta \hat{H}_0}, \quad (5.72)$$

where $\beta = 1/(k_B T)$ is the inverse temperature and $\mathcal{Z} = \text{Tr}[\hat{\rho}_0]$ is the partition sum. Don't confuse this $\hat{\rho}_0$ with the charge density $\rho = \rho_{ind} + \rho_{ext}$ that we had before! It's an unlucky notation convention that uses the Greek letter rho for both – there are only so many letters in the alphabet lest we switch to Chinese symbols. I will write the density matrix, being an operator, with a hat. Only in this section we will use the density matrix, afterwards we go back to using rho just for densities, so bear with me. If you know the density matrix, you also know all quantum statistical expectation values

$$\langle \hat{A} \rangle = \text{Tr}[\hat{\rho}_0 \hat{A}]. \quad (5.73)$$

The $\langle \dots \rangle$ bracket now includes both the quantum mechanical expectation value and the averaging over a statistical ensemble. At temperature zero this becomes

$$\text{Tr}[\hat{\rho}_0 \hat{A}] = \langle \Psi_G | \hat{\rho}_0 \hat{A} | \Psi_G \rangle = \langle \Psi_G | (|\Psi_G\rangle\langle\Psi_G|) \hat{A} | \Psi_G \rangle = \langle \Psi_G | \hat{A} | \Psi_G \rangle \quad (5.74)$$

as it should.

Now we introduce the perturbation. This adds an extra term to the Hamiltonian:

$$\hat{H}_1(t) = \hat{B}h(t). \quad (5.75)$$

Here the function $h(t)$ captures the time dependence of the probe (e.g. the electromagnetic field is only switched on for a certain time, and oscillates). The probe is treated as a macroscopic external field – so we still treat it classically. For example: we don't introduce operators for photons, we write the electric field. The operator \hat{B} is the observable to which the probe couples. For example, if we send in an electric field, then this will couple to the density of electrons. If we send in polarized neutrons, this will couple to the spin field or magnetization $\hat{\mathbf{M}}(\mathbf{r})$.

5.3.1 Linearized quantum Liouville equation

The main question to be solved is: how does the expectation value of the observable \hat{A} that we monitor change as a function of time, due to the perturbation? Again, we could be monitoring all sorts of things: \hat{A} can be the phonon density or the electron density or the spin density,... So, what we want to calculate is

$$\langle \hat{A}(t) \rangle = \text{Tr} [\hat{\rho}(t) \hat{A}], \quad (5.76)$$

where now $\hat{\rho}(t)$ is the time dependent density matrix of the whole system, including the perturbation.

The main approximation done by Kubo in 1957 is that we will linearize our result as a function of $h(t)$, taken as the small parameter of the expansion. So, we write

$$\hat{\rho}(t) = \hat{\rho}_0 + \Delta\hat{\rho}(t), \quad (5.77)$$

and assume $\Delta\hat{\rho}(t)$ is small, of first order in $h(t)$. We linearize the quantum Liouville equation

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)] = [\hat{H}_0 + \hat{H}_1, \hat{\rho}(t)], \quad (5.78)$$

by noting that $\hat{\rho}_0$ doesn't depend on time and expanding:

$$i\hbar \frac{\partial}{\partial t} [\Delta\hat{\rho}(t)] = \underbrace{[\hat{H}_0, \hat{\rho}_0]}_{\text{zero}} + [\hat{H}_1, \hat{\rho}_0] + [\hat{H}_0, \Delta\hat{\rho}(t)] + \underbrace{[\hat{H}_1, \Delta\hat{\rho}(t)]}_{\text{higher order}}. \quad (5.79)$$

The first term is zero because it is proportional to $\partial\hat{\rho}_0/\partial t$ and the last term is of second order. Now we go to the Dirac or interaction picture¹ and define

$$\delta\hat{\rho}(t) = e^{i\hat{H}_0 t/\hbar} \Delta\hat{\rho}(t) e^{-i\hat{H}_0 t/\hbar} \Leftrightarrow \Delta\hat{\rho}(t) = e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) e^{i\hat{H}_0 t/\hbar} \quad (5.80)$$

¹The quantum Liouville equation looks like the Heisenberg equation, but it is not in the Heisenberg picture. It is in the Schrödinger picture since it can be found by applying the Schrödinger equation to $\hat{\rho}(\mathbf{r}, \mathbf{r}') = \Psi_G^*(\mathbf{r}) \Psi_G(\mathbf{r}')$.

This gives us an alternative way of finding the time derivative of $\Delta\hat{\rho}(t)$. Indeed,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} [\Delta\hat{\rho}(t)] &= i\hbar \frac{\partial}{\partial t} \left[e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) e^{i\hat{H}_0 t/\hbar} \right] \\ &= i\hbar \left\{ -\frac{i}{\hbar} \hat{H}_0 e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) e^{i\hat{H}_0 t/\hbar} + e^{-i\hat{H}_0 t/\hbar} \frac{\partial [\delta\hat{\rho}(t)]}{\partial t} e^{i\hat{H}_0 t/\hbar} \right. \\ &\quad \left. + \frac{i}{\hbar} e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) \hat{H}_0 e^{i\hat{H}_0 t/\hbar} \right\}. \end{aligned} \quad (5.81)$$

The first and last terms combine into a commutator

$$i\hbar \frac{\partial}{\partial t} (\Delta\hat{\rho}(t)) = \left[\hat{H}_0, e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) e^{i\hat{H}_0 t/\hbar} \right] + i\hbar e^{-i\hat{H}_0 t/\hbar} \frac{\partial (\delta\hat{\rho}(t))}{\partial t} e^{i\hat{H}_0 t/\hbar}. \quad (5.82)$$

Also in the right hand side of (5.79) we can rewrite $\Delta\hat{\rho}(t)$ in the Dirac picture:

$$i\hbar \frac{\partial}{\partial t} (\Delta\hat{\rho}(t)) = \left[\hat{H}_0, e^{-i\hat{H}_0 t/\hbar} \delta\hat{\rho}(t) e^{i\hat{H}_0 t/\hbar} \right] + \left[\hat{H}_1, \hat{\rho}_0 \right]. \quad (5.83)$$

From comparing the previous two expressions we get

$$i\hbar e^{-i\hat{H}_0 t/\hbar} \frac{\partial (\delta\hat{\rho}(t))}{\partial t} e^{i\hat{H}_0 t/\hbar} = \left[\hat{H}_1, \hat{\rho}_0 \right] \quad (5.84)$$

$$\Leftrightarrow i\hbar \frac{\partial (\delta\hat{\rho}(t))}{\partial t} = e^{i\hat{H}_0 t/\hbar} \left[\hat{H}_1, \hat{\rho}_0 \right] e^{-i\hat{H}_0 t/\hbar}. \quad (5.85)$$

Since $\hat{\rho}_0$ commutes with \hat{H}_0 this becomes

$$i\hbar \frac{\partial (\delta\hat{\rho}(t))}{\partial t} = \left[e^{i\hat{H}_0 t/\hbar} \hat{H}_1 e^{-i\hat{H}_0 t/\hbar}, \hat{\rho}_0 \right]. \quad (5.86)$$

We can formally integrate both sides of this equation and obtain

$$\delta\hat{\rho}(t) = \frac{1}{i\hbar} \int_{-\infty}^t \left[e^{i\hat{H}_0 t'/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar}, \hat{\rho}_0 \right] dt'. \quad (5.87)$$

Going back from $\delta\hat{\rho}$ to $\Delta\hat{\rho}$ in the left hand side, we get

$$e^{i\hat{H}_0 t/\hbar} \Delta\hat{\rho}(t) e^{-i\hat{H}_0 t/\hbar} = \frac{1}{i\hbar} \int_{-\infty}^t \left[e^{i\hat{H}_0 t'/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0 t'/\hbar}, \hat{\rho}_0 \right] dt' \quad (5.88)$$

Again the factors $e^{\pm i\hat{H}_0 t/\hbar}$ can be brought to the other side and into the commutator:

$$\Delta\hat{\rho}(t) = \frac{1}{i\hbar} \int_{-\infty}^t \left[e^{i\hat{H}_0(t'-t)/\hbar} \hat{H}_1(t') e^{-i\hat{H}_0(t'-t)/\hbar}, \hat{\rho}_0 \right] dt' \quad (5.89)$$

Since $\hat{H}_1(t) = \hat{B}h(t)$ and the Dirac picture for \hat{B} is given by

$$\hat{B}(t' - t) = e^{i\hat{H}_0(t' - t)/\hbar} \hat{B} e^{-i\hat{H}_0(t' - t)/\hbar} \quad (5.90)$$

we get a nice convolution:

$$\Delta\hat{\rho}(t) = \frac{1}{i\hbar} \int_{-\infty}^t \left[\hat{B}(t' - t), \hat{\rho}_0 \right] h(t') dt' \quad (5.91)$$

5.3.2 Kubo formula

We can use the result (5.91) to find the change in the quantity that we monitor:

$$\langle \hat{A}(t) \rangle = \text{Tr} \left[(\hat{\rho}_0 + \Delta\hat{\rho}(t)) \hat{A} \right] = \underbrace{\text{Tr} \left[\hat{\rho}_0 \hat{A} \right]}_{\langle \hat{A} \rangle_0} + \text{Tr} \left[\Delta\hat{\rho}(t) \hat{A} \right]. \quad (5.92)$$

The first term is the unperturbed expectation value $\langle \hat{A} \rangle_0$ that we get without any external field. Now we can plug in our result for $\Delta\hat{\rho}(t)$ and find

$$\langle \hat{A}(t) \rangle - \langle \hat{A} \rangle_0 = \frac{1}{i\hbar} \int_{-\infty}^t \text{Tr} \left\{ \left[\hat{B}(t' - t), \hat{\rho}_0 \right] \hat{A} \right\} h(t') dt'. \quad (5.93)$$

We're going to play with the factors trace, realizing that we can perform cyclic permutations of the operators in the trace and that $\hat{\rho}_0$ and \hat{H}_0 commutes. Start with

$$\text{Tr} \left\{ \left[\hat{B}(t' - t), \hat{\rho}_0 \right] \hat{A} \right\} = \text{Tr} \left\{ \hat{B}(t' - t) \hat{\rho}_0 \hat{A} \right\} - \text{Tr} \left\{ \hat{\rho}_0 \hat{B}(t' - t) \hat{A} \right\}. \quad (5.94)$$

The first term is

$$\begin{aligned} \text{Tr} \left\{ \hat{B}(t' - t) \hat{\rho}_0 \hat{A} \right\} &= \text{Tr} \left\{ e^{i\hat{H}_0(t' - t)/\hbar} \hat{B} e^{-i\hat{H}_0(t' - t)/\hbar} \hat{\rho}_0 \hat{A} \right\} \\ &= \text{Tr} \left\{ e^{i\hat{H}_0 t'/\hbar} \hat{B} e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}_0 e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar} \right\} \\ &= \text{Tr} \left\{ \hat{B}(t') \hat{\rho}_0 \hat{A}(t) \right\} = \text{Tr} \left\{ \hat{\rho}_0 \hat{A}(t) \hat{B}(t') \right\}. \end{aligned} \quad (5.95)$$

Similarly,

$$\begin{aligned} \text{Tr} \left\{ \hat{\rho}_0 \hat{B}(t' - t) \hat{A} \right\} &= \text{Tr} \left\{ \hat{\rho}_0 e^{i\hat{H}_0(t' - t)/\hbar} \hat{B} e^{-i\hat{H}_0(t' - t)/\hbar} \hat{A} \right\} \\ &= \text{Tr} \left\{ \hat{\rho}_0 e^{i\hat{H}_0 t'/\hbar} \hat{B} e^{-i\hat{H}_0 t'/\hbar} \hat{\rho}_0 e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar} \right\} \\ &= \text{Tr} \left\{ \hat{\rho}_0 \hat{B}(t') \hat{A}(t) \right\}, \end{aligned} \quad (5.96)$$

so that

$$\text{Tr} \left\{ \left[\hat{B}(t' - t), \hat{\rho}_0 \right] \hat{A} \right\} = \text{Tr} \left\{ \hat{\rho}_0 \left[\hat{A}(t), \hat{B}(t') \right] \right\} = \left\langle \left[\hat{A}(t), \hat{B}(t') \right] \right\rangle_0 \quad (5.97)$$

This finally brings us to Kubo's famous formula:

$$\boxed{\left\langle \hat{A}(t) \right\rangle - \left\langle \hat{A} \right\rangle_0 = \frac{1}{i\hbar} \int_{-\infty}^t \left\langle \left[\hat{A}(t), \hat{B}(t') \right] \right\rangle_0 h(t') dt'} \quad (5.98)$$

The change in the monitored expectation value $\delta \langle \hat{A}(t) \rangle = \langle \hat{A}(t) \rangle - \langle \hat{A} \rangle_0$ is determined by the expectation value *in the unperturbed system* of the commutator of the monitored observable \hat{A} and the observable \hat{B} to which the perturbation couples! Note that the operators are calculated in the Dirac picture here. This is a very powerful formula: we can look at external fields that couple to currents, charge densities, spins,... and find out how the currents, charge densities, spins,... change just by taking expectation values of commutators with respect to the many-body system without the external perturbation.

Another way to write this, emphasizing the convolution, is to write

$$\Phi_{AB}(t - t') = \frac{1}{i\hbar} \left\langle \left[\hat{A}(t), \hat{B}(t') \right] \right\rangle_0. \quad (5.99)$$

The function $\Phi_{AB}(t - t')$ is called the response function. Once it is calculated, we can use it to find the influence of any arbitrary time sequence $h(t)$ of probing pulses by simply taking the convolution:

$$\delta \langle \hat{A}(t) \rangle = \int_{-\infty}^t \Phi_{AB}(t - t') h(t') dt'. \quad (5.100)$$

The nice thing about convolutions is that they become a simple product when Fourier or Laplace transformed. Here, since we usually have a specific starting time $t = 0$ before which $h(t)$ is zero, it is often convenient to introduce the Laplace transform

$$\tilde{\Phi}_{AB}(s) = \int_0^{\infty} \Phi_{AB}(t) e^{-st} dt.$$

If we have the Laplace transform $\tilde{h}(s)$ of $h(t)$, then we only need to compute $\tilde{h}(s)\tilde{\Phi}_{AB}(s)$ to get the Laplace transform of $\delta \langle \hat{A}(t) \rangle$.

5.4 Induced charge densities

The previous section was very general, and now we're going to focus back on shooting in an ion or another charged particle as an external perturbation, for

example a high-energy electron from an electron microscope beam. We'll also now use ρ (with and without hat!) exclusively for charge densities, no more density matrices here. The main result we want from a microscopic theory, as you'll remember, is to find the induced charge densities and currents. Indeed, if we compare

$$\nabla \cdot \mathbf{D} = \rho_{ext} \quad (5.101)$$

to

$$\nabla \cdot \mathbf{D} = \epsilon \nabla \cdot \mathbf{E} = \frac{\epsilon}{\epsilon_v} (\rho_{ext} + \rho_{ind}) \quad (5.102)$$

it is not hard to see that

$$\frac{\epsilon_v}{\epsilon} = 1 + \frac{\rho_{ind}}{\rho_{ext}} \quad (5.103)$$

If we know the induced charge density, we obviously can also find the permittivity. For those who read the second section, we now have the response of the charge in mind, to an external charge that we bring in, so this will be the *longitudinal* response that we study here! The response to light is in principle the transversal response and may be different although we already have a hunch from Lindhard that it will not be all that different at long wavelength and for $\omega\tau \gg 1$.

In Kubo's wording: the *observable that we want to monitor* is the density of the electron gas,

$$\hat{\rho}(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j), \quad (5.104)$$

or rather, it's Fourier components:

$$\hat{\rho}(\mathbf{q}) = \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \hat{\rho}(\mathbf{r}) = \sum_{j=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_j} \quad (5.105)$$

Using the prescriptions derived in chapter 1 we can write this in second quantized form as

$$\hat{\rho}(\mathbf{q}) = \sum_{\mathbf{k}, \sigma} \hat{a}_{\mathbf{k}-\mathbf{q}, \sigma}^\dagger \hat{a}_{\mathbf{k}, \sigma}, \quad (5.106)$$

where we have chosen plane waves as the single-particle states. When there's no perturbation, this density is homogeneous, so the Fourier transform $\hat{\rho}(\mathbf{q})$ only has a nonzero expectation value in $\mathbf{q} = \mathbf{0}$. That homogeneous charge is compensated by the jellium (which is the reason why we omitted the $\mathbf{q} = \mathbf{0}$ contributions in the chapter on electrons and phonons). So, we have

$$\rho_{ind}(\mathbf{q}) = e \langle \hat{\rho}(\mathbf{q}) \rangle. \quad (5.107)$$

and, in terms of the notation of the previous section,

$$\hat{A} = \hat{\rho}(\mathbf{q}). \quad (5.108)$$

Where does the external perturbation couple to? Well, if it is an external charge that we send in, it will obviously interact with the electrons in the medium through the Coulomb interaction. Remember the second quantized form that we used for the electron-electron Coulomb interaction:

$$\hat{H}_{coul} = \sum_{\mathbf{Q} \neq 0} \frac{e^2}{2\epsilon_v V} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_2 + \mathbf{Q}, \sigma_2}^\dagger \hat{a}_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_1, \sigma_1} \quad (5.109)$$

We can reshuffle the fermionic creation and annihilation operators using the anticommutation rules. What does it become if we have electrons interacting with an external charge that we can distinguish from the electrons? We could add another quantum label to say what kind of particle we have, and it would be like adding another spin state. Or we could use \hat{c} as operators. Anyway, the scattering process whereby a net momentum $\hbar \mathbf{Q}$ is transferred from an external charge to the electrons would become

$$\hat{H}_{ext} = \sum_{\mathbf{Q} \neq 0} \frac{e^2}{2\epsilon_v V} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{c}_{\mathbf{k}_2 + \mathbf{Q}}^\dagger \hat{c}_{\mathbf{k}_2} \hat{a}_{\mathbf{k}_1, \sigma_1} \quad (5.110)$$

Things get a bit trickier when we use electrons that cannot be distinguished from those of the system, then we must take care of the correct anticommutations which would lead to an energy shift, but here we can simply reshuffle the operators into

$$\begin{aligned} \hat{H}_{ext} &= \sum_{\mathbf{Q} \neq 0} \frac{e^2}{2\epsilon_v V} \frac{1}{Q^2} \sum_{\mathbf{k}_1, \sigma_1} \hat{a}_{\mathbf{k}_1 - \mathbf{Q}, \sigma_1}^\dagger \hat{a}_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2} \hat{c}_{\mathbf{k}_2 + \mathbf{Q}}^\dagger \hat{c}_{\mathbf{k}_2} \\ \Rightarrow \hat{H}_{ext} &= \sum_{\mathbf{Q} \neq 0} \frac{e^2}{2\epsilon_v V} \frac{1}{Q^2} \hat{\rho}(\mathbf{Q}) \hat{\rho}_{ext}(-\mathbf{Q}). \end{aligned} \quad (5.111)$$

In Kubo's formalism we always treat the external perturbation as a classical charge density, replacing $\hat{\rho}_{ext}(-\mathbf{Q})$ by its expectation value $\rho_{ext}(-\mathbf{Q}) = \langle \hat{\rho}_{ext}(-\mathbf{Q}) \rangle$, so we'll get

$$\hat{H}_{ext} = \sum_{\mathbf{Q} \neq 0} \frac{e^2}{2\epsilon_v V} \frac{1}{Q^2} \hat{\rho}(\mathbf{Q}) \rho_{ext}(-\mathbf{Q}). \quad (5.112)$$

We want to focus on an external charge that we are going to wiggle around with fixed wave number and oscillation frequency,

$$\rho_{ext}(\mathbf{r}, t) = \rho_{ext} e^{i\mathbf{q} \cdot \mathbf{r} - i\omega t} \rightarrow \rho_{ext}(\mathbf{q}, t) = \rho_{ext} e^{-i\omega t}. \quad (5.113)$$

We do this because in linear response, if you know the response to an arbitrary Fourier component, then you can simply sum up all the responses to get the response to any sum of Fourier components. With this form, our perturbation Hamiltonian becomes

$$\hat{H}_1 = \hat{\rho}(-\mathbf{q}) \frac{e^2}{2\epsilon_v V} \frac{1}{q^2} \rho_{ext} e^{-i\omega t}. \quad (5.114)$$

In terms of the notation of the previous section,

$$\hat{B} = \hat{\rho}(-\mathbf{q}), \quad (5.115)$$

$$h(t) = \frac{e^2}{2\varepsilon_v V} \frac{\rho_{ext}}{q^2} e^{-i\omega t}. \quad (5.116)$$

We see that the electron charge density is both the observable that we monitor and the observable to which the external perturbation couples.

Now the result for the induced charge is easy to find with Kubo's formula, we just have to plug in (5.108), (5.115) and (5.116):

$$\begin{aligned} \rho_{ind}(\mathbf{q}, t) &= \frac{1}{i\hbar} \int_{-\infty}^t \langle [\hat{\rho}(\mathbf{q}, t), \hat{\rho}(-\mathbf{q}, t')] \rangle \frac{e^2}{2\varepsilon_v V} \frac{\rho_{ext}}{q^2} e^{-i\omega t'} dt' \\ &= \frac{1}{i\hbar} \frac{e^2}{2\varepsilon_v V} \frac{\rho_{ext}}{q^2} \int_{-\infty}^t \langle [\hat{\rho}(\mathbf{q}, t), \hat{\rho}(-\mathbf{q}, t')] \rangle e^{-i\omega t'} dt'. \end{aligned} \quad (5.117)$$

Note that we could rewrite this also with the density-density response function (with $t' < t$ from the integral):

$$\Phi_{\rho\rho}(\mathbf{q}, t - t') = -i \langle [\hat{\rho}(\mathbf{q}, t), \hat{\rho}(-\mathbf{q}, t')] \rangle \quad (5.118)$$

as

$$\rho_{ind}(\mathbf{q}, t) = \frac{1}{\hbar} \frac{e^2 \rho_{ext}}{2\varepsilon_v V} \frac{1}{q^2} \int_{-\infty}^t \Phi_{\rho\rho}(\mathbf{q}, t - t') e^{-i\omega t'} dt'. \quad (5.119)$$

The good news is that we actually want the Fourier transform, to obtain the frequency dependent dielectric function

$$\frac{\varepsilon_v}{\varepsilon(\mathbf{q}, \omega)} = 1 + \frac{\rho_{ind}(\mathbf{q}, \omega)}{\rho_{ext}}. \quad (5.120)$$

As we've seen, this is good news because in the time domain our result for the induced charge is given by a convolution, which becomes a product in the frequency domain, so that

$$\rho_{ind}(\mathbf{q}, \omega) = \frac{1}{\hbar} \frac{e^2 \rho_{ext}}{2\varepsilon_v V} \frac{1}{q^2} \Phi_{\rho\rho}(\mathbf{q}, \omega). \quad (5.121)$$

From this we find

$$\frac{\varepsilon_v}{\varepsilon(\mathbf{q}, \omega)} = 1 + \frac{e^2}{2\hbar\varepsilon_v V} \frac{1}{q^2} \Phi_{\rho\rho}(\mathbf{q}, \omega), \quad (5.122)$$

and

$$\frac{\varepsilon(\mathbf{q}, \omega)}{\varepsilon_v} = \frac{1}{1 + \frac{e^2}{2\hbar\varepsilon_v V} \frac{1}{q^2} \Phi_{\rho\rho}(\mathbf{q}, \omega)}. \quad (5.123)$$

We have now re-expressed the (longitudinal) dielectric function as a function of the expectation value of the density-density correlation $\Phi_{\rho\rho}(\mathbf{q}, \omega)$, with respect to the ground state of the unperturbed system. But, remember that by “unperturbed” we here mean the system without the *external* perturbation, but still including all many-body interactions of the constituent particles in the material! So, we still have a hard job to do to calculate $\Phi_{\rho\rho}(\mathbf{q}, \omega)$, but once we did this we can figure out the response to any pump beam shape and time dependence.

5.5 Density-density correlations

Let’s write out the density-density correlator:

$$\begin{aligned} \Phi_{\rho\rho}(\mathbf{q}, t - t') &= -i \langle \Psi_G | [\hat{\rho}(\mathbf{q}, t), \hat{\rho}(-\mathbf{q}, t')] | \Psi_G \rangle \\ &= -i \left\langle \Psi_G \left| \left[\sum_{\mathbf{k}_1, \sigma_1} \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \hat{a}_{\mathbf{k}_1, \sigma_1}(t), \sum_{\mathbf{k}_2, \sigma_2} \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \right] \right| \Psi_G \right\rangle \end{aligned} \quad (5.124)$$

This is

$$\begin{aligned} \Phi_{\rho\rho}(\mathbf{q}, t - t') &= -i \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \langle \Psi_G | \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \hat{a}_{\mathbf{k}_1, \sigma_1}(t) \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \\ &\quad - \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \hat{a}_{\mathbf{k}_1, \sigma_1}(t) | \Psi_G \rangle \end{aligned} \quad (5.125)$$

Remember that $t' < t$. So, the above expression is equal to

$$\begin{aligned} \Phi_{\rho\rho}(\mathbf{q}, t - t') &= -2i \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \left\langle \Psi_G \left| \mathcal{T} \left\{ \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \hat{a}_{\mathbf{k}_1, \sigma_1}(t) \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \right\} \right| \Psi_G \right\rangle \end{aligned} \quad (5.126)$$

where we remove the constraint that $t' < t$. To lowest order approximation we set $|\Psi_G\rangle \rightarrow |\Psi_0\rangle$ and calculate the expectation value with respect to the Fermi sphere. We can apply Wick’s theorem to chop up this time-ordered product of four creation and annihilation operators in its component forms:

$$\begin{aligned} \Phi_{\rho\rho}(\mathbf{q}, t - t') &= -2i \sum_{\mathbf{k}_1, \sigma_1} \sum_{\mathbf{k}_2, \sigma_2} \\ &\quad \left(\left\langle \Psi_0 \left| \mathcal{T} \left\{ \hat{a}_{\mathbf{k}_1, \sigma_1}(t) \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \right\} \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \mathcal{T} \left\{ \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \right\} \right| \Psi_0 \right\rangle \right. \\ &\quad \left. - \left\langle \Psi_0 \left| \mathcal{T} \left\{ \hat{a}_{\mathbf{k}_1, \sigma_1}(t) \hat{a}_{\mathbf{k}_2 + \mathbf{q}, \sigma_2}^\dagger(t') \right\} \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \mathcal{T} \left\{ \hat{a}_{\mathbf{k}_2, \sigma_2}(t') \hat{a}_{\mathbf{k}_1 - \mathbf{q}, \sigma_1}^\dagger(t) \right\} \right| \Psi_0 \right\rangle \right). \end{aligned}$$

The first two expectation values are equal time expectations, and are become zero for $\mathbf{q} \neq 0$. The last two are unperturbed Green’s functions, so that

$$\Phi_{\rho\rho}(\mathbf{q}, t - t') = 2i \sum_{\mathbf{k}, \sigma} iG_0(\mathbf{k}, t - t') iG_0(\mathbf{k} - \mathbf{q}, t' - t) \quad (5.127)$$

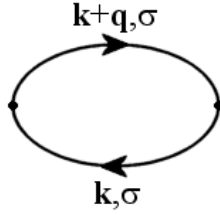
In the frequency domain this becomes

$$\Phi_{\rho\rho}(\mathbf{q}, \nu) = -4i \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d\omega}{(2\pi)} G_0(\mathbf{k}, \omega) G_0(\mathbf{k} - \mathbf{q}, \omega - \nu) \quad (5.128)$$

The dielectric function then satisfies

$$\frac{\varepsilon_v}{\varepsilon(\mathbf{q}, \omega)} = 1 - \frac{e^2}{\hbar\varepsilon_v} \frac{1}{q^2} 2i \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d\omega}{(2\pi)} G_0(\mathbf{k}, \omega) G_0(\mathbf{k} - \mathbf{q}, \omega - \nu) \quad (5.129)$$

What does this look like if we draw it as a Feynman diagram?



The polarization bubble diagram

There are two electron lines with a momentum $\hbar\mathbf{k}$ (and an energy $\hbar\omega$) running around in the loop. Note that in front of the integral we have $1/q^2$, the free photon propagator from the previous chapter, and $e^2/(\hbar\varepsilon_v)$, the electron-photon vertex squared. This is no coincidence!

5.6 Feynman diagrammatic approach

5.6.1 Coulomb propagator

You could have known! It's easy to derive the previous result from Feynman diagrams. Where did the photon propagator in the previous chapter come from? It was given by the Fourier transform of the Coulomb interaction

$$V_{coul}(\mathbf{r}) \propto \frac{1}{4\pi r} \rightarrow V_{coul}(\mathbf{q}) \propto \frac{1}{q^2}. \quad (5.130)$$

Now, in the material, the bare Coulomb propagator must be corrected, just like the bare electron propagator G_0 . Let's give the free Coulomb propagator also a name,

$$F_0(\mathbf{q}, v) = \frac{1}{q^2}. \quad (5.131)$$

The dielectric function, as we have argued before, appears as a correction factor screening the bare Coulomb interaction. In a medium

$$V_{coul}^{medium} \propto \frac{1}{4\pi(\varepsilon/\varepsilon_v)r} \rightarrow V_{coul}^{medium}(\mathbf{q}) \propto \frac{\varepsilon_v}{\varepsilon} \frac{1}{q^2}. \quad (5.132)$$

So, the ‘dressed’ or corrected Coulomb propagator corresponding to this is

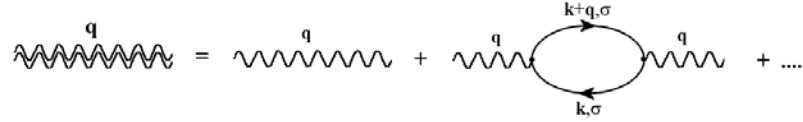
$$F(\mathbf{q}, v) = \frac{\varepsilon_v}{\varepsilon} \frac{1}{q^2} \quad (5.133)$$

$$\Rightarrow \frac{\varepsilon_v}{\varepsilon} = \frac{F(\mathbf{q}, v)}{F_0(\mathbf{q}, v)}. \quad (5.134)$$

This shows again that ε is just a way to rewrite the corrections due to the presence of the medium, i.e. a way to rewrite $F(\mathbf{q}, v)$.

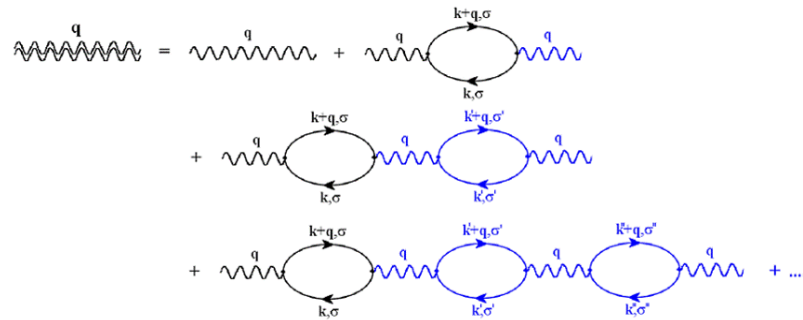
5.6.2 Polarization bubbles

Hey, but you know how to use diagrammatics to correct F_0 ! Let’s only look at corrections due to the electron-electron interactions, and not include any electron-phonon diagrams (these are higher order anyway). We’ll write the Coulomb propagator F_0 as a wavy line, and the corrected Coulomb propagator F as a bold or double wavy line (just like we drew the corrected electron Green’s function as a double line in the section on the Dyson equation). The only vertices we have involving photons connect two electron lines and one photon line. So we can draw:



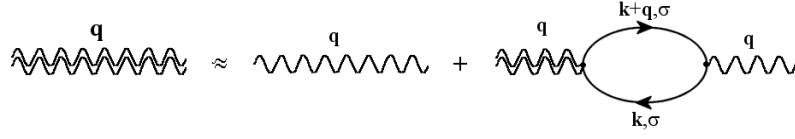
Lowest order correction to the Coulomb propagator

This is easy! The bubble shows up immediately. It has an electron line going back, so in fact it is an electron-hole bubble. It represents a story where the photon makes an electron hole pair, the electron and the hole wander along, and then they recombine and make again a photon. In fact, we can do a Dyson resummation by having a sequence of bubbles:



One polarization bubble after another...

The blue (grey) part is again the original series, so this becomes



Dyson equation for the Coulomb propagator

It doesn't matter that we put the double wiggly line first or last, the main point is that we can once again solve this Dyson equation easily. Let's use the Feynman diagrammatics to translate the drawings back into an equation:

$$F(\mathbf{q}, \nu) = F_0(\mathbf{q}, \nu) + F(\mathbf{q}, \nu) \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu) \quad (5.135)$$

Here the polarization bubble is written as $\Pi_0(\mathbf{q}, \nu)$, and this takes on the role that the self-energy $\Sigma_0(\mathbf{k}, \omega)$ had when we corrected the electron propagator. It contains the two vertices (each a factor $e/\sqrt{\hbar\varepsilon_v}$), and the two electron lines,

$$\Pi_0(\mathbf{q}, \nu) = \frac{e^2}{\hbar\varepsilon_v} (-2i) \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d\omega}{(2\pi)} G_0(\mathbf{k}, \omega) G_0(\mathbf{k} - \mathbf{q}, \omega - \nu) \quad (5.136)$$

The factor $-2i$ is the phase factor with 1 closed fermion loop, and $m = 1$ for the perturbation order. The solution for F is

$$F(\mathbf{q}, \nu) = \frac{F_0(\mathbf{q}, \nu)}{1 - \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu)}, \quad (5.137)$$

5.6.3 RPA versus first order perturbation

From the result for F this and expression (5.134) we immediately find

$$\frac{\varepsilon_v}{\varepsilon(\mathbf{q}, \nu)} = \frac{1}{1 - \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu)} \quad (5.138)$$

$$\Rightarrow \varepsilon(\mathbf{q}, \nu) = \varepsilon_v \{1 - \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu)\} \quad (5.139)$$

This is Lindhard's result for the (longitudinal) dielectric function. How is it linked to the result (5.129) that we had before? It is better! That's because we have made a Dyson resummation and included diagrams from all orders in calculation the Lindhard result. If we'd have stuck to the lowest order diagram, we would have

$$\begin{aligned} F_{1perturb}(\mathbf{q}, \nu) &= F_0(\mathbf{q}, \nu) + F_0(\mathbf{q}, \nu) \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu) \\ &\Rightarrow \frac{F(\mathbf{q}, \nu)}{F_0(\mathbf{q}, \nu)} = 1 + \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu). \end{aligned} \quad (5.140)$$

from which

$$\begin{aligned} \frac{\varepsilon_v}{\varepsilon_{1perturb}(\mathbf{q}, \nu)} &= 1 + \Pi_0(\mathbf{q}, \nu) F_0(\mathbf{q}, \nu) \\ &= 1 - \frac{e^2}{\hbar\varepsilon_v} \frac{1}{q^2} 2i \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d\omega}{(2\pi)} G_0(\mathbf{k}, \omega) G_0(\mathbf{k} - \mathbf{q}, \omega - \nu). \end{aligned} \quad (5.141)$$

And that is indeed the same result which we got in lowest order perturbation in (5.129). That lowest order includes only one polarization bubble. The Lindhard result has many subsequent events where a Coulomb line splits up in an electron-hole pair, that recombines back into a Coulomb line. Each time the phase of the photon is ‘randomized’, uncorrelated with the phase of the previous Coulomb line, so that is why the result (5.139) is sometimes called “Random Phase Approximation” or RPA. We now also know how to improve on this result! We could indeed take a better polarization contribution that just the Π_0 bubble. We could include for example such a line:



or include electron-phonon corrections.

5.7 Lindhard dielectric function

What does the result look like? In this section we go through the details of the calculation – again this can be skipped for a first reading of this course, and the reader just read the third subsection on the results for the dielectric functions without losing track. But I thought it would be instructive to at least include one detailed calculation of a diagrammatically obtained amplitude in these course notes. The first step is of course to substitute G_0 in Π_0 in order to work out the integrals:

$$\begin{aligned} \Pi_0(\mathbf{q}, \omega) = & -2i \frac{e^2}{\hbar \varepsilon_v} \int \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \left[\frac{\theta(k > k_F)}{\omega' - E_k/\hbar + i\delta} + \frac{\theta(k < k_F)}{\omega' - E_k/\hbar - i\delta} \right] \\ & \times \left[\frac{\theta(|\mathbf{k} + \mathbf{q}| > k_F)}{\omega + \omega' - E_{\mathbf{k}+\mathbf{q}}/\hbar + i\delta} + \frac{\theta(|\mathbf{k} + \mathbf{q}| < k_F)}{\omega + \omega' - E_{\mathbf{k}+\mathbf{q}}/\hbar - i\delta} \right] \quad (5.142) \end{aligned}$$

Here $E_{\mathbf{k}}$ is the single-particle energy $(\hbar k)^2/(2m)$. The integrand contains four terms with first order poles for the integration variable ω' . Two of the four terms have their poles on the same side of the real axis. By closing the contour in the complex plane along the half-plane that does not contain these poles, you can check that these terms do not contribute. The two other terms have their poles on opposite sides of the real axes and will contribute. Using the residue lemma we find

$$\begin{aligned} \Pi_0(\mathbf{q}, \omega) = & -2i \frac{e^2}{\hbar \varepsilon_v} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{2\pi i}{2\pi} \left[-\frac{\theta(k > k_F)\theta(k_F > |\mathbf{k} + \mathbf{q}|)}{\omega + E_k/\hbar - E_{\mathbf{k}+\mathbf{q}}/\hbar - i\eta} \right. \\ & \left. + \frac{\theta(k_F > k)\theta(|\mathbf{k} + \mathbf{q}| > k_F)}{\omega + E_k/\hbar - E_{\mathbf{k}+\mathbf{q}}/\hbar + i\eta} \right]. \quad (5.143) \end{aligned}$$

The different signs for these two terms appear because one is evaluated with a contour traversed in clockwise direction. The 2δ infinitesimal has been rewritten

as “ η ”. In the term with the minus sign, we change integration variables to $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ and then drop the prime:

$$\begin{aligned} \Pi_0(\mathbf{q}, \omega) = & -2 \frac{e^2}{\hbar \varepsilon_v} \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F > k) \theta(|\mathbf{k} + \mathbf{q}| > k_F) \\ & \times \left[\frac{1}{\omega + E_k/\hbar - E_{\mathbf{k}+\mathbf{q}}/\hbar + i\eta} - \frac{1}{\omega + E_{\mathbf{k}+\mathbf{q}}/\hbar - E_k/\hbar - i\eta} \right] \end{aligned} \quad (5.144)$$

The heaviside step functions restrict the integration domain in \mathbf{k} . For a value of \mathbf{k} to contribute firstly, \mathbf{k} must lie in the Fermi sphere ($\theta(k_F > k)$) and secondly, after adding \mathbf{q} to it, $\mathbf{k} + \mathbf{q}$ must lie outside the Fermi sphere. This means that only \mathbf{k} states that can absorb a wave vector \mathbf{q} according to Pauli's exclusion principle contribute. To find the real and imaginary parts, we use Plemelj's rule:

$$\frac{1}{x \pm i\eta} = \mathcal{P} \frac{1}{x} \mp i\pi \delta(x), \quad (5.145)$$

where δ represents the Dirac delta function and \mathcal{P} is the Cauchy prime value.

5.7.1 Real part of the polarization bubble amplitude

We note

$$\omega_{\mathbf{qk}} = E_{\mathbf{k}+\mathbf{q}}/\hbar - E_k/\hbar = \hbar(\mathbf{k} \cdot \mathbf{q} + q^2/2)/m, \quad (5.146)$$

$$\theta(|\mathbf{k} + \mathbf{q}| > k_F) = 1 - \theta(k_F > |\mathbf{k} + \mathbf{q}|) \quad (5.147)$$

and find

$$\text{Re} [\Pi_0(\mathbf{q}, \omega)] = 2 \frac{e^2}{\hbar \varepsilon_v} \mathcal{P} \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F > k) [1 - \theta(k_F > |\mathbf{k} + \mathbf{q}|)] \frac{2\omega_{\mathbf{qk}}}{\omega^2 - \omega_{\mathbf{qk}}^2}.$$

Note that $\omega_{\mathbf{qk}}$ is odd whereas $\theta(k_F > k)\theta(k_F > |\mathbf{k} + \mathbf{q}|)$ is even under interchanging $\mathbf{k} \leftrightarrow \mathbf{k} + \mathbf{q}$, so that

$$\text{Re} [\Pi_0(\mathbf{q}, \omega)] = 2 \frac{e^2}{\hbar \varepsilon_v} \mathcal{P} \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F > k) \frac{2\omega_{\mathbf{qk}}}{\omega^2 - \omega_{\mathbf{qk}}^2} \quad (5.148)$$

In order to keep notations simple, we'll write

$$v = \frac{\omega}{\hbar k_F^2/m} \quad (5.149)$$

and express the wave numbers in units of k_F , so that

$$\text{Re} [\Pi_0(\mathbf{q}, \omega)] = \frac{e^2}{\hbar \varepsilon_v} \frac{mk_F}{2\pi^2 \hbar} \int_0^1 dk \, k^2 \int_0^{2\pi} d\theta \, \sin \theta \left(\frac{2qk \cos \theta + q^2}{v^2 - (qk \cos \theta + q^2/2)^2} \right).$$

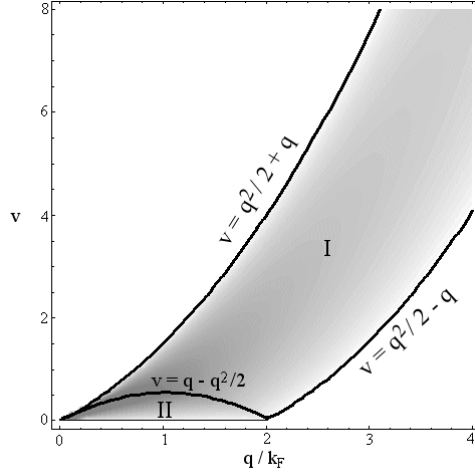


Figure 5.1: $\text{Im}[\Pi_0(\mathbf{q}, \omega)]$ as a function of q/k_F and $v = m\omega/(\hbar k_F^2)$. In the white areas, the result is zero. The curves show the boundaries of the different zones, and the grey scale shows the value of the function from 0 (lightest grey) to 0.5 (darkest).

The remaining integrations result in:

$$\begin{aligned} \text{Re}[\Pi_0(\mathbf{q}, \omega)] &= \frac{e^2}{\hbar \varepsilon_v} \frac{mk_F}{2\pi^2 \hbar} \left\{ -1 + \frac{1}{2q} \left[1 - \left(\frac{v}{q} - \frac{q}{2} \right)^2 \right] \ln \left| \frac{1 + (v/q - q/2)}{1 - (v/q - q/2)} \right| \right. \\ &\quad \left. - \frac{1}{2q} \left[1 - \left(\frac{v}{q} + \frac{q}{2} \right)^2 \right] \ln \left| \frac{1 + (v/q + q/2)}{1 - (v/q + q/2)} \right| \right\}. \end{aligned} \quad (5.150)$$

5.7.2 Imaginary part of the polarization bubble amplitude

The imaginary part is given by

$$\text{Im}[\Pi_0(\mathbf{q}, \omega)] = -2\pi \frac{e^2}{\hbar \varepsilon_v} \int \frac{d\mathbf{k}}{(2\pi)^3} \theta(k_F > k) \theta(|\mathbf{k} + \mathbf{q}| > k_F) \delta(\omega - \omega_{\mathbf{qk}}) \quad (5.151)$$

where we only look at the contributions with $\omega > 0$ (and keep in mind that $\omega_{\mathbf{qk}}$ is positive in the entire domain specified by the Heaviside functions). Using the property $\delta(ax) = \delta(x)/|a|$ of the Dirac delta function, we get in dimensionless variables:

$$\begin{aligned} \text{Im}[\Pi_0(\mathbf{q}, \omega)] &= -\frac{mk_F}{2\pi \hbar} \frac{e^2}{\hbar \varepsilon_v} \int dk k^2 \int_0^{2\pi} d\theta \sin \theta \delta(v - \mathbf{qk} - q^2/2) \\ &\quad \times \theta(1 > k) \theta(|\mathbf{k} + \mathbf{q}| > 1) \end{aligned} \quad (5.152)$$

The delta functions and step functions still constrain the integration domain. The step functions (taking into account the Pauli exclusion principle) constrain the wave vectors to those that lie in the Fermi sphere and that are taken outside of the Fermi sphere by addition of \mathbf{q} . The delta function (expressing the conservation of energy) fixes a plane in \mathbf{k} -space that lies perpendicular to \mathbf{q} , at a distance $v/q - q/2$ of the origin. Depending on the size of q and v these conditions give rise to different results. This is summarized in figure (5.1).

In the areas outside $q^2/2 + q \geq v \geq \max[q^2/2 - q, 0]$ the integral is zero. In area I of figure (5.1) the integral results in

$$\text{Im} [\Pi_0(\mathbf{q}, \omega)] = -\frac{mk_F}{2\pi\hbar} \frac{e^2}{\hbar\varepsilon_v} \frac{1}{2q} \left[1 - \left(\frac{v}{q} - \frac{q}{2} \right)^2 \right], \quad (5.153)$$

and in area II we get

$$\text{Im} [\Pi_0(\mathbf{q}, \omega)] = -\frac{mk_F}{2\pi\hbar} \frac{e^2}{\hbar\varepsilon_v} \frac{v}{q}. \quad (5.154)$$

5.7.3 Refinements in the dielectric function

Remember that we had our perturbation result,

$$\varepsilon_{\text{1st order}}^{-1}(\mathbf{q}, \omega) = 1 + \Pi_0(\mathbf{q}, v)/q^2, \quad (5.155)$$

where we've written out $F_0(\mathbf{q}, v) = 1/q^2$, the Coulomb propagator. We get a better result by resumming all improper sequences bubbles in a Dyson series. This gives the RPA or Lindhard dielectric function:

$$\varepsilon_{\text{Lindhard}}^{-1}(\mathbf{q}, \omega) = \frac{1}{1 - \Pi_0(\mathbf{q}, v)/q^2}. \quad (5.156)$$

Now you see why I write the result for ε^{-1} . As we expand the fraction in $\varepsilon_{\text{Lindhard}}^{-1}$ in orders of Π_0 , our lowest nontrivial result is precisely $\varepsilon_{\text{1st order}}^{-1}$. The real and imaginary parts of this result are plotted as a function of ω for different values of q in figure (5.2). The real part always tends to 1 as the frequency becomes very large, and it can become negative (typically for small q) in some frequency regions. The imaginary part is always positive, but is zero in large regions of the q, ω plane. This comes from the behavior of the imaginary part of $\Pi_0(\mathbf{q}, v)$. Indeed, in Lindhard's result

$$\text{Im} [\varepsilon_{\text{Lindhard}}(\mathbf{q}, \omega)] = -\text{Im} [\Pi_0(\mathbf{q}, \omega)] / q^2.$$

There have been further improvements on the Lindhard dielectric function, and we have barely lifted the veil on the theoretical of the dielectric function for metals and semiconductors, an area that is still evolving both as far as theory is concerned and as new experimental techniques becomes available. An important

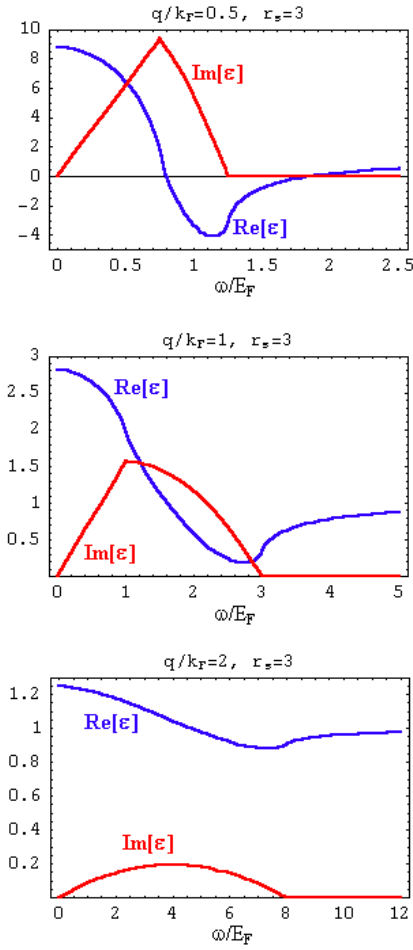


Figure 5.2: Real and imaginary parts of the Lindhard dielectric functions as a function of ω , for some chosen values of q .

improvement was suggested by Hubbard². He introduced a local field factor $G(q)$ in the RPA dielectric function:

$$\varepsilon_{\text{Lindhard}}(\mathbf{q}, \omega) = 1 - \Pi_0(\mathbf{q}, v)/q^2. \quad (5.157)$$

$$\hookrightarrow \varepsilon_{\text{Hubbard}}(\mathbf{q}, \omega) = 1 - \frac{\Pi_0(\mathbf{q}, v)/q^2}{1 + G(q)\Pi_0(\mathbf{q}, v)/q^2} \quad (5.158)$$

This local field factor corresponds to the exchange and correlation contributions to the Coulomb interaction, and is linked to the (Fourier transform) of the screening hole around a charge. Singwi, Tosi, Land and Sjölander³ refined the calculation for $G(q)$ and obtained the next improvement on the dielectric function. Finally, Devreese, Brosens en Lemmens⁴ here at the Universiteit Antwerpen took the dynamical exchange contribution into account – the screening hole needs some time to form – and derived the frequency dependence of the local field factor $G(q, \omega)$. Not so long ago, this Antwerpian result for the dielectric function was confirmed experimentally through inelastic X-ray scattering experiments on metals⁵, where it is the only theory to match these experiments. That little bit of Antwerpian chauvinism is also why I focused on the dielectric function as an application to Feynman diagrams in this course.

5.8 Plasmons

5.8.1 Structure factor

The density-density correlation $\Phi_{\rho\rho}$ can be interpreted itself as a kind of Green's function, related to

$$G_{\rho\rho}(\mathbf{q}, t - t') = -i \left\langle \Psi_G \left| \mathcal{T} \left\{ \hat{\rho}(\mathbf{q}, t) \hat{\rho}^\dagger(\mathbf{q}, t') \right\} \right| \Psi_G \right\rangle \quad (5.159)$$

where we used the property $\hat{\rho}^\dagger(\mathbf{q}, t) = \hat{\rho}(-\mathbf{q}, t)$ of the density operator. The spectral function of this Green's function is called the *structure factor*:

$$S(\mathbf{q}, \omega) = \sum_n |\langle \Psi_G | \hat{\rho}(\mathbf{q}) | \Psi_n \rangle|^2 \delta(\omega - \omega_{n0}). \quad (5.160)$$

Here $|\Psi_n\rangle$ is a many-body excited state. Compare this expression to (4.44), where we now use $\hat{\rho}(\mathbf{q})$ in stead of $\hat{a}_{\mathbf{q}}$. The structure factor is a very useful concept: $S(\mathbf{q}, \omega)$ gives the probability that the external perturbation will transfer a momentum $\hbar\mathbf{q}$ and an energy $\hbar\omega$ to the system. This also means that $S(\mathbf{q}, \omega)$ is the probability to create an excitation with given momentum $\hbar\mathbf{q}$ and given energy $\hbar\omega$ in the many-body system. If it is sharply peaked, we can

²J. Hubbard, Proc. Roy. Soc. London Ser. A **243**, 336 (1957).

³K. S. Singwi, M. P. Tosi, R.H. Land en A. Sjölander, Phys. Rev. **176**, 589 (1968).

⁴J.T. Devreese, F. Brosens en L. F. Lemmens, Phys. Rev. B **21**, 1349 (1980); F. Brosens, J.T. Devreese en L.F. Lemmens, Phys. Rev. B **21**, 1363 (1980).

⁵B. C. Larson, et al., Phys. Rev. Lett. **77**, 1346 (1996).

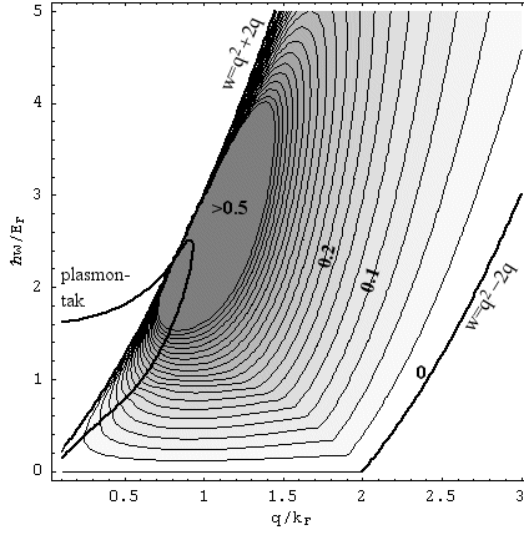


Figure 5.3: RPA structure factor (proportional imaginary part of $\epsilon_{\text{Lindhard}}^{-1}$).

interpret this excitation again as a quasiparticle with well defined momentum and energy (the sharpness of the peak as a function of the energy is related to the life time). It contains the same information as $\Phi_{\rho\rho}(\mathbf{q}, \omega)$:

$$\Phi_{\rho\rho}(\mathbf{q}, \omega) = \int d\omega' S(\mathbf{q}, \omega') \left(\frac{1}{\omega - \omega' + i\delta} - \frac{1}{\omega + \omega' + i\delta} \right) \quad (5.161)$$

and hence, is also related to the dielectric function: applying Plemelj's rule to (5.161) and using it in (5.122) we find

$$\begin{aligned} \text{Im} \left[\frac{1}{\epsilon(\mathbf{q}, \omega)} \right] &= \frac{e^2}{2\hbar\epsilon_v V} \frac{1}{q^2} \text{Im} [\Phi_{\rho\rho}(\mathbf{q}, \omega)] \\ \Rightarrow S(\mathbf{q}, \omega) &= -\frac{1}{\pi} \frac{\hbar\epsilon_v}{e^2} q^2 \text{Im} \left[\frac{1}{\epsilon(\mathbf{q}, \omega)} \right]. \end{aligned} \quad (5.162)$$

The structure factor is related to the imaginary part of ϵ . Figure (5.3) shows how this looks like as a function of \mathbf{q} and ω , for the Lindhard result. Since

$$\text{Im} \left[\frac{1}{\epsilon(\mathbf{q}, \omega)} \right] = \frac{\text{Im}[\epsilon(\mathbf{q}, \omega)]}{\{\text{Re}[\epsilon(\mathbf{q}, \omega)]\}^2 + \{\text{Im}[\epsilon(\mathbf{q}, \omega)]\}^2} \quad (5.163)$$

we expect it to be zero in the regions where $\text{Im}[\epsilon(\mathbf{q}, \omega)] = 0$, but there is an exception. When both the real and imaginary part of $\epsilon(\mathbf{q}, \omega)$ become zero, then there is a divergence. The locus of points where $\text{Re}[\epsilon(\mathbf{q}, \omega)]$ is drawn as a solid curve labeled “plasmon-tak” (plasmon branch) in figure (5.3). In the

region where $\text{Im}[\varepsilon(\mathbf{q}, \omega)] \neq 0$ this just gives rise to a bump or enhancement in the structure factor. This is the region with grey shading in figure (5.1) or (5.3), and this region is called the single-particle excitation region – the external perturbation will kick an electron from the Fermi sphere to outside the Fermi sphere, and this is the way in which energy and momentum is taken up by the many-body system. However, in the white region, there is now a sharp branch of excitations, delta function like when it is scanned as a function of ω . These excitations are the *plasmons*.

They are collective excitations: even when $q \rightarrow 0$, they survive at relatively high energy, and this means that the energy of the plasma oscillation is shared by many electrons performing a collective motion. It is known as a *collective mode*. The Greens function for the electron will only have the single-particle or energies as poles (albeit single quasiparticles). The Greens function $G_{\rho\rho}$ is a two-body Greens function (creating and annihilating two electrons) and it poles also contain the collective modes! When the plasmon branch hits the single-particle excitation band it transforms into a peak with a broad width, which tells us that the plasmons with those energies decay rapidly into single-particle excitations.

5.8.2 Collective mode

We can now use our expressions for the Lindhard dielectric function to find an analytical result for the location of the plasmon branch. Indeed, we have

$$\text{Im}[\varepsilon_{\text{Lindhard}}(\mathbf{q}, \omega)] = -\frac{1}{q^2} \text{Im}[\Pi_0(\mathbf{q}, v)], \quad (5.164)$$

$$\text{Re}[\varepsilon_{\text{Lindhard}}(\mathbf{q}, \omega)] = 1 - \frac{1}{q^2} \text{Re}[\Pi_0(\mathbf{q}, v)]. \quad (5.165)$$

Solving $\text{Re}[\varepsilon_{\text{Lindhard}}(\mathbf{q}, \omega)] = 0$ in the region outside the single-particle excitation band gives, for $q \ll k_F$

$$\omega_{pl}^2(\mathbf{q}) = \frac{ne^2}{m\varepsilon_v} \left(1 + \frac{3}{10} \frac{(\hbar k_F)^2}{n\varepsilon^2/\varepsilon_v} q^2 \right),$$

Here n is the density of electrons (it appears due to the presence of factors k_F). The plasmon branch starts at $\omega_{pl} = \sqrt{ne^2/(m\varepsilon_v)}$. This is exactly the value (5.46) that appears also in the Drude dielectric function and plays a special role there! For larger wavelengths, the energy grows quadratically with q . We can write the plasmon contribution to $S(\mathbf{q}, \omega)$ as a term proportional to $\delta(\omega - \omega_{pl}(\mathbf{q}))$.

It is also clear to see that this is a collective mode. What is $\rho_{ind}(\mathbf{q})$ for very small q (very large wave lengths)? It must be a uniform displacement of the electron density. If we start with a block of metal and shift all electrons over a distance u with respect to the lattice of metal ions, then at one side of the block of metal there will be a layer u of uncompensated electrons sticking out, and at the other side there will be a layer of thickness u of uncovered metal ions. These regions of uncompensated charge form a parallel-plate capacitor geometry, and

give rise to an electric field equal to $\mathbf{E} = ne\mathbf{u}/\varepsilon_v$ pulling the electrons back. The simplest, classical equation of motion then immediately reveals the plasma frequency:

$$\begin{aligned} mn \frac{d^2 \mathbf{u}}{dt^2} &= -ne\mathbf{E} = -(n^2 e^2 / \varepsilon_v) \mathbf{u} \\ \Leftrightarrow \mathbf{u} &\propto e^{i\omega_{pl} t} \text{ with } \omega_{pl}^2 = ne^2 / (m\varepsilon_v) \end{aligned} \quad (5.166)$$

In general, at higher \mathbf{k} 's, the plasmons will represent a density modulation in the electron gas, like an electron sound wave. It will have a frequency $\omega_{pl}(\mathbf{k})$. You can see that it is not just one electron, a single (quasi)particle, that has taken this energy, but it has been spread out over all electrons as they perform a collective dance.

I hope this chapter has illustrated the power of the diagrammatic technique in condensed matter physics. We have developed a microscopic theory of the electron response, based on the Kubo response formalism and found out how to calculate the dielectric function that appears in the Maxwell equations in a medium, from the microscopic Hamiltonian of the system. You might now think that the diagrammatic technique has no limits, and that anything can be calculated with it – that is certainly the viewpoint of those that want to solve problems in high energy physics by introducing new lines in the diagrams. But in condensed matter physics, we have an example where the perturbational approach, even with such a strong organizational tool as Feynman diagrams, fails. It fails because the right solutions have essential singularities that prohibit a series expansion. The example is superconductivity, the topic of the next chapter.

Addendum: Polaritons

For completeness' sake, let's have a look at the simplest classical estimate for the *dielectric function of an ionic or polar insulator*. This time we'll focus on the transversal dielectric function, so we're talking about photons mixing up with excitations in the material. These will primarily be phonons (when there are no conduction electrons), more precisely the transverse optical phonons. The electric field of the electromagnetic wave pulls positive and negative ions in the unit cell in different directions, hence it gives rise to an optical phonon, and it is orthogonal to the direction of propagator of the light wave, hence it's also a transversal phonon. So, the main actors in the story are

1. Electromagnetic waves satisfying

$$\frac{\partial^2}{\partial t^2}(\epsilon_v \mathbf{E} + \mathbf{P}) = \frac{1}{\mu_v} \nabla^2 \mathbf{E} \quad (5.167)$$

This is obtained from taking the curl of the third maxwell equation and substituting the fourth in it. We've also included the induced charges in the material and follow the "first way", namely by introducing the polarization field. For the electromagnetic wave, we assume $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$. Also the polarization field will be driven at the same oscillation frequency, so we can also write the above equation as

$$\omega^2 (\mathbf{E} + \mathbf{P}/\epsilon_v) = ck^2 \mathbf{E} \quad (5.168)$$

2. The transverse optical phonon whose amplitude \mathbf{u} of oscillation satisfies

$$M \frac{\partial^2 \mathbf{u}}{\partial t^2} = -M\omega_{TO}^2 \mathbf{u} \quad (5.169)$$

If there is an electric field present, then it will put an additional force $q\mathbf{E}$ on the ions with charge q . If once again we assume that both the electromagnetic field and the ions oscillate at the same frequency ω (to be determined), then we can also write the above equation as

$$-M\omega^2 \mathbf{u} = -M\omega_{TO}^2 \mathbf{u} + q\mathbf{E} \quad (5.170)$$

The two actors are clearly coupled. The electromagnetic field pulls on the ions, and the displaced ions (with density n_{ion}) give rise to a polarization density $\mathbf{P} = n_{ion}q\mathbf{u}$. Thus, we end up with two coupled equations

$$\begin{cases} -M\omega^2 \mathbf{u} = -M\omega_{TO}^2 \mathbf{u} + q\mathbf{E} \\ -\omega^2 (\mathbf{E} + n_{ion}q\mathbf{u}/\epsilon_v) = ck^2 \mathbf{E} \end{cases} \quad (5.171)$$

This can be nicely reshuffled to

$$\begin{cases} M(\omega_{TO}^2 - \omega^2) \mathbf{u} - q\mathbf{E} = 0 \\ \omega^2 n_{ion}q\mathbf{u}/\epsilon_v + (\omega^2 - ck^2) \mathbf{E} = 0 \end{cases} \quad (5.172)$$

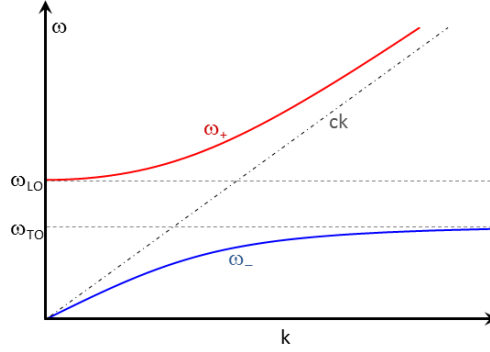


Figure 5.4: Dispersion of the mixed TO phonon and photon modes.

This set of linear equations only has a nonzero solution if the determinant of coefficients is zero, i.e. if

$$(\omega_{TO}^2 - \omega^2)(\omega^2 - ck^2) + \omega^2 \frac{n_{ion} q^2}{M \epsilon_v} = 0 \quad (5.173)$$

Note the appearance of a plasma frequency related to the ions in the material, $\omega_{pl,ion} = \sqrt{n_{ion} q^2 / (M \epsilon_v)}$. It is calculated with the density of ions, their charge and mass rather than the electron counterparts. Equation (5.173) has as its real roots

$$\omega_{\pm}^2 = \frac{1}{2} \left[\omega_{pl,ion}^2 + \omega_{TO}^2 + (ck)^2 \pm \sqrt{(\omega_{pl,ion}^2 + \omega_{TO}^2 + c^2 k^2)^2 - 4\omega_{TO}^2 (ck)^2} \right] \quad (5.174)$$

This result is shown in figure (5.4). The resulting solutions have both \mathbf{E} and \mathbf{u} nonzero, and are mixed phonon-photon modes. Whenever photons are hybridized with some source of polarization in a material, we call the resulting new modes “*polaritons*”. These sources of polarization can be the TO phonons, as in our case, or they can be excitons (electron-hole pairs that have an electric dipole moment), in which case they are called exciton-polaritons. The source can even come from surface plasmon modes, then we have surface plasmon polaritons. Don’t confuse them with the polarons from chapter 3. Below we’ll argue that $\omega_{pl,ion}^2 + \omega_{TO}^2 = \omega_{LO}^2$. You see that there is a gap between ω_{TO} and ω_{LO} : there are no light waves with frequencies between ω_{TO} and ω_{LO} in the ionic insulator. The result is a typical example of an avoided level crossing. The original energy levels ω_{TO} and ck cross. When we couple these two modes, we get hybrid modes (the polaritons) in the region of the crossing, and the original crossing is now avoided (there is level repulsion).

Now we still need to find the dielectric function. For that, we need to find the polarization \mathbf{P} . We can rewrite equation (5.170) using $\mathbf{u} = \mathbf{P}/(nq)$, and get

$$\begin{aligned} -M\omega^2\mathbf{P} &= -M\omega_{TO}^2\mathbf{P} + n_{ion}q^2\mathbf{E} \\ \Rightarrow \mathbf{P} &= \frac{1}{\omega_{TO}^2 - \omega^2} \frac{n_{ion}q^2}{M} \mathbf{E} \end{aligned} \quad (5.175)$$

To go from the polarization field to the dielectric function, we use $\varepsilon\mathbf{E} = \mathbf{D} = \varepsilon_v\mathbf{E} + \mathbf{P}$ from which

$$\begin{aligned} \varepsilon\mathbf{E} &= \varepsilon_v\mathbf{E} + \frac{1}{\omega_{TO}^2 - \omega^2} \frac{n_{ion}q^2}{M} \mathbf{E} \\ \Rightarrow \varepsilon(\omega) &= \varepsilon_v \left(1 + \frac{\omega_{pl,ion}^2}{\omega_{TO}^2 - \omega^2} \right) \end{aligned} \quad (5.176)$$

That is our result for the dielectric function of an ionic or polar insulator.

For very high frequencies $\varepsilon(\omega \rightarrow \infty) = \varepsilon_v$, the ions cannot follow the driving EM field and we retrieve the vacuum permittivity. For low frequencies,

$$\varepsilon(0) = \varepsilon_v \left(1 + \frac{\omega_{pl,ion}^2}{\omega_{TO}^2} \right) = \varepsilon_v + \frac{n_{ion}q^2}{M\omega_{TO}^2} \quad (5.177)$$

The static dielectric constant $\varepsilon(0)$ is not equal to the vacuum permittivity. It is the static dielectric constant that you determine by putting the crystal in between two capacitor plates and seeing how much energy can be stored in DC mode, this energy is $U = \varepsilon(0)E^2/2$ with E the electric field. If the static dielectric constant is large, then you can store a lot of energy in the capacitor. Note that we can use the static and high-frequency $\varepsilon(\infty)$ dielectric constants to rewrite $\varepsilon(\omega)$:

$$\varepsilon(\omega) = \varepsilon(\infty) + [\varepsilon(0) - \varepsilon(\infty)] \frac{\omega_{TO}^2}{\omega_{TO}^2 - \omega^2} \quad (5.178)$$

The analog of the “longitudinal plasmon mode” of the ions is a longitudinal optical phonon with frequency ω_{LO} , displacing all positive ions (and negative ones in the other direction), just as we did for the longitudinal plasmon in the electron gas by shifting the electrons from the background. It is found by solving $\varepsilon(\omega) = 0$, just as we did for the electron gas. This is how we can find the longitudinal optical phonon frequency

$$\begin{aligned} \varepsilon(\omega_{LO}) = 0 &\Leftrightarrow \varepsilon(\infty) + [\varepsilon(0) - \varepsilon(\infty)] \frac{\omega_{TO}^2}{\omega_{TO}^2 - \omega_{LO}^2} = 0 \\ \Leftrightarrow &\boxed{\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon(0)}{\varepsilon(\infty)}} \end{aligned} \quad (5.179)$$

This is known as the Lyddane-Sachs-Teller relation. We can use it to identify the LO phonon frequency with

$$\omega_{LO}^2 = \omega_{pl,ion}^2 + \omega_{TO}^2 \quad (5.180)$$

and to rewrite the dielectric function of the ionic or polar insulator in a particularly nice form:

$$\boxed{\varepsilon(\omega) = \varepsilon_v \frac{\omega_{LO}^2 - \omega^2}{\omega_{TO}^2 - \omega^2}} \quad (5.181)$$

So, all you need to know to write down a very estimate of the dielectric function of an ionic or polar semiconductor are its LO and TO phonon frequencies.

Chapter 6

Superconductivity

This final chapter provides an introduction to the phenomenon of superconductivity. We review the experimental properties and experimental milestones that led to the development of the theory of superconductor by Bardeen, Cooper and Schrieffer. The BCS theory of superconductivity is then derived using the Bogoliubov transformation. This topic is covered in more details in the course “superfluidity and superconductivity”, where however we take a slightly different approach.

6.1 Properties of superconductors

Superconductivity was discovered in 1911 by Kamerlingh Onnes and co-workers in Leiden¹. At the laboratory of Onnes, a technique had been developed to liquefy helium, and the liquid helium with its boiling point of 4.2 K could be used to cool down metals and see what happens. It was very quickly discovered that below a certain “critical” temperature T_c the resistivity of some metals vanish and they become perfect conductors. In this “superconducting” state, the resistivity is so low that persistent currents in a superconducting ring have been seen to flow without any dissipation or weakening for more than a year, when the experiment was finally halted. With nuclear magnetic resonance, follow-up experiments have sent a lower bound to the persistence of superconducting currents: they will keep running around for at least 100000 years without weakening. Theoretical predictions even find that it will not appreciably weaken in $10^{10^{10}}$ years, far more than the age of the universe. In other words, *perfect conduction of DC currents* is the first defining characteristic of the superconducting state. For AC currents there is also perfect conduction, but only for frequencies below the microwave region.

The second defining characteristic of the superconducting state was

¹H. Kamerlingh Onnes, Akad. van Wetenschappen **14**, 113, 818 (1911).

found in 1933 by Meissner and Ochsenfeld² and is *perfect diamagnetism*: in the superconducting state, all magnetic flux is expelled from the bulk superconductor (at least for the type I superconductors known in 1933). This, sadly for Ochsenfeld, is called the *Meissner effect*. It is very remarkable, and a first hint that quantum physics is involved at a fundamental level. Indeed, classically one expects that perfect conduction leads to freezing in of any magnetic field: when the resistivity ρ is zero, the electric fields $\mathbf{E} = \rho \mathbf{J}$ must also be zero according to Ohm's law, and from Maxwell's equation $\partial \mathbf{B} / \partial t = c \nabla \times \mathbf{E} = \mathbf{0}$ the magnetic field is not allowed to change in time. No surprise when we first cool down and then try to apply a magnetic field: it remains zero in the superconductor. But there's a big surprise when we first apply the field, and then cool down to below T_c (so-called "*field cooled experiments*"): rather than staying constant, the magnetic field gets expelled from the block of superconductor. Does this mean that the Maxwell equations won't hold? No, they do hold, it is Ohm's law which has to give way.

To expel a magnetic field \mathbf{H} , an energy $\mu H^2/2$ should be spent. The superconducting state is lower in energy than the normal state, but of course not infinitely lower in energy. So, increasing the magnetic field sooner or later one reaches a critical magnetic field beyond which the block of material becomes normal again and allows the magnetic field in. Empirically it was found that this critical magnetic field depends on temperature roughly as $H_c(T) = H_c(0)[1 - (T/T_c)^2]$. With the discovery of type-II materials, the result of Meissner and Ochsenfeld has to be generalized: in these materials there are two critical fields. Above the first critical field, the material still remains superconducting, but flux lines can penetrate the superconductor along thin tubes named vortices. These vortex lines dissipate energy when they move around and they can be pinned by impurities in the material. It is only at a much higher second critical magnetic field that the superconductivity vanishes everywhere. In this chapter we will restrict ourselves to the type-I superconductors.

A first phenomenological model that succeeded in describing the two main characteristics of the superconducting state was proposed by the London brothers³. In analogy with superfluid helium, they presume that a certain number n_s of charge carriers become superfluid and flows without friction. Ohm's law is replaced by stating that it is not the electric field, but the vector potential that is proportional to the current density:

$$\mathbf{A} \propto \mathbf{j}_s. \quad (6.1)$$

The essential constant of proportionality is determined by the length λ through

$$\mathbf{j}_s = -\frac{1}{\mu_v \lambda^2} \mathbf{A} \quad (6.2)$$

²W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).

³F. en H. London, *Proc. Roy. Soc.* **A149**, 71 (1935).

This parameter λ is called the *London penetration depth*, and it is related to the “plasma frequency of superconducting carriers”

$$\omega_{pl,sc}^2 = \frac{n_s Q^2}{M \varepsilon_v} \rightarrow \lambda = c/\omega_{pl,sc} = \frac{M \mu_v}{n_s Q^2} \quad (6.3)$$

where M and Q is the mass and charge of the superconducting charge carrier (now known to be a Cooper pair, as we’ll see later on). Using the London relation between current density and vector potential, we also find

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} = \mu_v \lambda^2 \frac{\partial \mathbf{j}_s}{\partial t} \quad (6.4)$$

$$\mathbf{B} = \nabla \times \mathbf{A} = -\mu_v \lambda^2 \nabla \times \mathbf{j}_s \quad (6.5)$$

These are the (phenomenological) London equations. From the second equation and the fourth Maxwell equation $\nabla \times \mathbf{B} = \mu_v \mathbf{j}_s$ we furthermore find:

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B} \quad (6.6)$$

Taking a semi-infinite superconductor, bounded by the $z = 0$ plane (with the material in the $z > 0$ half-space), and a magnetic induction field \mathbf{B}_0 in the $z < 0$ half-space, the solution of this equation is $\mathbf{B}(z) = \mathbf{B}_0 e^{-z/\lambda}$. This shows that the magnetic induction field is exponentially suppressed in the superconductor. Except for a surface layer of depth λ , it is exponentially small in the bulk of the material. In this surface layer, the Meissner supercurrents \mathbf{j}_s run and create a magnetization that cancels the magnetic induction field inside the material. Comparisons of this prediction with experiments that focus on this surface layer have revealed that the picture is slightly more complex and a second length scale is necessary: the coherence length or correlation length.

Pippard⁴ considers a non-local generalization of the London equation $\mathbf{j}_s(\mathbf{r}) = -\mathbf{A}(\mathbf{r})/(\mu_v \lambda^2)$. Also for Ohm’s law there exists such a generalization (Chalmer’s law), that takes into account that the current in a specific point is not proportional to the electric field in that same point, but is a function of the field in a small patch (of size ℓ) surrounding that point. The reason is that the charge carriers may have a finite size themselves, and so you need to look at the electric field over the entire “size” of the charge carrier. Pippard called this length scale (now for averaging the vector potential) the *correlation length*, denoted by ξ . He estimate its size as follows: only electrons within an energy band of width $k_B T_c$ around the Fermi energy can participate in building the superconducting charge carriers, so these electrons must have a momentum in a range $\Delta p \approx k_B T_c / v_F$ where v_F is the Fermi velocity. Then Heisenberg’s uncertainty relation tells you that these superconducting charge carriers have to be smeared out over at least an area $\xi \approx \Delta x \approx \hbar v_F / k_B T_c$. Pippard’s non-local equation was able to describe the experimental data very well, but it remains

⁴A. B. Pippard, Proc. Roy. Soc. **A216**, 547 (1953).

a macroscopic, phenomenological description. For a long time, a microscopic theory was lacking – until Bardeen, Cooper and Schrieffer⁵ came up with their “BCS” theory in 1957. First, we review the experimental clues that led to the theory.

6.2 Clues for a microscopic theory

Four milestone experiments provided crucial clues for a microscopic theory:

1. The first clue comes from the discovery of a band gap between the ground state of the system and the excited states. This band gap is manifested in experiments on microwave absorption; below the band gap frequency no photons can be absorbed.
2. The second clue is the analogy between superconductivity (flow without electrical resistance) and superfluidity (flow without friction). This is manifested for example in the specific heat: superfluid helium exhibits a specific “lambda peak” in the specific heat at T_c . Such a peak is not expected for fermions (electrons) since it requires Bose statistics, but nevertheless it is present at T_c in superconductors.
3. The third clue is that the magnetic flux in a superconducting ring is quantized with an effective flux quantum that corresponds to $2e$ instead of e . This means that the charge carriers have two electron charges.

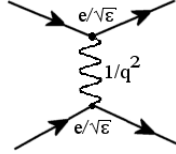
These first three clues give rise to an interesting assumption: electrons pair up two by two, forming a kind of “molecule” with charge $2e$. That molecule can be susceptible to Bose statistics since it is built from an even number of electrons, and hence undergo Bose-Einstein condensation. The binding energy of the molecule is precisely the superconducting band gap: if you provide this amount of energy, it can be absorbed by breaking up the pair. Whereas this nice assumption seems to fit the three clues above, there is a problem with it. Electrons repel, and don’t form molecules. There must be something providing the glue between the electrons.

4. This is where the fourth clue comes in. In an interesting experiment, the superconducting critical temperature was measured for isotopes of the same element. It turns out that T_c decreases as the mass M_i of the isotope increases, following $T_c \propto M_i^{-1/2}$. Since the chemistry (bond lengths, band structure, band mass,...) is unaffected by changing to a different isotope, the quantity in any microscopic picture that would depend on the mass of the isotope is the phonon frequency. Moreover, it would also depend as $M_i^{-1/2}$. This suggests that the phonons play an important role in superconductivity, and are a part of the glue that holds electrons together in pairs.

⁵J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

6.3 Cooper's intuition

So the experimental clues hint that the electrons bind together in pairs, even though they repel due to the Coulomb interactions between them. These Coulomb interactions are to lowest order represented by the exchange of a photon via a Coulomb line:



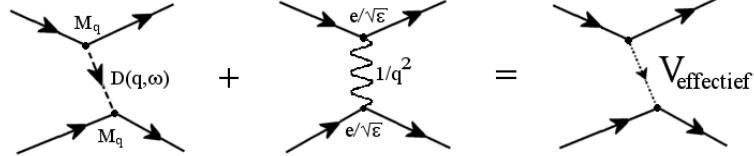
The vertex factor is essentially the charge, and the non-relativistic propagator is $1/q^2$. This agrees with the fact that we wrote the Coulomb interaction Hamiltonian in second quantization as

$$\hat{H}_{\text{coulomb}} = \frac{1}{2} \sum_{\mathbf{q}} V_{\text{coulomb}}(\mathbf{q}) \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \hat{a}_{\mathbf{k}+\mathbf{q}, \sigma}^+ \hat{a}_{\mathbf{k}-\mathbf{q}, \sigma'}^+ \hat{a}_{\mathbf{k}', \sigma'} \hat{a}_{\mathbf{k}, \sigma}, \quad (6.7)$$

with

$$V_{\text{coulomb}}(\mathbf{q}) = \frac{e^2}{\varepsilon q^2}. \quad (6.8)$$

The above diagram symbolizes this interaction. Cooper⁶ followed Fröhlich's conclusion that clue #4 means phonons are the glue. Indeed, two electrons in lowest order scattering can not only exchange a photon (via the Coulomb propagator line) but also a phonon. We also know the diagram for that:



We can now use the Feynman rules from Chapter 4 to see what the effective interaction potential would be, due to exchanging either a photon or a phonon. For the latter, the vertex factors are not the charges, but $M(q)$. The propagator (to lowest order) is not the free photon propagator F_0 , but the free phonon propagator $D_0(\mathbf{q}, \omega) = 2\omega_{\mathbf{q}}/(\omega^2 - \omega_{\mathbf{q}}^2 + i\delta)$. So, summing up both possibilities results in

$$V_{\text{eff}}(\mathbf{q}, \omega) = V_{\text{coulomb}} + V_{\text{phonon exch}} \quad (6.9)$$

$$= \frac{e^2}{\varepsilon q^2} + \frac{2\omega_{\mathbf{q}} |M(\mathbf{q})|^2}{\omega^2 - \omega_{\mathbf{q}}^2 + i\delta}. \quad (6.10)$$

⁶L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

We have to amend the pure Coulomb interaction and use the above effective interaction. For LO phonons, with the Fröhlich interaction amplitude $M(q) = A/q$ and a constant dispersion $\omega_{\mathbf{q}} = \omega_{LO}$ we get

$$V_{\text{eff}}(\mathbf{q}, \omega) = \frac{1}{q^2} \left(\frac{e^2}{\varepsilon} + \frac{2A\omega_{LO}}{\omega^2 - \omega_{LO}^2 + i\delta} \right), \quad (6.11)$$

and hence the electron-electron interaction Hamiltonian is

$$\frac{1}{2} \sum_{\mathbf{q}} V_{\text{eff}}(\mathbf{q}, \omega) \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} \hat{a}_{\mathbf{k}+\mathbf{q}, \sigma}^+ \hat{a}_{\mathbf{k}-\mathbf{q}, \sigma'}^+ \hat{a}_{\mathbf{k}', \sigma'} \hat{a}_{\mathbf{k}, \sigma}.$$

Starting from a ground state of non-interacting fermions with $E_{\mathbf{k}} = \hbar k^2/(2m)$ Fröhlich⁷, and Bardeen & Pines⁸ were able to show that $\omega = (\hbar \mathbf{k})^2/2m - (\hbar \mathbf{k}')^2/(2m)$. The effective interaction potential between an electron with wave number \mathbf{k} and an electron with wave number \mathbf{k}' due to the combination of exchanging a photon and an LO phonon then becomes

$$V_{\text{eff}}(\mathbf{q}, \mathbf{k}, \mathbf{k}') = \frac{1}{q^2} \left(\frac{e^2}{\varepsilon} + \frac{2A\omega_{LO}}{(E_{\mathbf{k}} - E_{\mathbf{k}'})^2 - \omega_{LO}^2 + i\delta} \right)$$

For energies $|E_{\mathbf{k}} - E_{\mathbf{k}'}| \ll \hbar\omega_{LO}$ this interaction potential is negative, and hence attractive. Indeed, we find

$$V_{\text{eff}}(\mathbf{q}, \omega \rightarrow 0) \approx \frac{1}{q^2} \left(\frac{e^2}{\varepsilon} - \frac{2A}{\omega_{LO}} \right) \quad (6.12)$$

so that a strong electron-phonon coupling combined with a small LO phonon frequency can make the term between brackets negative. The exchange of a phonon can indeed lead to an effective attraction between electrons.

Intuitively, this can be understood by imagining that the electron deforms the lattice around itself, as in the polaron picture. The positive polarization cloud induced by the electron in the lattice can attract another electron. Think of the electron as a negatively charged bowling ball on a trampoline surface. The bowling ball makes a dimple in the trampoline, and this dimple may be deep enough to overcome the repulsion that a second negatively charged bowling ball feels, so that they can stay in the same dimple. Such a bound state (of two electrons) is called a *Cooper pair*.

6.4 Bardeen-Cooper-Schrieffer (BCS) theory

6.4.1 BCS model

Rather than taking into account the full, complicated, effective interaction $V_{\text{eff}}(\mathbf{q}, \mathbf{k}, \mathbf{k}')$, Bardeen, Cooper and Schrieffer wanted to identify between which

⁷H. Fröhlich, Phys. Rev. **79**, 845 (1950).

⁸J. Bardeen en D. Pines, Phys. Rev. **99**, 1140 (1955).

pairs of electrons the effective interactions led to the strongest glue. Their aim was to set up a ‘minimal’ model of superconductivity, that is, they want to find the simplest Hamiltonian that would lead to Cooper pairing and superconductivity. Later models can add refinements and take into account additional terms to get better estimates of superconducting critical parameters, but it is important to understand first what it is that is needed for superconductivity to appear in the first place. So, let’s follow that reasoning and look for the electrons that feel the strongest attraction.

1. Firstly, we note that a large fraction of the electrons is incapable of exchanging a phonon because they are too deep in the Fermi sea and have no unoccupied states to scatter to. Only the electrons within a band of energies $\hbar\omega_{LO}$ (usually around 10-100 meV) around the Fermi energy E_F (usually about 10 eV) will be able to feel electron-electron attraction. This is called the “Debye” energy window since the Debye energy is the typical energy of a phonon.
2. Pick an electron in that Debye band, say with wave number \mathbf{k} and spin σ . It can feel attraction to other electrons in the Debye window, but to which electron will it be attracted most strongly? We’ve already seen that $E_{\mathbf{k}} - E_{\mathbf{k}'}$ should be small. Moreover, you want the resulting total momentum of the pair to be small as well (minimizing the kinetic energy of the Cooper pair, putting it in the translational ground state). This means $\mathbf{k} + \mathbf{k}' \approx 0$, so the attraction is strongest with the electron with wave number $\mathbf{k}' = -\mathbf{k}$.
3. Finally, remember that the exchange hole weakens the interactions. We already encountered this in the chapter on electrons and phonons, studying the effects of electron-electron interactions. These exchange interactions will also in the present case weaken the glue between electrons, but they are only present between electrons with the same spin. So, the attraction will be strongest if the electrons not only have opposite momentum, but also opposite spin.

From these considerations, Bardeen, Cooper and Schrieffer proposed the following model Hamiltonian:

$$\hat{H}^{(\text{BCS})} = \sum_{\mathbf{k}, \sigma} \frac{(\hbar\mathbf{k})^2}{2m_b} \hat{c}_{\mathbf{k}, \sigma}^\dagger \hat{c}_{\mathbf{k}, \sigma} + \hat{H}_{\text{int}}^{(\text{BCS})} \quad (6.13)$$

with the BCS interaction given by

$$\hat{H}_{\text{int}}^{(\text{BCS})} = -\tilde{V} \sum_{\mathbf{k} \in D} \sum_{\mathbf{k}' \in D} \hat{c}_{-\mathbf{k}', \downarrow}^\dagger \hat{c}_{\mathbf{k}', \uparrow}^\dagger \hat{c}_{\mathbf{k}, \uparrow} \hat{c}_{-\mathbf{k}, \downarrow}, \quad (6.14)$$

where D is the set of single-particle states in the Debye energy window:

$$D = \left\{ \mathbf{k} : \left[\left(\frac{(\hbar k_F)^2}{2m_b} - \hbar\omega_{LO} \right) < \frac{(\hbar k)^2}{2m_b} < \left(\frac{(\hbar k_F)^2}{2m_b} + \hbar\omega_{LO} \right) \right] \right\} \quad (6.15)$$

The interaction strength is replaced by a constant \tilde{V} , the only model parameter. In other words, rather than implementing the effective interaction V_{eff} between any two electrons, the BCS model only keeps those interactions that couple electrons with opposite spin, and opposite momentum in the Debye window, and moreover takes the interaction amplitude to be constant. This will indeed turn out to be the minimal assumptions for a model that exhibits superconductivity.

6.4.2 BCS ground state

BCS found a variational wave function for their Hamiltonian, that produces a lower energy than that of the filled Fermi sphere. Hence, the normal state (the filled Fermi sphere) is not the ground state that the system will attain as temperature is lowered towards zero. The variational wave function proposed by BCS is given by

$$|\Phi_{\text{BCS}}\rangle = \prod_{\mathbf{k}} (u_{\mathbf{k}}^* + v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger) |0\rangle, \quad (6.16)$$

Here $|0\rangle$ is the electron vacuum. The variational parameters are $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$, and these have to satisfy

$$|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1. \quad (6.17)$$

We can recover the filled Fermi sphere with a special choice of the variational parameters:

$$\begin{cases} u_{\mathbf{k}} = \theta(k > k_F) \\ v_{\mathbf{k}} = \theta(k < k_F) \end{cases}. \quad (6.18)$$

However, there is another choice for these variational parameters that leads to a lower energy, as we shall prove. The specific form of the BCS wave function is chosen because $\hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger$ creates a pair of electrons precisely in the suitable states $(\mathbf{k}, \uparrow), (-\mathbf{k}, \downarrow)$ where the attraction to form a Cooper pair is strongest. In essence, the interaction part of the BCS Hamiltonian represents scattering of a pair with \mathbf{k} to a pair with \mathbf{k}' .

For each \mathbf{k} , the two-particle wave function

$$(u_{\mathbf{k}}^* + v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger) |0\rangle \quad (6.19)$$

describes a *quantum superposition* of a state where the pair $(\mathbf{k}, \uparrow), (-\mathbf{k}, \downarrow)$ is occupied with electrons and where that pair is not occupied. Only for $v_{\mathbf{k}} = 1, u_{\mathbf{k}} = 0$ are we certain that the pair is occupied (2 electrons in the Cooper pair), and for $v_{\mathbf{k}} = 0, u_{\mathbf{k}} = 1$ we know with certainty that the pair is unoccupied (zero electrons in the Cooper pair). It is important to note that for all other choices of $u_{\mathbf{k}}, v_{\mathbf{k}}$ this superposition is *not a number state*! In other words, it is a superposition of different occupation representation basis vectors, and the number of electrons in the Cooper “pair” depends on $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$, it is not fixed. That means that expectation values such as $\langle \hat{c}_{\mathbf{k},\uparrow} \hat{c}_{-\mathbf{k},\downarrow} \rangle$ are not necessarily zero, as they are for the number states that we have been using all along in previous chapters. That also means that if we want to fix the total number of electrons

(summed over all \mathbf{k}) while performing the variational calculus, we'll need a Lagrange multiplier – the chemical potential μ .

The expectation value of the BCS Hamiltonian with respect to the BCS wave function needs to be calculated in order to minimize the energy as a function of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$:

$$\begin{aligned} \langle \Phi_{\text{BCS}} | \hat{H}^{(\text{BCS})} | \Phi_{\text{BCS}} \rangle - \mu N &= \sum_{\mathbf{k}, \sigma} \left(\frac{(\hbar \mathbf{k})^2}{2m_b} - \mu \right) \langle \Phi_{\text{BCS}} | \hat{c}_{\mathbf{k}, \sigma}^\dagger \hat{c}_{\mathbf{k}, \sigma} | \Phi_{\text{BCS}} \rangle \\ &\quad + \langle \Phi_{\text{BCS}} | \hat{H}_{\text{int}}^{(\text{BCS})} | \Phi_{\text{BCS}} \rangle. \end{aligned} \quad (6.20)$$

In other words, we look for the minimum in the energy $\langle \Phi_{\text{BCS}} | \hat{H}^{(\text{BCS})} | \Phi_{\text{BCS}} \rangle$, while fixing the number of electrons $N = \langle \sum_{\mathbf{k}, \sigma} \hat{c}_{\mathbf{k}, \sigma}^\dagger \hat{c}_{\mathbf{k}, \sigma} \rangle$ through the chemical potential. Denote

$$\xi_{\mathbf{k}} = \frac{(\hbar \mathbf{k})^2}{2m_b} - \mu \quad (6.21)$$

so that we can write

$$\begin{aligned} E &= \left\langle \Phi_{\text{BCS}} \left| \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} \hat{c}_{\mathbf{k}, \sigma}^\dagger \hat{c}_{\mathbf{k}, \sigma} \right| \Phi_{\text{BCS}} \right\rangle \\ &\quad - \tilde{V} \left\langle \Phi_{\text{BCS}} \left| \sum_{\mathbf{k} \in D} \sum_{\mathbf{k}' \in D} \hat{c}_{-\mathbf{k}', \downarrow}^\dagger \hat{c}_{\mathbf{k}', \uparrow}^\dagger \hat{c}_{\mathbf{k}, \uparrow} \hat{c}_{-\mathbf{k}, \downarrow} \right| \Phi_{\text{BCS}} \right\rangle \end{aligned} \quad (6.22)$$

6.4.3 Bogoliubov transformation

The calculation of the expectation values (and the interpretation of the results) is simplified a lot by first performing a unitary transformation, called the Bogoliubov transformation. We're going to follow this path since it is more insightful than the full calculation, even though it was found not by BCS, but afterwards by Bogoliubov and Valatin, and is based on Bogoliubov's work for superfluid helium. The idea is to introduce new operators $\hat{\alpha}$ that satisfy

$$\hat{\alpha}_{\mathbf{k}, \sigma} = u_{\mathbf{k}}^* \hat{c}_{\mathbf{k}, \sigma} - \sigma v_{\mathbf{k}} \hat{c}_{-\mathbf{k}, -\sigma}^\dagger \quad (6.23)$$

$$\Leftrightarrow$$

$$\hat{c}_{\mathbf{k}, \sigma} = u_{\mathbf{k}} \hat{\alpha}_{\mathbf{k}, \sigma} + \sigma v_{\mathbf{k}} \hat{\alpha}_{-\mathbf{k}, -\sigma}^\dagger, \quad (6.24)$$

where we impose that

$$u_{-\mathbf{k}} = u_{\mathbf{k}} \text{ and } v_{-\mathbf{k}} = v_{\mathbf{k}}.$$

We can make such restriction since the u 's and the v 's are variational parameters anyway – we'll make more restrictions later on. The BCS Hamiltonian can then be rewritten in terms of $\hat{\alpha}$'s rather than \hat{c} 's. It is easy to check that since the variational parameters satisfy (6.17),

$$u_{\mathbf{k}} u_{\mathbf{k}}^* + v_{\mathbf{k}} v_{\mathbf{k}}^* = 1, \quad (6.25)$$

the new operators $\hat{\alpha}_{\mathbf{k},\sigma}$ also satisfy anticommutation relations $\{\hat{\alpha}_{\mathbf{k}',\sigma'}, \hat{\alpha}_{\mathbf{k},\sigma}^\dagger\} = \delta_{\mathbf{k}-\mathbf{k}'}\delta_{\sigma\sigma'}$ so that they will be fermionic second quantization operators. The main usefulness of the Bogoliubov transformation follows from the fact that they have the BCS ground state as their vacuum. In other words, for any \mathbf{k}, σ the relation $\hat{\alpha}_{\mathbf{k},\sigma} |\Phi_{\text{BCS}}\rangle = 0$ holds. Indeed, we find:

$$\begin{aligned} \hat{\alpha}_{\mathbf{k},\uparrow} |\Phi_{\text{BCS}}\rangle &= (u_{\mathbf{k}}^* \hat{c}_{\mathbf{k},\uparrow} - v_{\mathbf{k}} \hat{c}_{-\mathbf{k},\downarrow}^\dagger)(u_{\mathbf{k}}^* + v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger) \prod_{\mathbf{k}' \neq \mathbf{k}} (u_{\mathbf{k}'}^* + v_{\mathbf{k}'} \hat{c}_{\mathbf{k}',\uparrow}^\dagger \hat{c}_{-\mathbf{k}',\downarrow}^\dagger) |0\rangle \\ &= \left(u_{\mathbf{k}}^* v_{\mathbf{k}} \hat{c}_{-\mathbf{k},\downarrow}^\dagger - v_{\mathbf{k}} u_{\mathbf{k}}^* \hat{c}_{-\mathbf{k},\downarrow}^\dagger \right) \prod_{\mathbf{k}' \neq \mathbf{k}} (u_{\mathbf{k}'}^* + v_{\mathbf{k}'} \hat{c}_{\mathbf{k}',\uparrow}^\dagger \hat{c}_{-\mathbf{k}',\downarrow}^\dagger) |0\rangle \\ &= 0. \end{aligned} \quad (6.26)$$

Furthermore, we note that the creation operator $\hat{\alpha}_{\mathbf{k},\uparrow}^\dagger$ is going to break up the Cooper pair with $\mathbf{k}, -\mathbf{k}$ and transform it into a single-electron state, the “broken Cooper pair”:

$$\begin{aligned} \hat{\alpha}_{\mathbf{k},\uparrow}^\dagger |\Phi_{\text{BCS}}\rangle &= (u_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger + v_{\mathbf{k}}^* \hat{c}_{-\mathbf{k},\downarrow})(u_{\mathbf{k}}^* + v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger) |0\rangle \\ &= |u_{\mathbf{k}}|^2 \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle + v_{\mathbf{k}}^* u_{\mathbf{k}}^* \hat{c}_{-\mathbf{k},\downarrow} |0\rangle + u_{\mathbf{k}} v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger |0\rangle \\ &\quad + |v_{\mathbf{k}}|^2 \hat{c}_{-\mathbf{k},\downarrow} \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle \\ &= (|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2) \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle = \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle. \end{aligned} \quad (6.27)$$

The third term drops out since $\hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle = 0$ (you cannot create two electrons in the same state). Summarizing:

$$0 \xleftarrow{\hat{\alpha}_{\mathbf{k},\sigma}} \left\{ \begin{array}{c} \text{Cooper pair} \\ (u_{\mathbf{k}}^* + v_{\mathbf{k}} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger) |0\rangle \end{array} \right\} \xrightleftharpoons[\hat{\alpha}_{\mathbf{k},\sigma}^\dagger]{\hat{\alpha}_{\mathbf{k},\sigma}} \left\{ \begin{array}{c} \text{Broken pair} \\ \hat{c}_{\mathbf{k},\uparrow}^\dagger |0\rangle \end{array} \right\} \xrightarrow{\hat{\alpha}_{\mathbf{k},\sigma}^\dagger} 0$$

The action of the fermionic operators $\hat{\alpha}_{\mathbf{k},\uparrow}$ is the excite, i.e. break up the Cooper pairs. The BCS state is the “vacuum” for broken Cooper pairs, and we can excite a gas of broken-up pairs by letting the creation operator work on this vacuum.

6.4.4 Variational calculation and gap equation

Optimal values of the variational parameters

The expectation value of the kinetic energy is

$$E_{\text{kin}} = \left\langle \Phi_{\text{BCS}} \left| \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} \hat{c}_{\mathbf{k},\sigma}^\dagger \hat{c}_{\mathbf{k},\sigma} \right| \Phi_{\text{BCS}} \right\rangle.$$

with $\xi_{\mathbf{k}} = \epsilon_{\mathbf{k}} - E_F$ the energy measured from the Fermi surface (setting $\mu = E_F$ at temperatures much below T_F). The Bogoliubov transformation changes this

into

$$\begin{aligned}
E_{\text{kin}} &= \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} \langle \Phi_{\text{BCS}} | \left(u_{\mathbf{k}}^* \hat{\alpha}_{\mathbf{k}, \sigma}^\dagger + \sigma v_{\mathbf{k}}^* \hat{\alpha}_{-\mathbf{k}, -\sigma} \right) \\
&\quad \times \left(u_{\mathbf{k}} \hat{\alpha}_{\mathbf{k}, \sigma} + \sigma v_{\mathbf{k}} \hat{\alpha}_{-\mathbf{k}, -\sigma}^\dagger \right) | \Phi_{\text{BCS}} \rangle.
\end{aligned} \tag{6.28}$$

Now we can use $\hat{\alpha}_{\mathbf{k}, \sigma} | \Phi_{\text{BCS}} \rangle = 0$ to simplify this to

$$\begin{aligned}
E_{\text{kin}} &= \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 \langle \Phi_{\text{BCS}} | \hat{\alpha}_{\mathbf{k}, \sigma} \hat{\alpha}_{\mathbf{k}, \sigma}^\dagger | \Phi_{\text{BCS}} \rangle \\
&= \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 \langle \Phi_{\text{BCS}} | 1 - \hat{\alpha}_{\mathbf{k}, \sigma}^\dagger \hat{\alpha}_{\mathbf{k}, \sigma} | \Phi_{\text{BCS}} \rangle \\
&= 2 \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2.
\end{aligned} \tag{6.29}$$

The interaction energy contribution,

$$\mathcal{I} = \langle \Phi_{\text{BCS}} | \hat{c}_{-\mathbf{k}', \downarrow}^\dagger \hat{c}_{\mathbf{k}', \uparrow}^\dagger \hat{c}_{\mathbf{k}, \uparrow} \hat{c}_{-\mathbf{k}, \downarrow} | \Phi_{\text{BCS}} \rangle$$

is calculated in the same way via the Bogoliubov transformation:

$$\begin{aligned}
\mathcal{I} &= \langle \Phi_{\text{BCS}} | \left(u_{-\mathbf{k}'}^* \hat{\alpha}_{-\mathbf{k}', \downarrow}^\dagger - v_{-\mathbf{k}'}^* \hat{\alpha}_{\mathbf{k}', \uparrow} \right) \left(u_{\mathbf{k}'}^* \hat{\alpha}_{\mathbf{k}', \uparrow}^\dagger + v_{\mathbf{k}'}^* \hat{\alpha}_{-\mathbf{k}', \downarrow} \right) \\
&\quad \times \left(u_{\mathbf{k}} \hat{\alpha}_{\mathbf{k}, \uparrow} + v_{\mathbf{k}} \hat{\alpha}_{-\mathbf{k}, \downarrow}^\dagger \right) \left(u_{-\mathbf{k}} \hat{\alpha}_{-\mathbf{k}, \downarrow} - v_{-\mathbf{k}} \hat{\alpha}_{\mathbf{k}, \uparrow}^\dagger \right) | \Phi_{\text{BCS}} \rangle \\
&= v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}} \langle \Phi_{\text{BCS}} | \hat{\alpha}_{-\mathbf{k}', \downarrow} \hat{\alpha}_{\mathbf{k}', \uparrow}^\dagger \hat{\alpha}_{\mathbf{k}, \uparrow} \hat{\alpha}_{\mathbf{k}, \uparrow}^\dagger | \Phi_{\text{BCS}} \rangle \\
&\quad + v_{\mathbf{k}'}^* v_{\mathbf{k}'}^* v_{\mathbf{k}} v_{\mathbf{k}} \langle \Phi_{\text{BCS}} | \hat{\alpha}_{\mathbf{k}', \uparrow} \hat{\alpha}_{-\mathbf{k}', \downarrow} \hat{\alpha}_{-\mathbf{k}, \downarrow}^\dagger \hat{\alpha}_{\mathbf{k}, \uparrow}^\dagger | \Phi_{\text{BCS}} \rangle \\
&= v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}} + |v_{\mathbf{k}}|^4 \delta_{\mathbf{k}-\mathbf{k}'}.
\end{aligned} \tag{6.30}$$

The first term in this result, (6.30), corresponds to

$$v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}} = \langle \Phi_{\text{BCS}} | \hat{c}_{-\mathbf{k}', \downarrow}^\dagger \hat{c}_{\mathbf{k}', \uparrow}^\dagger | \Phi_{\text{BCS}} \rangle \langle \Phi_{\text{BCS}} | \hat{c}_{\mathbf{k}, \uparrow} \hat{c}_{-\mathbf{k}, \downarrow} | \Phi_{\text{BCS}} \rangle,$$

If we'd calculate these expectation values with the Fermi sphere in stead of the BCS ground state, the expectation value would be zero. The reason that the expectation value of a product of two creation operators (or two annihilation operators) can be different from zero is because the BCS state contains superpositions of states with 0 and 2 particles! These type of expectation values were not present in our perturbational calculation of the energy of the interacting electron gas in Chapter 3 because we worked with the Fermi sphere, and that does not contain superpositions of different numbers of electrons. Therefore this type of expectation values are called “*anomalous averages*”. By making a suitable choice of the u 's and the v 's, we can make the anomalous averages different from zero, and thus reduce the energy.

The second term in (6.30) is more familiar:

$$|v_{\mathbf{k}}|^4 \delta_{\mathbf{k}-\mathbf{k}'} = \left\langle \Phi_{\text{BCS}} \left| \hat{c}_{\mathbf{k}';\uparrow}^\dagger \hat{c}_{\mathbf{k};\uparrow} \right| \Phi_{\text{BCS}} \right\rangle \left\langle \Phi_{\text{BCS}} \left| \hat{c}_{-\mathbf{k}';\downarrow}^\dagger \hat{c}_{-\mathbf{k};\downarrow} \right| \Phi_{\text{BCS}} \right\rangle. \quad (6.31)$$

This term would also appear in the normal state of the electron gas, it is the direct interaction. In Chapter 3, where we worked with the Coulomb interaction, the direct Coulomb interaction was cancelled by the background. Here, we work with the BCS interaction, and the direct contribution only results in a shift of the single-particle energies $\xi_{\mathbf{k}}$. When calculating the difference in energy between the superconducting and the normal state, it is the presence of the anomalous average that will matter.

Where is the exchange energy that we had in the calculation of the interaction energy of the electron gas in Chapter 3? It is not present here, because we have chosen the BCS interaction to act only between electrons of different spin.

The total energy now becomes

$$E = 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 - \tilde{V} \sum_{\mathbf{k} \in D} \sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}} - \tilde{V} \sum_{\mathbf{k} \in D} |v_{\mathbf{k}}|^4 \quad (6.32)$$

The condition $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$ is taken into account this time not with extra Lagrange multipliers, but simply by eliminating $u_{\mathbf{k}}$, replacing it everywhere with $(1 - v_{\mathbf{k}} v_{\mathbf{k}}^*)/u_{\mathbf{k}}^*$. This means in particular that

$$\frac{\partial u_{\mathbf{k}}}{\partial v_{\mathbf{k}}^*} = -\frac{v_{\mathbf{k}}}{u_{\mathbf{k}}^*}, \quad (6.33)$$

so that

$$\begin{aligned} \frac{\partial E}{\partial v_{\mathbf{k}}^*} &= 2\xi_{\mathbf{k}} v_{\mathbf{k}} - \tilde{V} \sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* \left(-\frac{v_{\mathbf{k}}}{u_{\mathbf{k}}^*} \right) v_{\mathbf{k}} \\ &\quad - \tilde{V} \sum_{\mathbf{k}' \in D} u_{\mathbf{k}}^* u_{\mathbf{k}'} v_{\mathbf{k}'} - 2\tilde{V} |v_{\mathbf{k}}|^2 v_{\mathbf{k}}. \end{aligned} \quad (6.34)$$

To solve the extremum condition $\partial E / \partial v_{\mathbf{k}}^* = 0$ we introduce an auxiliary function

$$\boxed{\Delta = \tilde{V} \sum_{\mathbf{k}' \in D} u_{\mathbf{k}'} v_{\mathbf{k}'}}. \quad (6.35)$$

The variational condition $\partial E / \partial v_{\mathbf{k}}^* = 0$ then becomes

$$2 \left(\xi_{\mathbf{k}} - \tilde{V} |v_{\mathbf{k}}|^2 \right) v_{\mathbf{k}} u_{\mathbf{k}}^* - \Delta (u_{\mathbf{k}}^*)^2 + \Delta^* (v_{\mathbf{k}})^2 = 0. \quad (6.36)$$

First, note that we've kept Δ constant when taking the partial derivative. So we're going to solve the problem assuming that we already know the value of Δ , and afterwards we'll have to plug in our solution in Δ to check if everything adds

up correctly. This is a so-called “self-consistent solution scheme” and it requires the self-consistency check at the end of the calculation. Second, we remark that the effect of the second term in (6.30), the direct interaction contribution, is clarified. As we mentioned before, it can be treated as a correction to the kinetic energy due to self-interaction of the electrons and as it is not important to the normal-superconducting transition, it can be absorbed in the definition of $\xi_{\mathbf{k}}$,

$$\xi'_{\mathbf{k}} = \xi_{\mathbf{k}} - \tilde{V} |v_{\mathbf{k}}|^2 \quad (6.37)$$

Also here, we could start from $\xi_{\mathbf{k}}$ without the correction, calculate the variational $v_{\mathbf{k}}$ for the “unperturbed” $\xi_{\mathbf{k}}$, and make a new $\xi'_{\mathbf{k}}$ with it. Then we iterate the calculation and keep on doing this until the result converges. In practice we just work with $\xi_{\mathbf{k}}$.

In order to satisfy the condition $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$ automatically we can choose the following form for $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$:

$$v_{\mathbf{k}} = \sin(\theta_{\mathbf{k}}/2) \exp\{i\phi_{\mathbf{k}}^{(1)}\}, \quad (6.38)$$

$$u_{\mathbf{k}}^* = \cos(\theta_{\mathbf{k}}/2) \exp\{i\phi_{\mathbf{k}}^{(2)}\}. \quad (6.39)$$

In this notation we find

$$\begin{aligned} & \xi_{\mathbf{k}} \sin(\theta_{\mathbf{k}}) - \Delta \exp\{-i(\phi_{\mathbf{k}}^{(1)} - \phi_{\mathbf{k}}^{(2)})\} \cos^2\left(\frac{\theta_{\mathbf{k}}}{2}\right) \\ & + \Delta^* \exp\{-i(\phi_{\mathbf{k}}^{(2)} - \phi_{\mathbf{k}}^{(1)})\} \sin^2\left(\frac{\theta_{\mathbf{k}}}{2}\right) = 0, \end{aligned} \quad (6.40)$$

Only if

$$\Delta = |\Delta| \exp\{i(\phi_{\mathbf{k}}^{(1)} - \phi_{\mathbf{k}}^{(2)})\} \quad (6.41)$$

all terms in the extremum condition (6.40) are real. A sufficient condition for this is that the phases $\phi_{\mathbf{k}}^{(1,2)}$ are independent of \mathbf{k} . Since we work with variational parameters anyway, we can restrict the domain in which we vary these parameters if we wish so, and choose the phases zero. The variational extremum condition now becomes

$$\xi_{\mathbf{k}} \sin(\theta_{\mathbf{k}}) - |\Delta| \cos(\theta_{\mathbf{k}}) = 0,$$

This is solved by

$$\sin(\theta_{\mathbf{k}}) = \frac{|\Delta|}{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}}, \quad (6.42)$$

$$\cos(\theta_{\mathbf{k}}) = \frac{\xi_{\mathbf{k}}}{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}}. \quad (6.43)$$

Now we need to impose the self-consistency condition for the gap Δ , by plugging in the results for the u 's and v 's back into expression (6.35):

$$\begin{aligned} |\Delta| &= \tilde{V} \sum_{\mathbf{k}' \in D} \cos(\theta_{\mathbf{k}'}/2) \sin(\theta_{\mathbf{k}'}/2) \\ &= \frac{1}{2} \tilde{V} \sum_{\mathbf{k}' \in D} \sin(\theta_{\mathbf{k}'}). \end{aligned}$$

With the help of (6.42) we then find

$$|\Delta| = \frac{1}{2} \tilde{V} \sum_{\mathbf{k}' \in D} \frac{|\Delta|}{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}'})^2}} \quad (6.44)$$

$$\Leftrightarrow \tilde{V} \sum_{\mathbf{k}' \in D} \frac{1}{2\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}'})^2}} = 1. \quad (6.45)$$

This is called the *gap equation*. It is solved by transforming the sum over wave numbers into an integral in energy space (with the density of states). Since in the Debye window around the Fermi energy the density of states does not vary much, we can keep it constant and equal to the density of states at the Fermi surface, $N(0)$. Remember that we've placed the zero of energy on the Fermi energy, so $\xi_k = E_k - \mu \Rightarrow \xi_{k_F} = E_{k_F} - \mu = 0$. The gap equation becomes

$$1 = \tilde{V} N(0) \int_{-\hbar\omega_{LO}}^{\hbar\omega_{LO}} dE \frac{1}{2\sqrt{|\Delta|^2 + E^2}} \quad (6.46)$$

The number $N(0)$ of states with energy between E_F and $E_F + dE$ depends of course on $\xi_{\mathbf{k}}$, but if we choose $\xi_k = (\hbar k)^2/2m - \mu$, then $N(0) = 3n/(2E_F)$ where n is the electron density in the normal state. The integral can be performed analytically:

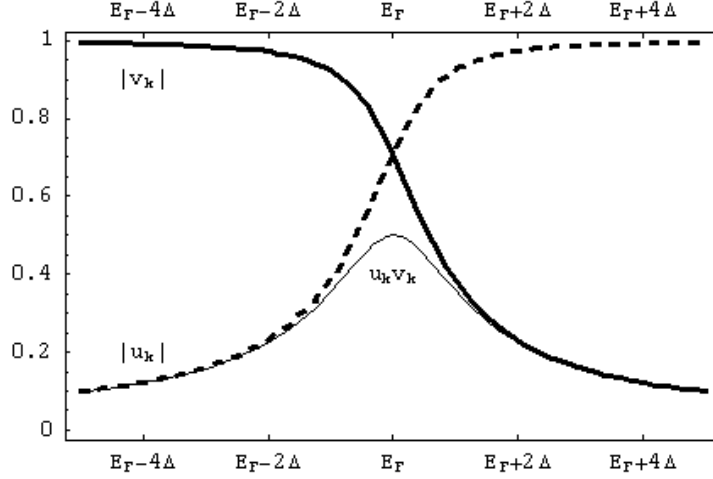
$$1 = \frac{1}{2} \tilde{V} N(0) 2 \operatorname{arcsinh} \left(\frac{\hbar\omega_{LO}}{|\Delta|} \right) \quad (6.47)$$

so that we find for the gap

$$\begin{aligned} |\Delta| &= \frac{\hbar\omega_{LO}}{\sinh \left\{ 1/[N(0)\tilde{V}] \right\}} \\ \Rightarrow |\Delta| &\approx 2\hbar\omega_{LO} \exp \left[-\frac{1}{N(0)\tilde{V}} \right], \end{aligned} \quad (6.48)$$

Where we have used that $N(0)\tilde{V} \ll 1$, i.e. we are working in the weak-coupling regime (since T_c is much, much smaller than T_F). Now, we can use these results to find the optimal variational results:

$$\begin{cases} v_{\mathbf{k}} = \sin(\theta_{\mathbf{k}}/2) \\ u_{\mathbf{k}}^* = \cos(\theta_{\mathbf{k}}/2) \end{cases} \text{ met } \begin{cases} \sin(\theta_{\mathbf{k}}) = -\frac{|\Delta|}{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}} \\ \cos(\theta_{\mathbf{k}}) = \frac{\xi_{\mathbf{k}}}{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}} \end{cases} \quad (6.49)$$



The variational parameters $u_{\mathbf{k}}$, $v_{\mathbf{k}}$, and $u_{\mathbf{k}}v_{\mathbf{k}}$ are shown in the neighbourhood of the Fermi surface as a function of the energy.

This figure shows the result that we obtained for $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$. When we move away from the Fermi energy, these parameters become equal to the values for the normal electron gas (the filled Fermi sphere):

$$\begin{cases} u_{\mathbf{k}} = \theta(k > k_F) \\ v_{\mathbf{k}} = \theta(k < k_F) \end{cases}.$$

But, near the Fermi energy $u_{\mathbf{k}}, v_{\mathbf{k}}$ deviate from these values. The change over the Fermi surface is no longer a step function, but it is smeared out over an energy range determined by the gap Δ , and in this range $u_{\mathbf{k}}v_{\mathbf{k}} \neq 0$ and anomalous averages appear. For this illustration, we choose a ridiculously large $\Delta = 0.02 E_F$.

BCS ground state energy

What is the result for the BCS variational energy? Is it indeed lower than the normal state energy? Note that $\Delta = 0$ is also a solution to the gap equation – in (6.45) we already divided by Δ , meaning that we still have to check that the solution we found has lower energy than the $\Delta = 0$ solution. We need to substitute the results for the u 's and v 's back into the variational energy

$$E_{\text{BCS}} = \sum_{\mathbf{k}} (2\xi_{\mathbf{k}} |v_{\mathbf{k}}|^2) - \sum_{\mathbf{k} \in D} \left(\tilde{V} \sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* \right) u_{\mathbf{k}} v_{\mathbf{k}}. \quad (6.50)$$

To compare this with the filled Fermi sphere, we first note that the electrons outside the Debye window notice no difference between $\Delta = 0$ and $\Delta \neq 0$. They

don't participate at all to the superconducting shift in energy. So, the difference in energy is

$$E_{\text{BCS}} - E_{\text{N}} = \left[\sum_{\mathbf{k} \in D} (2\xi_{\mathbf{k}} |v_{\mathbf{k}}|^2) - \frac{\Delta^2}{\tilde{V}} \right] - \left[\sum_{\mathbf{k} \in D, k < k_F} 2\xi_{\mathbf{k}} \right] \quad (6.51)$$

$$= - \sum_{k \in D, k < k_F} 2\xi_k |u_k|^2 + \sum_{k \in D, k > k_F} 2\xi_k |v_k|^2 - \frac{\Delta^2}{\tilde{V}} \quad (6.52)$$

$$= - \sum_{k \in D, k < k_F} \xi_k \left(1 + \frac{|\xi_k|}{\sqrt{|\xi_k|^2 + \Delta^2}} \right) + \sum_{k \in D, k > k_F} \xi_k \left(1 - \frac{|\xi_k|}{\sqrt{|\xi_k|^2 + \Delta^2}} \right) - \frac{\Delta^2}{\tilde{V}}. \quad (6.53)$$

Again the sums over \mathbf{k} are rewritten as integrals over the energy multiplied by the density of states, that we take constant in the Debye window:

$$E_{\text{BCS}} - E_{\text{N}} = -N(0) \int_{-\hbar\omega_{LO}}^0 dE E \left(1 + \frac{-|E|}{\sqrt{E^2 + \Delta^2}} \right) + N(0) \int_0^{\hbar\omega_{LO}} dE E \left(1 - \frac{E}{\sqrt{E^2 + \Delta^2}} \right) - \frac{\Delta^2}{\tilde{V}} \quad (6.54)$$

$$= 2N(0) \int_0^{\hbar\omega_{LO}} dE E \left(1 - \frac{E}{\sqrt{E^2 + \Delta^2}} \right) - \frac{\Delta^2}{\tilde{V}}. \quad (6.55)$$

The integral can be calculated using

$$\int \frac{x^2}{\sqrt{1+x^2}} dx = \frac{1}{2} x \sqrt{1+x^2} - \frac{1}{2} \text{arcsinh}(x). \quad (6.56)$$

This yields:

$$E_{\text{BCS}} - E_{\text{N}} = 2N(0)\Delta^2 \left[\frac{(\hbar\omega)^2}{2\Delta^2} - \frac{\hbar\omega}{2\Delta} \sqrt{1 + \left(\frac{\hbar\omega}{\Delta} \right)^2} + \frac{1}{2} \text{arcsinh} \left(\frac{\hbar\omega}{\Delta} \right) \right] - \frac{\Delta^2}{\tilde{V}} \quad (6.57)$$

Since

$$\text{arcsinh} \left(\frac{\hbar\omega}{\Delta} \right) = \frac{1}{N(0)\tilde{V}}$$

the hyperbolic arcsine cancels with $-\Delta^2/\tilde{V}$. In the limit $N(0)\tilde{V} \ll 1$ we also have $\Delta \ll \hbar\omega$ and so

$$\begin{aligned} E_{\text{BCS}} - E_{\text{N}} &= N(0) (\hbar\omega)^2 \left\{ 1 - \sqrt{\left(\frac{\Delta}{\hbar\omega}\right)^2 + 1} \right\} \\ &\approx -\frac{1}{2} N(0) \Delta^2. \end{aligned} \quad (6.58)$$

This confirms that the energy of electrons in the superconducting state is lowered. The filled Fermi sphere is not the true ground state of the electron gas with BCS attraction. The variational result with $\Delta \neq 0$ and anomalous averages has a lower energy. Indeed, the interaction energy now reduces the energy since:

$$\tilde{V} \left(\sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* \right) \left(\sum_{\mathbf{k} \in D} u_{\mathbf{k}} v_{\mathbf{k}} \right) \neq 0.$$

The pairs for which $u_{\mathbf{k}} v_{\mathbf{k}} \neq 0$ of course the Cooper pairs.

An important thing to note about this result is that the energy reduction is not an analytic function of \tilde{V} . In fact, it is clear from (6.48) that the result has an essential singularity in $\tilde{V} = 0$. This means that it is impossible to find any converging series expansion around the unperturbed $\tilde{V} = 0$ state. So, perturbative approaches (which set out to build such a series expansion for the energy) are bound to fail! This is the reason why it took so long to find the microscopic theory of superconductivity, and why it was in the end a variational approach that provided the answer.

6.5 Interpretation of the BCS state

6.5.1 Excited states and band gap

Now we come back to the issue of broken Cooper pairs, and calculate the energy it takes to break a Cooper pair. This will show that it is indeed correct to call the auxiliary function Δ a band gap. Remember, for a broken Cooper pair, we had a state

$$\hat{\alpha}_{\mathbf{k},\uparrow}^\dagger |\Phi_{\text{BCS}}\rangle = \hat{c}_{\mathbf{k},\uparrow}^+ |0\rangle \quad (6.59)$$

containing (with certainty) just 1 electron. The (unbroken) Cooper pairs correspond to a superposition of no electrons (with amplitude $u_{\mathbf{k}}^*$) and two electrons (amplitude $v_{\mathbf{k}}$) in the $\{\mathbf{k}, \uparrow\}, \{-\mathbf{k}, \downarrow\}$ states. So, for the Cooper pairs $u_{\mathbf{k}} v_{\mathbf{k}} \neq 0$, which, as we saw, lowers the total energy by

$$\tilde{V} \left(\sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* \right) \left(\sum_{\mathbf{k}'' \in D} u_{\mathbf{k}''} v_{\mathbf{k}''} \right). \quad (6.60)$$

If we now break up the $\{\mathbf{k}, \uparrow\}, \{-\mathbf{k}, \downarrow\}$ Cooper pair, this means we set $u_{\mathbf{k}} v_{\mathbf{k}} = 0$, and the interaction energy that is lost by breaking up the pair is the sum of all

the terms with the chosen $u_{\mathbf{k}}v_{\mathbf{k}}$ that we set equal to zero, or

$$2\tilde{V} \left(\sum_{\mathbf{k}' \in D} v_{\mathbf{k}'}^* u_{\mathbf{k}'}^* \right) u_{\mathbf{k}} v_{\mathbf{k}} = 2\Delta^* u_{\mathbf{k}} v_{\mathbf{k}}. \quad (6.61)$$

The factor 2 appears because we can either set $\mathbf{k}' = 0$ or $\mathbf{k}'' = 0$ in the double sum (6.60). Breaking up a pair also changes the kinetic energy: for the Cooper pair this was $2\xi_{\mathbf{k}}|v_{\mathbf{k}}|^2$, for the broken Cooper pair we just have the kinetic energy of the single electron, or $\xi_{\mathbf{k}}$. Hence, the energy difference between the state with one broken Cooper pair versus the ground state (with no broken pairs) is

$$E_{\text{BP}}(\mathbf{k}) - E_{\text{BCS}} = \xi_{\mathbf{k}} - 2\xi_{\mathbf{k}}|v_{\mathbf{k}}|^2 - 2\Delta^* u_{\mathbf{k}} v_{\mathbf{k}} \quad (6.62)$$

$$= \xi_{\mathbf{k}}[1 - 2\sin^2(\theta_{\mathbf{k}}/2)] - 2\Delta^* \sin(\theta_{\mathbf{k}}/2) \cos(\theta_{\mathbf{k}}/2) \quad (6.63)$$

$$= \xi_{\mathbf{k}} \cos(\theta_{\mathbf{k}}) - \Delta^* \sin(\theta_{\mathbf{k}}). \quad (6.64)$$

Here E_{BP} stands for the energy of the state with one broken pair. Substituting our results for the sine and cosine we find

$$E_{\text{BP}}(\mathbf{k}) - E_{\text{BCS}} = \sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2}. \quad (6.65)$$

This shows that the energy required to make an excitation with wave number \mathbf{k} equals $\sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2}$. This is the energy for an elementary excitation of the superconducting system, namely the breaking up of a Cooper pair.

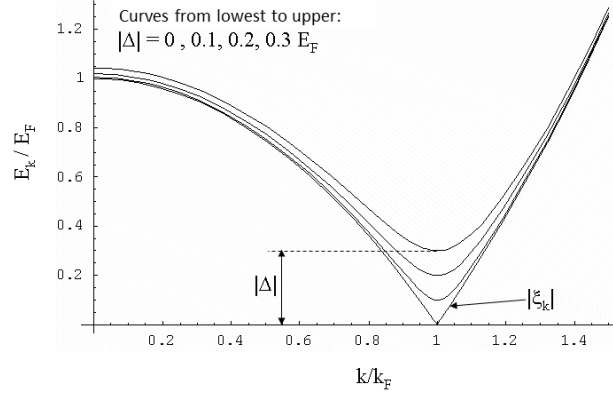
Summarizing: the operators $\hat{\alpha}_{\mathbf{k},\uparrow}^+$ create excited states with dispersion relation $\sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2}$. These excitations are broken Cooper pairs, and can be treated as fermionic quasiparticles since the $\hat{\alpha}_{\mathbf{k},\uparrow}^+$ satisfy fermionic commutation relations. This means that when we raise the temperature a little to T (still smaller than T_c) we make a gas of broken Cooper pairs where the number of broken pairs with wave number \mathbf{k} is given by the Fermi-Dirac distribution:

$$\langle \hat{\alpha}_{\mathbf{k},\uparrow}^+ \hat{\alpha}_{\mathbf{k},\uparrow} \rangle = f_{\mathbf{k}} = \frac{1}{\exp \left\{ -\sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2} / (k_B T) \right\} + 1}. \quad (6.66)$$

6.5.2 Density of states and resistivity

In stead of the original dispersion relation $\xi_{\mathbf{k}}$ we now have identified $\epsilon_{\mathbf{k}} = \sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2}$ as the energy of the excited states. The original dispersion relation was $\xi_{\mathbf{k}} = (\hbar k)^2 / 2m - \mu$. As we measure the energy from the Fermi level, the bottom of the band ($\mathbf{k} = 0$) has energy $-\mu = -E_F$. When $|\Delta| \rightarrow 0$, or for \mathbf{k} values such that $|\Delta| \ll |\xi_{\mathbf{k}}|$ the excitation energy $\epsilon_{\mathbf{k}} \rightarrow \sqrt{\xi_{\mathbf{k}}^2} = |\xi_{\mathbf{k}}|$. This is the non-interacting case, with elementary excitations being electrons for

$k > k_F$ and holes for $k < k_F$. Close to the Fermi surface ($k \approx k_F$, $\xi_{\mathbf{k}} \approx 0$) the effect of a non-zero $|\Delta|$ is clear: it opens a gap. The smallest energy excitation that we can make is to break up a Cooper pair precisely at the Fermi surface, and this costs energy $|\Delta|$. In the figure below, the new dispersion relation is shown. We used values of $|\Delta|/E_F$ that are unrealistically high to make the effect of the gap visible.



Bogoliubov energy of the excitations (broken Cooper pairs) as a function of \mathbf{k} .

These new excited states are still labeled by the wave vector and still have the same density of states in \mathbf{k} -space (namely 1 state per $(2\pi)^2/V$ of reciprocal space volume). However, the density of states in energy space is going to be different due to the different link between \mathbf{k} and the energy. We can use the fact that the density of states in \mathbf{k} -space is the same to link the normal density of states ($\approx N(0)$ near the Fermi level) to the superconducting density of states $N'(\epsilon)$:

$$N(\epsilon)d\epsilon = N(0)d\xi \Rightarrow N(\epsilon) = N(0)\frac{d\xi}{d\epsilon}$$

Since $\epsilon(\mathbf{k}) = \sqrt{\Delta^2 + \xi_{\mathbf{k}}^2}$, we find

$$N(\epsilon) = \begin{cases} 0 & \text{for } |\epsilon| < \Delta \\ \frac{N(0)\epsilon}{\sqrt{\epsilon^2 - \Delta^2}} & \text{for } |\epsilon| > \Delta \end{cases}.$$

The dispersion has a minimum (and hence a zero derivative), leading to Van Hove singularities at $|\epsilon| = |\Delta|$. There is an energy gap: for energies $\in [-|\Delta|, |\Delta|]$. The density of states in energy is shown in the figure on the next page, where we zoom in on the region close to E_F (still keeping Δ large so as to make the effects clearly visible at this scale).

Figure (6.1) shows results for the normal state (left two graphs) and the superconducting state (right two graphs). Both the energy dispersion (left panels of both cases) and the density of states (right panels of both cases)

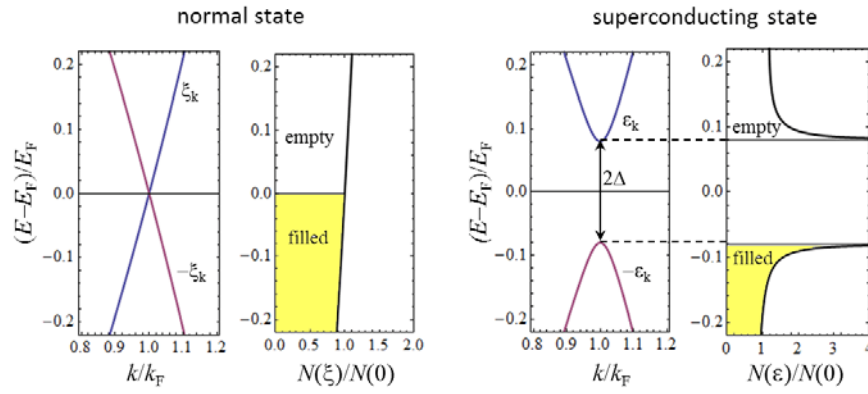


Figure 6.1: Energy spectrum and density of states close to the Fermi energy, in the normal and superconducting state.

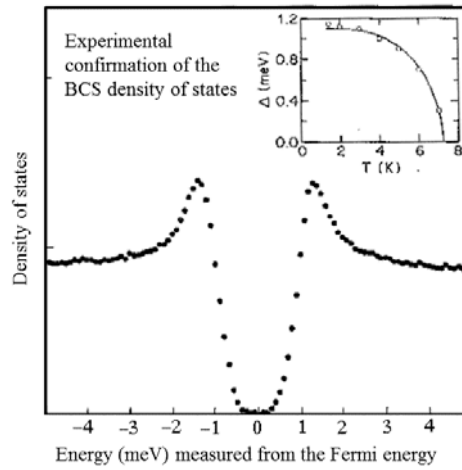


Figure 6.2: The theoretically predicted DOS was confirmed in scanning tunneling microscopy experiments.

are shown. In the density of states, levels are occupied up to the Fermi level, which is indicated by a filling. In order to make an excitation, a transition from an occupied to an unoccupied state has to be made. In the normal state, you only need a vanishingly small energy to make this transition, whereas you need the spectroscopic gap $2|\Delta|$ in the superconducting state. So, the gap measured in the microwave experiments (the first clue) is $2|\Delta|$. The density of states can be measured using a scanning tunneling microscope, since the tunneling current is proportional to the density of states. These measurements have been performed, and agree magnificently well with the BCS theory – one of the first experimental results is reproduced in figure (6.2). The rounding of the Van Hove singularity is due to limited experimental energy resolution – more recent experiments have sharpened up these peaks.

Another consequence of the presence of the gap, is that it is not possible to transfer an infinitesimal amount of energy to the superconductor. In a normal metal, an electric current can decay – the conducting electrons in the current scatter and transfer small amounts of energy to the material. However, the only way now to transfer energy to the system by breaking up Cooper pairs. This costs a finite amount of energy and as long as the current is below the critical current, this will not happen. This is the origin of the flow without dissipation, hence without resistance. Another way to formulate this is that all the Cooper pairs are in the $\mathbf{k} + (-\mathbf{k}) = 0$ momentum state, and form a Bose-Einstein condensate in this state. This corresponds to our second clue, and since Bose-Einstein condensates are superfluid, a Bose-Einstein condensate of charged Cooper pairs will be superconducting.

Furthermore, we can use the density of states to estimate the total lowering in energy that we have between the superconducting and normal states. Indeed, the filled states are lowered in energy! In the normal states, we have filled states from $-\Delta$ up to 0. The number of electrons in these states are $N(0) \times \Delta$. These are now brought down to make the Van Hove peak, so they are lowered by an average energy of $\Delta/2$. From this we estimate the energy difference between the superconductor and the normal state to be $N(0)\Delta^2/2$ in favour of the superconductor. This result, from a reasoning with density of states, agrees with our previous calculation (6.58).

Finally, note the difference in scales: E_F , being 10 eV, is huge with respect to the Debye window $\hbar\omega_D$ of 10-100 meV, which in turn is large in comparison to the band gap Δ of typically 0.1-1 meV.

6.6 Critical temperature

We have seen that at temperature zero, the BCS state is the ground state of the Hamiltonian $\hat{H}^{(\text{BCS})}$. What happens at non-zero temperature? We can look again at the scanning tunneling microscopy experiments and see (cf. the inset of figure (6.2)) that the gap closes down, and becomes zero at the critical temperature. Above the critical temperature, the material is in the normal state, with non-zero resistivity. We have also seen that excited states are created by

letting the operators $\hat{\alpha}_{\mathbf{k},\sigma}^\dagger$ act on the BCS state, and that these have an energy $\sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2}$. To find out what happens at finite temperature, we use the fact that the occupation of the excited states is given by the Fermi-Dirac distribution, as in (6.66) :

$$\langle \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \hat{\alpha}_{\mathbf{k},\sigma} \rangle = f_{\mathbf{k}} = \frac{1}{\exp \left\{ -\sqrt{|\Delta|^2 + \xi_{\mathbf{k}}^2} / (k_B T) \right\} + 1}, \quad (6.67)$$

$$\langle \hat{\alpha}_{\mathbf{k},\sigma} \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \rangle = 1 - f_{\mathbf{k}}. \quad (6.68)$$

As the temperature goes to zero, we find $\langle \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \hat{\alpha}_{\mathbf{k},\sigma} \rangle = 0$ and $\langle \hat{\alpha}_{\mathbf{k},\sigma} \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \rangle = 1$ just like before. Now we can use these finite-temperature quantum-statistical expectation values to calculate the free energy at any temperature $T \leq T_c$. The free energy is given by $E - TS$ with $E = \langle H_{\text{BCS}} \rangle$ and the entropy given by Shannon's rule

$$S = -k_B \sum_{\mathbf{k},\sigma} [f_{\mathbf{k}} \log(f_{\mathbf{k}}) + (1 - f_{\mathbf{k}}) \log(1 - f_{\mathbf{k}})] \quad (6.69)$$

As an example of the calculations, we evaluate the kinetic energy (expression (6.28)) for non-zero temperatures:

$$\begin{aligned} E_{\text{kin}} &= \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} \left\langle \left(u_{\mathbf{k}}^* \hat{\alpha}_{\mathbf{k},\sigma}^\dagger + \sigma v_{\mathbf{k}}^* \hat{\alpha}_{-\mathbf{k},-\sigma} \right) \right. \\ &\quad \left. \times \left(u_{\mathbf{k}} \hat{\alpha}_{\mathbf{k},\sigma} + \sigma v_{\mathbf{k}} \hat{\alpha}_{-\mathbf{k},-\sigma}^\dagger \right) \right\rangle. \\ &= \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} \left(|u_{\mathbf{k}}|^2 \langle \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \hat{\alpha}_{\mathbf{k},\sigma} \rangle + |v_{\mathbf{k}}|^2 \langle \hat{\alpha}_{\mathbf{k},\sigma} \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \rangle \right) \end{aligned} \quad (6.70)$$

$$= \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} \left[|u_{\mathbf{k}}|^2 f_{\mathbf{k}} + |v_{\mathbf{k}}|^2 (1 - f_{\mathbf{k}}) \right] \quad (6.71)$$

$$= 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left[f_{\mathbf{k}} + (1 - 2f_{\mathbf{k}}) |v_{\mathbf{k}}|^2 \right] \quad (6.72)$$

Note that we use $\langle \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \hat{\alpha}_{\mathbf{k},\sigma}^\dagger \rangle = 0 = \langle \hat{\alpha}_{\mathbf{k},\sigma} \hat{\alpha}_{\mathbf{k},\sigma} \rangle$: there are anomalous averages in the electron creation and annihilation operators, but not for the Bogoliubov excitations – we do not have superpositions of different numbers of broken Cooper pairs in our theory. For the details of the complete calculation I refer to for example the book ‘Superfluidity and Superconductivity’ of D. R. Tilley and J. Tilley (IOP Publishing Ltd., Bristol, UK, 1994), pp. 131-134. In order to find the optimal values of the parameters $v_{\mathbf{k}}$ in the case of non-zero temperatures, the free energy is minimized with respect to these parameters, from which we again obtain a gap equation. This gap equation is a generalization of our temperature

zero result (6.45) and is now given by

$$\tilde{V} \sum_{\mathbf{k}' \in D} \frac{1}{2\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}} \tanh \left(\frac{\sqrt{|\Delta|^2 + (\xi_{\mathbf{k}})^2}}{2k_B T} \right) = 1. \quad (6.73)$$

It can be used to compute $\Delta(T)$, the gap as a function of temperature. The result (matching with the experimental points) is shown in the inset of figure (6.2). If the temperature becomes equal to the critical temperature T_c then Δ should become zero. Hence, we can find the critical temperature by searching for the temperature at which (6.73) is satisfied for $\Delta = 0$:

$$\tilde{V} \sum_{\mathbf{k}' \in D} \frac{1}{2|\xi_{\mathbf{k}}|} \tanh \left(\frac{|\xi_{\mathbf{k}}|}{2k_B T_c} \right) = 1. \quad (6.74)$$

This is once more calculated by changing the \mathbf{k} -sum in an energy domain integral:

$$N(0)\tilde{V} \int_0^{\hbar\omega_{LO}} d\xi \frac{1}{2|\xi|} \tanh \left(\frac{|\xi|}{2k_B T_c} \right) = 1. \quad (6.75)$$

At weak coupling this simplifies to

$$k_B T_c = 1.14 \hbar\omega_{LO} \exp \left\{ -1 / \left[N(0)\tilde{V} \right] \right\}. \quad (6.76)$$

This result nicely fits the fourth clue, the isotope effect. The critical temperature is proportional to the phonon frequency ω_{LO} (or in general the Debye frequency of the phonons), which in turn is proportional to $1/\sqrt{M}$ with M the mass of the atoms in the crystal lattice. The expression (6.76) for T_c contains the same exponential with the same essential singularity as the result for the temperature-zero band gap (6.48). From this we find that the ratio of the temperature-zero band gap to the critical temperature is a constant, and given by

$$\frac{2\Delta}{k_B T_c} = 3.52. \quad (6.77)$$

Even though the BCS model represents a strongly distilled version of the interaction between the electrons, and as such should be expected to be a quite crude approximation, this ratio corresponds well to what is measured for most BCS superconductors:

Superconductor	$2\Delta/(k_B T_c)$
Aluminium	3.37 ± 0.1
Cadmium	3.20 ± 0.1
Mercury	4.60 ± 0.1
Indium	3.63 ± 0.1
Niobium	3.83 ± 0.06
Lead	4.29 ± 0.04
Tin	3.46 ± 0.1

We can also use expression (6.77) to rewrite the lowering of the energy achieved at temperature zero by becoming superconducting, as a function of the critical temperature:

$$E_{\text{BCS}} - E_{\text{N}} = -1.55N(0) \times (k_B T_c)^2. \quad (6.78)$$

6.7 Critical magnetic field

The simple BCS model is a big success! It fits all the experimental data and has only one fitting parameter. It explains the lack of resistance, has a gap linked to the critical temperature, a Bose condensate of Cooper pairs (so that flux is quantized using 2 electron charges and we get the correct specific heat), and fits the isotope effect. The last thing we want it to explain is of course the Meissner effect. Cooper pairs don't like magnetic fields.

There is of course the fact that spins like to align with the magnetic field and Cooper pairs contain two electrons with opposite spin. For that 'wrongly' spinning electron we have to subtract the Zeemann energy cost from the binding energy of the pair. If the spin of one of the electrons were forced flip, the glue might become too weak. But it turns out that this effect is rather weak, the Zeeman cost is not the main reason why magnetic fields break up the Cooper pairs. A larger effect is due to the orbital angular momentum of the pair. The electrons have momentum $\hbar\mathbf{k}$ and $-\hbar\mathbf{k}$, and in a magnetic field they experience oppositely directed Lorentz forces $e(\hbar\mathbf{k}/m) \times \mathbf{B}$ and $-e(\hbar\mathbf{k}/m) \times \mathbf{B}$ that pull the two electrons of the Cooper pair apart.

This is why type-I materials have only two options available to them: either they are superconducting but have to expel the magnetic field, or they let the magnetic field in and become normal. The critical magnetic field occurs when the gain in energy from becoming superconducting becomes exactly equal to the cost in energy to expel the magnetic field.

We know what the gain in energy is, due to making Cooper pairs:

$$\Delta E_{\text{N-SC}} = \frac{1}{2}N(0)\Delta^2 \quad (6.79)$$

We also know what the cost in electromagnetic energy is to expel a magnetic field \mathbf{H}_c from a volume V of material:

$$\Delta E_{\text{magn}} = \frac{\mu H_c^2}{2}V \quad (6.80)$$

Equating those two results in

$$H_c = \sqrt{\frac{1}{\mu} \frac{N(0)}{V}} \Delta \quad (6.81)$$

Here, $N(0)$ is the density of states at the Fermi energy in the normal state. If we assume a normal state dispersion $(\hbar k)^2 / (2m)$ for the electrons, then this becomes

$$H_c = \sqrt{\frac{1}{\mu} \frac{3n}{2E_F}} \Delta \quad (6.82)$$

with n the density of electrons in the normal state. We can also reformulate this using the relation between $\Delta(T = 0)$ and T_c as

$$H_c(T = 0) = 1.75 \sqrt{\frac{1}{\mu} \frac{3n}{2E_F}} k_B T_c \quad (6.83)$$

Note that when the temperature is nonzero, we have to use equation (6.82) and plug in the value of the gap $\Delta(T)$ that we find from solving the temperature-dependent gap equation, expression (6.73).

Final remarks on superconductivity

The BCS theory is tremendously successful in explaining the strange superconducting properties of many materials, as we have seen. Several other authors, such as Eliashberg, Migdal, de Gennes, Kirchnitz, Usadel, have refined the description by taking into account better expressions for the effective electron-electron interaction amplitude, and for the electron band structure. They show that the remaining differences between the predictions of T_c , H_c , c_V , ... can be corrected for. This result could never have been found using a perturbation series start starts from the unperturbed Fermi sphere ($\tilde{V} = 0$) and calculates successive corrections to that unperturbed result, because of the presence of an essential singularity at $\tilde{V} = 0$. A variational calculation has shown the way. A perturbation calculation could still work if we build a series expansion around another point, $\tilde{V} \neq 0$, but that is much more difficult.

However, since 1987 we know that there is another class of superconducting materials, the so-called ‘high- T_c ’ materials. These turn out to be perovskite materials (ceramics) with charge carries running on copper oxide planes. They are technologically important because the critical temperature is much higher (in stead of a few kelvin, it lies close to 100 K). But they are not understood, and such a high T_c does not seem compatible with standard BCS theory. The point of the matter seems to be that the nature of the glue between the electrons is not yet known. More recently, high temperature superconductivity (of a few tens of kelvin) has been discovered in related materials where now iron arsenic planes play the role of copper oxide planes. No-one had been expecting this, as iron is magnetic and magnetism seems to be antagonistic to superconductivity. It is fair to say that the problem of finding the microscopic mechanism of these high temperature superconductors, and the related goal of finding a room-temperature superconductor, is one of the main unsolved problems in modern solid state physics. You probably have all the basic knowledge to start thinking about it. Have fun solving it.

Afterword and bibliography

In this course we introduced some theoretical techniques of modern solid state physics and applied them to systems of electrons and phonons, to calculate for example dielectric and superconducting properties. Of course, this cannot be an exhaustive review, and we have just skimmed the surface of this very dynamical field of physics. The interested student can look into more detail at some topic in specialized courses such as “superfluidity and superconductivity”, “physics of low dimensional systems”,... or find further information in a number of good textbooks, among which:

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