
Introduction to solid state theory

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Contents

1	The solid as quantum system	5
1.1	The Hamiltonian of a solid	6
1.2	Born-Oppenheimer approximation	8
2	Mathematical background	13
2.1	Elements of many-body theory	14
2.1.1	Indistinguishability and permutations	14
2.1.2	Bosons and fermions	15
2.1.3	Basis vectors of \mathcal{H}_N^+ and \mathcal{H}_N^-	16
2.1.4	Fock space of variable particle number	19
2.1.5	Fock space representation of operators	22
2.2	Statistical description of quantum many-body systems	28
3	The homogeneous electron gas	31
3.1	The noninteracting electron gas	32
3.1.1	Ground state properties	33
3.1.2	Evaluation of \vec{k} -sums – Density of States	35
3.1.3	Excited states of the electron gas	36
3.1.4	Finite temperatures	37
3.1.5	The Fermi gas in a magnetic field	42
3.2	Beyond the independent electron approximation	50
3.2.1	Hartree-Fock approximation	50
3.2.2	Landau’s Fermi liquid theory	54
3.2.3	Beyond Hartree-Fock	67
3.2.4	Density functional theory	67
4	Lattices and crystals	73
4.1	The Bravais lattice	74
4.2	Crystals	76
4.3	Classification of crystal structures	78

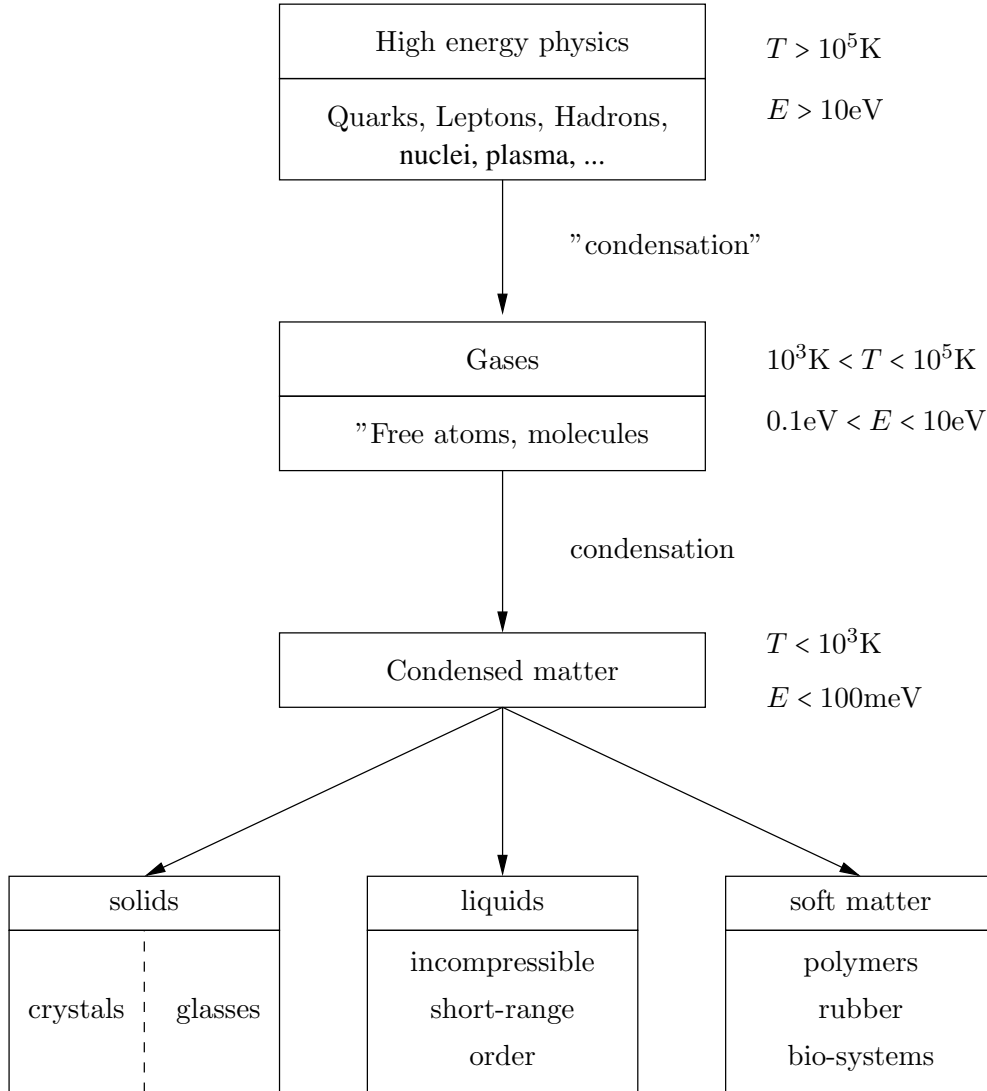
4.4	The reciprocal lattice	79
4.5	Bloch's theorem	82
5	Electrons in a periodic potential	85
5.1	Consequences of Bloch's theorem	86
5.2	Weak periodic potential	91
5.3	Calculating the band structure	96
5.4	Effective mass and electrons and holes	101
6	Lattice dynamics	105
6.1	The harmonic approximation	106
6.2	Ionic motion in solids	106
6.2.1	Repititorium: Normal modes of the 1d Bravais lattice . .	106
6.2.2	Normal modes of a crystal	108
6.3	Quantum theory of the harmonic crystal	112
6.3.1	The Hamilton operator	112
6.3.2	Thermodynamic properties of the crystal	114
6.4	Beyond the harmonic approximation	116
7	Electron Dynamics	119
7.1	Semiclassical approximation	120
7.2	Electrical conductivity in metals	123
7.2.1	Boltzmann equation	124
7.2.2	Boltzmann equation for electrons	125
7.2.3	dc-conductivity	129
7.2.4	Thermal conductivity	131
8	Magnetism	135
8.1	Absence of magnetism in a classical theory	136
8.2	Basics of magnetism	137
8.3	The Heisenberg model	138
8.3.1	Free spins on a lattice	138
8.3.2	Effects of the Coulomb interaction	139
8.3.3	Mean-field solution of the Heisenberg model	141
8.4	Delocalizing the spins	147
8.4.1	The Hubbard model	147
8.4.2	Mean-field solution of the Hubbard model	148
8.4.3	The limit $U \rightarrow \infty$	152

CONTENTS

9 Superconductivity	155
9.1 Phenomenology	156
9.2 The BCS theory	158
9.2.1 The Cooper instability	158
9.2.2 BCS-Theorie	161
9.2.3 The gap function $\Delta_{\vec{k}}$	164
9.2.4 Density of states and tunneling experiments	168
9.2.5 Meißner effect	169
9.3 Origin of attractive interaction	173
10 Theory of scattering from crystals	175
10.1 Experimental setup and dynamical structure factor	176
10.2 Evaluation of $S(\vec{q}, \omega)$ in the harmonic approximation	179
10.3 Bragg scattering and experimental determination phonon branches	182
A Sommerfeld expansion	187
B Hartree-Fock approximation	188
B.1 Hartree-Fock equations for finite temperature	189
B.2 Application to the Jellium model	190

Introductory remarks

Physical systems cover a huge range of energy scales:



The focus of this lecture will be on the lower left corner of this hierarchy, i.e. quite obviously a very small regime given the many orders of magnitude compressed in the scheme. Nevertheless, this small portion contains a fascinating broad facet of phenomena, for example magnets, metals and insulators, superconductors (with the up to now only observed Higgs boson and Higgs mass generation¹) and without it our modern world would be impossible.²

Let us start the excursion into this fascinating world by an attempt of a definition: A solid is a (sometimes) regular compound of a macroscopic number

¹The Higgs mechanism was in fact first proposed by Phil W. Anderson, a famous solid state theoretician, based on the BCS theory of superconductivity.

²Which one might consider as good or bad, depending on ones philosophy.

of atoms ($\sim 10^{23}$), which are strongly interacting. The most important new elements in the physics of solids³ are

- electrical conductivity (metals, insulators, semiconductors)
- mechanical strength (chemical bonding, crystal structure)
- phase transitions (magnetism, superconductivity).

All these effects cannot be observed in individual atoms or molecules, in fact the mere notion of conductivity or phase transitions does not make any sense for those “nanoscopic” systems. Using a modern notion, they are also referred to as *emergent phenomena*.

The aim of this lecture is to investigate the properties of the many-body problem “solid”. A solid is a macroscopic system, but its properties are determined by microscopic length scales (distances between atoms $O(1\text{nm})$) and microscopic time scales (life times of atomic excitations $O(1\text{fs})$). Thus, we have to deal with a quantum mechanical many-body problem. Fortunately, we know – at least in principle – the Hamilton operator, which we write as

$$\begin{aligned} H_0 = & H_N && \text{nuclei} \\ & +H_e && \text{electrons} \\ & +K_{eN} && \text{interaction between nuclei and electrons.} \end{aligned}$$

This funny way of splitting may seem strange at first sight, but we will see later that it is actually quite natural and opens the route to an important approximation, the *Born-Oppenheimer* or *adiabatic* approximation.

Given the Hamiltonian, we of course want to find the solution of Schrödinger’s (eigenvalue) equation

$$H_0|u_n\rangle = E_n|u_n\rangle .$$

Once we know *all* eigenvalues E_n and eigenvectors $|u_n\rangle$, we can calculate the thermodynamic properties of the solid by Boltzmann’s formula.⁴ For the expectation value of an observable \hat{O} , for example, we get

$$\begin{aligned} \langle \hat{O} \rangle &= \frac{1}{\mathcal{Z}} \sum_n \langle u_n | \hat{O} | u_n \rangle e^{-E_n/k_B T} \\ \mathcal{Z} &= \sum_n e^{-E_n/k_B T} . \end{aligned}$$

For the ground state we in particular have the relation

$$E_G = \langle u_G | \hat{H}_0 | u_G \rangle = \underline{\text{absolute}} \text{ minimum.}$$

³Actually: Condensed matter in general.

⁴You will learn the details of this in “Statistical Mechanics” or take a quick look at section 2.2.

The ground state is thus the absolute energetic minimum with respect to

- (i) crystal structure, i.e. the spatial arrangement of the nuclei, and
- (ii) electronic structure, i.e. the distribution of charges and the energetic spectrum of the electrons, the so-called *band-structure*.

Of course these two points are interrelated, in particular the electronic configurations are responsible for chemical bonding and hence the energetics of a crystal structure, which in return defines the bonding properties.

Once we have determined crystal structure and charge density, we may become bold and ask the question how the solid reacts to an external perturbation, for example an electromagnetic field, a temperature gradient, particle beams, sound, ... Apparently, this is what we do in experiments, when we measure properties of solids. Thus, one of the “tasks” of solid state theory is to understand the physical origin of experimentally observed phenomena or in a perfect world even predict such phenomena. A certain complication arises due to the fact, that any such perturbation inevitably introduces a time dependence into the problem (one has to switch it on at some time at minimum), i.e. we will have to deal with a Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_{ext}(t) .$$

This is a true non-equilibrium problem, and even if we knew the solution to \hat{H}_0 a formidable task to solve. Fortunately, a large variety of applications allow to assume $\hat{H}_{ext}(t)$ as “small” (in whatever sense) and treat it in lowest order perturbation theory, which in statistical physics is called *linear response theory*. The prerequisites necessary for this lecture are a solid knowledge of quantum mechanics. Furthermore, we will in the course of the lecture touch some topics from “Quantenmechanik II” and “Statistischer Physik”. As I cannot assume that these things will be provided in time, I will briefly introduce the necessary concepts and tools in the beginning of the lecture. I am pretty sure, that such redundancy will not be considered as boring anyway.

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Chapter 1

The solid as quantum system

1.1 The Hamiltonian of a solid

In solid state physics we are in a lucky position in the sense that we do know the Hamilton operator of our system exactly: A solid consists of a collection of nuclei of charge Ze and the corresponding Z electrons per nucleus, each of charge $-e$, so that charge neutrality is preserved. As solids are stable up to temperatures $T \approx 10^3\text{K}$ only, we need not bother with the question of the internal structure of the nuclei or things like the weak or strong interaction. Consequently, both nuclei and electrons can be treated as point charges which interact via the Coulomb interaction only.

In the following, I will assume that our solid consists of N_N nuclei¹ each having a mass M and a nuclear charge Z . Likewise, there will be $N_e = Z \cdot N_N$ electrons in the system. We will denote the position vector of the i -th electron as \vec{r}_i ($i = 1, \dots, N_e$), and the collection of all those position vectors as $\underline{r} := \{\vec{r}_i\}$. The electron mass we will simply call m . Likewise, the nuclei are located at positions \vec{R}_α ($\alpha = 1, \dots, N_N$), the collection of which we will call $\underline{R} = \{\vec{R}_\alpha\}$.

After these preliminaries, we can write down the operators for the kinetic energies as

$$\begin{aligned}\hat{T}_e &= -\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \vec{\nabla}_i^2 \quad (\text{electrons}) \\ \hat{T}_N &= -\frac{\hbar^2}{2M} \sum_{\alpha=1}^{N_N} \vec{\nabla}_\alpha^2 \quad (\text{nuclei}).\end{aligned}$$

The interaction potentials we denote as $V_{NN}(\vec{R}_\alpha - \vec{R}_\beta)$, $V_{ee}(\vec{r}_i - \vec{r}_j)$ and $V_{eN}(\vec{r}_i - \vec{R}_\beta)$ for nucleus-nucleus, electron-electron and electron-nucleus interactions, respectively. These are explicitly given by the expressions²

$$\begin{aligned}V_{NN}(\vec{R}_\alpha) &= \frac{(Ze)^2}{|\vec{R}_\alpha|} \\ V_{ee}(\vec{r}_i) &= \frac{e^2}{|\vec{r}_i|} \\ V_{eN}(\vec{r}_i - \vec{R}_\beta) &= -\frac{Ze^2}{|\vec{r}_i - \vec{R}_\beta|}.\end{aligned}$$

¹For simplicity we assume a monoatomic solid. Extending the concepts to different types of nuclei is straightforward, but the nomenclature gets somewhat tedious.

²I will use the Gaussian system in this lecture.

Finally, we can write down the total Hamilton operator in the form

$$\begin{aligned}
 \hat{H}_0 &= \hat{H}_e + \hat{H}_N + \hat{H}_{eN} \\
 \hat{H}_e &= -\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \vec{\nabla}_i^2 + \frac{1}{2} \sum_{i \neq j} V_{ee}(\hat{r}_i - \hat{r}_j) \\
 \hat{H}_N &= -\frac{\hbar^2}{2M} \sum_{\alpha=1}^{N_N} \vec{\nabla}_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \beta} V_{NN}(\hat{R}_\alpha - \hat{R}_\beta) \\
 \hat{H}_{eN} &= \sum_{\alpha, i} V_{eN}(\hat{r}_i - \hat{R}_\alpha) .
 \end{aligned}$$

Note that this formulation does not include spin-dependent potentials like spin-orbit coupling, as these derive from a relativistic theory of the solid. If necessary, approximate expressions valid in the limit $v/c \ll 1$ can be added.

Up to now we did not take into account the fact that for solids the nuclei cannot move freely but are restricted in their movement to the vicinity of certain fixed positions. We thus assume that for our nuclei there exist distinguished positions $\vec{R}_\alpha^{(0)}$, we will call equilibrium positions of the nuclei. As our solid does not melt, it is safe to assume further that the nuclei perform only small oscillations about these equilibrium positions. Note that this is true even for $T = 0$, as quantum mechanics dictates that the more localized an object is the larger is its uncertainty in kinetic energy. Thus all nuclei will perform *zero-point motion* at $T = 0$. You should know this phenomenon from the quantum-mechanical harmonic oscillator, where the ground state energy is $\hbar\omega/2$. This is not a trivial effect: e.g. for ${}^4\text{He}$ it means that you can solidify this substance only under very high pressure.

With these observations and definitions we can rewrite the Hamiltonian further as

$$\hat{H}_0 = E_N^{(0)} + \hat{H}_{ph} + \hat{H}_e + \hat{V}_{eN}^{(0)} + \hat{H}_{e-ph} . \quad (1.1)$$

The different parts have the following meaning:

1. $E_N^{(0)}$ describes the energy of the *static* nuclei in their equilibrium positions. This part encodes the crystal lattice we will introduce in chapter 4 and is responsible for electrical neutrality.
2. $\hat{V}_{eN}^{(0)}$ is the interaction potential between the electrons and the nuclei located at their equilibrium positions. Note that this is a pure potential term for the electrons, but it has a profound effect on the properties of the electrons.
3. $\hat{H}_{ph} := \hat{H}_N - E_N^{(0)}$ describes the displacement of the nuclei from their equilibrium positions. This part will be responsible for the lattice vibrations or *phonons* we will consider in chapter 6.

4. $\hat{H}_{e-ph} := \hat{H}_{eN} - \hat{V}_{eN}^{(0)}$ finally collects all effects that are due to coupling of electron and nuclei dynamics.

The reason for this funny rearrangement of terms lies in the fact that the Hamiltonian in the form (1.1) allows to motivate and introduce approximations that make the otherwise unsolvable problem “solid” at least treatable to some extent. Even with the most powerful modern computer resources (for example the world top one: Blue Gene/Q at Lawrence Livermore National Laboratory, 100000 nodes with 18 cores each and overall 1.6PB memory, approximately 20 PFLOP/s peak performance) the attempt to solve the full problem \hat{H}_0 would restrict N_N to something of the order 5 (assuming that only one electron per nucleus is taken into account) to obtain all states or 10 if only the ground state is sought for. To give you a flavor what that means, note that a cluster of say 50 Iron atoms does not behave even slightest like a solid. Only when you come to clusters of the order of several 1000 atoms, the physics starts to resemble this of a solid.

Thus we need approximations. However, these approximations must be such that they are based on systematic and well-founded dismissal of individual terms in \hat{H}_0 .

1.2 Born-Oppenheimer approximation

The by far most important and most commonly used approximation is the so-called *adiabatic approximation* or *Born-Oppenheimer approximation*. It is based on the insight that due to $m \ll M = O(10^4)m$ the electrons move much faster than the nuclei.

If we idealise to infinitely heavy nuclei, the nuclei would indeed be static and the electrons at each time see a momentaneous (and here indeed static) arrangement of nuclei. From a quantum mechanical point of view, the wave function would be a simple product

$$|\Psi\rangle = |\phi_e(\underline{R}^{(0)})\rangle|\chi\rangle .$$

Here, $|\chi\rangle$ is an unimportant wave function describing the static nuclei, and $|\phi_e(\underline{R})\rangle$ contains the dynamics of the electrons at positions \underline{r} , parametrized by the c-numbers \underline{R} , i.e. the momentarily positions of the nuclei.

For a solid with $m \ll M$ we may now try the ansatz

$$|\Psi\rangle \approx |\phi_e(\underline{R})\rangle|\chi\rangle$$

which is called *adiabatic* or *Born-Oppenheimer* approximation. Note that the nuclei can actually perform motions, but these are assumed to be so slow, that

the electrons “instantaneously” adjust to the new nuclei positions. In that sense the electrons move in a “static” environment, while the nuclei move in an “effective” electronic background.

Let us try to give a somewhat more mathematical argument for the adiabatic approximation, which will also tell us when it actually may be valid. To this end we will rescale all quantities in the Hamiltonian by atomic scales, i.e. a_B for the length and $E_R = \hbar^2/ma_B^2$ for the energy. Further we define the ratio $\kappa^4 := m/M$. The quantities appearing in the Hamiltonian then take the form

$$\tilde{r}_i := \frac{\hat{r}_i}{a_B}, \quad \tilde{R}_\alpha := \frac{\hat{R}_\alpha}{a_B}, \quad \tilde{\nabla} := a_B \vec{\nabla}, \quad \tilde{H}_0 = \frac{\hat{H}_0}{E_R}$$

and the Hamiltonian becomes

$$\tilde{H}_0 = \underbrace{-\frac{1}{2}\kappa^4 \sum_\alpha \tilde{\nabla}_\alpha^2}_{=: \tilde{T}_N} - \underbrace{\frac{1}{2} \sum_i \tilde{\nabla}_i^2}_{=: \tilde{T}_e} + \tilde{V}_{ee} + \tilde{V}_{NN} + \tilde{V}_{eN} .$$

As the solid is stable, we may assume small harmonic motions of the nuclei, the frequency of which will be $\omega \propto \sqrt{M}^{-1}$. From the theory of the harmonic oscillator we on the other hand know that typical displacements about the equilibrium position are of the order $\sqrt{\omega} \propto \sqrt[4]{M}^{-1}$. This means that $\tilde{R}_\alpha - \tilde{R}_\alpha^{(0)} = O(\kappa)$ and hence $\tilde{\nabla}_\alpha = O(\kappa^{-1})$. Putting these estimates together, we may deduce that $\tilde{T}_N = O(\kappa^2) \ll 1$, while all the other terms are $O(1)$. Hence the ionic motion can be viewed as small perturbation to the system consisting of static ions and mobile electrons.

Note that we started with the assumption that the small parameter is the ratio m/M , which is $O(10^{-4})$ for typical atoms like iron. However, it is actually only the square root of this ratio that governs the validity of the Born-Oppenheimer approximation. Thus, if for example the mass m of the charge carriers increases by a factor 100, we are suddenly faced with a completely different situation. This may seem to be an academic discussion to you, but we will learn in chapter 3 that due to electron-electron interactions such a situation may indeed arise effectively.

Let us discuss some qualitative consequences of the Born-Oppenheimer approximation. We start with the nuclei sitting at fixed positions \underline{R} (not necessarily the equilibrium positions) and assume that we solved the Schrödinger equation

$$(\hat{H}_e + \hat{H}_{eN}) |\phi_e(\underline{R})\rangle = E_e(\underline{R}) |\phi_e(\underline{R})\rangle \quad (1.2)$$

for the electrons. The quantity $E(\underline{R})$ is the energy of the electron system depending *parametrically* on the positions of the nuclei. Now let us apply the

Born-Oppenheimer approximation $|\Psi\rangle = |\phi_e(\underline{R})\rangle|\chi\rangle + O(\kappa^2)$ to the eigenvalue problem of the full Hamiltonian, yielding

$$\begin{aligned} \hat{H}_0|\Psi\rangle &= |\chi\rangle(\hat{H}_e + \hat{H}_{eN})|\phi_e\rangle + |\phi_e\rangle\hat{H}_{NN}|\chi\rangle + O(\kappa^2) \\ &= |\phi_e\rangle(\hat{H}_{NN} + E_e(\underline{R}))|\chi\rangle = E_{\text{tot}}|\Psi\rangle . \end{aligned} \tag{1.3}$$

We may now multiply this equation from the left by $\langle\phi_e|$ and obtain

$$\langle\phi_e|\hat{H}_0|\phi_e\rangle|\chi\rangle = (\hat{T}_N + V_{NN}(\underline{R}) + E_e(\underline{R}))|\chi\rangle + O(\kappa^2) = E_{\text{tot}}|\chi\rangle .$$

as effective Schrödinger equation for the nuclei. Thus, under the adiabatic approximation the nuclei “see” an effective potential

$$V_{NN}^{\text{eff}}(\underline{R}) := V_{NN}(\underline{R}) + E_e(\underline{R})$$

due to the presence of the electrons.

Up to now we have considered atoms completely stripped off their electrons with charge eZ and the corresponding Z electrons. However, most of these electrons are rather tightly bound to the nucleus with energies $O(10\text{eV})$ or even much larger. Instead of treating these electrons exactly, one can use an extended adiabatic principle: We divide the electrons in those *core electrons* that form closed electronic shells tightly bound to the nucleus, yielding the *ion*, and the *valence electrons*. We thus reduce the number of particles to treat considerably. How good is that approximation? To see this, note that the core electrons are very strongly localized at the position of the ion. By Heisenberg’s uncertainty principle the fluctuations $\langle\hat{p}^2\rangle$ of the momentum and hence the kinetic energy will be large, and by the same reasoning as for the original adiabatic approximation one can deduce a hierarchy of velocities

$$v_{\text{core}} \gg v_{\text{valence}} \gg v_{\text{ion}} ,$$

which tells us that the valence electrons “see” an average potential originating from the system consisting of the nuclei plus the core electrons, while the ions “see” an effective potential due to the (now also) effective potential between the ions and the contribution from the valence electrons. At this point we very much start to depart from our “exactly known” Hamiltonian. The potential produced by the nuclei plus core electrons is anything but a pure Coulomb potential, neither for the valence electrons nor for the ion-ion interaction.³ To determine these effective potentials is a formidable task, and quite often they are treated in an approximate way introducing new parameters to the theory.

³The latter may though be dominated by the Coulomb part, however modified by a “dielectric constant” due to the polarizability of the ion.

Moreover, while the separation of energy scales between electrons and nuclei is rather well founded, the distinction between core and valence electrons often is not that straightforward, in particular when electrons from the d - or f -shells are involved. Depending on the compound and chemical environment, these may be counted to the core or must be added to the valence states. These materials are a major research area of modern solid state physics.

1.2. BORN-OPPENHEIMER APPROXIMATION

Chapter 2

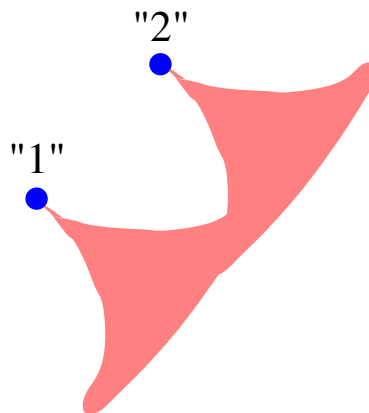
Mathematical background

2.1 Elements of many-body theory

2.1.1 Indistinguishability and permutations

In classical physics we are able to at least in principle identify particles uniquely by their trajectory. Thus we can attach a label or number to each particle, even if they are identical. One of the major concepts of quantum mechanics is that the mere notion of “particle” and “trajectory” becomes meaningless.

A pictorial representation of this property is given in the figure to the right. The objects “1” and “2” represent some quantum mechanical entities, for example electrons, which start at different places with different initial velocities. However, due to the quantum mechanical nature these trajectories will be “smeared out” in course of time and eventually their probability distributions will start to overlap. Once this happens it does not make sense to talk of object “1” being at position \vec{r}_1 and “2” being at position \vec{r}_2 any more: The otherwise *identical particle* are from a physical point of view *indistinguishable*.



Obviously, experiments must give the same result independently of the way we number our particles, i.e. the result cannot change when we *exchange* the particles. In mathematical terms, the physical properties like probabilities and expectation values must be invariant under any *permutation* of the quantum numbers of identical particles. In the following I assume that you are familiar with permutations, in particular the meaning of *even* and *odd* permutations. The permutations of the set $\{1, 2, \dots, n\}$ form a group denoted as \mathcal{S}_n with $n!$ elements. With χ_ρ for $\rho \in \mathcal{S}_n$ we denote the number of transpositions necessary to construct the permutation ρ , in particular χ_ρ is even (odd) for even (odd) permutations

After these preliminaries let us start to discuss the structure of the Hilbert space of a system of N identical particles.¹ As we discussed before, the physical properties must be invariant under permutations of the particles, or in mathematical terms

$$[\hat{L}, \hat{P}_\rho] = 0$$

for any *observable* \hat{L} of the N particle system and all permutations $\rho \in \mathcal{S}_N$. The object \hat{P}_ρ is the linear operator associated with the permutation ρ .

¹Instead of the neutral word “objects” I will use “particles” henceforth.

Group theory now tells us that the Hilbert space of the N particle system can be decomposed as $\mathcal{H}_N = \mathcal{H}_N^+ \oplus \mathcal{H}_N^- \oplus \mathcal{H}_N^Q$, where \mathcal{H}_N^\pm denotes the Hilbert spaces belonging to the states even (+) respectively odd (-) under particle exchange, and \mathcal{H}_N^Q collects the rest. Each of these subspaces induce so-called *representations* of the group \mathcal{S}_n as (unitary) matrices. Obviously, in \mathcal{H}_N^\pm the permutation operators simply act as $\hat{P}_\rho = \pm 1$. An important property of the permutation group now is that in \mathcal{H}_N^Q the \hat{P}_ρ are at least 2×2 matrices, i.e. there are no further *one-dimensional representations*.

In the following we will also frequently need the operators

$$\hat{S} := \frac{1}{N!} \sum_{\rho \in \mathcal{S}_N} \hat{P}_\rho \quad (2.1a)$$

$$\hat{A} := \frac{1}{N!} \sum_{\rho \in \mathcal{S}_N} (-1)^{\chi_\rho} \hat{P}_\rho \quad (2.1b)$$

$$\hat{Q} := \hat{1} - \hat{S} - \hat{A} ,$$

which project onto \mathcal{H}_N^+ , \mathcal{H}_N^- and \mathcal{H}_N^Q , respectively. Some properties of these operators are (proofs left as exercises)

$$\hat{P}_\alpha \hat{S} = \hat{S} \text{ for all } \alpha \in S_N \quad (2.2a)$$

$$\hat{P}_\alpha \hat{A} = (-1)^{\chi_\alpha} \hat{A} \text{ for all } \alpha \in S_N \quad (2.2b)$$

$$\hat{S}^\dagger = \hat{S} \quad (2.2c)$$

$$\hat{A}^\dagger = \hat{A} \quad (2.2d)$$

$$\hat{S}^2 = \hat{S} \quad (2.2e)$$

$$\hat{A}^2 = \hat{A} \quad (2.2f)$$

$$\hat{S} \hat{A} = \hat{A} \hat{S} = 0$$

$$\hat{S} \hat{Q} = \hat{A} \hat{Q} = 0 .$$

With these operators we can represent $\mathcal{H}_N^+ = \hat{S} \mathcal{H}_N$, $\mathcal{H}_N^- = \hat{A} \mathcal{H}_N$ and $\mathcal{H}_N^Q = \hat{Q} \mathcal{H}_N$.

2.1.2 Bosons and fermions

Let us first consider the space \mathcal{H}_N^Q . Group theory² provides us with *Schur's lemma* which states that any operator which commutes with all representation operators of a group different from the identity operator must be proportional to the identity. As in general not all \hat{L} are proportional to the identity, the requirement that $[\hat{L}, \hat{P}_\rho] = 0$ for arbitrary observables \hat{L} and all \hat{P}_ρ leads to a contradiction. In other words, the space \mathcal{H}_N^Q cannot appear in physical systems.

²Indeed a very resourceful mathematical toolbox for physicists. There are very nice books about it, for example by Tinkham or Falter & Ludwig.

Let now $|\varphi^\pm\rangle$ be a state in \mathcal{H}_N^\pm . As $[\hat{L}, \hat{P}_\rho] = 0$ for *all* observables \hat{L} and *all* permutations $\rho \in \mathcal{S}_N$, we must have

$$\begin{aligned} \langle \varphi^- | \hat{L} | \varphi^+ \rangle &= \langle \hat{A} \varphi^- | \hat{L} | \hat{S} \varphi^+ \rangle = \langle \varphi^- | \underbrace{\hat{A} \hat{L} \hat{S}}_{\hat{L} \hat{A} \hat{S}} | \varphi^+ \rangle = \langle \varphi^- | \underbrace{\hat{L} \hat{A} \hat{S}}_{= 0} | \varphi^+ \rangle = 0 . \end{aligned}$$

It therefore does not exist any observable that maps states from \mathcal{H}_N^+ into \mathcal{H}_N^- and vice versa. The physically allowed states of an N particle system³ belong all to either \mathcal{H}_N^+ or \mathcal{H}_N^- , with no possible transitions between them.

The previous statements in particular hold for the Hamiltonian \hat{H} and thus also for the time evolution operator $\hat{U}(t, t_0)$, i.e.

$$\begin{aligned} |\varphi^+(t)\rangle &= \hat{U}(t, t_0) |\varphi^+(t_0)\rangle \in \mathcal{H}_N^+ \\ |\varphi^-(t)\rangle &= \hat{U}(t, t_0) |\varphi^-(t_0)\rangle \in \mathcal{H}_N^- \end{aligned}$$

for all times t .

The description of a physical system of N identical particles must happen *completely* in either \mathcal{H}_N^+ or \mathcal{H}_N^- . Particles, which are described by states from \mathcal{H}_N^+ are called *bosons*, those described by states from \mathcal{H}_N^- are called *fermions*.

In 1940, Pauli formulated the spin-statistic theorem

Bosons are all particles with integer spin $S = 0, 1, 2, \dots$, fermions are all particles with half-integer spin $S = \frac{1}{2}, \frac{3}{2}, \dots$

2.1.3 Basis vectors of \mathcal{H}_N^+ and \mathcal{H}_N^-

In order to be able to do calculations in the representation spaces \mathcal{H}_N^\pm we need a basis for each of these spaces. We start again with the canonical basis of the product space \mathcal{H}_N , which consists of the product states

$$|v_{k_1}^{(1)} v_{k_2}^{(2)} \dots v_{k_N}^{(N)}\rangle := |v_{k_1}^{(1)}\rangle |v_{k_2}^{(2)}\rangle \dots |v_{k_N}^{(N)}\rangle .$$

The index k_j contains *all* relevant quantum numbers, for example for electrons in an atom n, l, m_l, s, m_s . The states are ortho-normal,

$$\langle v_{k_1}^{(1)} v_{k_2}^{(2)} \dots v_{k_N}^{(N)} | v_{l_1}^{(1)} v_{l_2}^{(2)} \dots v_{l_N}^{(N)} \rangle = \delta(k_1, l_1) \dots \delta(k_N, l_N) ,$$

³Please remember: We here talk about identical particles. For a proton and an electron in an H atom for example, these concepts do not apply!

if the individual factors are, and by construction they represent a partition of unity

$$\sum_{\{k_i\}} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)}| = \hat{1}$$

in \mathcal{H}_N . The claim now is that the states

$$|v_{k_1 k_2 \dots k_N}^\pm\rangle := \frac{1}{\sqrt{N!}} \sum_{\rho \in \mathcal{S}_N} (\pm 1)^{X_\rho} \hat{P}_\rho |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle = \sqrt{N!} \left\{ \begin{matrix} \hat{S} \\ \hat{A} \end{matrix} \right\} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle$$

constitute a basis of \mathcal{H}_N^\pm . The proof goes as follows:

We start with the observation that with the relations (2.2c)-(2.2f)

$$\begin{aligned} \langle v_{m_1 \dots m_N}^\pm | v_{k_1 \dots k_N}^\pm \rangle &= N! \left\langle \left\{ \begin{matrix} \hat{S} \\ \hat{A} \end{matrix} \right\} v_{k_1}^{(1)} \dots v_{k_N}^{(N)} \middle| \left\{ \begin{matrix} \hat{S} \\ \hat{A} \end{matrix} \right\} v_{m_1}^{(1)} \dots v_{m_N}^{(N)} \right\rangle \\ &= N! \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \left\{ \begin{matrix} \hat{S} \\ \hat{A} \end{matrix} \right\} v_{m_1}^{(1)} \dots v_{m_N}^{(N)} \rangle \\ &= \sum_{\rho \in \mathcal{S}_N} (\pm 1)^{X_\rho} \langle v_{m_1}^{(1)} \dots v_{m_N}^{(N)} | \hat{P}_\rho | v_{k_1}^{(1)} \dots v_{k_N}^{(N)} \rangle \\ &= \sum_{\rho \in \mathcal{S}_N} (\pm 1)^{X_\rho} \prod_{l=1}^N \delta(m_l, k_{\rho(l)}) \end{aligned}$$

There now exist two possibilities. Either, the sets $\{m_l\}$ and $\{k_l\}$ cannot be mapped onto each other by a permutation $\rho \in \mathcal{S}_N$. In this case

$$\langle v_{m_1 \dots m_N}^\pm | v_{k_1 \dots k_N}^\pm \rangle = 0 \quad .$$

Or, for one $\rho_0 \in \mathcal{S}_N$ we have $\{m_l\} = \{k_{\rho_0(l)}\}$, which then means

$$\langle v_{m_1 \dots m_N}^\pm | v_{k_1 \dots k_N}^\pm \rangle = (\pm 1)^{X_{\rho_0}} \quad .$$

We can thus draw the first conclusion, viz that $|v_{k_1 \dots k_N}^\pm\rangle$ are normalized to 1.

Let now $|\varphi\rangle \in \mathcal{H}_N$ be arbitrary. For example, for \mathcal{H}_N^- we can then deduce

$$\begin{aligned} \mathcal{H}_N^- \ni |\varphi^- \rangle = \hat{A} |\varphi \rangle &= \sum_{\{k_i\}} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \hat{A} |\varphi \rangle \\ &= \sum_{\{k_i\}} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle \langle \hat{A} v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \hat{A} |\varphi \rangle \quad , \end{aligned}$$

where we again used (2.2d) and (2.2f) in the last step. Furthermore,

$$|\varphi^- \rangle = \hat{A} |\varphi^- \rangle \frac{1}{N!} \sum_{\{k_i\}} |v_{k_1}^- \dots v_{k_N}^- \rangle \langle v_{k_1}^- \dots v_{k_N}^- | \varphi^- \rangle \quad .$$

As $|\varphi^- \rangle \in \mathcal{H}_N^-$ was arbitrary, we have the result

$$\frac{1}{N!} \int_{\{k_i\}} |v_{k_1 \dots k_N}^- \rangle \langle v_{k_1 \dots k_N}^-| = \hat{1} \text{ in } \mathcal{H}_N^- . \quad (2.3)$$

The same line of argument obviously holds for \mathcal{H}_N^+ , i.e. the vectors $|v_{k_1 \dots k_N}^\pm \rangle$ form a complete orthonormal system in \mathcal{H}_N^\pm .

The special structure of \hat{A} can be used to write $|v_{k_1 \dots k_N}^- \rangle$ in a very intuitive fashion, namely as

$$|v_{k_1 \dots k_N}^- \rangle = \frac{1}{\sqrt{N!}} \hat{A} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)} \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |v_{k_1}^{(1)} \rangle & \dots & |v_{k_1}^{(N)} \rangle \\ |v_{k_2}^{(1)} \rangle & \dots & |v_{k_2}^{(N)} \rangle \\ \vdots & \ddots & \vdots \\ |v_{k_N}^{(1)} \rangle & \dots & |v_{k_N}^{(N)} \rangle \end{vmatrix} . \quad (2.4)$$

This determinant is also called *Slater determinant*. One of the properties of determinants is that they vanish if two (or more) columns are linearly dependent. For the Slater determinant this means that if (at least) two quantum numbers are identical, $k_i = k_j$ for $i \neq j$, then $|v_{k_1 \dots k_N}^- \rangle = 0$. This property you may know as *Pauli's exclusion principle*:

Two identical Fermions cannot agree in all their quantum numbers.

A more general formulation of Pauli's principle, which does not rely on the representation as determinant of "single-particle states" $|v_{k_i}^{(m)} \rangle$, can be obtained from the property (2.2b), $\hat{P}_\rho \hat{A} = (-1)^{\chi_\rho} \hat{A}$. Consider an arbitrary vector $|\varphi_{k_1 \dots k_N}^- \rangle \in \mathcal{H}_N^-$ with a set of quantum numbers k_i . As we know, $|\varphi_{k_1 \dots k_N}^- \rangle = \hat{A} |\varphi_{k_1 \dots k_N}^- \rangle$ and thus on the one hand $\hat{P}_\rho |\varphi_{k_1 \dots k_N}^- \rangle = |\varphi_{k_{\rho(1)} \dots k_{\rho(N)}}^- \rangle$, while use of (2.2b) yields $\hat{P}_\rho |\varphi_{k_1 \dots k_N}^- \rangle = (-1)^{\chi_\rho} |\varphi_{k_1 \dots k_N}^- \rangle$. Put together, we obtain

$$|\varphi_{k_{\rho(1)} \dots k_{\rho(N)}}^- \rangle = (-1)^{\chi_\rho} |\varphi_{k_1 \dots k_N}^- \rangle .$$

If now ρ is a simple transposition, say $i \leftrightarrow j$, and $k_i = k_j$, this implies $|\varphi_{k_1 \dots k_N}^- \rangle = 0$. Thus, Pauli's principle is indeed an intrinsic property of the Fermionic sector and does not depend on a particular type of interaction or representation of the basis of \mathcal{H}_N^- .

In the case of \mathcal{H}_N^+ (Bosons), on the other hand, such a restriction does not exist, in particular all "particles" can occupy the same single-particle state. This phenomenon is also known as *Bose condensation*.

2.1.4 Fock space of variable particle number

In classical physics one usually distinguishes between point mechanics, where one studies systems consisting of a given number of particles, and field theories, where the physical objects are more or less abstract quantities called *fields*, which vary continuously as function of space and time. Well-known examples for the latter are electromagnetism, general theory of relativity, theory of elastic media or fluids, and so on.

In quantum mechanics the “Schrödinger field” is to some extent a mixture between both views: On the one hand, it is a field in the original sense of classical physics. On the other hand, this field is designed to describe the “particles” living in the microscopic world. It is thus quite natural to ask the question whether one can reconcile these seemingly contradicting point of views. This brings us into the realms of *quantum-field theories*.

Let us start with an old friend, the harmonic oscillator. In fact, the quantum mechanical solution presented you with the first quantum-field theory. The “field” for the harmonic oscillator is the amplitude of the oscillation, or rather $\langle \hat{x}^2 \rangle$. In solving the harmonic oscillator one introduces operators $\hat{b}^{(\dagger)}$, with which the Hamiltonian becomes $\hat{H} = \hbar\omega (\hat{b}^\dagger \hat{b} + \frac{1}{2})$. The operator $\hat{N} = \hat{b}^\dagger \hat{b}$ has integer eigenvalues $n \in \mathbb{N}_0$, and $\hat{b}^{(\dagger)}$ decrease (increase) n by one. The field amplitude, finally, is given by $\langle \hat{x}^2 \rangle \propto \langle \hat{b}^\dagger \hat{b} \rangle$.

The alternative quantum mechanical interpretation now is to view n as the number of fundamental oscillator modes, we call *oscillator quanta*, and which because of the discreteness of n have some features we know from particles. Consequently, one can now interpret n as number of (in this case abstract) *particles* contained in the *field*, and the operators $\hat{b}^{(\dagger)}$ *destroy* (*create*) a particle. After this motivation the further procedure is obvious: We now consider a system with *variable particle number*, which allows us to access the associated *field* adequately. To this end we introduce a hierarchy of states ($\alpha = \pm$ distinguishes between bosons and fermions)

$$\begin{aligned} |0\rangle &\in \mathcal{H}_0 \hat{=} \text{vacuum, i.e. no particle in the system} \\ |v_k\rangle &\in \mathcal{H}_1 \hat{=} \text{one particle with quantum number } k \\ |v_{k_1 k_2}^\alpha\rangle &\in \mathcal{H}_2 \hat{=} \text{two particles with quantum numbers } k_1 \text{ and } k_2 \\ |v_{k_1 k_2 k_3}^\alpha\rangle &\in \mathcal{H}_3 \dots \end{aligned}$$

The Hilbert space of our system then is formally defined as direct sum

$$\mathcal{H}^\alpha := \mathcal{H}_0^\alpha \oplus \mathcal{H}_1^\alpha \oplus \mathcal{H}_2^\alpha \oplus \dots$$

A general state from \mathcal{H}^α we write as

$$|\Phi\rangle := |0\rangle\langle 0|\Phi\rangle + \int_k |v_k\rangle\langle v_k|\Phi\rangle + \frac{1}{2!} \int_{k_1} \int_{k_2} |v_{k_1 k_2}^\alpha\rangle\langle v_{k_1 k_2}^\alpha|\Phi\rangle + \dots$$

For consistency, we furthermore *require*

$$\langle v_{k_1 \dots k_N}^\alpha | v_{q_1 \dots q_M}^\alpha \rangle \propto \delta_{NM} .$$

The quantity $|\langle v_{k_1 \dots k_N}^\alpha | \Phi \rangle|^2$ can be interpreted as probability to find N identical (!) “particles” with quantum numbers k_1, \dots, k_N in the state $|\Phi\rangle$. The Hilbert space \mathcal{H}^α is called *Fock space of variable particle number*.

Let us now define an operator

$$\hat{a}^\dagger : \mathcal{H}_N^\alpha \rightarrow \mathcal{H}_{N+1}^\alpha$$

with

$$\begin{aligned} \hat{a}_k^\dagger |0\rangle &:= |v_k\rangle \\ \hat{a}_k^\dagger |v_{k_1}\rangle &:= |v_{k k_1}^\alpha\rangle \\ &\vdots \\ \hat{a}_k^\dagger |v_{k_1 \dots k_N}^\alpha\rangle &:= |v_{k k_1 \dots k_N}^\alpha\rangle \\ &\vdots \end{aligned}$$

We call \hat{a}_k^\dagger *creation operator* of a particle with quantum number k . At this point one at last has to distinguish between bosons and fermions. As for bosons ($\alpha = +$) the vector has to be symmetric under particle exchange, we must require $\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger = \hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger$, while antisymmetry for fermions ($\alpha = -$) enforces $\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger = -\hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger$. The latter property in particular means $\hat{a}_k^\dagger \hat{a}_k^\dagger = 0$, which again is a variant of Pauli’s principle.

What is the action of the adjoint operator $\hat{a}_k := (\hat{a}_k^\dagger)^\dagger$? When we assume that the vectors $|0\rangle, |v_k\rangle, |v_{k_1 k_2}^\alpha\rangle, \dots$ are a complete orthonormal set in their respective Hilbert spaces, then we have

$$\mathbb{1}^\alpha = |0\rangle\langle 0| + \int_k |v_k\rangle\langle v_k| + \frac{1}{2!} \int_{k_1} \int_{k_2} |v_{k_1 k_2}^\alpha\rangle\langle v_{k_1 k_2}^\alpha| + \dots$$

as decomposition of unity in \mathcal{H}^α . Consequently, the operator \hat{a}_k^\dagger can be represented as

$$\hat{a}_k^\dagger = |v_k\rangle\langle 0| + \int_{k_1} |v_{k k_1}^\alpha\rangle\langle v_{k_1}| + \frac{1}{2!} \int_{k_1} \int_{k_2} |v_{k k_1 k_2}^\alpha\rangle\langle v_{k_1 k_2}| + \dots$$

Thus,

$$\hat{a}_k = |0\rangle\langle v_k| + \int_{k_1} |v_k\rangle\langle v_{kk_1}^\alpha| + \frac{1}{2!} \int_{k_1} \int_{k_2} |v_{k_1k_2}^\alpha\rangle\langle v_{kk_1k_2}^\alpha| + \dots$$

Together with orthonormalization of the $|v_{k_1\dots k_N}^\alpha\rangle$ and $\langle v_{k_1\dots k_N}^\alpha|v_{k_1\dots k_M}^\alpha\rangle \propto \delta_{NM}$ we obtain

$$\begin{aligned} \hat{a}_k|0\rangle &= 0 \\ \hat{a}_k|v_{k_1}\rangle &= \delta_{k,k_1}|0\rangle \\ \hat{a}_k|v_{k_1k_2}^\alpha\rangle &= \int_{k_3} |v_{k_3}\rangle\langle v_{kk_3}^\alpha|v_{k_1k_2}^\alpha\rangle \\ &= \int_{k_3} |v_{k_3}\rangle (\delta_{k,k_1}\delta_{k_3,k_2} + \alpha \cdot \delta_{k,k_2}\delta_{k_3,k_1}) \\ &= \delta_{k,k_1}|v_{k_2}\rangle + \alpha \cdot \delta_{k,k_2}|v_{k_1}\rangle \\ &\vdots \\ \hat{a}_k|v_{k_1\dots k_N}^\alpha\rangle &= \dots \\ &= \delta_{kk_1}|v_{k_2\dots k_N}^\alpha\rangle + \alpha \cdot \delta_{kk_2}|v_{k_1k_3\dots k_N}^\alpha\rangle \\ &\quad + \delta_{kk_3}|v_{k_1k_2k_4\dots k_N}^\alpha\rangle \\ &\quad + \dots \\ &\quad + \alpha^{N-1}\delta_{kk_N}|v_{k_1\dots k_{N-1}}^\alpha\rangle . \end{aligned}$$

Therefore, the operator \hat{a}_k maps

$$\hat{a}_k : \mathcal{H}_N \rightarrow \mathcal{H}_{N-1} ,$$

and is consequently called *annihilation operator*.

Now consider

$$\begin{aligned} \hat{a}_k \hat{a}_{k'}^\dagger |v_{k_1\dots k_N}^\alpha\rangle &= \delta_{k,k'} |v_{k_1\dots k_N}^\alpha\rangle + \alpha \cdot \delta_{k,k_1} |v_{k'k_2\dots k_N}^\alpha\rangle + \alpha^2 \cdot \delta_{k,k_2} |v_{k'k_1k_3\dots k_N}^\alpha\rangle + \dots \\ \hat{a}_{k'}^\dagger \hat{a}_k |v_{k_1\dots k_N}^\alpha\rangle &= \delta_{k,k_1} |v_{k'k_2\dots k_N}^\alpha\rangle + \alpha \cdot \delta_{k,k_2} |v_{k'k_1k_3\dots k_N}^\alpha\rangle + \dots \end{aligned}$$

There are two cases:

- (i) For bosons ($\alpha = +$) we subtract the two equations to obtain

$$(\hat{a}_k \hat{a}_{k'}^\dagger - \hat{a}_{k'}^\dagger \hat{a}_k) |v_{k_1\dots k_N}^\alpha\rangle = \delta_{k,k'} |v_{k_1\dots k_N}^\alpha\rangle .$$

- (ii) For fermions ($\alpha = -$) we add the two equations to obtain

$$(\hat{a}_k \hat{a}_{k'}^\dagger + \hat{a}_{k'}^\dagger \hat{a}_k) |v_{k_1\dots k_N}^\alpha\rangle = \delta_{k,k'} |v_{k_1\dots k_N}^\alpha\rangle .$$

As $|v_{k_1\dots k_N}^\alpha\rangle$ was arbitrary and a basis vector we may conclude

$$[\hat{a}_k, \hat{a}_{k'}] = [\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger] = 0 \quad , \quad [\hat{a}_k, \hat{a}_{k'}^\dagger] = \delta_{k,k'} \text{ for bosons} \quad (2.5)$$

$$\{\hat{a}_k, \hat{a}_{k'}\} = \{\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger\} = 0 \quad , \quad \{\hat{a}_k, \hat{a}_{k'}^\dagger\} = \delta_{k,k'} \text{ for fermions} \quad (2.6)$$

where $[A, B] := AB - BA$ is the conventional commutator and $\{A, B\} := AB + BA$ the *anti-commutator*. Sometimes a unifying notation

$$[A, B]_\alpha := AB + \alpha \cdot BA$$

is used.

Just like in usual quantum mechanics, there are of course infinitely many possibilities to choose a basis. Changes between two such basis sets are achieved via a basis transformation

$$|v_\alpha\rangle = \int_k |v_k\rangle \langle v_k | v_\alpha\rangle \quad .$$

Since we can write $|v_\alpha\rangle = \hat{a}_\alpha^\dagger |0\rangle$, the same formula holds as

$$\begin{aligned} \hat{a}_\alpha^\dagger &= \int_k \hat{a}_k^\dagger \langle v_k | v_\alpha\rangle \\ \hat{a}_\alpha &= \int_k \hat{a}_k \langle v_\alpha | v_k\rangle \quad . \end{aligned}$$

A particularly important basis is the position representation, i.e. $\alpha = \{\vec{r}, \sigma\}$. For fermions, the corresponding operator is conventionally denoted as $\hat{\Psi}_\sigma(\vec{r})$ and called *field operator*. It has the anti-commutator rules

$$\begin{aligned} \{\hat{\Psi}_\sigma(\vec{r}), \hat{\Psi}_{\sigma'}(\vec{r}')\} &= \{\hat{\Psi}_\sigma(\vec{r})^\dagger, \hat{\Psi}_{\sigma'}(\vec{r}')^\dagger\} = 0 \\ \{\hat{\Psi}_\sigma(\vec{r}), \hat{\Psi}_{\sigma'}(\vec{r}')^\dagger\} &= \delta_{\sigma,\sigma'} \delta(\vec{r} - \vec{r}') \quad . \end{aligned} \quad (2.7)$$

2.1.5 Fock space representation of operators

Let us now consider an arbitrary observable \hat{L} . For identical particles we know that $\hat{S}\hat{L}\hat{S} = \hat{L}$ respectively $\hat{A}\hat{L}\hat{A} = \hat{L}$. To simplify the discussion I will concentrate on \mathcal{H}^- , the argumentation for \mathcal{H}^+ is analogous.

We first keep N fixed. In \mathcal{H}_N we have

$$\hat{L} = \int_{\{k_i\}} \int_{\{n_i\}} |v_{k_1}^{(1)} \dots v_{k_N}^{(N)}\rangle \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \hat{L} |v_{n_1}^{(1)} \dots v_{n_N}^{(N)}\rangle \langle v_{n_1}^{(1)} \dots v_{n_N}^{(N)} |$$

and, using $\hat{L} = \hat{A}\hat{L}\hat{A}$ and $|v_{k_1 \dots k_N}^- \rangle = \sqrt{N!}\hat{A}|v_{k_1}^{(1)} \dots v_{k_N}^{(N)} \rangle$, we can write

$$\hat{L} = \frac{1}{N!} \int \int_{\{k_i\} \{n_i\}} |v_{k_1 \dots k_N}^- \rangle \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \hat{L} |v_{n_1}^{(1)} \dots v_{n_N}^{(N)} \rangle \langle v_{n_1 \dots n_N}^- |$$

in \mathcal{H}_N^- . The important result is that the matrix elements of \hat{L} are calculated with respect to the product space \mathcal{H}_N and not within \mathcal{H}_N^- !

There are two important types of operators:

Single-particle operators

The observable \hat{L} has the form

$$\hat{L} = \underbrace{\hat{f} \otimes 1 \otimes 1 \otimes \dots \otimes 1 + 1 \otimes \hat{f} \otimes \dots \otimes 1 + \dots + 1 \otimes 1 \otimes \dots \otimes 1 \otimes \hat{f}}_{N \text{ factors}}$$

where the operator \hat{f} acts only on one particle, for example the kinetic energy $\hat{p}^2/(2m)$ or an external potential $U(\hat{r})$. We employ a short-hand notation

$$\begin{aligned} \hat{f}_\nu &:= 1 \otimes 1 \otimes \dots \otimes \hat{f} \otimes 1 \otimes \dots \otimes 1 \\ &\quad \uparrow \\ &\quad \nu\text{-th place} \end{aligned}$$

i.e.

$$\hat{L} = \sum_{\nu=1}^N \hat{f}_\nu .$$

Then,

$$\begin{aligned} \langle v_{k_1}^{(1)} \dots v_{k_N}^{(N)} | \hat{L} |v_{n_1}^{(1)} \dots v_{n_N}^{(N)} \rangle &= \langle v_{k_1}^{(1)} | \hat{f} |v_{n_1}^{(1)} \rangle \delta_{k_2, n_2} \dots \delta_{k_N, n_N} + \dots + \\ &\quad \langle v_{k_N}^{(N)} | \hat{f} |v_{n_1}^{(1)} \rangle \delta_{k_1, n_1} \dots \delta_{k_{N-1}, n_{N-1}} \end{aligned}$$

Obviously,

$$\langle v_k^{(1)} | \hat{f} |v_n^{(1)} \rangle = \langle v_k^{(2)} | \hat{f} |v_n^{(2)} \rangle = \dots = \langle v_k^{(N)} | \hat{f} |v_n^{(N)} \rangle = \langle v_k | \hat{f} |v_n \rangle$$

Consequently, using the delta functions,

$$\begin{aligned} \sum_{\nu=1}^N \hat{f}_\nu &= \frac{1}{N!} \int \int |v_{k_1 \dots k_N}^- \rangle \langle v_{k_1} | \hat{f} |v_{n_1} \rangle \langle v_{n_1 k_2 \dots k_N}^- | + \\ &\quad \frac{1}{N!} \int \int |v_{k_1 \dots k_N}^- \rangle \langle v_{k_2} | \hat{f} |v_{n_2} \rangle \langle v_{k_1 n_2 \dots k_N}^- | + \dots \end{aligned}$$

In the second term, we perform a substitution $k_1 \leftrightarrow k_2$ and $n_1 \leftrightarrow n_2$ and use

$$|v_{k_2 k_1 \dots k_N}^- \rangle \langle v_{k_2 n_1 k_3 \dots k_N}^- | = |v_{k_1 k_2 \dots k_N}^- \rangle \langle v_{n_1 k_2 \dots k_N}^- |$$

and similarly for all other terms in the series. We then obtain

$$\sum_{\nu=1}^N \hat{f}_{\nu} = \frac{1}{(N-1)!} \int |v_{k_1 \dots k_N}^{-}\rangle \langle v_{k_1} | \hat{f} | v_{n_1} \rangle \langle v_{n_1 k_2 \dots k_N}^{-} |$$

Now use $|v_{k_1 \dots k_N}^{-}\rangle = \hat{a}_{k_1}^{\dagger} |v_{k_2 \dots k_N}^{-}\rangle$, $\langle v_{k_1 \dots k_N}^{-} | = \langle v_{k_2 \dots k_N}^{-} | \hat{a}_{k_1}$ and

$$\frac{1}{(N-1)!} \int |v_{k_2 \dots k_N}^{-}\rangle \langle v_{k_2 \dots k_N}^{-} | = \mathbb{1}$$

to obtain

$$\sum_{\nu=1}^N \hat{f}_{\nu} = \int_{k,k'} \hat{a}_k^{\dagger} \langle v_k | \hat{f} | v_{k'} \rangle \hat{a}_{k'} \quad (2.8)$$

This result has a very intuitive interpretation: In \mathcal{H}_N^{α} the operator \hat{L} “scatters a particle” from the single-particle state k' into the single-particle state k . The “scattering amplitude” from $k' \rightarrow k$ is given by the matrix element $\langle v_k | \hat{f} | v_{k'} \rangle$ of the *single-particle operator* \hat{f} .

Up to now we have kept N fixed. How about the Fock space \mathcal{H}^- ? To this end we introduce the projection operator \hat{P}_N^- with $\hat{P}_N^- \mathcal{H}^- = \mathcal{H}_N^-$. Obviously,

$$\sum_{N=0}^{\infty} \hat{P}_N^- = \mathbb{1} \text{ in } \mathcal{H}^-.$$

Furthermore, the operator $\hat{a}_k^{\dagger} \hat{a}_{k'}$ does not change the number of particles (only their quantum numbers), thus

$$\hat{P}_N^- \hat{a}_k^{\dagger} \hat{a}_{k'} \hat{P}_N^- = \hat{a}_k^{\dagger} \hat{a}_{k'} (\hat{P}_N^-)^2 = \hat{a}_k^{\dagger} \hat{a}_{k'} \hat{P}_N^- ,$$

where we have used $(\hat{P}_N^-)^2 = \hat{P}_N^-$. Putting all things together we can conclude

$$\sum_{N=0}^{\infty} \hat{P}_N^- \hat{L} \hat{P}_N^- = \int_{k,k'} \hat{a}_k^{\dagger} \langle v_k | \hat{f} | v_{k'} \rangle \hat{a}_{k'} \text{ in } \mathcal{H}^- . \quad (2.9)$$

Some examples:

- (i) The momentum operator is given by

$$\hat{P} = \sum_{\nu} \hat{p}_{\nu} .$$

If we in particular choose as basis the momentum eigenstates $|\vec{k}, \sigma\rangle$, the matrix element is given by $\langle \vec{k}, \sigma | \hat{p} | \vec{k}', \sigma' \rangle = \hbar \vec{k} \delta(\vec{k} - \vec{k}') \delta_{\sigma, \sigma'}$ and

$$\hat{P} = \sum_{\sigma} \int d^3k \hbar \vec{k} \hat{a}_{k\sigma}^{\dagger} \hat{a}_{\vec{k}\sigma} .$$

Alternatively, we may choose $|\vec{r}, \sigma\rangle$ as basis and use

$$\langle \vec{r}, \sigma | \hat{p} | \vec{r}', \sigma' \rangle = -\frac{\hbar}{i} \vec{\nabla}_{\vec{r}'} \delta(\vec{r} - \vec{r}') \delta_{\sigma, \sigma'}$$

with the result⁴

$$\hat{P} = \frac{\hbar}{i} \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}(\vec{r}) \vec{\nabla} \hat{\Psi}_{\sigma}(\vec{r})$$

- (ii) Hamilton operator $\hat{H} = \sum \hat{h}_{\nu}$ with $\hat{h}_{\nu} = \frac{1}{2m} \hat{p}_{\nu}^2 + U(\hat{r}_{\nu})$. With our above results

$$\hat{H} = \sum_{kk'} h_{kk'} \hat{a}_k^{\dagger} \hat{a}_{k'} , \quad h_{kk'} = \langle v_k | \hat{h} | v_{k'} \rangle .$$

As special case we can again use $|\vec{r}, \sigma\rangle$ to obtain

$$h_{\sigma\sigma'}(\vec{r}, \vec{r}') = \delta_{\sigma\sigma'} \left(-\frac{\hbar^2}{2m} \vec{\nabla}_{\vec{r}'}^2 + U(\vec{r}) \right) \delta(\vec{r} - \vec{r}')$$

or

$$\hat{H} = \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}(\vec{r})^{\dagger} \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + U(\vec{r}) \right] \hat{\Psi}_{\sigma}(\vec{r}) .$$

Note that this looks very much like the definition of an expectation value in QM I, except that $\hat{\Psi}_{\sigma}(\vec{r})$ now is an operator and not a complex function.

Another frequent choice are the eigenstates of \hat{h} , $\hat{h}|u_k\rangle = \epsilon_k|u_k\rangle$, which then means

$$\hat{H} = \sum_k \epsilon_k \hat{a}_k^{\dagger} \hat{a}_k .$$

Compare this to the harmonic oscillator $\hat{H} = \hbar\omega \hat{b}^{\dagger} \hat{b}$ of your choice!

- (iii) Particle number

Consider the projection operator $\hat{P}_k := |v_k\rangle\langle v_k|$. Its meaning is “has the particle the quantum number k ?”. In \mathcal{H}^{α} we use $\sum_{\nu} \hat{P}_k^{(\nu)}$ with the meaning “how many particle do have the quantum number k ?” and it can be represented as

$$\sum_{\nu} \hat{P}_k^{(\nu)} = \sum_{qq'} \hat{a}_q^{\dagger} \langle v_q | v_k \rangle \langle v_k | v_{q'} \rangle \hat{a}_{q'} = \hat{a}_k^{\dagger} \hat{a}_k .$$

The observable $\hat{N}_k := \hat{a}_k^{\dagger} \hat{a}_k$ is called *occupation number operator of the single-particle state k* . From its definition we can infer

$$\hat{N}_k |v_{k_1 \dots k_N}^{\alpha}\rangle = \delta_{kk_1} |v_{k_2 \dots k_N}^{\alpha}\rangle + \delta_{kk_2} |v_{k_1 k_3 \dots k_N}^{\alpha}\rangle + \dots ,$$

⁴Remember: $\int f(x) \frac{d^n}{dx^n} \delta(x-y) = (-1)^n \frac{d^n f}{dy^n}$.

i.e. \hat{N}_k has the eigenvectors $|v_{k_1 \dots k_N}^\alpha\rangle$ with eigenvalue 0, if $k \notin \{k_1, \dots, k_N\}$, or $n_k \in \mathbb{N}$ if k appears n_k times in $\{k_1, \dots, k_N\}$. This property is made explicit in the *occupation number representation*, where the basis is written as $|n_{k_1} n_{k_2} \dots n_{k_N}\rangle$. In particular for fermions only $n_k = 0, 1$ is allowed due to Pauli's principle and a possible vector for example reads $|101100\dots\rangle$, which obviously is very nicely suited for coding on a computer.

Finally, the observable

$$\hat{N} = \sum_k \hat{N}_k$$

is the operator of the total particle number with eigenvalues $n = 0, 1, \dots$

As

$$\hat{a}_k = \sum_\sigma \int d^3r \hat{\Psi}_\sigma(\vec{r}) \langle v_k | \vec{r}, \sigma \rangle$$

and

$$\sum_k \langle \vec{r}', \sigma' | v_k \rangle \langle v_k | \vec{r}, \sigma \rangle = \delta(\vec{r} - \vec{r}') \delta_{\sigma\sigma'}$$

we have

$$\hat{N} = \sum_\sigma \int d^3r \hat{\Psi}_\sigma(\vec{r})^\dagger \hat{\Psi}_\sigma(\vec{r})$$

and thus

$$\hat{\Psi}_\sigma(\vec{r})^\dagger \hat{\Psi}_\sigma(\vec{r}) = \sum_\nu \delta(\vec{r}_\nu - \vec{r}) \mathbb{1}$$

is the operator of the *particle-density at point \vec{r} with spin σ* . Note that this is the operator version of “ $|\Psi_\sigma(\vec{r})|^2$ is the probability density to find a particle at \vec{r} with spin σ ”.

From the (anti-) commutation rules we obtain (independent of whether we have bosons or fermions)

$$\begin{aligned} [\hat{a}_{k_1}^\dagger \hat{a}_{k_2}, \hat{a}_k] &= -\delta_{k_1 k} \hat{a}_{k_2} \\ [\hat{a}_{k_1}^\dagger \hat{a}_{k_2}, \hat{a}_k^\dagger] &= \delta_{k_2 k} \hat{a}_{k_1}^\dagger \\ [\hat{N}_k, \hat{a}_{k'}] &= -\delta_{kk'} \hat{a}_{k'} \\ [\hat{N}_k, \hat{a}_{k'}^\dagger] &= \delta_{kk'} \hat{a}_{k'}^\dagger \\ [\hat{N}_k, \hat{N}_{k'}] &= [\hat{N}_k, \hat{a}_{k_1}^\dagger \hat{a}_{k_2}] = 0 \end{aligned}$$

The last two commutators represent the particle conservation. With these commutators we can set up the equations of motion

$$\frac{d}{dt} \hat{a}_k = \frac{i}{\hbar} [\hat{H}, \hat{a}_k] = -\frac{i}{\hbar} \sum_{k'} h_{kk'} \hat{a}_{k'} .$$

If we in particular choose the eigenstates of \hat{h} , the equation of motion reduces to

$$\frac{d}{dt}\hat{a}_k = -\frac{i}{\hbar}\epsilon_k\hat{a}_k \Rightarrow \hat{a}_k(t) = e^{-\frac{i}{\hbar}\epsilon_k t}\hat{a}_k, ,$$

while for the position eigenstates of fermions

$$\frac{d}{dt}\hat{\Psi}_\sigma(\vec{r}, t) = -\frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r})\right]\hat{\Psi}_\sigma(\vec{r}, t)$$

follows. This is the operator form of Schrödinger's equation for the matter field. One often also talks about *quantization of the matter field*, *field quantization* or *second quantization*.

Interaction operators

The typical form of an interaction operator between two particles is (c.f. the Coulomb interaction)

$$\hat{H}_W = \frac{1}{2} \sum_{\mu \neq \nu} \hat{h}_{\mu\nu}$$

Going through the same steps as for the single particle operator, we find

$$\begin{aligned} \hat{H}_W &= \frac{1}{2} \int \int_{k_1, k_2, q_1, q_2} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger W_{k_1 k_2; q_2 q_1} \hat{a}_{q_2} \hat{a}_{q_1} \quad (2.10) \\ W_{k_1 k_2; q_2 q_1} &= \langle v_{k_1}^{(1)} v_{k_2}^{(2)} | \hat{h}_{12} | v_{q_2}^{(2)} v_{q_1}^{(1)} \rangle \end{aligned}$$

Note that here the proper order of operators and indexes is essential!

This result has again an intuitive interpretation: Interaction is “scattering” of two particles from initial states q_1 and q_2 into final states k_1 and k_2 . In particular, for the Coulomb interaction between two fermions and within position representation

$$\begin{aligned} W(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2; \vec{r}'_2 \sigma'_2, \vec{r}'_1 \sigma'_1) &= \langle \vec{r}_1 \sigma_1 | \langle \vec{r}_2 \sigma_2 | \frac{e^2}{|\hat{r}_1 - \hat{r}_2|} | \vec{r}'_2 \sigma'_2 \rangle | \vec{r}'_1 \sigma'_1 \rangle \\ &= \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \delta(\vec{r}_1 - \vec{r}'_1) \delta(\vec{r}_2 - \vec{r}'_2) \delta_{\sigma_1 \sigma'_1} \delta_{\sigma_2 \sigma'_2} \end{aligned}$$

i.e.

$$\hat{H}_W = \frac{e^2}{2} \sum_{\sigma_1 \sigma_2} \int d^3 r_1 \int d^3 r_2 \frac{\hat{\Psi}_{\sigma_1}(\vec{r}_1)^\dagger \hat{\Psi}_{\sigma_2}(\vec{r}_2)^\dagger \hat{\Psi}_{\sigma_2}(\vec{r}_2) \hat{\Psi}_{\sigma_1}(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|}$$

Again, the order of the operators is essential here.

Last but not least let us write down the expression in momentum eigenspace (plane waves), where we obtain

$$\begin{aligned}\hat{H}_W &= \frac{e^2}{2} \int d^3q \frac{1}{q^2} \hat{\rho}(\vec{q}) \hat{\rho}(-\vec{q}) \\ \hat{\rho}(\vec{q}) &= \sum_{\sigma} \int \frac{d^3k}{(2\pi)^3} \hat{a}_{\vec{k}+\vec{q},\sigma}^{\dagger} \hat{a}_{\vec{k},\sigma} = \hat{\rho}(-\vec{q})^{\dagger}\end{aligned}$$

The operators $\hat{\rho}(\vec{q})$ are called *density operators*.

2.2 Statistical description of quantum many-body systems

Usually, one is not really interested in the microscopic details of a system such as a solid but rather in the macroscopic properties like specific heat, resistivity and so on. The details of this statistical description will be discussed in the lecture “Statistische Physik”, here I will only briefly introduce the concepts. Experimentally, we can control external quantities like temperature, pressure etc. of a macroscopic system, while from the microscopic point of view the relevant quantities are energy, volume or particle number. The connection is made by assuming that in the limit as the particle number N becomes large, keeping particle density $n = N/V$ constant,⁵ these quantities can be computed as expectation values

$$\langle \hat{A} \rangle := \text{Tr} \hat{\rho} \hat{A} ,$$

where \hat{A} is some observable describing the microscopic property and $\hat{\rho}$ a measure for the weight of states occurring in the calculation of the trace (the *statistical operator* or *density matrix*). For example, in the usual quantum mechanical description of a system by some single state $|\Psi\rangle$, this operator is simply given by $\hat{\rho} = |\Psi\rangle\langle\Psi|$.

A particularly important expectation value is $\langle \hat{H} \rangle$. One typically equates it to the *internal energy* $U(T)$ of the system, i.e. for a given temperature T one has to determine $\hat{\rho}$ under the constraint that

$$U(T) \stackrel{!}{=} \langle \hat{H} \rangle = \text{Tr} \hat{\rho} \hat{H} , \quad \text{Tr} \hat{\rho} = 1 .$$

The proper approach, which requires additional prior knowledge will be discussed in “Statistische Physik”. Here we will take a “top-down” approach. To this end I remind you that in classical statistical physics the probability for the realization of a state with energy E and particle number N is given by the Boltzmann factor

$$P(E) = \frac{1}{\mathcal{Z}} e^{-\beta E} , \quad \beta = \frac{1}{k_B T} ,$$

⁵This limit is called *thermodynamic limit*.

CHAPTER 2. MATHEMATICAL BACKGROUND

where T is the temperature and \mathcal{Z} a normalization. We now generalize this expression to the quantum mechanical case by replacing

$$\begin{aligned} P(E) &\rightarrow \langle u_E | \hat{\rho} | u_E \rangle \\ E = H &\rightarrow \hat{H} \end{aligned}$$

and obtain

$$\hat{\rho} = \frac{1}{\mathcal{Z}} e^{-\beta \hat{H}} .$$

As obviously $\text{Tr} \hat{\rho} = 1$ must hold, we can identify

$$\mathcal{Z} = \text{Tr} e^{-\beta \hat{H}} .$$

The quantity \mathcal{Z} is called *partition function* and is related to the free energy as

$$F = -k_B T \ln \mathcal{Z} .$$

From the latter relation and thermodynamics we can now calculate the entropy via

$$\begin{aligned} S = -\frac{\partial F}{\partial T} &= k_B \ln \mathcal{Z} + k_B T \frac{\partial \beta}{\partial T} \frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ &= k_B [\ln \mathcal{Z} + \langle -\beta \hat{H} \rangle] . \end{aligned}$$

We now write

$$\begin{aligned} \langle -\beta \hat{H} \rangle &= \text{Tr} (-\beta \hat{H}) \hat{\rho} = \text{Tr} \ln [\hat{\rho} \mathcal{Z}] \hat{\rho} \\ &= \langle \ln \hat{\rho} \rangle + \ln \mathcal{Z} . \end{aligned}$$

Therefore we obtain

$$S = -k_B \langle \ln \hat{\rho} \rangle \quad (2.11)$$

as expression for the entropy. In information theory this expression is actually used to *define* the entropy of a statistical measure (*Shannon entropy*). In recent years the problem of suitably defining entropy in information transmission has become important in connection with quantum computing and the concept of *entanglement* of quantum systems.

2.2. STATISTICAL DESCRIPTION OF QUANTUM MANY-BODY SYSTEMS

Chapter 3

The homogeneous electron gas

The homogeneous electron gas is in connection with solid state physics also sometimes called *jellium model* or *free-electron model* for the solid. One here approximates the ions of a solid by a homogeneous positive background guaranteeing charge neutrality.

3.1 The noninteracting electron gas

In addition to neglecting a possible regular arrangement of the ions, we now also ignore the Coulomb interaction between the electrons. This seems an even more rude approximation at first sight. However, as we will learn later, it is the one that is usually better justified than the assumption of a homogeneous system.

The Hamiltonian for the noninteracting electron gas is simply given by

$$\hat{H}_e = \frac{1}{2m} \sum_{i=1}^N \hat{p}_i^2 \quad (3.1)$$

$$\stackrel{\text{Eq. (2.8)}}{=} \sum_{\vec{k}\sigma} \langle \varphi_{\vec{k}\sigma} | \frac{\hat{p}^2}{2m} | \varphi_{\vec{k}\sigma} \rangle \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \quad (3.2)$$

Since electrons are fermions, the operators $\hat{c}_{\vec{k}\sigma}$ and $\hat{c}_{\vec{k}\sigma}^\dagger$ must fulfill anticommutation relations, i.e. $\{\hat{c}_{\vec{k}'\sigma'}, \hat{c}_{\vec{k}\sigma}^\dagger\} = \delta_{\vec{k},\vec{k}'} \delta_{\sigma,\sigma'}$. Furthermore, as we are now working with solids, which occupy a finite region in space, we assume that the electrons are confined to a finite but large volume¹ $V = L^3$. A certain mathematical problem arises from the existence of the boundaries, which would require $\Psi(\vec{r} \in \partial V) = 0$ or at least an exponential decay outside the cube, and the potential barrier to overcome the boundaries is called *work function*. Far enough away from the surface, the wave functions are then in principle standing waves, described by either sin or cos functions. For practical purposes it is however more convenient to work with travelling waves described by a complex exponential function. Quite obviously, the type of solution is determined by the existence of boundaries. However, quite often we are not interested in properties at the boundary, but in the *bulk* properties far away from the boundary. These bulk properties can on the other hand not depend on the details of boundary, i.e. we are free to choose convenient boundary conditions in such a situation. This fact has first been observed by Born and von Karmann, who introduced the concept of *periodic boundary conditions* or *Born-von Karman boundary conditions*, which identify the properties at position at $x_i + L$ with those at x_i . For a chain this amounts to closing it into a ring, in two dimensions one ends up with a torus, and so on.

¹For simplicity we assume a cube of base length L .

Employing periodic boundary conditions we have

$$\varphi(x, y, z) = \varphi(x + L, y, z) = \varphi(x, y + L, z) = \varphi(x, y, z + L)$$

for the wave functions entering (3.2). These conditions lead to discrete \vec{k} vectors which have the components

$$k_i = \frac{2\pi}{L} n_i, \quad n_i \in \mathbb{Z};.$$

As the set of vectors \vec{k} numbers all possible inequivalent single-particle states it serves as quantum number. We in addition need the spin as further quantum number, which we denote by σ with $\sigma = \pm 1$ or $\sigma = \uparrow / \downarrow$ depending on the context. We then have

$$\begin{aligned} \varphi_{\vec{k}\sigma}(\vec{r}) &= \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \chi_{\sigma} \\ \chi_{\sigma} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \delta_{\sigma,\uparrow} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \delta_{\sigma,\downarrow} \end{aligned}$$

and with this for the matrix element of the kinetic energy

$$\langle \varphi_{\vec{k}\sigma} | \frac{\hat{p}^2}{2m} | \varphi_{\vec{k}\sigma} \rangle = \frac{\hbar^2 k^2}{2m} =: \epsilon_{\vec{k}}.$$

The discrete \vec{k} points form a lattice in \vec{k} space, where each lattice point can accommodate two single-particle states with different spin orientation. The volume per \vec{k} point is $(2\pi)^3/V$.

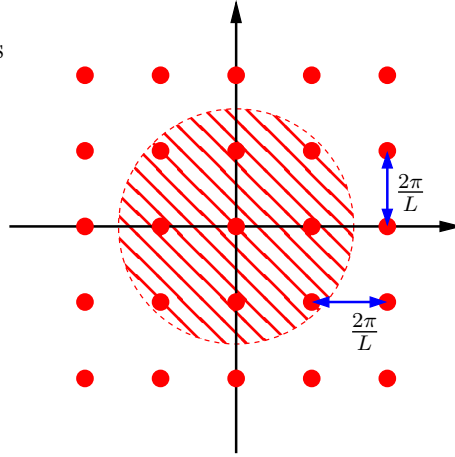
3.1.1 Ground state properties

In particular, the ground state is obtained by occupying the set $\{\vec{k}_i\}$ of \vec{k} points with the smallest possible energies respecting Pauli's principle, i.e.

$$\langle \Psi_G | \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} | \Psi_G \rangle = \begin{cases} 1, & \text{for } \vec{k} \in \{\vec{k}_i\} \\ 0, & \text{else} \end{cases}.$$

As $\epsilon_{\vec{k}} \propto k^2$, these states can be found within a sphere (*Fermi sphere*) with a certain radius k_F (*Fermi wave vector*) about $\vec{k} = 0$. The value of k_F can be determined from the requirement, that the sum over all occupied states must equal to the number of particles, i.e.

$$N = \sum_{\sigma} \sum_{k \leq k_F}$$



3.1. THE NONINTERACTING ELECTRON GAS

For simplicity we assume that N is even.

How does one evaluate such sums? To this end let me remind you, that the Volume V of the system is very large and consequently the volume per \vec{k} point $d^3k = \frac{(2\pi)^3}{V}$ is very small. Then,

$$\sum_{\vec{k}} \dots = V \sum_{\vec{k}} \frac{d^3k}{(2\pi)^3} \dots \xrightarrow{V \rightarrow \infty} V \int \frac{d^3k}{(2\pi)^3} \dots$$

With this observation we find in the thermodynamic limit $V \rightarrow \infty$ and $n = N/V$ finite

$$n = \frac{N}{V} = \frac{1}{V} \sum_{\sigma} \sum_{k \leq k_F} = \sum_{\sigma} \int \frac{d^3k}{(2\pi)^3} = \frac{1}{4\pi^3} \int_0^{k_F} 4\pi k^2 dk = \frac{1}{3\pi^2} k_F^3 ,$$

which leads to

$$k_f = (3\pi^2 n)^{1/3} \quad (3.3)$$

as expression for the Fermi wave vector. The corresponding energy

$$\epsilon_{k_F} = \frac{\hbar^2 k_F^2}{2m}$$

is called *Fermi energy* and usually denoted as E_F .

We can now calculate the ground state energy of the noninteracting electron gas

$$\begin{aligned} E_0 &= \sum_{\vec{k}, k \leq k_F} \sum_{\sigma} \epsilon_{\vec{k}} \\ &= \underset{\uparrow}{2} V \int_0^{k_F} \frac{4\pi}{(2\pi)^3} k^2 \frac{\hbar^2 k^2}{2m} dk \\ &\quad \text{spin} \\ &= \frac{\hbar^2 V}{2m\pi^2} \int_0^{k_F} k^4 dk = V \frac{\hbar^2}{2m\pi^2} \frac{k_F^5}{5} \\ &= V \frac{3}{5} \underbrace{\frac{\hbar^2 k_F^2}{2m}}_{= E_F} \underbrace{\frac{k_F^3}{3\pi^2}}_{= \frac{N}{V}} = \frac{3}{5} N E_F \end{aligned} \quad (3.4)$$

and the energy per particle

$$\epsilon_0 = \frac{E_0}{N} = \frac{3}{5} E_F .$$

With the knowledge of the ground state energy we can calculate physical properties. As examples let us determine the pressure P and bulk modulus B_0 of the Fermi gas at $T = 0$. These two quantities are related to the ground state energy through

$$\begin{aligned} P &= -\left(\frac{\partial E_0}{\partial V}\right)_N \\ B_0 &= -V\left(\frac{\partial P}{\partial V}\right)_N . \end{aligned}$$

As E_0 is given by

$$E_0 = \frac{3}{5}NE_F = \frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3}$$

the pressure is

$$P = -\frac{3}{5}N\frac{\hbar^2}{2m}\left(-3\pi^2\frac{N}{V^2}\right)\frac{2}{3}\left(3\pi^2\frac{N}{V}\right)^{-1/3} = \frac{2}{3}\frac{E_0}{V} = \frac{2}{5}nE_F$$

and for the bulk modulus one finds

$$B_0 = \dots = \frac{5}{3}P = \frac{2}{3}nE_F .$$

3.1.2 Evaluation of \vec{k} -sums – Density of States

In the following we will rather often have to deal with expressions of the type

$$\frac{1}{V}\sum_{\vec{k}}F(\epsilon_{\vec{k}}) ,$$

where $F(\epsilon_{\vec{k}})$ is some function depending on \vec{k} through the dispersion only. Such a sum can be rewritten as

$$\frac{1}{V}\sum_{\vec{k}}F(\epsilon_{\vec{k}}) = \int_{-\infty}^{\infty}\mathcal{N}(\epsilon)F(\epsilon)d\epsilon ,$$

where we have introduced the *density of states* (DOS)

$$\mathcal{N}(\epsilon) := \frac{1}{V}\sum_{\vec{k}}\delta(\epsilon - \epsilon_{\vec{k}}) .$$

Note that this definition also holds for a more general dispersion appearing in a real lattice. Let us calculate the DOS for $\epsilon_{\vec{k}} = \frac{\hbar^2k^2}{2m}$. From the definition one firstly obtains

$$\mathcal{N}(\epsilon) = \frac{1}{V}\sum_{\vec{k}}\delta(\epsilon - \epsilon_{\vec{k}}) = \int_0^{\infty}\frac{4\pi k^2 dk}{(2\pi)^3}\delta(\epsilon - \epsilon_{\vec{k}}) . \quad (3.5)$$

3.1. THE NONINTERACTING ELECTRON GAS

To evaluate this expression further I remind you of the relation

$$\delta(\epsilon - \epsilon_{\vec{k}}) = \sum_{k_i} \frac{1}{|\vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}=\vec{k}_i}|} \delta(k - k_i), \quad \epsilon - \epsilon_{\vec{k}_i} = 0, \quad \vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}=\vec{k}_i} \neq 0.$$

In the present case as $\epsilon_{\vec{k}} \geq 0$ we also must have $\epsilon \geq 0$ and hence there exist two roots for a given ϵ , namely $k_0 = \pm \sqrt{\frac{2m\epsilon}{\hbar^2}}$. As also $k \geq 0$ in the integral (3.5), we only need the positive root here. Furthermore, $|\vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}}| = \frac{\hbar^2 k}{m} \neq 0$ for $k \neq 0$ and therefore

$$\begin{aligned} \mathcal{N}(\epsilon) &= \frac{1}{(2\pi)^3} 4\pi k_0^2 \frac{m}{\hbar^2 k_0} = \frac{m}{2\pi^2 \hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} \\ &= \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2 k_F^2} \right)^{\frac{3}{2}} k_F^3 \sqrt{\epsilon} \end{aligned}$$

With the definitions of k_f in (3.3) and E_F we finally obtain

$$\mathcal{N}(\epsilon) = \frac{3}{4} \frac{n}{E_F} \sqrt{\frac{\epsilon}{E_F}} \quad (3.6)$$

for the DOS. Some warning: Sometimes the spin factor 2 is included in the definition of the DOS, which then reads $\tilde{\mathcal{N}}(\epsilon) = 2\mathcal{N}(\epsilon) = \frac{3}{2} \frac{n}{E_F} \sqrt{\frac{\epsilon}{E_F}}$. A particularly important value is the DOS at the Fermi energy $\mathcal{N}(E_F)$, which is

$$\mathcal{N}(E_F) = \frac{3}{4} \frac{n}{E_F} \propto \frac{1}{E_F} \propto m \quad (3.7)$$

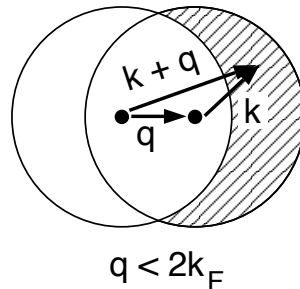
This is an important proportionality you should memorize!

3.1.3 Excited states of the electron gas

To construct excited states of the noninteracting, free electron gas we have only one possibility, viz taking one electron from a state with $\leq k_F$ and putting it into a state with $k' > k_F$. Let us denote the difference in momentum by $\vec{q} = \vec{k}' - \vec{k}$. We now must distinguish two possibilities:

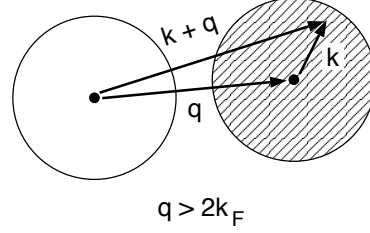
- (i) $q \leq 2k_F$:

Not all states inside the Fermi sphere are possible final states for a given \vec{q} , but only those that fulfil the requirement $k' = |\vec{k} + \vec{q}| \geq k_F$. Further, as \vec{k} cannot be outside the Fermi sphere, we can restrict k' to $k_F \leq k' \leq |\vec{k}_F + \vec{q}|$ or equivalently $E_F \leq \epsilon_{\vec{k}'} \leq \frac{\hbar^2}{2m} (\vec{q} + \vec{k}_F)^2$.

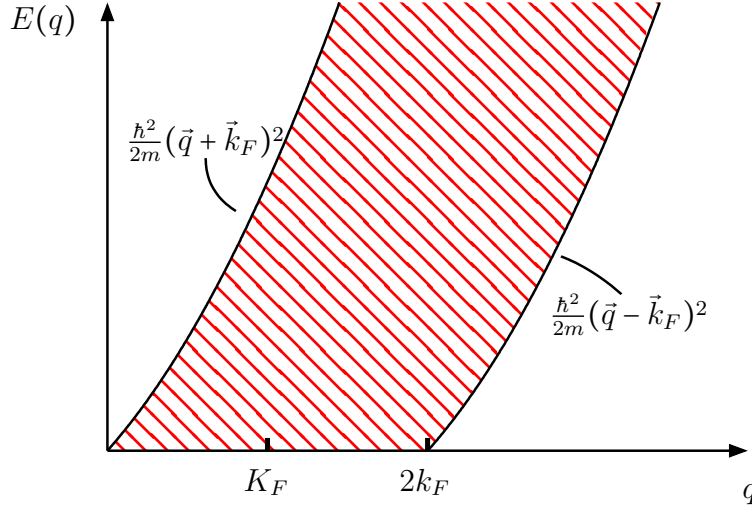


(ii) $q > 2k_F$:

All states inside the Fermi sphere are possible final states and $|\vec{q} - \vec{k}_F| \leq k' \leq |\vec{q} + \vec{k}_F|$, which is the “Fermi sphere” about the point \vec{q} , respectively $E_F < \frac{\hbar^2}{2m}(\vec{q} - \vec{k}_F)^2 \leq \epsilon_{\vec{k}'}, \leq \frac{\hbar^2}{2m}(\vec{q} + \vec{k}_F)^2$ for the energies.



Defining the excitation energy as $E(\vec{q}) := \epsilon_{\vec{k}'} - E_F$ we obtain the region where excitations are possible as the shaded area in the figure below.



Until $q = 2k_F$, the excitations are gapless, i.e. the minimal excitation energy $E_{min} = 0$. For $q > 2k_F$, there is a minimum excitation energy $E_{min}(\vec{q}) = \frac{\hbar^2}{2m}(\vec{q} - \vec{k}_F)^2$. The structure of the excitations is such that an electron is transferred from the interior of the filled Fermi sphere to its outside, leaving a hole at \vec{k} in the Fermi sphere. We thus call the excitations of the Fermi sphere *particle-hole pairs*. It is important to understand that this is more than just a name. In fact, the dynamics of the “hole” must be taken into account. The reason is that in the ground state for every \vec{k} occupied there is another occupied state with $-\vec{k}$, which implies that the total momentum $\vec{K} = 0$. An excited state then has an electron in state $|\vec{k}'| > k_F$ and a “lonely” electron at $-\vec{k}$ in the Fermi sphere. Therefore the total momentum now is $\vec{K} = \vec{k}' + (-\vec{k}) = \vec{q}$. We thus formally need the electron at $-\vec{k}$. However, the tradition is to rather work with the hole at $+\vec{k}$ instead, which is treated like a particle with charge $+e$ and momentum $-\vec{k}$.

3.1.4 Finite temperatures

In contrast to $T = 0$, the properties of the Fermi gas at finite temperatures will be influenced by the excited states. One also talks of *thermal excitation of*

3.1. THE NONINTERACTING ELECTRON GAS

particle-hole pairs in this connection. To describe the thermal effects, we need the partition function or more precisely the probability for the realization of a certain excited state. Let us take as example the expectation value of the Hamilton operator, which for finite T leads to the internal energy. For our jellium model we then have

$$U(T) = \langle \hat{H}_e \rangle_T = \sum_{\vec{k}\sigma} \frac{\hbar^2 k^2}{2m} \langle \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \rangle_T .$$

We thus need to evaluate the thermal expectation value $\langle \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \rangle_T$. The combination of creation and annihilation operator just represents the particle number operator for the state with quantum numbers \vec{k} and σ , and because fermions can occupy each state at most once, $0 \leq \langle \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \rangle_T \leq 1$ must hold, and we can interpret this expectation value also as *occupation probability* of this particular single-particle state. One simple way to calculate it will be discussed in the exercise. Here, I want to use a different approach, which at the same time introduces the important concept of the *chemical potential*.

Quite generally, the probability for a certain state with eigenenergy E in an N -particle system can be written as

$$P_N(E) = \frac{e^{-\beta E}}{\mathcal{Z}} = e^{-\beta(E-F_N)}$$

where $\beta = 1/(k_B T)$, \mathcal{Z} is the partition function and $F_N = -k_B T \ln \mathcal{Z}$ the free energy of the N -particle system. As Fermions can occupy each state at most once, the specification of N different single-particle states defines an N -particle state in the case without interactions.

The probability that a given single-particle state i is occupied can then be written as

$$f_i^N \equiv \langle \hat{c}_i^\dagger \hat{c}_i \rangle_T = \sum'_{\nu} P_N(E_{\nu,i}^N) ,$$

where the sum runs over all states ν with N particles and single-particle state i occupied. The energy corresponding to such a state is $E_{\nu,i}^N$. If we denote with $E_{\nu,i}^{N+1}$ the energy of a system with $N+1$ particles in a state with single-particle level i occupied, the energy of the N -particle system with this level i *not* occupied is given as $E_{\nu,-i}^N = E_{\nu,i}^{N+1} - \epsilon_i$, where ϵ_i is the corresponding energy of the single-particle state i . Thus,

$$f_i^N = 1 - \sum'_{\nu} P_N(E_{\nu,i}^{N+1} - \epsilon_i)$$

and from its definition

$$P_N(E_{\nu,i}^{N+1} - \epsilon_i) = e^{\beta(\epsilon_i + F_N - F_{N+1})} P_{N+1}(E_{\nu,i}^{N+1}) .$$

The quantity $\mu := F_{N+1} - F_N$ is called *chemical potential* and with its help we may write

$$f_i^N = 1 - e^{\beta(\epsilon_i - \mu)} f_i^{N+1}$$

In the thermodynamic limit $N \rightarrow \infty$ we may assume $f_i^N = f_i + O(\frac{1}{N})$ and obtain

$$f(\epsilon_i) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}}$$

the famous *Fermi-Dirac* distribution function.

Some remarks are in order:

- It is very important to remember, that the derivation is only true for noninteracting particles. If an interaction is present, the notion of single-particle states does not make sense any more, and the distribution function can become more complicated.
- For the free electron (or more generally Fermi) gas we have

$$\lim_{T \rightarrow 0} \mu(T) = E_{N+1} - E_N \equiv E_F$$

where the Fermi energy denotes the energy of the *last occupied state*. Again, this identification becomes meaningless for interacting particles. Moreover, there exist situations (semiconductors and insulators), where even for noninteracting particles this relation is not true any more: In this case there is a gap between the last occupied and first unoccupied state, and while E_F is still given by the definition of representing the energy of the last occupied single particle state, the chemical potential can take any value in the gap.

- For temperatures $k_B T \ll E_F$ the physics is dominated by Pauli principle and one speaks of the *degenerate Fermi gas*. The “word” degenerate is meant here in the sense “different from the norm”, which up to the advent of quantum statistics was the Boltzmann distribution.
- To study the limit $k_B T \gg E_F$ one needs to understand what $\mu(T)$ does first. To this end let us take a look at the particle density. We can write

$$n = 2e^{\beta\mu} \int_0^\infty d\epsilon \mathcal{N}(\epsilon) \frac{1}{e^{\beta\mu} + e^{\beta\epsilon}},$$

3.1. THE NONINTERACTING ELECTRON GAS

where we made use of the fact that $\mathcal{N}(\epsilon)$ has to be bounded from below,² choosing this bound to be 0 without loss of generality. In the limit $T \rightarrow \infty$ we have $\beta \rightarrow 0$. If now $\lim_{\beta \rightarrow 0} e^{\beta\mu} = c > 0$, then

$$\lim_{\beta \rightarrow 0} \frac{1}{e^{\beta\mu} + e^{\beta\epsilon}} = \frac{1}{c} \neq 0$$

and the integral diverges. Thus, we *must* have $\mu(T \rightarrow \infty) \rightarrow -\infty$. In that case we however find

$$f(\epsilon_k) \propto e^{-\beta\epsilon_k} ,$$

i.e. we recover the Boltzmann distribution, and we speak of the *non-degenerate Fermi gas*.

With the Fermi-Dirac distribution we now can evaluate the formula for the internal energy and obtain

$$U(T) = \sum_{\vec{k}\sigma} \frac{\hbar^2 k^2}{2m} f_{\vec{k}\sigma} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} f_{\vec{k}\sigma} .$$

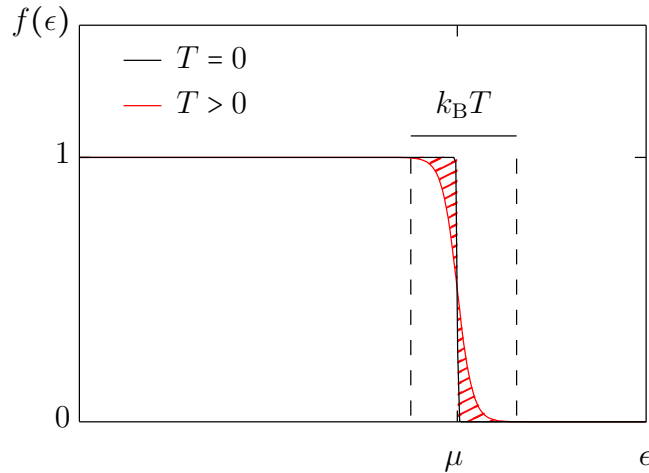


Figure 3.1: Fermi function for $T = 0$ (black line) and $T > 0$ (red line). The states in a region $O(k_B T)$ around the chemical potential is redistributed according to the red shaded area.

The evaluation of this sum (or integral) is in general pretty cumbersome. However, because $f_{\vec{k}\sigma} = f(\epsilon_{\vec{k}})$, one can approximately evaluate the sum for $k_B T/E_F \ll 1$ using the *Sommerfeld expansion* (see appendix A and exercises). To convey the idea let me note that the Fermi function has the structure shown in Fig. 3.1, i.e. it sharply changes in a region $O(k_B T)$ around the Fermi level.

²Otherwise we would find an energy $U(T = 0) = -\infty$.

Thus, only those excitations which are available in this region will actually contribute to the expectation values and it seems naturally that one can expand physical quantities as series in $k_B T$.

After these preliminaries, we are now in the position to calculate physical quantities, for example the internal energy and from it the specific heat. We assume $N = \text{const.}$ together with $V = \text{const.}$ and obtain (exercise) consistent in $O(T^4)$

$$u(T, n) = u(0, n) + \frac{\pi^2}{3} (k_B T)^2 \mathcal{N}(E_F) \quad (3.8)$$

Note that the inclusion of the temperature dependence of μ is essential to obtain this result (otherwise we would find an additional term involving $\mathcal{N}'(E_F)$). From this result we can calculate the specific heat at constant volume heat as

$$c_V = \frac{1}{V} \left(\frac{\partial E(T, N)}{\partial T} \right)_{N, V} = \frac{2\pi^2}{3} k_B^2 \mathcal{N}(E_F) \cdot T \quad (3.9)$$

With $\mathcal{N}(E_F) = \frac{3}{4} \frac{n}{E_F}$ this can be cast into

$$c_V(T) = \frac{\pi^2}{2} k_B n \frac{k_B T}{E_F} \propto \frac{T}{E_F} \propto m \cdot T \quad .$$

The latter proportionality, i.e. $\frac{c_V}{T} \propto m$, is very important as it opens the road to a phenomenological understanding of the properties of the *interacting* Fermi gas. The quantity

$$\lim_{T \rightarrow 0} \frac{c_V(T)}{T} =: \gamma$$

is called *Sommerfeld coefficient of the specific heat*.

In anticipation of what we will learn in chapter 6 let us add to this *electronic contribution* the part coming from lattice vibrations (see eq. (6.4))

to obtain for the total specific heat of a crystal at low temperatures

$$c_V(T) = \gamma \cdot T + \beta \cdot T^3 \quad .$$

Therefore, plotting $\frac{c_V(T)}{T}$ versus T^2 will yield at the same time information about the lattice part (slope) and the electronic part (offset).

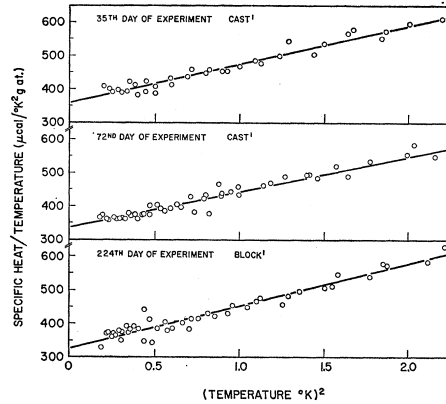


Figure 3.2: Low-temperature specific heat of sodium.

3.1. THE NONINTERACTING ELECTRON GAS

Taking into account the fact, that the result (3.9) was derived for non-interacting electrons in free space, it is quite astonishing that one actually finds such a behavior in the experiment for a large number of metals. As an example Fig. 3.2³ shows experimental data for the specific heat plotted versus T^2 for three different sodium samples.

However, although for low enough temperatures the dependence on T qualitatively agrees with the Fermi gas prediction, one observes important differences in the details. For example, the free Fermi gas predicts values

$$\gamma_0 \approx 1 \dots 10 \frac{\text{mJ}}{\text{mol K}^2}$$

for the Sommerfeld coefficient, while experiments yield

$$10^{-3} \frac{\text{mJ}}{\text{mol K}^2} \lesssim \gamma \lesssim 10^3 \frac{\text{mJ}}{\text{mol K}^2} ,$$

depending on the class of compounds studied. This deviation has two major reasons. Firstly, electrons of course do interact. Typically, interactions have the tendency to enhance γ . Why they do not completely destroy the Fermi gas behaviour will be discussed in section 3.2.2. Secondly, we so far also have neglected the existence of a lattice. Its influence can go in both directions. In semiconductors for example it is responsible for the extremely small values of the Sommerfeld coefficient.

3.1.5 The Fermi gas in a magnetic field

The classical theory of charges in a homogeneous magnetic field leads to a circular motion in a plane perpendicular to the field due to the Lorentz force. Without interaction, the classical Hamilton function of an electron with charge $q = -e$ is

$$H = \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 .$$

For a homogeneous field B_0 in z -direction one can choose $\vec{A} = (0, B_0 x, 0)$ (*Landau gauge*) and obtains as equations of motion

$$\begin{aligned} \dot{\vec{r}} &= \frac{1}{m} \left(\vec{p} + \frac{e}{c} \vec{A} \right) \\ \dot{\vec{p}} &= -\frac{e}{c} \dot{\vec{r}} \times \vec{B} \end{aligned}$$

or as $\vec{B} = B_0 \vec{e}_z$

$$\begin{aligned} \ddot{x} &= -\omega_c (\dot{y} + \omega_c x) \\ \ddot{y} &= \omega_c \dot{x} \\ \ddot{z} &= 0 , \end{aligned}$$

³Taken from D.L. Martin, Phys. Rev. **124**, 438 (1961).

i.e. circular orbits in the x - y plane with a circular frequency

$$\omega_c = \frac{eB_0}{mc}$$

called *cyclotron frequency*.

Quantum mechanically, the Hamilton function is mapped to the Hamilton operator and one has to include the spin (we neglect spin-orbit coupling, though).

The result is

$$\hat{H} = \frac{1}{2m} \left(\hat{\vec{p}} + \frac{e}{c} \vec{A}(\hat{\vec{r}}) \right)^2 + \frac{g\mu_B}{\hbar} \hat{\vec{s}} \cdot \vec{B}, \quad \mu_B = \frac{e\hbar}{2mc}, \quad g = 2.$$

As usual, $[\hat{H}, \hat{p}_z] = 0$, i.e. the eigenvectors and -values of \hat{H} can be characterised by the quantum number $p_z = \hbar k_z$. The physical reason is that the magnetic field does not destroy the translational invariance parallel to the magnetic field. The components of the operator $\hat{\Pi} := \hat{\vec{p}} + \frac{e}{c} \vec{A}(\hat{\vec{r}})$ on the other hand have the commutators

$$\begin{aligned} [\hat{\Pi}_z, \hat{\Pi}_y] &= [\hat{\Pi}_z, \hat{\Pi}_x] = 0 \\ [\hat{\Pi}_x, \hat{\Pi}_y] &= \frac{e}{c} [\hat{p}_x \hat{A}_y - \hat{A}_y \hat{p}_x] = -i \frac{\hbar e}{c} B_0 \neq 0. \end{aligned}$$

The last equation tells us, that we cannot diagonalise $\hat{\Pi}_x$ and $\hat{\Pi}_y$ simultaneously, for example using plane waves. We may however pick one, say $\hat{\Pi}_y$, and diagonalise that together with $\hat{\Pi}_z$ using plane waves. For the eigenfunctions of the Hamiltonian we then can try the separation ansatz

$$\Psi(\vec{r}) = e^{i(k_y y + k_z z)} \varphi(x).$$

The action of $\hat{\Pi}_y$ on this wave function is

$$\begin{aligned} \hat{\Pi}_y \Psi(\vec{r}) &= \left(-\frac{\hbar}{i} \partial_y + \frac{e}{c} B_0 x \right) \Psi(\vec{r}) = \left(-\hbar k_y + \frac{e}{c} B_0 x \right) \Psi(\vec{r}) \\ \hat{\Pi}_y^2 \Psi(\vec{r}) &= \left(-\hbar k_y + \frac{e}{c} B_0 x \right) \hat{\Pi}_y \Psi(\vec{r}) \\ &= \left(\underbrace{m \frac{eB_0}{mc}}_{= \omega_c} x - \hbar k_y \right)^2 \Psi(\vec{r}) \\ &= m^2 \omega_c^2 \left(x - \underbrace{\frac{\hbar k_y}{m\omega_c}}_{=: x_0} \right)^2 \Psi(\vec{r}). \end{aligned}$$

Together with $\hat{\Pi}_x^2 = -\hbar^2 \partial_x^2$ one arrives at the differential equation

$$-\frac{\hbar^2}{2m} \varphi'' + \frac{m\omega_c^2}{2} (x - x_0)^2 \varphi = \left(\epsilon - \frac{\hbar^2 k_z^2}{2m} \right) \varphi.$$

3.1. THE NONINTERACTING ELECTRON GAS

This differential equation is nothing but a shifted one dimensional harmonic oscillator. The eigenvalues of \hat{H} thus are

$$\epsilon_{nk_z\sigma} = \hbar\omega_c \left(n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m} + g \frac{\hbar\mu_B}{2} \sigma B_0 \quad , \quad (3.10)$$

where $n \in \mathbb{N}_0$ and $\sigma = \pm$. We further assume our standard box of dimension L_z in z -direction yielding discrete values $k_z = \frac{2\pi}{L_z} n_z$ with $n_z \in \mathbb{Z}$. Since $\mu_B B_0 = \frac{e\hbar B_0}{2mc} = \frac{\hbar\omega_c}{2}$ and $g = 2$ this expression can be simplified to

$$\epsilon_{nk_z\sigma} = \hbar\omega_c \left(n + \frac{1 + \sigma}{2} \right) + \frac{\hbar^2 k_z^2}{2m} \quad . \quad (3.11)$$

The motion of a quantum mechanical charged particle in a homogeneous magnetic field is thus quantized in the plane perpendicular to the field. This effect is called *Landau quantization* and the resulting levels are called *Landau levels*. A very important aspect is that the Landau levels are highly degenerate. The coordinate of the center $x_0 \sim k_y$. If we assume a periodicity L_y in y -direction, $k_y = \frac{2\pi}{L_y} n_y$ with $n_y \in \mathbb{Z}$, i.e.

$$x_0 = \frac{\hbar}{m\omega_c} \frac{2\pi}{L_y} n_y \quad .$$

Furthermore, $0 \leq x_0 \leq L_x$ or

$$0 \leq n_y \leq \frac{m\omega_c L_x L_y}{2\pi\hbar} = \frac{B_0}{2\pi\hbar c/e} L_x L_y =: N_L \quad .$$

The combination $\Phi_0 := \frac{2\pi\hbar c}{e}$ is called *flux quantum*. The quantity $\Phi := B_0 L_x L_y$ on the other hand is the magnetic flux through the x - y -plane of our system. One therefore can write the degeneracy as

$$N_L = \frac{\Phi}{\Phi_0} \quad ,$$

i.e. the number of flux quanta piercing the x - y -plane.

In order to calculate physical quantities we need an expression for the free energy. As we have learned in chapter 2, the Hamiltonian for a noninteracting system can be represented with the help of creation and annihilation operators as

$$\hat{H} = \sum_{\alpha} \epsilon_{\alpha} \hat{c}_{\alpha}^{\dagger} \hat{c}_{\alpha} \quad ,$$

where α collects the relevant quantum numbers and the anticommutator relations $\{\hat{c}_\alpha^\dagger, \hat{a}_\beta\} = \delta_{\alpha\beta}$ hold. The partition function is then given as

$$\begin{aligned}\mathcal{Z} &= \text{Tr} e^{-\beta(\hat{H}-\mu\hat{N})} \\ \hat{N} &= \sum_{\alpha} \hat{c}_\alpha^\dagger \hat{c}_\alpha ,\end{aligned}$$

with the chemical potential μ . The free energy finally is obtained via

$$F = -k_B T \ln \mathcal{Z} + \mu N .$$

With

$$\hat{H} - \mu\hat{N} = \sum_{\alpha} (\epsilon_{\alpha} - \mu) \hat{c}_\alpha^\dagger \hat{c}_\alpha$$

we find

$$\begin{aligned}\mathcal{Z} &= \text{Tr} \exp \left[-\beta \sum_{\alpha} (\epsilon_{\alpha} - \mu) \hat{c}_\alpha^\dagger \hat{c}_\alpha \right] \\ &= \prod_{\alpha} \sum_{n_{\alpha}=0}^1 e^{-\beta(\epsilon_{\alpha}-\mu)n_{\alpha}} \\ &= \prod_{\alpha} \left[1 + e^{-\beta(\epsilon_{\alpha}-\mu)} \right] .\end{aligned}$$

For the free energy, inserting the actual quantum numbers n , σ and k_z again for α , one thus gets

$$\begin{aligned}F &= \mu N - k_B T \sum_{nk_z\sigma} \ln \left[1 + e^{-\beta(\epsilon_{nk_z\sigma}-\mu)} \right] \\ &= \mu N - V k_B T \int_{-\infty}^{\infty} d\epsilon \mathcal{N}(\epsilon) \ln \left[1 + e^{-\beta(\epsilon-\mu)} \right]\end{aligned}\quad (3.12)$$

where we again introduced the density of states. To obtain an expression for $\mathcal{N}(\epsilon)$, let us first recall that each set of quantum numbers $\{n, k_z, \sigma\}$ has a degeneracy N_L . The density of states then is

$$\frac{N_L}{V} \sum_{nk\sigma} \delta(\epsilon - \epsilon_{nk\sigma}) \rightarrow \frac{N_L}{V} \frac{L_z}{2\pi} \int_{-\infty}^{\infty} dk \delta(\epsilon - \epsilon_{nk\sigma}) = \frac{N_L L_z}{2\pi V} \int dk \left(\left| \frac{\partial \epsilon_{nk\sigma}}{\partial k} \right|_{k=k_0} \right)^{-1} \delta(k - k_0) ,$$

where $\epsilon_{nk_0\sigma} = \epsilon$. With $V = L_x L_y L_z$ and the definition of N_L we finally obtain

$$\mathcal{N}(\epsilon) = \frac{1}{8\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \hbar\omega_c \sum_{n\sigma} \frac{\Theta\left(\epsilon - \hbar\omega_c \left(n + \frac{1+\sigma}{2}\right)\right)}{\sqrt{\epsilon - \hbar\omega_c \left(n + \frac{1+\sigma}{2}\right)}} .$$

The density of states is shown in Fig. 3.3. It features characteristic square root singularities for energies $\epsilon = n\hbar\omega_c$.

3.1. THE NONINTERACTING ELECTRON GAS

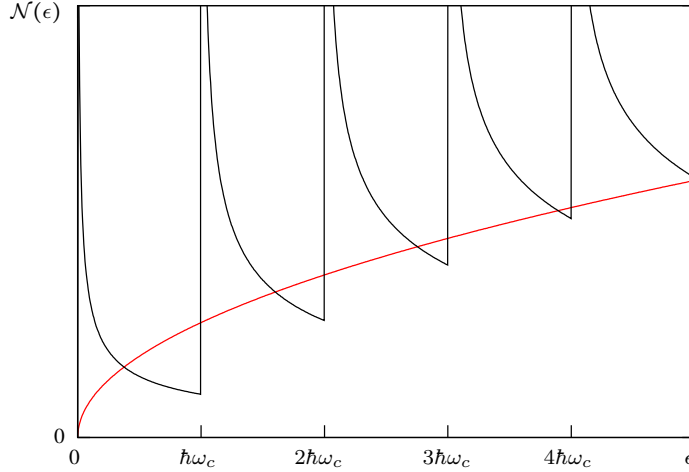


Figure 3.3: Density of states for finite magnetic field. The red line represents the corresponding density of states for $B_0 = 0$.

Another question one can ask is what happens to the Fermi sphere present for $B_0 = 0$. Due to the Landau quantisation there exist only discrete values for $k_{\perp} = (k_x^2 + k_y^2)^{1/2}$. In other words, the possible states live on concentric cylinders in \vec{k} space parallel to the z axis. This is schematically depicted in Fig. 3.4. The degeneracy of each level N_L together with the requirement that

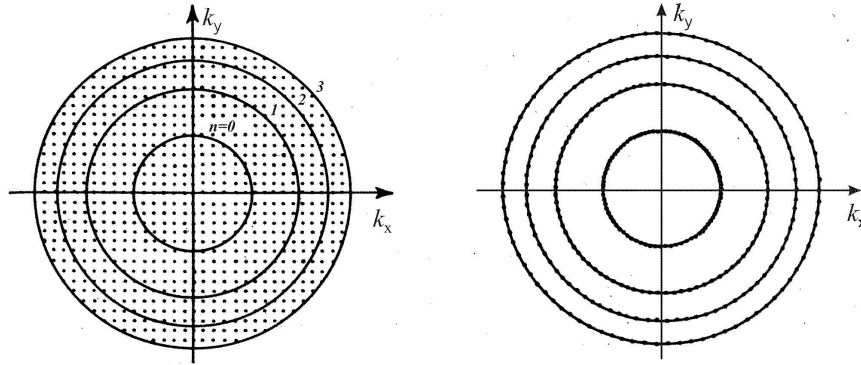


Figure 3.4: Left: Distribution of states in \vec{k} space without magnetic field. Right: Landau cylinders as location of electronic states for finite magnetic field.

the integral over all \vec{k} vectors must equal to the number of electrons in the system determines the number of cylinders and for each cylinder a maximal value of k_z . One then finds that the Fermi points are given by the intersection of the Fermi sphere for $B_0 = 0$ with the set of Landau cylinders. Increasing the magnetic field will enlarge the radius of the cylinders and periodically some cylinder will just touch the Fermi sphere. Quite obviously such situation will

occur periodically in the field and lead to some kind of oscillations. We will discuss later how these oscillations depend on B_0 and give an idea how they can be used to measure for example the Fermi surface.

Let us first turn to the calculation of the magnetization

$$m_z = -\frac{1}{V} \left(\frac{\partial F}{\partial B_0} \right)_{T,N}$$

induced by the external field and the susceptibility

$$\chi = \frac{\partial m_z}{\partial B_0} .$$

To this end we must evaluate the expression (3.12) for the free energy and differentiate it with respect to B_0 . This task turns out to be rather tedious (see for example W. Nolting, *Quantum Theory of Magnetism*), therefore I quote the result only. For low T and field B_0 , more precisely $\frac{k_B T}{E_F}$, $\frac{\mu_B B_0}{E_F} \ll 1$, and within a Sommerfeld expansion one finds

$$m_z = \frac{2}{3} n \frac{\mu_B^2}{E_F} B_0 \left\{ 1 - \frac{1}{3} + \mathcal{F}_{\text{osz}}(B_0) \right\} \quad (3.13a)$$

$$\mathcal{F}_{\text{osz}}(B_0) = \frac{\pi k_B T}{\mu_B B_0} \sqrt{\frac{E_F}{\mu_B B_0}} \sum_{l=1}^{\infty} \frac{1}{\sqrt{l}} \frac{\sin\left(\frac{\pi}{4} - l\pi \frac{E_F}{\mu_B B_0}\right)}{\sinh\left(l\pi \frac{\pi k_B T}{\mu_B B_0}\right)} + \mathcal{O}\left(\frac{\mu_B B_0}{E_F}\right) \quad (3.13b)$$

Note that in particular $\frac{\mu_B B_0}{E_F} \ll 1$ is fulfilled for any reasonable field strength, because a field of 1T roughly corresponds to an energy of $1e^{-4}$ eV. On the other hand, except for some exotic materials, $E_F \approx 1$ eV. As even in the best high-field laboratories one cannot achieve fields beyond 60T,⁴ the condition is hardly in danger to become violated.

Let us discuss the three individual terms:

- The contribution

$$m_z^{(1)} := \frac{2}{3} n \frac{\mu_B^2}{E_F} B_0$$

describes the *Pauli spin paramagnetism*. The corresponding contribution

$$\chi_P = \frac{m_z^{(1)}}{B_0} = \frac{2}{3} n \frac{\mu_B^2}{E_F} \quad (3.14)$$

⁴The highest man-made fields were produced in nuclear explosions and went up to ~ 200 T for the duration of a few nanoseconds. Of course, the probe is evaporized afterwards, and whether such an experiment really measures thermal equilibrium is all but clear.

3.1. THE NONINTERACTING ELECTRON GAS

to the susceptibility is called *Pauli susceptibility*. Its origin is very simply the Zeeman splitting $\pm g\mu_B B_0$ of the electronic energy levels. To see this let us note that for spin up the energy levels are *lowered* by an amount $g\mu_B B_0/2 = \mu_B B_0$, while spin down becomes higher in energy by the same amount. For the particle density this means

$$n = n_{\uparrow} + n_{\downarrow} = \int_{-\infty}^{E_F + \mu_B B_0} d\epsilon \mathcal{N}(\epsilon) + \int_{-\infty}^{E_F - \mu_B B_0} d\epsilon \mathcal{N}(\epsilon) = 2 \int_{-\infty}^{E_F} d\epsilon \mathcal{N}(\epsilon) + \mathcal{O} \left[\left(\frac{\mu_B B_0}{E_F} \right)^2 \right],$$

i.e. E_F does not change to lowest order in the field, while for the difference of up and down particles we find

$$\Delta N = n_{\uparrow} - n_{\downarrow} = \int_{-\infty}^{E_F + \mu_B B_0} d\epsilon \mathcal{N}(\epsilon) - \int_{-\infty}^{E_F - \mu_B B_0} d\epsilon \mathcal{N}(\epsilon) \approx 2\mu_B B_0 \mathcal{N}(E_F) = \frac{2}{3} n \frac{\mu_B}{E_F} B_0.$$

For the magnetization one finally obtains $m_z = \frac{g\mu_B}{2} (n_{\uparrow} - n_{\downarrow})$, and hence the above expression.

- The second term

$$m_z^{(2)} = -\frac{1}{3} \frac{3}{2} n \frac{\mu_B^2}{E_F} B_0 = -\frac{1}{3} m_z^{(1)}$$

is negative and describes *Landau-Peierls diamagnetism*. It has a contribution

$$\chi_L = -\frac{1}{3} \chi_P \quad (3.15)$$

to the susceptibility. Here, a rather intuitive interpretation is possible, too. The electrons “move” on circles (“cyclotron orbits”), which induces a magnetic orbital moment. As this moment is connected to a circular current, Lenz’s rule applies, which states, that this moment counteracts an external field, hence the diamagnetic response.

Quite obviously Pauli paramagnetism always wins for free electrons. However, up to now we did not take into account the existence of a periodic lattice potential. Without going into detail here, one of its actions is the change the properties of the electronic dispersion. In most cases this can be taken into account by a replacement $m_e \rightarrow m^*$ for the mass of the electrons entering in the free dispersion, i.e. use a relation $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m^*}$. Now a subtle difference in deriving the contributions $m_z^{(1)}$ and $m_z^{(2)}$ comes into play. For the former, μ_B is a fundamental constant connected to the spin degree of freedom. For the latter, on the other hand, it is the orbital

motion that leads to the response, which in turn is intimately connected with the dispersion via $\frac{1}{2m^*} (\vec{p} - \frac{e}{c} \vec{A})^2$. Hence, for Landau diamagnetism we must use

$$\mu_B \rightarrow \mu_B^* = \frac{e\hbar}{2m^*c}$$

instead, and obtain

$$\begin{aligned} \chi_L &= -\frac{1}{3} \frac{3}{2} \left(\frac{e\hbar}{2m^*c} \right)^2 \frac{n}{E_F} = -\frac{1}{3} \frac{3}{2} \left(\frac{e\hbar}{2m_e c} \right)^2 \left(\frac{m_e}{m^*} \right)^2 \\ &= -\frac{1}{3} \left(\frac{m_e}{m^*} \right)^2 \chi_P . \end{aligned} \quad (3.16)$$

This has as one consequence, that for $m^* > m_e/\sqrt{3}$ always Pauli paramagnetism wins. However, for $m^* < m_e/\sqrt{3}$ the system can actually show diamagnetic response. This is in particular observed in semiconductors, where effective masses can take on values as small as $10^{-3}m_e$.

- The last part $m_z^{(3)}$ leads to *quantum oscillations* as function of the external field B_0 . The susceptibility in *lowest order* in $\mu_B B_0/E_F$ and $k_B T/E_F$ is given by

$$\chi_{\text{osz}} \approx \frac{3}{2} n \sqrt{\frac{E_F}{\mu_B B_0}} \frac{\pi^2 k_B T}{\mu_B B_0} \frac{\mu_B}{B_0} \sum_{l=1}^{\infty} \sqrt{l} \frac{\cos\left(\frac{\pi}{4} - \pi l \frac{E_F}{\mu_B B_0}\right)}{\sinh\left(\pi l \frac{\pi k_B T}{\mu_B B_0}\right)} \quad (3.17)$$

According to our previous discussion, there will appear certain modifications in the presence of a periodic lattice potential (see e.g. W. Nolting, *Quantum Theory of Magnetism*), we will however not further discuss here.

Inspecting the relation (3.17) more closely, it becomes apparent that this contribution plays only a role for $k_B T \ll \mu_B B_0$, as otherwise the denominator in the sum will lead to an exponential suppression of even the lowest order terms. If this condition is fulfilled, one can expect oscillations with a fundamental period

$$\begin{aligned} 2\pi &= \frac{\pi E_F}{\mu_B} \frac{1}{B_0^{(1)}} - \frac{\pi E_F}{\mu_B} \frac{1}{B_0^{(2)}} \\ &= \frac{\pi E_F}{\mu_B} \Delta \left(\frac{1}{B_0} \right) , \end{aligned}$$

where we have assumed $B_0^{(1)} < B_0^{(2)}$. The period in $1/B_0$ thus becomes

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

$$\Delta\left(\frac{1}{B_0}\right) = \frac{2\mu_B}{E_F} . \quad (3.18)$$

These oscillation in the magnetic susceptibility are called *de Haas - van Alphen effect*. Similar oscillations appear in several other physical quantities, for example in the resistivity, where they are called *Shubnikov - de Haas oscillations*.

An important experimental implementation is based on the picture of Landau cylinders intersecting the Fermi surface. As already mentioned in the discussion of Fig. 3.4, increasing the field will increase the radius of the cylinders, and eventually the outermost will barely touch the Fermi surface along some extremal direction. As for the free electron gas, the Fermi surface is a sphere, the effect will be homogeneous for all field directions. One can however imagine, that for a real crystal the Fermi surface will be deformed in accordance with the space group of the crystal. Now there may actually be different extremal cross sections, and hence also different oscillation periods. Measuring χ_{osz} and analysing these different periods one can obtain rather detailed experimental information about the Fermi surface.

3.2 Beyond the independent electron approximation

Up to now we have assumed that the electrons can be treated as non-interacting particles (the so-called *independent electron approximation*). In the following we will discuss some effects of the interaction and in particular how to take them into account. We will not yet include the periodic lattice, but stay within the free electron approximation.

3.2.1 Hartree-Fock approximation

Let me start with a rather simple approximation, which however is quite useful to obtain some idea what type of effects interactions and Pauli's principle will have. To this end we write the Hamiltonian of the free electron gas in second quantization as

$$\hat{H} = \sum_{\vec{k}\sigma} \frac{\hbar^2 k^2}{2m} \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} + \frac{1}{2} \sum_{\vec{q}} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} V_{\vec{q}} \hat{c}_{\vec{k}+\vec{q}\sigma}^\dagger \hat{c}_{\vec{k}'-\vec{q}\sigma'}^\dagger \hat{c}_{\vec{k}'\sigma'} \hat{c}_{\vec{k}\sigma} \quad (3.19)$$

where

$$V_{\vec{q}} = \frac{4\pi e^2}{V q^2}$$

is the Fourier transform of the Coulomb interaction. At first, the term $\vec{q} = 0$ seems to be troublesome. To see its meaning, let us rewrite

$$V_{\vec{q}} \rightarrow V_{\vec{q}} = \lim_{\alpha \rightarrow 0} \frac{4\pi}{V} \frac{e^2}{q^2 + \alpha^2}$$

and study the contribution from $\vec{q} \rightarrow 0$ for α finite. We then have

$$\begin{aligned} E_{ee} &= \frac{4\pi}{V} \frac{e^2}{\alpha^2} \frac{1}{2} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} \langle \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}'\sigma'}^\dagger \hat{c}_{\vec{k}'\sigma'} \hat{c}_{\vec{k}\sigma} \rangle = \frac{4\pi}{V} \frac{e^2}{\alpha^2} \frac{1}{2} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} \langle \hat{n}_{\vec{k}\sigma} (\hat{n}_{\vec{k}'\sigma'} - \delta_{\vec{k}\vec{k}'} \delta_{\sigma\sigma'}) \rangle \\ &= \frac{4\pi}{V} \frac{e^2}{\alpha^2} \frac{1}{2} N(N-1) \quad , \end{aligned}$$

where N is the particle number. Even with $\alpha > 0$ this term is disturbing, because it is extensive and thus represents a relevant contribution to the energy of the system. However, up to now we have not cared for the positive homogeneous charge background ensuring charge neutrality. Calculating its energy, we find a contribution

$$\begin{aligned} E_{NN} &= \frac{4\pi}{V} \frac{e^2}{\alpha^2} \frac{1}{2} \sum_{i \neq j} \\ &= \frac{4\pi}{V} \frac{e^2}{\alpha^2} \frac{1}{2} N(N-1) \quad . \end{aligned}$$

On the other hand, the interaction energy between electrons and this positive background charge contributes

$$E_{eN} = -\frac{4\pi}{V} \frac{e^2}{\alpha^2} N^2 \quad .$$

Thus, taking all three terms together, we find the $\vec{q} = 0$ part is almost cancelled exactly due to charge neutrality. There is one term remaining, namely

$$\delta E = -\frac{4\pi}{V} \frac{e^2}{\alpha^2} N = -\frac{4\pi e^2}{\alpha^2} n = -V_{\vec{q}=0} \frac{1}{V} \sum_{\vec{k}\sigma} f(\epsilon_{\vec{k}}) \quad .$$

The details of the Hartree-Fock treatment are given in appendix B with the result (B.3). Note that Fock part with $\vec{q} = 0$, when summed over \vec{k} and spin σ , yields precisely the contributions to δE above. Put into a Hamiltonian one finds

$$\begin{aligned} \hat{H}_{\text{HF}} &= \sum_{\vec{k}\sigma} E_{\vec{k}} \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \\ E_{\vec{k}} &= \epsilon_{\vec{k}} - \sum_{\vec{q}} V_{\vec{q}} f(E_{\vec{k}+\vec{q}}) \quad . \end{aligned}$$

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

According to the discussion at the end of appendix B the \vec{q} integral can be evaluated for $T = 0$ as

$$\begin{aligned} \sum_{\vec{q}} V_{\vec{q}} f(E_{\vec{k}+\vec{q}}) &= 4\pi e^2 \int_{k' \leq k_F} \frac{d^3 k'}{(2\pi)^3} \frac{1}{|\vec{k} - \vec{k}'|^2} \\ &= \frac{e^2}{\pi} \int_0^{k_F} (k')^2 dk' \int_{-1}^1 d \cos \vartheta \frac{1}{k^2 + (k')^2 - 2kk' \cos \vartheta} \\ &= \dots \\ &= \frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right) \\ F(x) &= \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \end{aligned}$$

Finally, for the dispersion one arrives at

$$E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right) .$$

The function $F(x)$ is called *Lindhard function*. Its graph is shown in the left

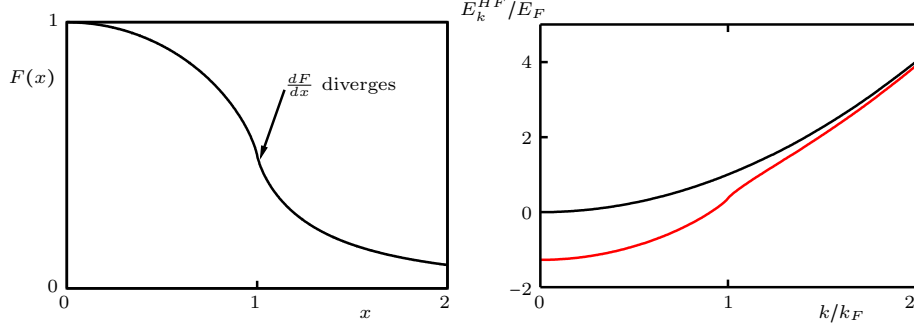


Figure 3.5: Lindhard function and Hartree-Fock dispersion.

panel of Fig. 3.5, and the Hartree-Fock dispersion as red curve in the right panel in comparison to the non-interacting dispersion included as black line.

The ground-state energy can be calculated, too, with the result

$$\frac{E_0}{V} = \sum_{k \leq k_F} E_k^{HF} = \frac{3}{5} E_F - \frac{3e^2}{4\pi} k_F .$$

Note that we have a reduction of the ground state energy, although the Coulomb repulsion at first sight should give a positive contribution. This negative contribution is again a quantum effect arising from the exchange or Fock part.

It is custom to represent the energy in atomic units $\frac{e^2}{2a_B} = 13.6\text{eV}$. Then

$$\frac{E_0}{V} = \frac{e^2}{2a_B} \left[\frac{3}{5} (k_F a_B)^2 - \frac{3}{2\pi} k_F a_B \right] = \left[\frac{2.21}{(r_s/a_B)^2} - \frac{0.916}{r_s/a_B} \right] \frac{e^2}{2a_B} .$$

In the last step we introduced the quantity r_s , which is defined as the radius of the sphere which has the volume equivalent to the volume per electron:

$$\frac{V}{N_e} = \frac{1}{n} =: \frac{4\pi}{3} r_s^3 \Leftrightarrow r_s = r_s[n] = \left(\frac{3}{4\pi n} \right)^{1/3} . \quad (3.20)$$

As r_s is a “functional” of the electron density n , the same is true for the ground state energy, i.e. $E_0 = E[n]$.

The result for E_k^{HF} has one deficiency, namely $\vec{\nabla}_{\vec{k}} E_k^{HF} \rightarrow \infty$ as $k \rightarrow k_F$. As $\vec{v}_{\vec{k}} := \vec{\nabla}_{\vec{k}} E_k^{HF}$ is the group velocity of the electrons, such a divergence is a serious problem. The reason for this divergence is that the Coulomb repulsion is extremely long-ranged. Obviously, this divergence has to be removed somehow, as nature is stable. We will come back to this point later.

The exchange contribution to the Hartree-Fock energy can be rewritten as

$$\begin{aligned} \sum_{\vec{q}} V_{\vec{q}} f(E_{\vec{k}+\vec{q}}) &= \int_V d^3r \frac{e}{r} \rho_{\vec{k}}^{xc}(\vec{r}) \\ \rho_{\vec{k}}^{xc}(\vec{r}) &= -\frac{e}{V} \sum_{k' \leq k_F} e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}} . \end{aligned}$$

The quantity $\rho_{\vec{k}}^{xc}(\vec{r})$ is called *exchange charge density* and is non-local even for the homogeneous electron gas. It can be evaluated to

$$\rho_{\vec{k}}^{xc}(\vec{r}) = -\frac{3en}{2} \frac{e^{ikr}}{(k_F r)^3} [k_F r \cos(k_F r) - \sin(k_F r)] .$$

A more intuitive quantity is the total exchange charge density obtained from summing $\rho_{\vec{k}}^{xc}(\vec{r})$ over $k \leq k_F$. The result is

$$\langle \rho_{\vec{k}}^{xc}(\vec{r}) \rangle := \frac{1}{V} \sum_{k \leq k_F, \sigma} \rho_{\vec{k}}^{xc}(\vec{r}) = -\frac{9ne}{2} \frac{1}{(k_F r)^6} [k_F r \cos(k_F r) - \sin(k_F r)]^2 .$$

It describes the *average change of the charge density induced by an electron at the origin in a distance r due to Pauli’s principle*. Again it must be emphasized that this is a purely quantum mechanical phenomenon! This exchange charge density oscillates in a characteristic manner. These oscillations are caused by the existence of a sharp Fermi surface and called *Friedel oscillations*.

For large r the exchange charge density $\langle \rho_{\vec{k}}^{xc}(\vec{r}) \rangle$ goes to zero $\propto r^{-4}$. For small r , on the other hand, we can expand the different parts and obtain

$$\begin{aligned} \langle \rho_{\vec{k}}^{xc}(\vec{r} \rightarrow 0) \rangle &\approx -\frac{9en}{2} \frac{1}{(k_F r)^6} \left[k_F r - \frac{1}{2} (k_F r)^3 - k_F r + \frac{1}{6} (k_F r)^3 \right]^2 \\ &= -\frac{1}{2} en . \end{aligned}$$

Thus, in the vicinity of a given electron, the “effective” charge density seen by another electron is $\rho_{eff} = \rho_0 + \langle \rho_{\vec{k}}^{xc}(\vec{r} \rightarrow 0) \rangle \approx en - \frac{1}{2} en = \frac{1}{2} en!$ This characteristic

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

reduction of the effective charge density is called *exchange hole*. In Hartree-Fock theory one considers only contributions among one spin species. If one takes into account the Coulomb correlations beyond Hartree-Fock, one obtains due to the presence of the other spin species a further *correlation hole* $-\frac{1}{2}en$, i.e. the effective *electronic* charge density in the vicinity of a given electron is

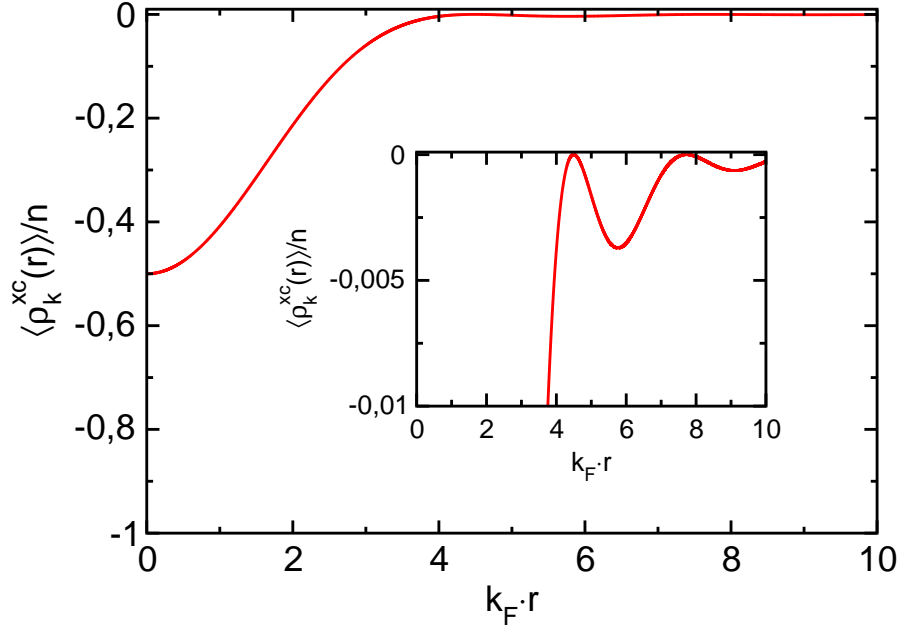


Figure 3.6: Exchange charge density $\langle \rho_k^{xc}(\vec{r}) \rangle / n$ as function of $k_F \cdot r$.

actually reduced to zero! Thus, in practice, every electron can be thought of being “dressed” with an *exchange-correlation hole* it has to carry along during its motion. Such a parcel will of course hinder the motion, and to an “outsider” the electron will appear as having a larger mass. In this sense it will no longer be the electron we know from vacuum, but some modified creature one calls *quasi electron* or more general *quasi particle*.

The concept of quasi-particles is a very common and powerful one. In fact, all “particles” you know (electrons, quarks, mesons, photons, ...) are actually quasi-particles, because we never see them as completely isolated individuals, but in an interacting environment which usually completely modifies their properties.

3.2.2 Landau’s Fermi liquid theory

The properties of the noninteracting electron gas can be summarized as follows: It has a specific heat $c_V(T) = \gamma T$ with a temperature independent Sommerfeld constant γ , a magnetic Pauli susceptibility $\chi_P(T) = \text{const.}$ and a bulk modulus

$B_T(T) = \text{const.}$ for $k_B T \ll E_F$. Another interesting quantity is the so-called *Wilson ratio*

$$R_W := \frac{4\pi^2 k_B^2}{3(g\mu_B)^2} \frac{\chi_P}{\gamma} . \quad (3.21)$$

For the noninteracting electron gas we have $R_W = 1$.

The astonishing *experimental* observation now is that for many metallic solids at low temperature⁵ one again finds the same behavior for the electronic contributions to specific heat, susceptibility and bulk modulus, together with a Wilson ratio $R_W = O(1)$. It thus seems that in spite of the long-ranged and strong Coulomb repulsion among the electrons the low-temperature properties can be well approximated by ignoring the Coulomb interaction.

A partial solution to this puzzle is provided by inspecting the response of the electron gas to an external charge or electrostatic potential. With standard arguments from electrostatics such an external charge will, due to the mobility of the electrons, lead to a total charge density $\rho(\vec{r}) = \rho^{\text{ext}}(\vec{r}) + \rho^{\text{ind}}(\vec{r})$ and a total electrostatic potential $\Phi(\vec{r}) = \Phi^{\text{ext}}(\vec{r}) + \Phi^{\text{ind}}(\vec{r})$, which are related through Poisson's equation. For a homogeneous and isotropic system, the total and external potential are related via a dielectric function according to

$$\Phi(\vec{r}) = \int d^3r' \varepsilon(\vec{r} - \vec{r}') \Phi^{\text{ext}}(\vec{r}') .$$

After a spatial Fourier transformation this relation becomes

$$\Phi^{\text{ext}}(\vec{q}) = \varepsilon(\vec{q}) \Phi(\vec{q}) .$$

In Fourier space the Poisson equations for the external and total charge have the form⁶ $q^2 \Phi^{\text{ext}}(\vec{q}) = 4\pi \rho^{\text{ext}}(\vec{q})$ and $q^2 \Phi(\vec{q}) = 4\pi \rho(\vec{q})$. Together with $\rho^{\text{ext}} = \rho - \rho^{\text{ind}}$ one can identify

$$\varepsilon(\vec{q}) = 1 - \frac{4\pi \rho^{\text{ind}}(\vec{q})}{q^2 \Phi(\vec{q})} .$$

Thus, what we need is a relation between the total potential and the induced charge density.

To this end we try to approximately solve the Schrödinger equation for our test charge in the presence of the total electrostatic potential, i.e.

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi_i(\vec{r}) - e\Phi(\vec{r})\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) .$$

To proceed we assume that $\Phi(\vec{r})$ (and consequently also $\rho(\vec{r})$) varies only little over atomic length scales as shown in Fig. 3.7, i.e. we assume that $|\vec{\nabla}^2 \Phi| \ll |\vec{\nabla}^2 \psi_i|$

⁵Typically well below 300K.

⁶Remember: $\vec{\nabla}^2 \xrightarrow{\text{FT}} -q^2$.

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

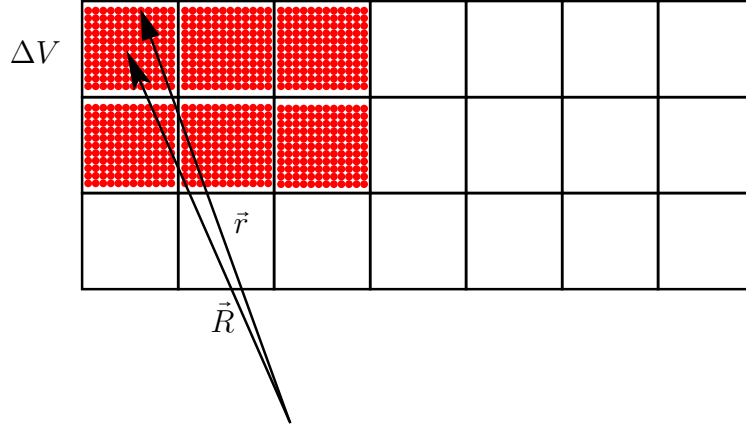


Figure 3.7: Macroscopic versus microscopic structure

and $\Phi(\vec{r}) \approx \Phi(\vec{R})$ within the small but macroscopic volume element ΔV . In this case we can approximate the solution of the Schrödinger equation by plane waves with a position dependent dispersion

$$\epsilon_{\vec{k}}(\vec{R}) = \frac{\hbar^2 k^2}{2m} - e\Phi(\vec{R}) .$$

This dispersion leads to a position dependent particle density

$$n(\vec{R}) = \frac{1}{V} \sum_{\vec{k}} f(\epsilon_{\vec{k}}(\vec{R}))$$

and a corresponding charge density $\rho(\vec{R}) = -en(\vec{R})$. The induced charge density then becomes $\rho^{\text{ind}}(\vec{R}) = -en(\vec{R}) + en_0$, where

$$n_0 = \frac{1}{V} \sum_{\vec{k}} f\left(\frac{\hbar^2 k^2}{2m}\right) .$$

We then obtain from a Taylor expansion with respect to ϕ

$$\begin{aligned} \rho^{\text{ind}}(\vec{R}) &= -e \frac{1}{V} \sum_{\vec{k}} \left[f\left(\frac{\hbar^2 k^2}{2m} - e\Phi(\vec{R})\right) - f\left(\frac{\hbar^2 k^2}{2m}\right) \right] \\ &= -e^2 \frac{\partial n_0}{\partial \mu} \Phi(\vec{R}) + \text{O}(\Phi^2) . \end{aligned}$$

After Fourier transformation with respect to \vec{R} we insert this into the formula for the dielectric function to obtain the *Thomas-Fermi dielectric function*

$$\begin{aligned} \epsilon(\vec{q}) &= 1 + \frac{4\pi e^2}{q^2} \frac{\partial n}{\partial \mu} \\ &= 1 + \left(\frac{q_{TF}}{q}\right)^2 \end{aligned} \quad (3.22)$$

$$q_{TF}^2 = 4\pi e^2 \frac{\partial n}{\partial \mu} \quad (3.23)$$

with the *Thomas-Fermi wave vector* q_{TF} . Note that we have neglected all contributions from *short length scales*, i.e. possible modifications for *large wave vectors*.

As a special case let us calculate the effective potential of a point charge Q with

$$\Phi^{\text{ext}}(\vec{q}) = \frac{4\pi Q}{q^2}$$

to obtain

$$\Phi(\vec{q}) = \frac{1}{\varepsilon(\vec{q})} \frac{4\pi Q}{q^2} = \frac{4\pi Q}{q^2 + q_{TF}^2} .$$

Note that $\Phi(\vec{q})$ now is finite for $\vec{q} \rightarrow 0$. Furthermore, transformed into real space, we find

$$\Phi(\vec{r}) = \frac{Q}{r} e^{-q_{TF} r}$$

for the potential, i.e. a short ranged Yukawa potential. We may even evaluate the expression for q_{TF} for $k_B T \ll E_F$ to obtain

$$\frac{q_{TF}^2}{k_F^2} = \frac{4}{\pi} \frac{1}{k_F a_B} = \text{O}(1) .$$

Thus $q_{TF} \approx k_F$, and the range of $\Phi(\vec{r})$ is only sizeable over distances a_B .

This peculiar property of the electron gas is called *screening* and very efficiently cuts off the range of the Coulomb interaction, even among the electrons themselves.⁷ Nevertheless, the remaining short-ranged effective repulsion still poses a problem, because in its presence a single-particle state $|n_{\vec{k}\sigma}\rangle$ is not an eigenstate of the system, but will evolve in time under the action of the total Hamiltonian. In general, one can identify a time scale τ , the *lifetime*, after which the state $|n_{\vec{k}\sigma}(t)\rangle$ has lost all “memory” of its initial form.

After this discussion we can now give an operational definition, under what conditions it makes sense at all to talk of electrons: When $\tau \rightarrow \infty$ or at least $\tau \gg$ relevant time scales, the state $|n_{\vec{k}\sigma}(t)\rangle \approx |n_{\vec{k}\sigma}(0)\rangle$ is called *quasi-stationary*. We thus need an idea of the lifetime τ of a single-particle state in the presence of the Coulomb interaction. To this end we put an electron in a state close to the Fermi surface, i.e. with an energy $\epsilon_{\vec{k}} > E_F$. This electron can interact with a second electron just below the Fermi energy, leading to an excited state where the two electrons must have energies just above the Fermi energy (Pauli principle). If we denote with $\epsilon_i = \epsilon_{\vec{k}_i} - E_F$ the energies relative to the Fermi energy, energy conservation requires $\epsilon_3 + \epsilon_4 = \epsilon_1 - |\epsilon_2| \geq 0$ or $|\epsilon_2| \leq \epsilon_1$. Therefore, the fraction of electrons in the Fermi volume, that can actually interact with

⁷This is not a trivial statement, but must (and can) be actually proven by inspecting the interaction energy between two electrons.

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

an additional electron with energy slightly above the Fermi energy, can be estimated as

$$\begin{aligned}
 \delta_i &\approx \frac{\text{volume of Fermi sphere in } [-\epsilon_1, 0]}{\text{volume of Fermi sphere}} \\
 &= \frac{V(E_F) - V(E_F - \epsilon_1)}{V(E_F)} = 1 - \frac{V(E_F - \epsilon_1)}{V(E_F)} \\
 &= 1 - \left(\frac{E_F - \epsilon_1}{E_F} \right)^{3/2} \approx \frac{3}{2} \frac{\epsilon_1}{E_F} \ll 1 ,
 \end{aligned}$$

where we used $V(\epsilon) \sim k^3 \sim \epsilon^{3/2}$. In particular, for $\epsilon_1 \rightarrow 0$ the phase space for interactions vanishes, i.e. for the state ϵ_1 the lifetime $\tau \rightarrow \infty$. As for the final states after the interaction process $0 \leq \epsilon_3 + \epsilon_4 \leq \epsilon_1$ must hold and $\epsilon_1 \rightarrow 0$, we may approximately assume $\epsilon_3 \approx \epsilon_4 \approx \epsilon_1/2$, and hence find as phase space fraction for final states of the interaction process

$$\delta_f \approx \frac{3}{2} \frac{\epsilon_3}{E_F} \sim \frac{\epsilon_1}{E_F} .$$

Taking together, the total phase space for an interaction process becomes

$$\delta \sim \left(\frac{\epsilon_1}{E_F} \right)^2 .$$

If we take finite temperature into account, the Fermi surface becomes “soft” in a region $O(k_B T)$ around the Fermi energy, and the previous estimate must be modified to

$$\delta \sim a \left(\frac{\epsilon_1}{E_F} \right)^2 + b \left(\frac{k_B T}{E_F} \right)^2 .$$

Using Fermi’s golden rule, we can estimate the decay rate or equivalently the inverse lifetime of an additional electron placed into a state close to the Fermi surface according to

$$\frac{1}{\tau} \sim \delta |V(\vec{q})|^2 \sim \left(\frac{k_B T}{E_F} \right)^2 |V(\vec{q})|^2 ,$$

where \vec{q} denotes a typical momentum transfer due to the interaction. For the bare Coulomb interaction one then finds $\frac{1}{\tau} \sim \frac{T^2}{q^2}$, which is indetermined in the limit $T \rightarrow 0$ and $q \rightarrow 0$. However, for the screened Coulomb interaction we have $\frac{1}{\tau} \sim \frac{T^2}{q^2 + q_T^2}$, i.e. $\tau \sim 1/T^2 \rightarrow \infty$ as $T \rightarrow 0$.

For non-singular interactions, the concept of single-particle states remains valid in a quasi-stationary sense for energies at the Fermi surface and low temperatures.

Based on this observation, Landau 1957 made the suggestion that the low-energy excitations of the interacting Fermi gas can be described by quasi-stationary single-particle states $|n_{\vec{k}}(t)\rangle$ that evolve adiabatically⁸ from corresponding states $|n_{\vec{k}}^{(0)}\rangle$ of the noninteracting Fermi gas. However, because these quasi-stationary states are not true eigenstates of the interacting system, one cannot use the notion of “electrons” in association with them any more. Thus Landau further suggested to call the interacting Fermi system with these properties a *Fermi liquid* and the objects described by the quasi-stationary states *quasi electrons* or more general *quasi particles*. For these quasi particles Landau proposed the following axioms:

- Quasi particles have a spin $s = \hbar/2$, i.e. are Fermions.
- Quasi particles interact (Landau quasi particles).
- The number of quasi particles equals the number of electrons (uniqueness).

In particular the last axiom means that the particle density $n = N/V$ and consequently $k_F = (3\pi^2 n)^{3/2}$ remains unchanged. This observation can be rephrased as

The volume of the Fermi body is not changed by non-singular interactions (Luttinger theorem).

Let us discuss the consequences of the concepts of quasi particles. First, we note that for the noninteracting electron gas we have a distribution function $f(\epsilon_k) \equiv n_{k\sigma}^{(0)}$, the Fermi function. With this function we can write the ground state energy of the system as

$$E_{GS} = \sum_{\vec{k}\sigma} \epsilon_k n_{k\sigma}^{(0)} ,$$

while for the system in an excited state we will in general have a different distribution n_k and

$$E = \sum_{\vec{k}\sigma} \epsilon_k n_{k\sigma} .$$

In particular, if we add or remove one electron in state k_0 , we have $\delta n_{k\sigma} := n_{k\sigma} - n_{k\sigma}^{(0)} = \pm \delta_{k,k_0}$ and $\delta E = E - E_{GS} = \epsilon_{k_0} \delta_{k,k_0}$. Therefore

$$\frac{\delta E}{\delta n_{k\sigma}} = \epsilon_k .$$

⁸i.e. one switches on the interaction from $t = -\infty$ to $t = 0$ sufficiently slow (for example as $e^{\eta t}$) and assumes that the state always is uniquely identifiable with $|n_k(t = -\infty)\rangle$.

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

As the quasi particles are objects that evolve in one-to-one correspondence from the free particles of the electron gas, we add another axiom for the interacting system, namely

- There exists a *distribution function* $n_{\vec{k}\sigma}$ such that the energy of the system can be written as a functional $E[n_{\vec{k}\sigma}]$ of this function. In particular, there exists a *ground-state distribution function* $n_{\vec{k}\sigma}^{(0)}$ with $E_{GS} = E[n_{\vec{k}\sigma}^{(0)}]$. The low-energy excitations are characterised by deviations $\delta n_{\vec{k}\sigma} = n_{\vec{k}\sigma} - n_{\vec{k}\sigma}^{(0)}$, $|\delta n_{\vec{k}\sigma}| \ll 1$ from the ground state distribution and a corresponding change of energy

$$\delta E[n_{\vec{k}\sigma}] = E[n_{\vec{k}\sigma}] - E_0 = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}\sigma} \delta n_{\vec{k}\sigma} + \frac{1}{2} \sum_{\vec{k}\sigma} \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma; \vec{k}'\sigma'} \delta n_{\vec{k}\sigma} \delta n_{\vec{k}'\sigma'} + \dots \quad (3.24)$$

in the sense of a Volterra expansion (= Taylor expansion for functionals).

From the first term in this expression we can define in correspondence to the structure of the noninteracting electron gas the *energy of a quasi particle* as

$$\epsilon[n_{\vec{k}\sigma}] := \frac{\delta E[n_{\vec{k}\sigma}]}{\delta n_{\vec{k}\sigma}}$$

If $\epsilon[n_{\vec{k}\sigma}] \equiv \epsilon_{\vec{k}\sigma} > E_F$, we talk of a *quasi particle*, in the other case of a *quasi hole*. The convention is to drop the word “quasi” and talk of particles and holes, always keeping in mind that these notions are meant in the sense of Landau’s axioms.

The determination of the distribution function, based on general thermodynamic principles and the expansion (3.24), is somewhat tedious. The final result, however, looks quite intuitive and reasonable. It reads

$$n_{\vec{k}\sigma} = [1 + \exp\{\beta(\epsilon_{\vec{k}\sigma} - \mu)\}]^{-1}$$

and formally looks like the Fermi function. In reality it however is a very complicated implicit equation, as $\epsilon_{\vec{k}\sigma} = \epsilon[n_{\vec{k}\sigma}]$ is a (usually unknown) functional of the distribution function.

Let us now concentrate on the ground state, where we have $\epsilon_{\vec{k}\sigma}^{(0)} := \epsilon[n_{\vec{k}\sigma}^{(0)}]$. We can then define a *group velocity* for the particles in the usual way as $\vec{v}_{\vec{k}\sigma} := \vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}\sigma}^{(0)}$. To keep things simple we proceed without external magnetic field, ignore spin-orbit coupling and assume an isotropic system. In this case everything depends on k only, and in particular $\vec{v}_{\vec{k}\sigma} = v_k \frac{\vec{k}}{k}$. For⁹ $k = k_F$ we now *define*

⁹Remember: k_F is the same as for the noninteracting system!

$$\begin{aligned} v_{k_F} &=: \frac{\hbar k_F}{m^*} \\ \epsilon_k^{(0)} &=: \mu + \hbar v_F (k - k_F) . \end{aligned}$$

The constant m^* introduced in this way is called *effective mass of the particles*. Having an explicit form for the dispersion, we can now also calculate the density of states as

$$\begin{aligned} \mathcal{N}(\epsilon) &= \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon_k^{(0)} - \mu - \epsilon) \\ &= \int \frac{d^3k}{(2\pi)^3} \delta(\epsilon_k^{(0)} - \mu - \epsilon) = \frac{1}{\hbar v_F} \int \frac{k^2 dk}{2\pi^2} \delta(k - k_0)|_{k_0=k_F+\epsilon/(\hbar v_F)} \\ &= \frac{1}{2\pi^2 \hbar v_F} \left(k_F + \frac{\epsilon}{\hbar v_F} \right)^2 . \end{aligned}$$

The convention is such that $\epsilon = 0$ represents the Fermi energy. In particular, for the density of states at the Fermi energy one then finds

$$\mathcal{N}(0) = \frac{k_F^2}{2\pi^2 \hbar v_F} = \frac{m^* k_F}{2\pi^2 \hbar^2} = \frac{m^*}{m} \mathcal{N}^{(0)}(E_F) .$$

The second term in the expansion (3.24) defines the *quasi particle interaction*

$$f_{\vec{k}\sigma; \vec{k}'\sigma'} := \frac{\delta^2 E[n_{\vec{k}\sigma}]}{\delta n_{\vec{k}\sigma} \delta n_{\vec{k}'\sigma'}} .$$

An obvious question is how important this part actually is. To this end let us consider a variation in the ground state energy

$$\begin{aligned} \delta E &= \delta\epsilon - \mu \delta n \\ &= \sum_{\vec{k}\sigma} \bar{\epsilon}_{\vec{k}\sigma}^{(0)} (\epsilon_{\vec{k}\sigma}^{(0)} - \mu) \delta n_{\vec{k}\sigma} + \frac{1}{2} \sum_{\vec{k}\sigma} \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma; \vec{k}'\sigma'} \delta n_{\vec{k}\sigma} \delta n_{\vec{k}'\sigma'} + \dots \end{aligned}$$

As we are interested in low energy excitations, we have $|\epsilon_{\vec{k}\sigma}^{(0)} - E_F| \ll E_F$ and may assume

$$\frac{\epsilon_{\vec{k}\sigma}^{(0)} - E_F}{E_F} \propto \delta n_{\vec{k}\sigma}$$

to leading order, respectively $(\epsilon_{\vec{k}\sigma}^{(0)} - E_F) \delta n_{\vec{k}\sigma} = O(\delta n^2)$. On the other hand, the “interaction term” is $O(\delta n^2)$ by construction, and thus of the same order. Consequently, both terms are actually important for the consistency of the

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

theory. Therefore, we will in general have to deal with a *renormalised particle energy*

$$\epsilon_{\vec{k}\sigma} = \epsilon_{\vec{k}\sigma}^{(0)} + \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma;\vec{k}'\sigma'} \delta n_{\vec{k}'\sigma'} .$$

Due to isotropy and without spin-orbit interaction the interaction can only depend on the relativ orientation of \vec{k} and \vec{k}' respectively σ and σ' . Moreover, for Fermions all the action is concentrated to within a small shell around the Fermi energy, and thus $\vec{k} \cdot \vec{k}' \approx k_F^2 \cos \vartheta$. We can then define

$$\begin{aligned} f^S(\cos \vartheta) &:= f_{\vec{k}\uparrow;\vec{k}'\uparrow} + f_{\vec{k}\uparrow;\vec{k}'\downarrow} \text{ spin-symmetric interaction,} \\ f^A(\cos \vartheta) &:= f_{\vec{k}\uparrow;\vec{k}'\uparrow} - f_{\vec{k}\uparrow;\vec{k}'\downarrow} \text{ spin-antisymmetric interaction.} \end{aligned}$$

As f^α depends only on $\cos \vartheta$, we can further expand it into Legendre polynomials according to

$$f^\alpha(\cos \vartheta) = \sum_{l=0}^{\infty} f_l^\alpha P_l(\cos \vartheta)$$

and finally obtain

$$f_{\vec{k}\sigma;\vec{k}'\sigma'} = \frac{1}{2V\mathcal{N}(0)} \sum_{l=0}^{\infty} (F_l^S + \sigma \cdot \sigma' F_l^A) P_l(\cos \vartheta) . \quad (3.25)$$

The quantities $F_l^\alpha := V\mathcal{N}(0)f_l^\alpha$ are called *Landau parameters*. Note that by definition they are dimensionless.

We now are ready to calculate physical quantities.

1. Let us start with the specific heat, which is defined via

$$c_V = \frac{1}{V} \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{1}{V} \sum_{\vec{k}\sigma} \left[\epsilon_{\vec{k}\sigma}^{(0)} + \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma;\vec{k}'\sigma'} \delta n_{\vec{k}'\sigma'} \right] \frac{\partial n_{\vec{k}\sigma}}{\partial T} .$$

As the second part is by construction of at least $O(\delta n) = O(T)$, we can stick to the first as $T \rightarrow 0$. This leads to¹⁰

$$\begin{aligned} c_V &= \gamma T \\ \gamma &= \frac{\pi^2}{3} k_B^2 \mathcal{N}(0) = \frac{m^*}{m} \gamma^{(0)} . \end{aligned}$$

As there are now corrections to the “pure” Fermi gas, one can also calculate the deviations from this particular law, which behave as

$$\frac{\Delta c_V}{T} \sim - \left(\frac{k_B T}{E_F} \right)^3 \ln \frac{k_B T}{E_F} .$$

¹⁰The calculation is identical to the one for the electron gas.

This prediction by Fermi liquid theory has been observed experimentally. In recent years several materials have been found that actually show a behavior

$$\frac{c_V}{T} \sim \ln \frac{k_B T}{E_F}$$

all the way down to the lowest temperatures. For these systems the rather meaningless notion of a “non-Fermi liquid” has been introduced. It just tells you, that they do not behave like predicted by Landau’s theory, but otherwise is as precise as to call an apple a “non-banana”.

2. A second interesting quantity is the *compressibility* defined as

$$\kappa := -\frac{1}{V} \frac{\partial V}{\partial p}, \quad p = -\frac{\partial E_{GS}}{\partial V}.$$

With some manipulations this can be cast into the form

$$\kappa = \frac{1}{n^2} \frac{\partial n}{\partial \mu}$$

This result is again quite reasonable, as the compressibility is something that tells us how easy it is to make the system more dense or how easy it is to add particles to the system. Both are related to the density n , and a change in particle number is regulated by the chemical potential.

We thus have to calculate

$$\delta n = \frac{1}{V} \sum_{\vec{k}\sigma} \delta n_{\vec{k}\sigma}.$$

From the definition of the quasi particle energy we can now infer

$$\delta n_{\vec{k}\sigma} = \frac{\partial n_{\vec{k}\sigma}}{\partial (\epsilon_{\vec{k}\sigma} - \mu)} (\delta \epsilon_{\vec{k}\sigma} - \delta \mu)$$

or

$$\delta n = \frac{1}{V} \sum_{\vec{k}\sigma} \left(-\frac{\partial n_{\vec{k}\sigma}}{\partial \epsilon_{\vec{k}\sigma}} \right) (\delta \mu - \delta \epsilon_{\vec{k}\sigma}).$$

Now the quasi particle interaction becomes important. The change in the energy is given by

$$\delta \epsilon_{\vec{k}\sigma} = \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma; \vec{k}'\sigma'} \delta n_{\vec{k}'\sigma'}.$$

Furthermore, as we vary the chemical potential, the resulting variations are better isotropic and spin independent, i.e. we find

$$\delta \epsilon_{\vec{k}\sigma} = \sum_{\vec{k}} \left[f_{\vec{k}\sigma; \vec{k}'\sigma} + f_{\vec{k}\sigma; \vec{k}-\sigma} \right] \delta n_{\vec{k}'\sigma} = \frac{F_0^S}{V \mathcal{N}(0)} \sum_{\vec{k}} n_{\vec{k}'\sigma} = \frac{F_0^S}{V \mathcal{N}(0)} \frac{1}{2} \sum_{\vec{k}\sigma'} n_{\vec{k}'\sigma'},$$

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

where in the last step we made use of the fact that the distribution function does not depend on spin explicitly for a variation of μ . We therefore can conclude that from the Landau parameters only F_0^S plays a role, i.e. with the definition (3.25)

$$\delta\epsilon_{\vec{k}\sigma} = \frac{F_0^S}{2V\mathcal{N}(0)} \sum_{\vec{k}'\sigma'} \delta n_{\vec{k}'\sigma'} = \frac{F_0^S}{2\mathcal{N}(0)} \delta n .$$

Collecting all terms one arrives at

$$\delta n = \left(\delta\mu - \frac{F_0^S}{2\mathcal{N}(0)} \delta n \right) \frac{1}{V} \sum_{\vec{k}\sigma} \left(-\frac{\partial n_{\vec{k}\sigma}}{\partial \epsilon_{\vec{k}\sigma}} \right) .$$

The \vec{k} sum can be cast into an integral yielding

$$\frac{1}{V} \sum_{\vec{k}\sigma} \left(-\frac{\partial n_{\vec{k}\sigma}}{\partial \epsilon_{\vec{k}\sigma}} \right) \int d\epsilon \mathcal{N}(\epsilon) \left(-\frac{\partial n(\epsilon)}{\partial \epsilon} \right) \xrightarrow{T=0} 2\mathcal{N}(0) .$$

We therefore find

$$\delta n = \mathcal{N}(0) \delta\mu - F_0^S \delta n \Leftrightarrow \frac{\delta n}{\delta\mu} = \frac{\mathcal{N}(0)}{1 + F_0^S} .$$

For the noninteracting system one can do an equivalent calculation, which leads to the compressibility $\kappa^{(0)}$ and with the relation between the density of states of the Fermi liquid and the noninteracting gas we arrive at the final expression

$$\kappa = \frac{1}{n^2} \frac{\mathcal{N}(0)}{1 + F_0^S} = \frac{m^*/m}{1 + F_0^S} \kappa^{(0)}$$

The important things are, that we again find a renormalisation $\propto m^*/m$ with respect to the specific heat. The novel aspect however is that a further renormalisation occurs due to the quasi particle interactions. In fact, depending on the sign of F_0^S , this can lead to a sizeable change in κ . Moreover, if $F_0^S \leq -1$, the above expression leads to a divergence of κ or a negative sign. This immediately tells us that the Fermi liquid is unstable and the whole concept of quasi particles breaks down.

- From the Fermi gas we know already that the susceptibility is another important quantity. To calculate it we apply a small external field $\vec{B} = b\vec{e}_z$ and obtain

$$\delta\epsilon_{\vec{k}\sigma} = -g\mu_B b\sigma \frac{\hbar}{2} + \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma; \vec{k}'\sigma'} \delta n_{\vec{k}'\sigma'} .$$

Again we use

$$\delta n_{\bar{k}\sigma} = \left(-\frac{\partial n_{\bar{k}\sigma}}{\partial \epsilon_{\bar{k}\sigma}} \right) (\delta\mu - \delta\epsilon_{\bar{k}\sigma})$$

and observe that $\delta\mu$ cannot depend on the sign of b . Hence, $\delta\mu \propto b^2$, i.e. we can ignore $\delta\mu$ in leading order in b . Therefore, $\delta n_{\bar{k}\sigma} \propto \delta\epsilon_{\bar{k}\sigma}$ and furthermore $\delta n_{\bar{k}\uparrow} = -\delta n_{\bar{k}\downarrow}$. For a given σ the quasi particle interaction part then becomes

$$\sum_{\bar{k}'\sigma'} f_{\bar{k}\sigma;\bar{k}'\sigma'} \delta n_{\bar{k}'\sigma'} = \sum_{\bar{k}'} (f_{\bar{k}\sigma;\bar{k}'\sigma} - f_{\bar{k}\sigma;\bar{k}'\bar{\sigma}}) \delta n_{\bar{k}'\sigma} = \frac{F_0^A}{\mathcal{N}(0)} \delta n_{\sigma} .$$

Note that here naturally F_0^A comes into play.

With this result we have

$$\begin{aligned} \delta n_{\sigma} &= \frac{1}{V} \sum_{\bar{k}} \delta n_{\bar{k}\sigma} = -\frac{1}{V} \sum_{\bar{k}} \left(-\frac{\partial n_{\bar{k}\sigma}}{\partial \epsilon_{\bar{k}\sigma}} \right) \delta \epsilon_{\bar{k}\sigma} \\ &= -\left(-g\mu_B b \sigma \frac{\hbar}{2} + \frac{F_0^A}{\mathcal{N}(0)} \delta n_{\sigma} \right) \mathcal{N}(0) \\ \delta n_{\sigma} &= g\mu_B b \sigma \frac{\hbar}{2} \frac{\mathcal{N}(0)}{1 + F_0^A} . \end{aligned}$$

For the difference of up and down changes one then obtains

$$\delta n_{\uparrow} - \delta n_{\downarrow} = \frac{g\mu_B \hbar}{2} \frac{\mathcal{N}(0)}{1 + F_0^A} b$$

and with the magnetization given by $m = \frac{g\mu_B \hbar}{2} (n_{\uparrow} - n_{\downarrow})$ the expression for the susceptibility becomes

$$\chi_P = \frac{\partial m}{\partial b} = \left(\frac{g\mu_B \hbar}{2} \right)^2 \frac{\mathcal{N}(0)}{1 + F_0^A} = \frac{m^*/m}{1 + F_0^A} \chi_P^{(0)}$$

As already for the compressibility, we here observe two contributions to the renormalisation with respect to the noninteracting electron gas: One from the effective mass and a second from the quasi particle interactions. If we calculate now the Wilson ratio (3.21), we find

$$R_W = \dots = \frac{1}{1 + F_0^A} .$$

It is thus important to note that the Fermi gas value $R_W = 1$ can easily be changed to values of the order $1 \dots 10$ by the quasi particle interactions. Furthermore, we again have to require $F_0^A > -1$ in order for the Fermi liquid concept to be valid. Otherwise we will in general observe a magnetic instability.

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

4. Let us now ask how the effective mass is related to the true electron mass. This can be achieved by invoking Galileian invariance, i.e. according to Noether the conservation of the momentum of center of mass.

Let us assume we change the momentum of an electron by $\vec{k} \rightarrow \vec{k} + \delta\vec{k}$. The change in quasi particle energy induced by this “kick” is then

$$\delta\epsilon_{\vec{k}\sigma} = \vec{\nabla}_{\vec{k}}\epsilon_{\vec{k}\sigma}\delta\vec{k} + \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma;\vec{k}'\sigma'}\delta n_{\vec{k}'\sigma'} .$$

We now restrict to $T = 0$ and an isotropic system and use

$$\begin{aligned} \vec{\nabla}_{\vec{k}}\epsilon_{\vec{k}\sigma} &\approx \vec{\nabla}_{\vec{k}}\epsilon_{\vec{k}\sigma}^{(0)} = \hbar^2 \frac{k_F}{m^*} \frac{\vec{k}}{k} \\ \delta n_{\vec{k}\sigma} &= -\vec{\nabla}_{\vec{k}}\bar{n}_{\vec{k}\sigma}\delta\vec{k} \\ &= -\frac{\partial\bar{n}_{\vec{k}\sigma}}{\partial\epsilon_{\vec{k}\sigma}}\vec{\nabla}_{\vec{k}}\epsilon_{\vec{k}\sigma}\delta\vec{k} \\ &\approx \delta(\epsilon_{\vec{k}\sigma} - \mu) \frac{\hbar^2\vec{k} \cdot \delta\vec{k}}{m^*} . \end{aligned}$$

On the other hand, Galilein invariance enforces that for real particles

$$\delta\epsilon_{\vec{k}\sigma} = \frac{\hbar^2\vec{k} \cdot \delta\vec{k}}{m} .$$

Now we invoke the fact that there must be a one-to-one correspondence between real particles and quasi particles, i.e.

$$\frac{\hbar^2\vec{k} \cdot \delta\vec{k}}{m} \stackrel{!}{=} \frac{\hbar^2\vec{k} \cdot \delta\vec{k}}{m^*} + \sum_{\vec{k}'\sigma'} f_{\vec{k}\sigma;\vec{k}'\sigma'}\delta(\epsilon_{\vec{k}'\sigma'} - \mu) \frac{\hbar^2\vec{k}' \cdot \delta\vec{k}}{m^*}$$

For $T = 0$, we now can replace $\vec{k} \cdot \delta\vec{k} \rightarrow k_F \frac{\vec{k}}{k} \cdot \delta\vec{k}$ and $\vec{k}' \cdot \delta\vec{k} \rightarrow k_F \frac{\vec{k}'}{k'} \cdot \delta\vec{k} = \cos\vartheta' \frac{\vec{k}}{k} \cdot \delta\vec{k}$. The latter is achieved by choosing a proper axis of reference in the sum on \vec{k}' . We thus have to evaluate

$$\begin{aligned} \sum_{l=0}^{\infty} F_0^S \int \frac{d\Omega'}{4\pi} P_l(\cos\vartheta') \cos\vartheta' &= \frac{F_1^S}{3} \\ &= \frac{1}{3}\delta_{l,1} \end{aligned}$$

and finally

$$\boxed{\frac{m^*}{m} = 1 + \frac{1}{3}F_1^S}$$

Again, we see that we have a stability criterion, namely $F_1^S > -3$ in order to have meaningful results. In general, the criterion is $F_l^S > -(2l + 1)$ respectively $F_l^A > -(2l + 1)$.

3.2.3 Beyond Hartree-Fock

As the Hartree-Fock approximation can be viewed as the lowest order in a perturbation expansion of the ground-state energy of the system, one is tempted to calculate higher orders and thus obtain an improvement. It is however a quite general observation, that typically low-order terms give an apparently reasonable result, but taking into account higher orders in the perturbation expansion leads to a disaster. The same happens here: Beyond second order the individual contributions diverge. Sometimes such a divergence can be overcome by resummation of parts of the perturbation series to infinite orders. For the homogeneous electron gas this has been done by Gell-Mann and Brückner in 1957 with the result

$$\frac{E_0}{V} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s + O(r_s) \right) \text{Ry}$$

for the ground state energy. The proper expansion parameter thus is the quantity r_s defined by equation (3.20). Note that $r_s \propto n^{-1/3}$, i.e. small r_s means high electron density. In typical metals one has $r_s = 2 \dots 6$ and one might wonder how relevant such an expansion actually is. For very low density, i.e. $r_s \rightarrow \infty$, Wigner has shown that the system actually should undergo a phase transition into a localized, i.e. insulating state. This is the famous *Wigner crystal*, people actually are trying to find since then. Candidates for such a phenomenon are at first glance those wonderful realizations of the electron gas in semiconductor heterostructures. However, those systems have actually a rather high carrier density and are thus rather in the limit $r_s \ll 1$.

Besides these analytical approaches one can also try to make use of modern computer power, for example by devising a Monte-Carlo algorithm for performing these perturbation expansions numerically. This can indeed be done and is used to calculate further terms in the expansion in r_s . That such an effort is worth its price will become clear in a moment.

3.2.4 Density functional theory

Another approach is based on the observation, that the ground state energy depends on r_s and thus n only. This is the fundament of the *density functional theory* or abbreviated *DFT*, honoured with a Nobel prize for Walter Kohn in 1999 (for chemistry!). As it is the standard approach to calculate properties of solids nowadays, let us discuss this in more detail.

We begin by defining what we actually mean by electron density. The N electrons in a solid (or any N particle quantum system) are described by a wave

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

function (we restrict to the ground state here)

$$\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) .$$

The quantity

$$n(\vec{r}) := \int d^3r_1 \int d^3r_2 \dots \int d^3r_N |\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2$$

is the *inhomogeneous electron density in the ground state* of the interacting electron gas, possibly subject to an additional *external potential* $V(\vec{r})$. Obviously, when $n(\vec{r}) \neq n'(\vec{r})$ then surely $V(\vec{r}) \neq V'(\vec{r})$. The more interesting question is if the reverse is also true, i.e. if from $V = V'$ unambiguously $n = n'$ follows. This is the *Hohenberg-Kohn theorem*. The proof goes as follows:

Let us assume that $n = n'$, but we have $V \neq V'$ in the ground state. Then

$$\begin{aligned} E_0 &= \langle \Psi_0 | T + U + V | \Psi_0 \rangle \\ E'_0 &= \langle \Psi'_0 | T + U + V' | \Psi'_0 \rangle \end{aligned}$$

where T is the kinetic energy, U the Coulomb interaction and $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ denote the exact ground state wave functions for V and V' , respectively.

As the energy is the total minimum with respect to the exact ground state, we necessarily have

$$\begin{aligned} E'_0 &< \langle \Psi_0 | T + U + V' | \Psi_0 \rangle \\ &= E_0 + \langle \Psi_0 | V' - V | \Psi_0 \rangle \\ &= E_0 + \int d^3r n(\vec{r}) [V'(\vec{r}) - V(\vec{r})] \end{aligned} \tag{I}$$

$$\begin{aligned} E_0 &< \langle \Psi'_0 | T + U + V | \Psi'_0 \rangle \\ &= E'_0 + \int d^3r n'(\vec{r}) [V(\vec{r}) - V'(\vec{r})] \end{aligned} \tag{II}$$

Using our assumption we then obtain from (I) + (II) that $E_0 + E'_0 < E_0 + E'_0$ which is a contradiction.

We thus have the nice result that the ground state energy is a unique functional of the ground state density

$$E_0 = E_0[n(\vec{r})]$$

We did actually encounter this property already for the Hartree-Fock approximation and the lowest order perturbation series.

The formulation via $n(\vec{r})$ has an apparent advantage: Instead of $3N$ coordinates for the wave function we only need 3 here. But how can we make use of this theorem in a practical sense? Here we again employ the variational property

of the ground state energy, which is minimal for the true ground state density. There is however one problem: We do not know this functional. The ingenious idea of Hohenberg and Kohn now was to propose as ansatz

$$\begin{aligned} E[n] &= T[n] + \int d^3r n(\vec{r}) V(\vec{r}) + \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\text{xc}}[n] \\ &\stackrel{!}{=} F_{\text{HK}}[n(\vec{r})] + \int d^3r n(\vec{r}) V(\vec{r}) . \end{aligned}$$

In this formulation, the first term $T[n]$ denotes the kinetic energy,¹¹ the second ist the contribution by the external potential, the third the Hartree energy due to the Coulomb interaction and the last ist the *REST*, i.e. everything we cannot write in terms of the first three contributions. This unknown quantity is called *exchange-correlation energy*, as it will contain effects due to fermionic exchange (the unpleasant part in Hartree-Fock) and further contributions from the Coulomb interaction (“correlations”, everything beyond Hartree-Fock). Sometimes one puts this part, the Hartree energy and the kinetic energy into a universal functional $F_{\text{HK}}[n]$, the *Hohenberg-Kohn functional*.

Although this formula looks rather appealing, it does not help the least in the task to calculate n and E_0 practically for a given V . Here one must use an ansatz for the density $n(\vec{r})$, the kinetic energy and finally E_{xc} . Such an ansatz was proposed by Kohn and Sham in 1965. It reads

$$\begin{aligned} n(\vec{r}) &= \sum_{i=1}^N |\varphi_i(\vec{r})|^2 \\ T[n(\vec{r})] &= \sum_{i=1}^N \int d^3r \varphi_i(\vec{r})^* \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 \right] \varphi_i(\vec{r}) + \Delta T[n] . \end{aligned}$$

The last term $\Delta T[n]$ collects all contributions to the kinetic energy that are not included in the first form. Again, as we do not know these, we simply add them to the quantity $E_{\text{xc}}[n]$. Now we know that the energy has an absolute minimum for the ground state density, i.e. we perform a variation of $E[n]$ with respect to $n(\vec{r})$, which we can transfer to a variation with respect to $\varphi(\vec{r})^*$ as in the Hartree-Fock case. There is a constraint to be fulfilled, namely

$$\int d^3r \sum_{i=1}^N |\varphi_i(\vec{r})|^2 = N .$$

The variation under this constraint leads to the equations

$$\left\{ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r}) + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{xc}}(\vec{r}) \right\} \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r}) \quad (3.26)$$

¹¹Note that we do not know even that expression!

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

with

$$V_{\text{xc}}(\vec{r}) := \frac{\delta E_{\text{xc}}[n(\vec{r})]}{\delta n(\vec{r})} .$$

These are the *Kohn-Sham equations*. Formally they are a single-particle problem as the Hartree-Fock equations, and like them they contain the solution via the density in the differential operator as both $n(\vec{r})$ and $V_{\text{xc}}(\vec{r})$ depend on $\varphi_i(\vec{r})$. Thus, they are again a system that has to be solved self-consistently (for example by iteration). The “energies” ϵ_i appearing in the equations (3.26) guarantee the constraints, but have no physical meaning whatsoever.

Up to now we have not specified what E_{xc} is. Quite obviously, it is not known exactly, and we have to specify a reasonable approximation. The crazy idea now is to use $E_{\text{xc}}[n]$ from the homogeneous electron gas. In this case we have $n(\vec{r}) = n = \text{const.}$ and we then can write

$$E_{\text{xc}}^{\text{hom}}[n] = V n \mathcal{E}_{\text{xc}}^{\text{hom}}(n) = \int d^3r' n \mathcal{E}_{\text{xc}}^{\text{hom}}(n) .$$

The *local-density approximation* or *LDA* now simply replaces the constant density in the above formula by a spatially varying one to obtain

$$E_{\text{xc}} \approx \int d^3r' n(\vec{r}') \mathcal{E}_{\text{xc}}^{\text{hom}}(n(\vec{r}')) . \quad (3.27)$$

as an approximation to the exchange-correlation functional. With this explicit expression we can also write down the exchange-correlation potential

$$V_{\text{xc}}^{\text{LDA}}(\vec{r}) = \frac{d}{dx} [x \mathcal{E}_{\text{xc}}^{\text{hom}}(x)] \Big|_{x=n(\vec{r})} .$$

Finally, the form for $\mathcal{E}_{\text{xc}}^{\text{LDA}}(n)$ we can obtain either from perturbation expansion or from high-quality quantum Monte-Carlo calculations. This shows, why these calculations are still of relevance.

Some remarks are in place:

- The combination of DFT and LDA is frequently used for very inhomogeneous systems like molecules (quantum chemistry) or solids. The results are surprisingly good and one may wonder why this is the case. No really satisfactory answer to this question has been found yet, all we know is “that it works when it works”.
- DFT together with LDA is typically problematic in connection with systems containing $3d$, $4f$ or $5f$ electrons, because the d and f states are more tightly bound to the core and consequently the electron density here is extremely inhomogeneous, which invalidates the use of LDA.

- The lagrange multiplier have no physical meaning. Nevertheless they are quite happily interpreted as “single-particle” energies by the majority of the people using DFT and LDA. This may be permissible in the sense of Fermi liquid theory¹² or one tries to invoke something called *Koopmann’s theorem*. For the for Hartree-Fock approximation it simply says that

$$\Delta E = \langle \Psi_{N+1}^{HF} | H | \Psi_{N+1}^{HF} \rangle - \langle \Psi_N^{HF} | H | \Psi_N^{HF} \rangle = \epsilon_i^{HF} .$$

However, due to self-consistency the removal of one electron will severely modify the charge distribution and thus the effective potential in DFT. As this in general can lead to completely different structures of the wave function, it is absolutely unclear if or under which conditions Koopmann’s theorem actually holds for the DFT.

¹²Although one in principle had to show that the Kohn-Sham wave functions are indeed the single-particle states Landau talks of.

3.2. BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

Chapter 4

Lattices and crystals

As already noted in the introduction, a solid is a collection of a macroscopic number of atoms or molecules. The characteristic distance between two constituents is of the order of $5 \cdots 10 \text{ \AA}$ or $10 \cdots 20 a_B$. The obvious question is how the atoms or molecules are arranged and what their dynamics is. This chapter is devoted to the former question, i.e. the possible structures of static crystals and types of bonding present in solids.

As theoreticians we are allowed to make a simplifying abstraction:

An *ideal crystal* is the *infinite* recurrence of identical elementary structures.

In the following, we will always consider such ideal crystals.

4.1 The Bravais lattice

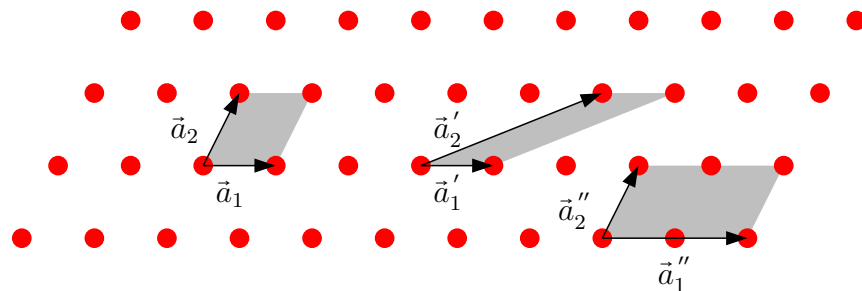
The fundamental concept of the theory of crystals is the Bravais lattice:

Definition 4.1. A *Bravais lattice* is the set of all points, called *lattice points* or *lattice sites*, with position vectors

$$\vec{R} = \sum_{i=1}^D n_i \vec{a}_i, \quad n_i \in \mathbb{Z}, \quad \vec{a}_i \in \mathbb{R}^D \text{ linearly independent.}$$

For $D = 2$ one also talks of a *net*. The vectors \vec{a}_i are called *primitive vectors*.

For example, in the net below several vectors \vec{a}_i , \vec{a}'_i and \vec{a}''_i are included. The



vectors \vec{a}_1 and \vec{a}_2 are primitive vectors in the sense of the definition, the same is true for \vec{a}'_1 and \vec{a}'_2 . However, \vec{a}''_1 cannot be a primitive vector, because not all points in the net can be reached. Thus, the primitive vectors are not unique, and not all vectors connecting two lattice points are primitive. Moreover, not all regular lattices are Bravais lattices. A counter example is the honeycomb lattice (see exercise).

From the definition follows, that arrangement and orientation of the lattice points look the same independent of the choice of origin. Furthermore, the

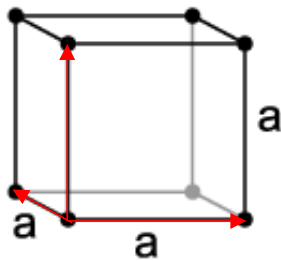
lattice is translationally invariant in the sense that any translation through a vector

$$\vec{T} = \sum_{i=1}^D n_i \vec{a}_i, \quad n_i \in \mathbb{Z}$$

maps the lattice onto itself.

Some important Bravais lattices are:

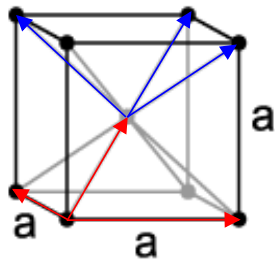
1. Simple cubic (sc) lattice:



Primitive vectors are shown in red. Their coordinates are

$$\begin{aligned} \vec{a}_1 &= a\vec{e}_1 \\ \vec{a}_2 &= a\vec{e}_2 \\ \vec{a}_3 &= a\vec{e}_3 \end{aligned}$$

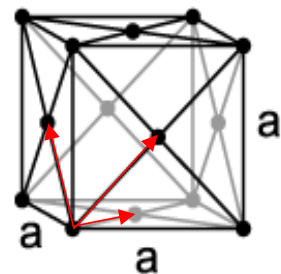
2. Body-centered cubic (bcc) lattice:



Two different sets of primitive vectors are shown in red and blue. Their coordinates are

$$\begin{aligned} \vec{a}_1 &= a\vec{e}_1 & \vec{a}_4 &= \frac{a}{2}(\vec{e}_2 + \vec{e}_3 - \vec{e}_1) \\ \vec{a}_2 &= a\vec{e}_2 & \vec{a}_5 &= \frac{a}{2}(\vec{e}_1 + \vec{e}_3 - \vec{e}_2) \\ \vec{a}_3 &= \frac{a}{2}(\vec{e}_1 + \vec{e}_2 + \vec{e}_3) & \vec{a}_6 &= \frac{a}{2}(\vec{e}_1 + \vec{e}_2 - \vec{e}_3) \end{aligned}$$

3. Face-centered cubic (fcc) lattice:



The primitive vectors are shown in red. Their coordinates are

$$\begin{aligned} \vec{a}_1 &= \frac{a}{2}(\vec{e}_2 + \vec{e}_3) \\ \vec{a}_2 &= \frac{a}{2}(\vec{e}_1 + \vec{e}_3) \\ \vec{a}_3 &= \frac{a}{2}(\vec{e}_1 + \vec{e}_2) \end{aligned}$$

In these examples the *conventional elementary or unit cell* of the lattice was shown. This unit cell is nice to visualise the full symmetries of the lattice. There are, however, many different ways to construct elementary cells. Another, quite convenient one is the *primitive elementary or unit cell*, which

- contains exactly one lattice point,
- has a volume independent of its shape, but
- does not necessarily show the symmetries of the lattice.

There is one possible choice of the primitive cell that actually has the symmetry of the lattice, namely the *Wigner-Seitz cell*. It is the region of space that is closer to a given lattice point than to any other.

It can be geometrically constructed by picking a lattice point and then drawing the lines connecting this point and its neighboring points. Then one draws the perpendicular bisectors of these lines. The region of space enclosed by these bisectors is just the Wigner-Seitz cell. For the simple-cubic lattice this construction is shown in the figure on the right. The Wigner-Seitz cell for the fcc and bcc lattices is shown in Fig. 4.1.

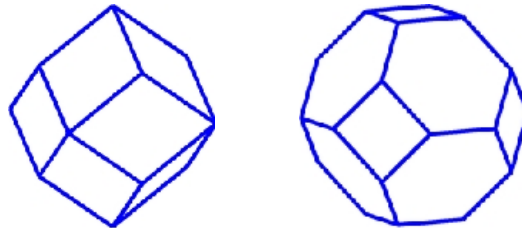
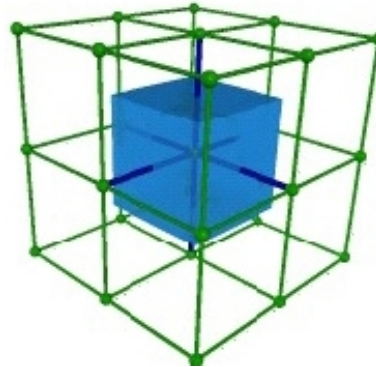
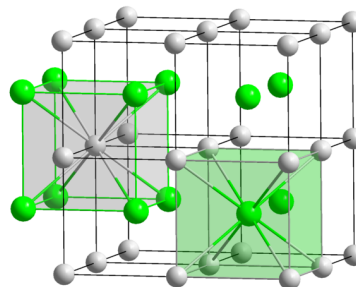


Figure 4.1: Wigner-Seitz cells of the fcc (left) and bcc (right) lattices.

While it is rarely used in representing lattices, the Wigner-Seitz cell becomes an important construct for the so-called *reciprocal space* as it defines the *first Brillouin zone*.

4.2 Crystals

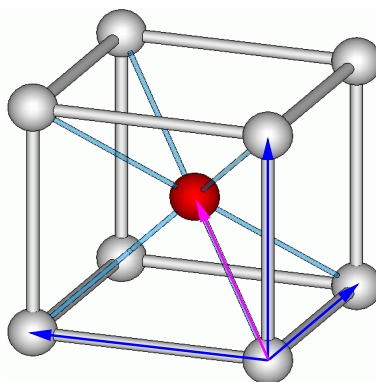
The Bravais lattice is the fundamental periodic structure of solids. However, the actual *crystal structure* must in general not be identical. Let us for example look at the CsCl crystal, which schematically is shown to the right.



The Cesium and Chlorine ions both occupy the sites of a simple cubic Bravais lattice in an alternating fashion. Obviously, the resulting crystal is not a Bravais

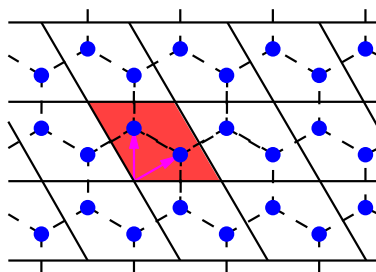
lattice, as not all points of the simple cubic lattice are equivalent. However, one can relate the structure to a certain Bravais lattice by giving the lattice points an additional internal structure.

The set of objects, or rather the set of locations of the objects, that form this internal structure, here the Cs and Cl ions, is called *basis*. The basis for the CsCl crystal is shown in the figure at the right-hand side. The primitive vectors of the underlying sc Bravais lattice are shown in blue, the basis consists of the objects located at $\vec{r}_1 = (0, 0, 0)$ (Cs ions, for example) and $\vec{r}_2 = \frac{a}{2}(1, 1, 1)$ (magenta vector).



This concept of a *lattice with basis* is not only applicable to structures with non-identical constituents, but also to regular arrangements of points in space that by themselves are not Bravais lattices.

A simple instructive example is the honeycomb net, which consists of hexagons *without the midpoint* as defined by the blue dots in the figure on the right. The underlying Bravais net is given by the midpoints of the honeycomb net, and the corresponding conventional unit cell shaded in red.



The basis finally are the two magenta arrows pointing to the two netpoints of the honeycomb net contained in one unit cell of the Bravais lattice. Further examples from real crystals are (the unit cells are shown in Fig. 4.2)

- (i) the diamond structure, which is an fcc lattice with basis $\{(0, 0, 0), \frac{a}{4}(1, 1, 1)\}$,
- (ii) NaCl structure, which is an fcc lattice with basis $\{(0, 0, 0), \frac{a}{2}(1, 1, 1)\}$ for Na and Cl, respectively,
- (iii) the CsCl structure discussed before and
- (iv) the ZnS (zincblende) structure, which is like the diamond structure an fcc Bravais lattice with basis $\{(0, 0, 0), \frac{a}{4}(1, 1, 1)\}$ occupied by Zn and S,

respectively.

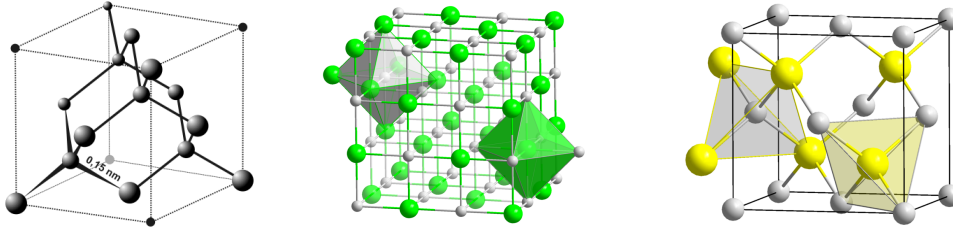


Figure 4.2: The diamond, NaCl and zincblende structures

Note that these structures are named after certain specific compounds, but are actually realized by a large number of compounds. For example, the zincblende structure occurs for at least 28 other diatomic compounds.

4.3 Classification of crystal structures

After the previous discussion it seems rather impossible to give a total account of all possible crystal structures in nature. The fascinating thing however is that this is indeed possible, namely by application of group theory. This classification has already been done in the late 19th century and amounts to number all possible Bravais lattices and their symmetry groups.

Quite generally, the symmetry group or *space group* of a crystal is a subgroup of the *euclydean group*. The primitive vectors of the Bravais lattice define the Abelian¹ *translation group*, which is a subgroup of the space group. All other elements of the space group, which are *not* pure translations, constitute the *point group* of the crystal, which in general is non-Abelian. While without the constraint of a connected translation group, the number of possible mathematical point groups is prohibitively large, the existence of the Bravais lattice reduces the number dramatically. First, let us list the possible point group elements. This can be done by remembering that we here deal with three dimensional geometric objects, i.e. all elements must be related to the $SO(3)$ somehow. They are

1. Rotations about n -fold axes. For example a rotation about the z -axis with rotation angle $\pi/4$ would be a fourfold axis.
2. Mirror reflections about a plane.
3. Point inversions.

¹For an Abelian group all elements commute with each other.

4. Rotation-reflections, i.e. a rotation followed by a mirror reflection about a plane containing the rotation axis.
5. Rotation-inversions, i.e. a rotation followed by an inversion through a point on the rotation axis.

It may be surprising, but these are indeed all possible point group elements. Furthermore one can show that the Bravais lattice permits only rotation axes with $n = 2, 3, 4$ and 6 , which is the actual limitation to the possible number of crystal structures. Note that in certain alloys one also observes five-fold symmetries. These compounds can however not be described by conventional three dimensional crystallography and have been coined *quasicrystals*.²

Adding together the possible point group elements with the definition of a Bravais lattice one can define seven *crystal systems* and altogether 14 Bravais lattices, shown in Table 4.2. Up to now we did not allow for any internal structure of the objects located at the lattice sites. As already discussed, physical objects have an internal structure, for example a basis or molecular symmetries etc., which will in general not have the full spherical symmetry. One thus has to introduce a further point group representing the physical objects. Here, too, the freedom is not infinite, but one finds that with the symmetry operations discussed previously³ from the 14 Bravais lattices one can construct 73 *symmorphic* space groups, i.e. crystal structures.

There are some additional symmetry operations not considered hitherto. These are

1. *Glide planes*, consisting of a reflection on a plane and a simultaneous translation through a vector not element of the Bravais lattice parallel to the plane.
2. *Screw axes*, consisting of a rotation about $2\pi/n$ and a simultaneous translation through a vector not element of the Bravais lattice.

Space groups with such symmetry elements are called *non-symmorphic* and constitute the remaining of the in total 230 space groups for crystals.

4.4 The reciprocal lattice

A consequence of the discrete translational symmetry of the lattice is that all quantities (potentials, densities, ...) are periodic functions with respect to

²See for example the review by N.D. Mermin, Rev. Mod. Phys. **64**, 3 (1992).

³Obviously, the local point group cannot add symmetry elements not compatible with the lattice.

4.4. THE RECIPROCAL LATTICE

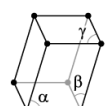
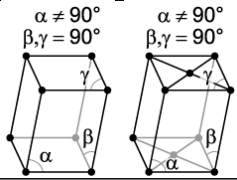
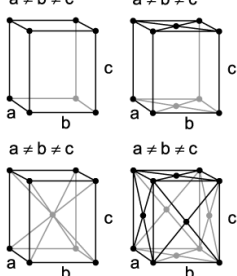
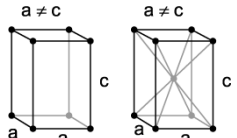
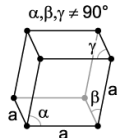
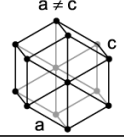
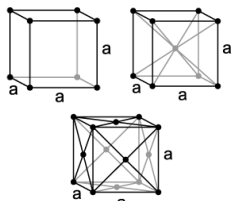
System	Relations	Symmetry (Schönflies)	Bravais lattices
Triclinic	$a \neq b \neq c \neq a$ $\alpha \neq \beta \neq \gamma \neq \alpha$	C_i	$\alpha, \beta, \gamma \neq 90^\circ$ 
Monoclinic	$a \neq b \neq c \neq a$ $\alpha = \gamma = \frac{\pi}{2} \neq \beta$ or $\alpha = \beta = \frac{\pi}{2} \neq \gamma$	C_{2h}	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ $\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 
Orthorhombic	$a \neq b \neq c \neq a$ $\alpha = \beta = \gamma = \frac{\pi}{2}$	D_{2h}	$a \neq b \neq c$ $a \neq b \neq c$ 
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = \frac{\pi}{2}$	D_{4h}	$a \neq c$ $a \neq c$ 
Rhombohedral Trigonal	$a = b = c$ $\frac{\pi}{2} \neq \alpha = \beta = \gamma < \frac{2\pi}{3}$	D_{3d}	$\alpha, \beta, \gamma \neq 90^\circ$ 
Hexagonal	$a = b \neq c$ $\alpha = \beta = \frac{\pi}{2}; \gamma = \frac{2\pi}{3}$	D_{6h}	$a \neq c$ 
Cubic	$a = b = c$ $\alpha = \beta = \gamma = \frac{\pi}{2}$	O_h	

Table 4.2: The 14 Bravais lattices

translations through lattice vectors. Formally, if $\vec{R} \in$ Bravais lattice and $f(\vec{r})$ some physical quantity at position \vec{r} , then $f(\vec{r} + \vec{R}) = f(\vec{r})$.

Let me remind you of periodic functions in dimension one with an “unit cell” of length L , i.e. $f(x+L) = f(x)$. Then one can expand $f(x)$ in a Fourier series as

$$f(x) = \sum_k f(k) e^{ikx}, \quad f(k) = \frac{1}{L} \int_{EZ} f(x) e^{-ikx} dx, \quad k = \frac{2\pi n}{L}, \quad n \in \mathbb{Z}.$$

In higher dimensions $d > 1$, one can use an identical concept, viz write for a lattice with volume V_{EZ} of the unit cell

$$f(\vec{r}) = \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot\vec{r}}, \quad f(\vec{G}) = \frac{1}{V_{EZ}} \int_{V_{EZ}} f(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^3r, \quad \vec{G} = ?$$

In order to determine \vec{G} we make use of the periodicity $f(\vec{r} + \vec{R}) = f(\vec{r})$ to obtain

$$f(\vec{r} + \vec{R}) = \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot(\vec{r} + \vec{R})} = \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot\vec{r}} e^{i\vec{G}\cdot\vec{R}} \stackrel{!}{=} \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot\vec{r}}.$$

In other words, $e^{i\vec{G}\cdot\vec{R}} = 1$ or $\vec{G}\cdot\vec{R} = 2\pi n$ with $n \in \mathbb{Z}$, as $e^{i\vec{G}\cdot\vec{r}}$ are linearly independent.

All vectors $\vec{G} \in \mathbb{R}^d$ with $\vec{G}\cdot\vec{R} = 2\pi\mathbb{Z}$ for all $\vec{R} \in \text{Bravais lattice}$ define the *reciprocal lattice* of the Bravais lattice. The Bravais lattice is also called *direct lattice*.

Obviously, the choice of the vectors \vec{G} is not unique. However, as the condition $\vec{G}\cdot\vec{R} = 2\pi\mathbb{Z}$ must hold for all \vec{R} , it must in particular be fulfilled for $\vec{R} = \vec{a}_i$, i.e. the primitive vectors of the Bravais lattice. A reasonable *convention* then is to choose a basis \vec{b}_i for the reciprocal lattice which fulfills $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$. In $d = 3$ this requirement can be satisfied by the vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (4.1a)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad (4.1b)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}. \quad (4.1c)$$

With this basis, a vector \vec{G} of the reciprocal lattice can be written as

$$\vec{G} = \sum_{i=1}^3 g_i \vec{b}_i.$$

We then obtain with

$$\vec{R} = \sum_{i=1}^3 n_i \vec{a}_i, \quad n_i \in \mathbb{Z},$$

and $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$ the result

$$\vec{G} \cdot \vec{R} = 2\pi \sum_{i=1}^3 g_i n_i.$$

As the right hand side must be $2\pi\mathbb{Z}$ for all possible combinations $n_i \in \mathbb{Z}$, $g_i \in \mathbb{Z}$ necessarily follows.

We can therefore conclude:

The reciprocal lattice is a Bravais lattice, too, with basis vectors \vec{b}_i . If the vectors \vec{a}_i are primitive, then the \vec{b}_i are also primitive.

Note that the reciprocal lattice of the reciprocal lattice is again the direct lattice. Important examples are:

1. A sc lattice with lattice constant a has as reciprocal lattice a sc lattice with lattice constant $2\pi/a$.
2. A fcc lattice with lattice constant a has as reciprocal lattice a bcc lattice with lattice constant $4\pi/a$ (and vice versa).

A very important concept of the reciprocal lattice is the Wigner-Seitz cell. This special unit cell is also called *first Brillouin zone* of the direct lattice; For example, the first Brillouin zone of an fcc lattice with lattice constant a is the Wigner-Seitz cell of the bcc lattice with lattice constant $4\pi/a$.

Finally, one can interpret the condition $\vec{G} \cdot \vec{R} = 2\pi n$ in a geometrical fashion. You may remember from linear algebra the Hessian normal form of a plane, which applied to the previous condition tells us that every \vec{G} from the reciprocal lattice defines a family of planes in the direct lattice which have \vec{G} as normal and which have a distance $d = 2\pi/|\vec{G}|$. The application of this interpretation is the indexing of crystal planes with vectors from the reciprocal lattice by *Miller's indexes* (hkl), which are the coordinates (in the basis \vec{b}_i) of the *shortest* \vec{G} from the reciprocal lattice normal to the crystal plane. If one of the coordinates is has a minus sign, for example $-l$, one writes \bar{l} , for example $(h\bar{l}k)$. Some care is necessary here, as directions in crystals are also denoted by a similar symbol, namely $[hkl]$. Thus, $[00\bar{1}]$ denotes the $-z$ -direction in a simple-cubic lattice, while $(00\bar{1})$ are all planes parallel to the xy -plane with distance a .

4.5 Bloch's theorem

We frequently will be faced with the task to solve eigenvalue problems in the presence of the crystal lattice. As already noted before, its existence implies that *all* physical properties are invariant under operations from the space group of the crystal, in particular from the translational subgroup. If we denote such

a translation through a vector \vec{a} by an operator $\hat{T}_{\vec{a}}$ and the Hamiltonian of our solid as \hat{H} , we can recast the previous statement as

$$[\hat{H}, \hat{T}_{\vec{R}}] = 0$$

for all \vec{R} from the Bravais lattice. We know from linear algebra, that we can choose the eigenvectors of \hat{H} simultaneously as eigenvectors of $\hat{T}_{\vec{R}}$. Using the property $\hat{T}_{\vec{a}} \cdot \hat{T}_{\vec{b}} = \hat{T}_{\vec{b}} \cdot \hat{T}_{\vec{a}} = \hat{T}_{\vec{a}+\vec{b}}$ one can prove *Bloch's theorem*

$$T_{\vec{R}}|u_{\vec{k}}\rangle = e^{i\vec{k}\cdot\vec{R}}|u_{\vec{k}}\rangle, \quad \vec{k} \in \mathbb{R}^3. \quad (4.2)$$

The actual proof is left as exercise.

Translational symmetry thus enforces the appearance of a *quantum number* \vec{k} for the eigenvectors of any observable in the system. In free space we know what this quantum number is: Neother's theorem tells us that translational invariance is connected to conservation of momentum and we may identify $\vec{p} = \hbar\vec{k}$ as the momentum of the particle or quantum mechanical state. Here, however, we have only a discrete translational symmetry, and consequently Mrs. Noether has nothing to tell us in such a case. Nevertheless, one uses this analogy to coin the name *crystal momentum* for $\hbar\vec{k}$, often also loosely called momentum. It is utterly important to remember this subtle distinction between *crystal momentum* $\hbar\vec{k}$ and *physical momentum* $\vec{p} \neq \hbar\vec{k}$, because due to $e^{i\vec{G}\cdot\vec{R}} = 1$ for an arbitrary vector \vec{G} of the reciprocal lattice we can always add such a \vec{G} to \vec{k} without changing anything. Therefore, crystal momentum conservation is always only up to an *arbitrary* vector of the reciprocal lattice. This feature is not only a mathematical nuisance, but in fact very important for all relaxation processes in crystals, as crystal momentum transfers with $\vec{G} \neq 0$ – so-called “Umklapp scattering” processes – are largely responsible for changes in *physical* momentum \vec{p} .

Chapter 5

Electrons in a periodic potential

We now reintroduce the periodic lattice, but ignore the interactions between the electrons. As we have learned in the previous chapter, this is a reasonable approximation in many cases, provided one replaces the electron mass by an effective mass in the spirit of Landau's Fermi liquid picture. We still do not consider the motion of the ions, but assume that they are localized at the sites of the perfect crystal lattice. Furthermore we again use periodic boundary conditions.

5.1 Consequences of Bloch's theorem

From Bloch's theorem we know that the electron wave function must obey

$$\hat{T}_{\vec{R}}|\Psi\rangle = e^{i\vec{k}\cdot\vec{R}}|\Psi\rangle$$

with suitably chosen \vec{k} . We call electrons in a periodic potential also *Bloch electrons*.

There are several consequences that follow immediately from Bloch's theorem:

- All non-equivalent \vec{k} vectors can be chosen from the first Brillouin zone of the lattice.

Proof: For any $\vec{k} \notin 1. \text{ BZ}$, but $\vec{k}' = \vec{k} + \vec{G} \in 1. \text{ BZ}$ for suitable \vec{G} from the reciprocal lattice it follows¹

$$\begin{aligned} \hat{T}_{\vec{R}}|\Psi_{\vec{k}}\rangle &= e^{i\vec{k}\cdot\vec{R}}|\Psi_{\vec{k}}\rangle = e^{i(\vec{k}+\vec{G})\cdot\vec{R}}|\Psi_{\vec{k}}\rangle = e^{i\vec{k}'\cdot\vec{R}}|\Psi_{\vec{k}}\rangle \\ \hat{T}_{\vec{R}}|\Psi_{\vec{k}'}\rangle &= e^{i\vec{k}'\cdot\vec{R}}|\Psi_{\vec{k}'}\rangle . \end{aligned}$$

Group theory now tells us that for Abelian groups like the translation group such a degeneracy is not possible, consequently

$$|\Psi_{\vec{k}}\rangle = |\Psi_{\vec{k}'}\rangle .$$

The number of non-equivalent \vec{k} points in the first BZ is given by (V_{WSZ} is the volume of the Wigner-Seitz cell)

$$\frac{(2\pi)^3}{V_{WSZ}} = \frac{V}{V_{WSZ}} = N$$

i.e. precisely the number of Bravais lattice points contained in the volume V .

¹Remember: $e^{i\vec{G}\cdot\vec{R}} = 1$.

- Bloch's theorem can be reformulated in position representation as

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

with $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$ for all vectors \vec{R} of the Bravais lattice. The proof is left as exercise. Since

$$\left(\frac{1}{i}\vec{\nabla}\right)^2 \Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{R}} \left(\frac{1}{i}\vec{\nabla} + \vec{k}\right)^2 u_{\vec{k}}(\vec{r})$$

we find for the Schrödinger equation ($V(\vec{r})$ is the potential due to the periodic arrangements of the ions)

$$\left[\frac{\hbar^2}{2m} \left(\frac{1}{i}\vec{\nabla} + \vec{k}\right)^2 + V(\vec{r})\right] u_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} u_{\vec{k}}(\vec{r}) .$$

The boundary conditions are $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{a}_i)$, i.e. the eigenvalue problem is reduced to the primitive cell of the lattice. This eigenvalue problem has for each value of \vec{k} an infinite set of discrete eigenvalues $\epsilon_{n\vec{k}}$. The positive integer n is called *band index*.

The eigenvectors $|\Psi_{n\vec{k}}\rangle$ and eigenvalues $\epsilon_{n\vec{k}}$ are periodic functions with respect to the reciprocal lattice, i.e.

$$|\Psi_{n,\vec{k}+\vec{G}}\rangle = |\Psi_{n\vec{k}}\rangle, \quad \epsilon_{n,\vec{k}+\vec{G}} = \epsilon_{n\vec{k}} .$$

Both $|\Psi_{n\vec{k}}\rangle$ and $\epsilon_{n\vec{k}}$ are continuous functions with respect to \vec{k} , and the family of functions $\epsilon_{n\vec{k}}$ is called *band structure*. An individual $\epsilon_{n\vec{k}}$ with fixed n viewed as function of \vec{k} is denoted as *energy band*.

- We have just noted, that for fixed n , $\epsilon_{n\vec{k}}$ as function of \vec{k} is continuous and periodic, i.e. there exists minimum and maximum. The quantity

$$W_N := \max_{\vec{k}} (\epsilon_{n\vec{k}}) - \min_{\vec{k}} (\epsilon_{n\vec{k}})$$

is called *bandwidth* of the energy band n .

- From elementary quantum mechanics we know, that an electron in the state $|\Psi_{n\vec{k}}\rangle$ with dispersion $\epsilon_{n\vec{k}}$ has a mean velocity or group velocity

$$\vec{v}_{n\vec{k}} = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon_{n\vec{k}}$$

As $|\Psi_{n\vec{k}}\rangle$ is a stationary state, Bloch electrons occupying that state have a mean velocity that does not vary in time, i.e. a current imposed will not decay. Consequently, electrons in a perfect crystal without interactions will show infinite conductivity. Note that this “theorem” only holds under the condition of a perfect crystal, i.e. any imperfection will lead to a finite conductivity.

- Another funny effect arises from the periodicity of $\epsilon_{n\vec{k}}$, which is of course inherited by $\vec{v}_{n\vec{k}}$. Applying for example an external electric field \vec{E} will lead to a change $\hbar\vec{k} \rightarrow \hbar\vec{k} - e\vec{E}t$ of the crystal momentum of an electron. As soon as \vec{k} crosses the Brillouin zone boundary, the velocity will go through a new periodicity cycle. As $\epsilon_{n\vec{k}}$ takes on minimum and maximum, $\vec{v}_{n\vec{k}}$ will oscillate and the electron will actually not translate but oscillate, too. These oscillations are called *Bloch oscillations*. In normal metals they are not observable, because defect scattering happens on time scales much faster than the oscillation period. However, in artificial lattices built for example from modulated electron gases in semiconductor heterostructures, one can achieve extremely large scattering times together with short Bloch frequencies, and the Bloch oscillations become observable.²

A schematic picture of a bandstructure with two bands is shown in Fig. 5.1. We here also assume, that both bands are separated by a *band gap* Δ_g , i.e. the energy supports of both bands do not overlap. This is quite often, but not necessarily always, the case in real band structures. We already know that electrons are Fermions, i.e. each k -state can occupy two electrons, and one has to occupy the available states until the number N_e of electrons in the system is accommodated. Two distinct situations are possible:

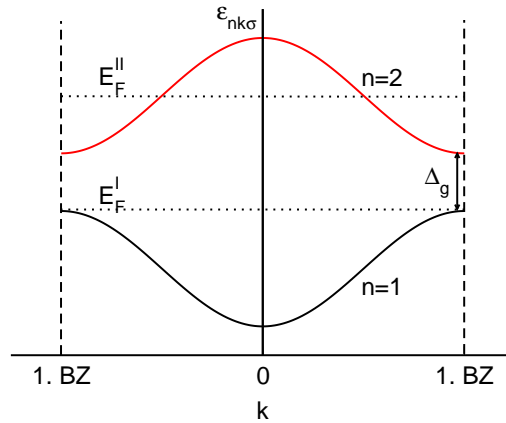


Figure 5.1: Schematic sketch of a bandstructure with two bands.

- (I) Band $n = 1$ is completely filled, and band $n = 2$ is empty. The Fermi energy, denoted as E_F^I in Fig. 5.1, then lies at the top of band $n = 1$. The next free state is separated by a finite gap Δ_g and the electronic system cannot respond to external perturbations providing energies smaller than Δ_g . Thus, the system will behave as an insulator.

When can such a situation be realized? Remember, that the number of allowed k values is equal to the number of elementary cells in the crystal. As each k can take two electrons with opposite spin, a necessary condition for the appearance of such a *Slater* or *band insulator* is that each elementary cell must contain an even number of electrons.

²J. Feldmann et al., *Optical Investigation of Bloch Oscillations in a Semiconductor Superlattice*, Phys. Rev. B **46**, 7252 (1992).

- (II) Some bands are partially filled. In this case the Fermi energy lies in this band, for example E_F^{II} in Fig. 5.1. For each band n that crosses the Fermi energy,

$$\epsilon_{n\bar{k}} = E_F$$

defines a surface of constant energy for this band. The set of all such surfaces is called *Fermi surface* of the electronic system, and the individual pieces are the *branches* of the Fermi surface. A system with a Fermi surface is always metallic.

As one cannot draw the dispersion of Fermi of a threedimensional lattice, one usually defines certain cuts through the first Brillouin zone. The end points of

Symbol	Description
Γ	Center of the Brillouin zone
Simple cube	
M	Center of an edge
R	Corner point
X	Center of a face
Face-centered cubic	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face
Body-centered cubic	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three edges
Hexagonal	
A	Center of a hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face

Table 5.1: Symbols for certain special points of important Brillouin zones.

such cuts are labeled with special symbols. For the most important Brillouin zones these symbols and their meaning are tabulated in Tab. 5.1. As specific examples you find below you the band structures and Fermi surfaces of Aluminum (left) and Copper (right), calculated with a density functional approach

5.1. CONSEQUENCES OF BLOCH'S THEOREM

discussed in the previous chapter. Both crystallize in an fcc structure and are metals according to the above classification. Note that the bandstructure does

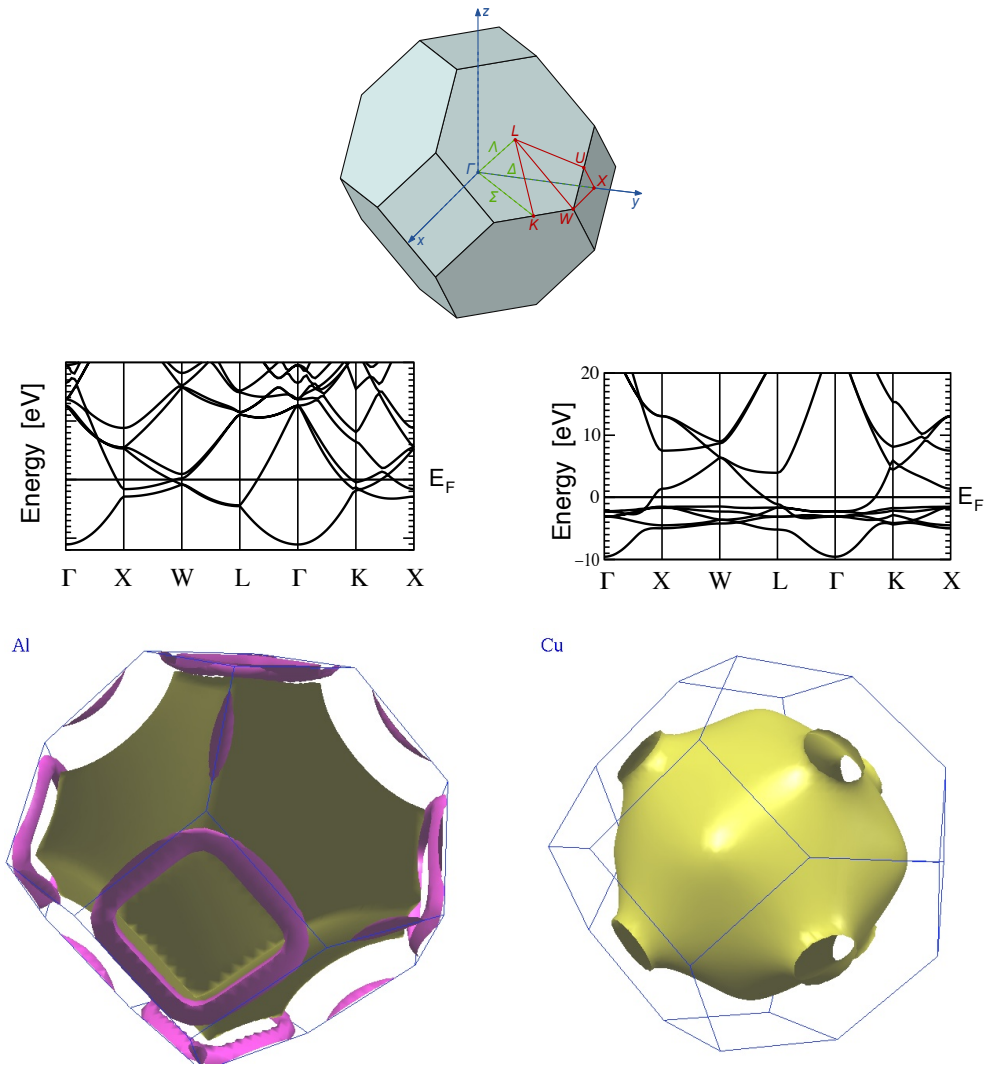


Figure 5.2: Top: High-symmetry points of the first Brillouin zone of the fcc lattice according to Tab. 5.1. Middle: Bandstructure of fcc Aluminum and Copper. Bottom: Fermi surfaces of Aluminum and Copper.

not show bands below -10eV (“core states”), which are separated by a gap from the “valence states”.

Another important property of the band structure follows from the invariance of the Hamilton operator under time reversal. Let us denote the operator performing a time reversal with $\hat{\mathcal{K}}$, then its properties are $\hat{\mathcal{K}}^{-1} \hat{p} \hat{\mathcal{K}} = -\hat{p}$ and

$\hat{\mathcal{K}}^{-1} \hat{s} \hat{\mathcal{K}} = -\hat{s}$. Then, because $\hat{\mathcal{K}}^{-1} \hat{H} \hat{\mathcal{K}} = \hat{H}$ and $\hat{\mathcal{K}}^{-1} \hat{T}_{\vec{R}} \hat{\mathcal{K}} = \hat{T}_{\vec{R}}$,

$$\hat{H} \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle = \hat{\mathcal{K}} \hat{H} |\Psi_{n\vec{k}\sigma}\rangle = \epsilon_{n\vec{k}\sigma} \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle$$

and with Bloch's theorem

$$\hat{T}_{\vec{R}} \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle = \hat{\mathcal{K}} \hat{T}_{\vec{R}} |\Psi_{n\vec{k}\sigma}\rangle = \hat{\mathcal{K}} \left(e^{i\vec{k}\cdot\vec{R}} |\Psi_{n\vec{k}\sigma}\rangle \right) = e^{-i\vec{k}\cdot\vec{R}} \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle .$$

Finally,

$$\hat{s}_z \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle = -\hat{\mathcal{K}} \hat{s}_z |\Psi_{n\vec{k}\sigma}\rangle = -\frac{\hbar\sigma}{2} \hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle$$

and thus

$$\hat{\mathcal{K}} |\Psi_{n\vec{k}\sigma}\rangle = |\Psi_{n,-\vec{k},-\sigma}\rangle, \quad \epsilon_{n\vec{k}\sigma} = \epsilon_{n,-\vec{k},-\sigma} .$$

Without an external magnetic field the band energies are thus at least twofold degenerate. This degeneracy is named *Kramer's degeneracy*.

5.2 Weak periodic potential

While the bare potential of the ions is quite strong, Pauli's principle prohibits too close distances. Thus the screening of the potential due to the core electrons leads to a "softening" of the potential seen by the valence electrons. Therefore, as a first step to understand the effect of a periodic potential, the assumption of a weak potential is quite reasonable.

From the discussion in the previous section we know that the eigenfunctions $\Psi_{\vec{k}}(\vec{r})$ are periodic with respect to vectors \vec{G} of the reciprocal lattice, i.e.

$$\Psi_{\vec{k}+\vec{G}}(\vec{r}) = \Psi_{\vec{k}}(\vec{r}) .$$

A suitable ansatz therefore is

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G} \in \text{RG}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} .$$

Likewise, we can expand the periodic potential in a Fourier series

$$V(\vec{r}) = \sum_{\vec{G} \in \text{RG}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} .$$

Inserting these expressions into the Schrödinger equation, we obtain

$$\begin{aligned} \hat{H} \Psi_{\vec{k}}(\vec{r}) &= \sum_{\vec{G}} \frac{\hbar^2}{2m} (\vec{k} - \vec{G})^2 c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} + \sum_{\vec{G}, \vec{G}'} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} c_{\vec{k}-\vec{G}'} e^{i(\vec{k}-\vec{G}')\cdot\vec{r}} \\ &= \epsilon_{\vec{k}} \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} . \end{aligned}$$

Since the $e^{i\vec{k}\cdot\vec{r}}$ form a linearly independent set of functions, the coefficients of the above equation have to fulfil

$$\left[\epsilon_{\vec{k}-\vec{G}}^{(0)} - \epsilon_{\vec{k}} \right] c_{\vec{k}-\vec{G}} + \sum_{\vec{G}'} U_{\vec{G}'-\vec{G}} c_{\vec{k}-\vec{G}'} = 0$$

where we introduced $\epsilon_{\vec{k}}^{(0)} := \hbar^2 k^2 / (2m)$. As noted before, for each $\vec{k} \in 1$. BZ there exist countably many solutions, labeled by the reciprocal lattice vectors \vec{G} . As we will see in a moment, this way of labelling is equivalent to the use of the band index introduced in the previous section.

We now use the assumption that $V(\vec{r})$ is weak, i.e. determine its effects within a perturbation theory. To this end we have to distinguish two cases:

- (i) For a certain pair \vec{k} and \vec{G}_1 we have no (near) degeneracy,³ i.e. for all $\vec{G} \neq \vec{G}_1$ we have

$$\left| \epsilon_{\vec{k}-\vec{G}_1}^{(0)} - \epsilon_{\vec{k}-\vec{G}}^{(0)} \right| \gg \bar{U} ,$$

where \bar{U} denotes a typical Fourier component of the potential. This tells us that we can use non-degenerate perturbation theory.

As you have learned in Quantum Mechanics I, we can then expand the energy and wave function in terms of $U_{\vec{G}}$, the lowest order being given by

$$\begin{aligned} |\Psi_{\vec{k}}^{(1)}\rangle &= |\phi_{\vec{k}-\vec{G}_1}\rangle \\ \langle \vec{r} | \phi_{\vec{k}-\vec{G}_1} \rangle &= \frac{1}{\sqrt{V}} e^{i(\vec{k}-\vec{G}_1) \cdot \vec{r}} \\ \epsilon_{\vec{k}}^{(1)} &= \epsilon_{\vec{k}-\vec{G}_1}^{(0)} + \langle \phi_{\vec{k}-\vec{G}_1} | \hat{V} | \phi_{\vec{k}-\vec{G}_1} \rangle \\ &= \epsilon_{\vec{k}-\vec{G}_1}^{(0)} + U_{\vec{0}} . \end{aligned}$$

If we furthermore assume $U_{\vec{0}} = 0$ (choice of energy zero), the lowest-order solution to Schrödinger's equation reduces to

$$\begin{aligned} c_{\vec{k}-\vec{G}_1} &\neq 0 \\ c_{\vec{k}-\vec{G}} &= 0 \quad (\forall \vec{G} \neq \vec{G}_1) \\ \epsilon_{\vec{k}} &\approx \epsilon_{\vec{k}-\vec{G}_1}^{(0)} . \end{aligned}$$

To find out how accurate this approximation is, we calculate the next order in the perturbation expansion. For every $\vec{G} \neq \vec{G}_1$ we find from Schrödinger's equation the correction to $c_{\vec{k}-\vec{G}_1}$ as

$$c_{\vec{k}-\vec{G}} \approx \frac{U_{\vec{G}_1-\vec{G}} c_{\vec{k}-\vec{G}_1}}{\epsilon_{\vec{K}-\vec{G}_1}^{(0)} - \epsilon_{\vec{k}-\vec{G}}^{(0)}} \Rightarrow \left[\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{G}_1}^{(0)} \right] c_{\vec{k}-\vec{G}_1} = \sum_{\vec{G} \neq \vec{G}_1} \frac{U_{\vec{G}-\vec{G}_1} U_{\vec{G}_1-\vec{G}}}{\epsilon_{\vec{K}-\vec{G}_1}^{(0)} - \epsilon_{\vec{k}-\vec{G}}^{(0)}} c_{\vec{k}-\vec{G}_1} ,$$

³The term “near degeneracy” means that all energy differences are huge compared to typical values of the perturbation.

or as by assumption $c_{\vec{k}-\vec{G}_1} \neq 0$

$$\epsilon_{\vec{k}} = \epsilon_{\vec{k}-\vec{G}_1}^{(0)} + \sum_{\vec{G} \neq \vec{G}_1} \frac{|U_{\vec{G}-\vec{G}_1}|^2}{\epsilon_{\vec{k}-\vec{G}_1}^{(0)} - \epsilon_{\vec{k}-\vec{G}}^{(0)}} + O(\bar{U}^3).$$

Therefore, the correction is indeed of order \bar{U}^2 in this case.

(ii) We have a certain \vec{k} and a set \vec{G}_i from the reciprocal lattice with

$$\begin{aligned} \left| \epsilon_{\vec{k}-\vec{G}_i}^{(0)} - \epsilon_{\vec{k}-\vec{G}}^{(0)} \right| &\gg \bar{U} \quad \forall \vec{G} \neq \vec{G}_i \\ \left| \epsilon_{\vec{k}-\vec{G}_i}^{(0)} - \epsilon_{\vec{k}-\vec{G}_j}^{(0)} \right| &= O(\bar{U}) , \end{aligned}$$

i.e. the energy values are almost degenerate and we now have to use degenerate perturbation theory. This means that we must take into account the full set of wave functions $\left\{ |\phi_{\vec{k}-\vec{G}_i}\rangle \right\}_{i=1}^m$ and set up the secular equation, which with the notation introduced above takes the form

$$\left[\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{G}_i}^{(0)} \right] c_{\vec{k}-\vec{G}_i} = \sum_{j=1}^m U_{\vec{G}_j-\vec{G}_i} c_{\vec{k}-\vec{G}_j} , \quad (5.1)$$

which is the standard expression within degenerate perturbation theory. To proceed we need to specify m , and as especially important case we study $m = 2$. We can choose without loss of generality $\vec{G}_1 = 0$ and assume that \vec{G}_2 points into one of the neighboring unit cells in reciprocal space. We thus look for solutions to $\epsilon_{\vec{k}}^{(0)} = \epsilon_{\vec{k}-\vec{G}_2}^{(0)}$, i.e. $|\vec{k}| = |\vec{k} - \vec{G}_2|$. From a geometrical point of view this relation means that \vec{k} must lie in the plane perpendicular to \vec{G}_2 including the point $\vec{G}_2/2$. This, however, is nothing but the definition of the boundary of the Wigner-Seitz cell in the direction of \vec{G}_2 , i.e. the definition of the first Brillouin zone.

In the present case we have only one \vec{G}_2 fulfilling this condition, i.e. only one such plane is involved. As usual eq. (5.1) has non-trivial solutions iff

$$\begin{vmatrix} \epsilon_{\vec{k}} - \epsilon_{\vec{k}}^{(0)} & -U_{\vec{G}_2} \\ U_{\vec{G}_2}^* & \epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{G}_2}^{(0)} \end{vmatrix} = 0 ,$$

where we have used $U_{-\vec{G}} = U_{\vec{G}}^*$. This leads to a quadratic equation with the solutions

$$\epsilon_{i,\vec{k}} = \frac{1}{2} \left(\epsilon_{\vec{k}}^{(0)} + \epsilon_{\vec{k}-\vec{G}_2}^{(0)} \right) \pm \sqrt{\frac{\left(\epsilon_{\vec{k}}^{(0)} - \epsilon_{\vec{k}-\vec{G}_2}^{(0)} \right)^2}{4} + |U_{\vec{G}_2}|^2} .$$

In particular, for \vec{k} on the Brillouin zone boundary, we have exactly $\epsilon_{\vec{k}}^{(0)} = \epsilon_{\vec{k}-\vec{G}_2}^{(0)}$ and hence $\epsilon_{1,\vec{k}} = \epsilon_{\vec{k}}^{(0)} - |U_{\vec{G}_2}|$ respectively $\epsilon_{2,\vec{k}} = \epsilon_{\vec{k}}^{(0)} + |U_{\vec{G}_2}|$, i.e.

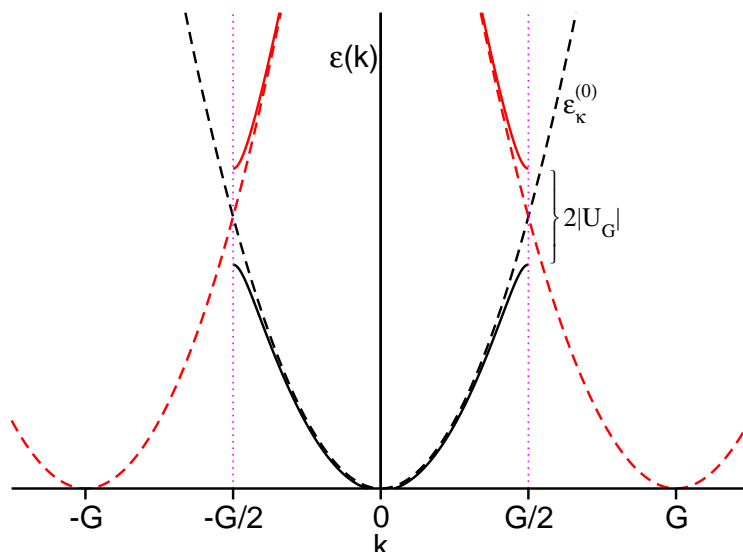


Figure 5.3: Schematic view of the action of a weak periodic potential on the dispersion. Around the boundary of the Brillouin zone at $k = \pm G/2$ a gap appears.

degenerate levels are split and an energy gap $2|U_{\vec{G}_2}|$ appears between them. The resulting dispersion is schematically shown in Fig. 5.3 and should be compared to the prediction in Fig. 5.1 obtained from general arguments based on Bloch's theorem.

Another feature of the dispersion in a weak periodic potential is obtained from looking at the gradient of $\epsilon_{i,\vec{k}}$ for \vec{k} on the Brillouin zone boundary. One finds

$$\vec{\nabla}_{\vec{k}} \epsilon_{i,\vec{k}} = \frac{\hbar^2}{2m} \left(\vec{k} - \frac{1}{2} \vec{G} \right) ,$$

i.e. the gradient is a vector in the plane constituting the BZ boundary. As the gradient is always perpendicular to the surfaces of constant energy, we can conclude that the surfaces of constant energy are perpendicular to the boundaries of the Brillouin zone. Although this result was obtained for a weak potential, one quite often observes this behavior for general periodic potentials, too.

Quite obviously, the above discussion holds for any set of vectors from the reciprocal lattice. For any such \vec{G} , the requirement $|\vec{k}| = |\vec{k} - \vec{G}|$ defines a plane perpendicular to \vec{G} including the point $\vec{G}/2$. Such a plane is called *Bragg plane*.⁴ With this identification we can introduce the following definition:

⁴In scattering theory Bragg planes define the planes for which constructive interference occurs.

The n -th Brillouin zone consists of all \vec{k} -points which can be reached by crossing exactly $n - 1$ Bragg planes.

An example of the first four Brillouin zones of the square net and the auxiliary lines used to construct them is shown in Fig. 5.4. What is the relevance of these higher-order Brillouin zones? As we have seen in Fig. 5.3, the second band in the first Brillouin zone is obtained from the branch of the dispersion which runs in the interval $k \in [G/2, G]$, which precisely is the second Brillouin zone in this one-dimensional sketch. Therefore, one uses the following identification: The band index n of the dispersion relation $\epsilon_{n,\vec{k}}$ is related to a reciprocal lattice vector \vec{G}_n through the requirement that (i) $\vec{k} + \vec{G}_n \in n$. BZ and (ii) $\epsilon_{n,\vec{k}} = \epsilon_{n,\vec{k} + \vec{G}_n}$, using the periodicity of the dispersion. One thus has two ways to represent a dispersion. On the one hand, one can plot

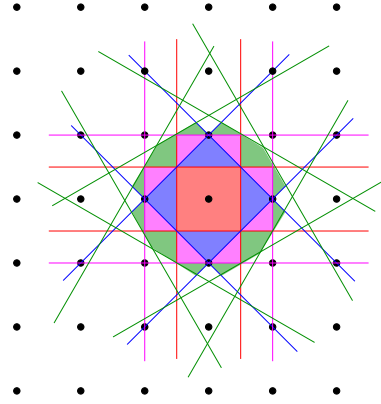


Figure 5.4: First 4 Brillouin zones of the square net.

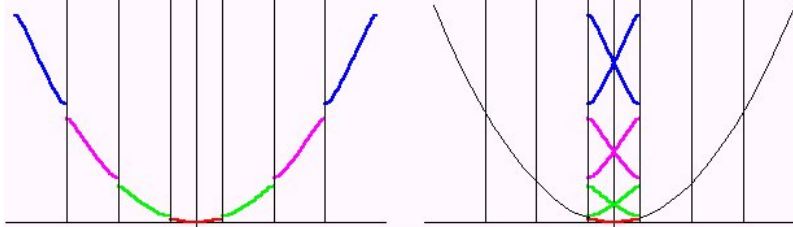


Figure 5.5: Left: Band structure in the *extended zone scheme*, i.e. the dispersion is shown as function of k from all \mathbb{R} . Right: Bandstructure in the *reduced zone scheme* by folding back the dispersion to the first Brillouin zone via translations through reciprocal lattice vectors from the n -th Brillouin zone.

$\epsilon_{n,\vec{k}}$ as function of $\vec{k} \in \mathbb{R}^d$, displaying the n -th branch only in the n -th Brillouin zone. This way of representation is called *extended zone scheme*. On the other hand, using the periodicity it is sufficient to visualize the band structure for $\vec{k} \in 1$. BZ, the so-called *reduced zone scheme*. A one-dimensional sketch is shown in Fig. 5.5. Note that due to the periodic potential each branch hits the zone boundary orthogonal, and a gap separates two different branches of the dispersion. As mentioned before, every time one of these branches is completely filled one will obtain an insulator or semi-conductor, depending on the actual size of the gap.

Last but not least the Fermi surface of a metal is obtained by fixing E_F and then collecting all pieces with $\epsilon_{n,\vec{k}} = E_F$. All contributions lying in the n -th BZ then constitute the n -th branch of the Fermi surface.

5.3 Calculating the band structure

Calculating the band structure for a given lattice is, even in the absence of interactions, not a trivial task. In general, we must solve a Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + U(\vec{r}) \right\} \phi_{n,\vec{k}\sigma}(\vec{r}) = \epsilon_{n,\vec{k}\sigma} \phi_{n,\vec{k}\sigma}(\vec{r}) .$$

The potential $U(\vec{r})$ includes the periodic potential due to the ions, and the solutions have to fulfil Bloch's theorem. If we want to go beyond independent electrons, we for example can think of the density-functional approach described in section 3.2.4, and $U(\vec{r})$ would then also contain the Hartree energy and the exchange-correlation potential.

There are two possibilities to proceed:

1. One can pick a suitable basis set and then try to solve Schrödinger's equation numerically. The problem already starts with the first task, the basis set. A natural choice seems to be plane waves, i.e.

$$\phi_{n,\vec{k}\sigma}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}}^{n,\sigma} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} .$$

There is however a certain problem, as the lattice potential usually is rather steep around the ions and more or less flat between them. To treat such a "localized" function in Fourier space, one needs a really huge number of plane waves, making the ansatz inefficient. One way out is to replace the potential of the nuclei and core electrons by something smooth (as it will be due to screening) and hope that this replacement does not affect the physical properties too much. The "pseudo-potential method" thus usually works fine when the energetic separation between core and valence electrons is good.

Another approach surrounds every atom by an imaginary sphere and expands the $\phi_{n,\vec{k}\sigma}(\vec{r})$ into spherical harmonics within each sphere. If one cuts through this system, it looks like the tool used to bake muffins, a so-called muffin tin, and the setup is consequently coined *muffin-tin approximation*. The wave-functions constructed this way are called *muffin-tin orbitals* (MTO). Since even for the heaviest elements the angular quantum

numbers do not exceed $L = 5$, one cuts off the basis set at a certain spherical harmonic, say $L = 5$, and can include all electrons up to this orbital quantum number into the calculation (including those of the core).⁵

There are certain problems connected with this method. Firstly, it is evident that one cannot cover the space with non-intersecting spheres. One therefore always will find some unaccounted space, called *interstitials*. Presently, there is a standard way to cope with this part, namely expand the wave function in plane waves in the interstitial and *augment* these plane waves to the expansion within the spheres (so-called *augmented plane waves*, APW).

Secondly, the boundary conditions at the surfaces of the sphere (with or without augmented plane waves) explicitly depend on the wave vector and hence the energy. The resulting eigenvalue equations are thus non-linear in nature and thus quite hard to solve. The standard approach is to linearize the energy dependence of the boundary conditions, recovering a standard eigenvalue problem. This leads to the *linearized muffin-tin orbitals* (LMTO). Confused? Don't relax yet: There are many other approaches (NMTO, ASW, PAW, ...) living happily together and of course everybody swears that his/her approach is the most efficient and accurate one.

2. A more analytical approach is the *linear combination of atomic orbitals* (LCAO) or *tight-binding approximation*. It is to some extent an extension of the Heitler-London approach to the hydrogen atom and starts from the observation that for a lattice constant $a \rightarrow \infty$ all atoms are independent and the electronic states can be described by atomic orbitals, those for different atoms being degenerate. If we start to push the atoms closer, the atomic wave-functions will start to "see" each other and an electron on site A can tunnel to site B and vice versa. Within a variational treatment one then would encounter two solutions $\phi_A \pm \phi_B$, the *bonding* for $+$ and the *anti-bonding* for $-$. The reason for these names comes from the fact that state with $+$ has a higher probability to find the electrons between the nuclei, thus reducing the repulsive energy of the nuclei, which is responsible for the binding between the two atoms. Moreover, the formerly degenerate energies of state A and B will be split, leading to the energy bands in a lattice.

To deduce the equations let us start with defining $\hat{H}_{at}(\vec{R}_i)$ to be the Hamiltonian of an isolated atom at site \vec{R}_i . We assume that we have

⁵That's why it is also called *all-electron method*.

5.3. CALCULATING THE BAND STRUCTURE

solved the eigenvalue problem for the bound states of this atom, i.e. $\hat{H}_{at}(\vec{R}_i)|\Psi_n(\vec{R}_i)\rangle = E_n|\Psi_n(\vec{R}_i)\rangle$. Let us further define

$$\Delta\hat{U} := \hat{H} - \sum_i \hat{H}_{at}(\vec{R}_i)$$

where \hat{H} is the Hamiltonian of the full system. If $\Delta\hat{U} = 0$ we can construct a wave function obeying Bloch's theorem as

$$|\phi_{n,\vec{k}}\rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} |\Psi_n(\vec{R}_i)\rangle$$

The proof is left as exercise. The energies in this case are simply $\epsilon_{n,\vec{k}} = E_n$, i.e. are independent of \vec{k} . Such a \vec{k} -independence is a general sign of localized states in a lattice.

With $\Delta\hat{U} \neq 0$ we now use as ansatz

$$|\phi_{n,\vec{k}}\rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} |\Phi_n(\vec{R}_i)\rangle$$

and try to generate a reasonable approximation for $|\Phi_n(\vec{R}_i)\rangle$, called *Wannier states*. Note that in general these Wannier states are not atomic states! As our atomic wave functions form a complete set, we may however expand

$$|\Phi_n(\vec{R}_i)\rangle = \sum_\gamma c_{n,\gamma} |\Psi_\gamma(\vec{R}_i)\rangle$$

To distinguish the band index n from the atomic quantum numbers I use Greek indices for the latter. We now multiply Schrödinger's equation

$$\left(\sum_i \hat{H}_{at}(\vec{R}_i) + \Delta\hat{U} \right) |\phi_{n,\vec{k}}\rangle = \epsilon_{n,\vec{k}} |\phi_{n,\vec{k}}\rangle$$

from the left by $\langle\Psi_\alpha(\vec{R}_j)|$ to obtain

$$E_\alpha \langle\Psi_\alpha(\vec{R}_j)|\phi_{n,\vec{k}}\rangle + \langle\Psi_\alpha(\vec{R}_j)|\Delta\hat{U}|\phi_{n,\vec{k}}\rangle = \epsilon_{n,\vec{k}} \langle\Psi_\alpha(\vec{R}_j)|\phi_{n,\vec{k}}\rangle$$

We now may use the orthonormality $\langle\Psi_\alpha(\vec{R}_j)|\Psi_\gamma(\vec{R}_j)\rangle = \delta_{\alpha\gamma}$ to obtain

$$\langle\Psi_\alpha(\vec{R}_j)|\phi_{n,\vec{k}}\rangle = e^{i\vec{k}\cdot\vec{R}_j} c_{n,\alpha} + \sum_{i \neq j} \sum_\gamma e^{i\vec{k}\cdot\vec{R}_i} c_{n,\gamma} \langle\Psi_\alpha(\vec{R}_j)|\Psi_\gamma(\vec{R}_i)\rangle .$$

Note that the atomic wave function for different sites are not necessarily orthogonal, i.e. $\langle\Psi_\alpha(\vec{R}_j)|\Psi_\gamma(\vec{R}_i)\rangle \neq 0$ in general!

Finally, we have

$$\begin{aligned} \langle\Psi_\alpha(\vec{R}_j)|\Delta\hat{U}|\phi_{n,\vec{k}}\rangle &= \sum_\beta e^{i\vec{k}\cdot\vec{R}_j} c_{n,\beta} \langle\Psi_\alpha(\vec{R}_j)|\Delta\hat{U}|\Psi_\beta(\vec{R}_j)\rangle + \\ &\quad \sum_{i \neq j} \sum_\beta e^{i\vec{k}\cdot\vec{R}_i} c_{n,\beta} \langle\Psi_\alpha(\vec{R}_j)|\Delta\hat{U}|\Psi_\beta(\vec{R}_i)\rangle . \end{aligned}$$

We now introduce the following definitions:

$$\begin{aligned}
 a_{\alpha\beta}(\vec{R}_i - \vec{R}_j) &:= \langle \Psi_\alpha(\vec{R}_i) | \Psi_\beta(\vec{R}_j) \rangle \\
 &= \int d^3r \Psi_\alpha^*(\vec{r} - \vec{R}_i) \Psi_\beta(\vec{r} - \vec{R}_j) \\
 &\quad \text{overlap integral}
 \end{aligned}$$

$$\begin{aligned}
 t_{\alpha\beta}(\vec{R}_i - \vec{R}_j) &:= -\langle \Psi_\alpha(\vec{R}_i) | \Delta \hat{U} | \Psi_\beta(\vec{R}_j) \rangle \\
 &= -\int d^3r \Psi_\alpha^*(\vec{r} - \vec{R}_i) \Delta U(\vec{r}) \Psi_\beta(\vec{r} - \vec{R}_j) \\
 &\quad \text{tunneling matrix element or hopping matrix element}
 \end{aligned}$$

$$\begin{aligned}
 \Delta \varepsilon_{\alpha\beta} &:= \langle \Psi_\alpha(\vec{R}_j) | \Delta \hat{U} | \Psi_\beta(\vec{R}_j) \rangle \\
 &= \int d^3r \Psi_\alpha^*(\vec{r} - \vec{R}_j) \Delta U(\vec{r}) \Psi_\beta(\vec{r} - \vec{R}_j)
 \end{aligned}$$

Due to the translational invariance we can choose $\vec{R}_j = 0$ to obtain

$$\begin{aligned}
 (\epsilon_{n,\vec{k}} - E_\alpha) c_{n,\alpha} &= -(\epsilon_{n,\vec{k}} - E_\alpha) \sum_{i \neq 0} \sum_{\beta} e^{i\vec{k} \cdot \vec{R}_i} a_{\alpha\beta}(\vec{R}_i) c_{n,\beta} + \sum_{\beta} \Delta \varepsilon_{\alpha\beta} c_{n,\beta} \\
 &\quad - \sum_{i \neq 0} \sum_{\beta} e^{i\vec{k} \cdot \vec{R}_i} t_{\alpha\beta}(\vec{R}_i) c_{n,\beta}
 \end{aligned}$$

If we define the matrices

$$\begin{aligned}
 t_{\vec{k}}^{\alpha\beta} &:= \sum_{i \neq 0} e^{i\vec{k} \cdot \vec{R}_i} t_{\alpha\beta}(\vec{R}_i) \\
 a_{\vec{k}}^{\alpha\beta} &:= \sum_{i \neq 0} e^{i\vec{k} \cdot \vec{R}_i} a_{\alpha\beta}(\vec{R}_i) \\
 \varepsilon^{\alpha\beta} &:= \varepsilon_{\alpha\beta}(\vec{R}_i)
 \end{aligned}$$

we can write the equation in compact matrix notation as

$$\boxed{
 \begin{aligned}
 \left[\underline{t}_{\vec{k}} - \underline{\varepsilon} - \left(\underline{E} - \epsilon_{n,\vec{k}} \underline{I} \right) \underline{B}_{\vec{k}} \right] \underline{c}_n &= 0 \\
 \underline{B}_{\vec{k}} &:= \underline{I} + \underline{a}_{\vec{k}}
 \end{aligned}
 }$$

This linear equation is a so-called *generalized eigenvalue problem*.

While the LCAO looks rather appealing, its application is all but straightforward. There are infinitely many atomic wave functions and one has to pick a suitable or rather manageable subset. Again, the observation, that usually angular momentum $L < 5$ is sufficient to account for all interesting elements, reduces the set of states from the onset. However, expanding a spherical harmonic $Y_{lm}(\varphi, \vartheta)$ centered at a given site \vec{R}_i about a different site \vec{R}_j , all l appear again, and the system to solve would grow

5.3. CALCULATING THE BAND STRUCTURE

quickly. To avoid this problem one typically assumes that the relevant atomic wave functions are well localized, i.e. their overlap is zero except for a few orbitals. To what extent this is a reasonable argument strongly depends on the material and the relevant orbitals at the Fermi level. For example, in transition metal compounds one often finds that the states at the Fermi level are dominated by $3d$ -like electrons, and a description within this subset of states is often quite accurate. A good example is LaMnO_3 . In other cases, for example La_2CuO_4 ,⁶ one needs the $3d$ - and $2p$ -states for a reasonable description.

To see how the method works let us study a simple example, namely one single “s-like” orbital with energy E_s in a simple-cubic lattice. In this case the equation collapses to

$$[t_{\vec{k}} - \varepsilon - (E_s - \epsilon_{\vec{k}}) B_{\vec{k}}] c_s = 0 .$$

The existence of a nontrivial solution requires

$$\epsilon_{\vec{k}} = -\frac{t_{\vec{k}} + \varepsilon}{1 + a_{\vec{k}}} + E_s .$$

As discussed before, to make sense the LCAO requires $|a_{\vec{k}}| \ll 1$ and we obtain

$$\epsilon_{\vec{k}} = E_s - \varepsilon - t_{\vec{k}} .$$

Also, within the assumption that the overlap between wave functions at different sites decreases strongly with distance, one typically makes the ansatz

$$t(\vec{R}) = \begin{cases} t & \text{for } \vec{R} = \vec{a}_i \\ 0 & \text{otherwise} \end{cases} .$$

We also used the inversion symmetry of the cubic lattice, which means $\Delta U(\vec{r}) = \Delta U(-\vec{r})$ and hence $t(-\vec{R}) = t(\vec{R})$. We then can perform the Fourier transformation explicitly to obtain

$$t_{\vec{k}} = t \sum_{i=1}^3 (e^{i\vec{k}\cdot\vec{a}_i} + e^{-i\vec{k}\cdot\vec{a}_i}) = 2t \sum_{i=1}^3 \cos(k_i a)$$

and finally, with $\tilde{E}_s = E_s - \varepsilon$,

$$\epsilon_{\vec{k}} = \tilde{E}_s - 2t \sum_{i=1}^3 \cos(k_i a) . \quad (5.2)$$

⁶This is one of the famous high- T_c superconductors.

This formula describes the so-called *nearest-neighbor tight-binding band* in the simple-cubic lattice, which plays an important role in the theory of transition metal oxides.

The behavior of the dispersion (5.2) around $\vec{k} = 0$ is obtained by expanding $\cos(k_i a)$ and leads to the expression

$$\epsilon_{\vec{k}} \approx \tilde{E}_s - 6t + ta^2 k^2 \stackrel{!}{=} \epsilon_0 + \frac{\hbar^2 k^2}{2m^*} .$$

Around the minimum of the dispersion, one again finds the behavior like for the free electron gas, and can even read off the effective mass as

$$m^* = \frac{\hbar^2}{2ta^2} .$$

Note that in the atomic limit $t \rightarrow 0$ the effective mass diverges. As rule of thumb one can use that narrow or tight bands can be modelled by “free electrons” with large effective mass.

5.4 Effective mass and electrons and holes

Semiconductors are solids for which one finds the following qualitative situation of their band structure: One group of bands is completely filled and the next empty band – the conduction band – is separated from the filled ones – the valence bands – by a comparatively small energy gap. Another class of systems, the so-called semimetals, differ from the semiconductors in that the Fermi energy is situated close to the edge of the valence band, i.e. it is almost but not completely filled. A typical realisation is sketched in Fig. 5.6. Note that the extrema of the valence and conduction band need not necessarily be right above each other. As we already have learned, the physical properties of a solid are dominated by the electronic structure close to the Fermi energy, i.e. the extremal points and their close environment in the present case. Let us now assume for simplicity⁷ that the extrema of valence and conduction band are situated at $k = 0$ and that

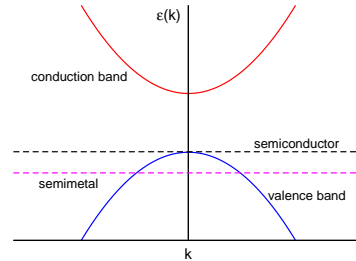


Figure 5.6: Schematic view of valence and conduction bands and the position of the Fermi energy in semimetals and semiconductors.

⁷This is actually quite often the case in real materials anyway. Otherwise we get an additional shift.

both have a parabolic extremum, i.e.

$$\epsilon_{\vec{k}} = \epsilon_0 + \frac{\hbar^2}{2} \vec{k}^T \frac{1}{\underline{\underline{M}}} \vec{k} + \dots$$

The matrix $\underline{\underline{M}}$ is called *tensor of effective masses* and with the above notes its knowledge suffices to describe the influence of electronic properties on physical quantities. This naming convention however has one flaw, namely for example for the valence band we have a maximum and hence the matrix $\underline{\underline{M}}$ is negative definite. As physicist one does not like negative masses and avoids this problem by defining $\underline{\underline{M}}^h := -\underline{\underline{M}}$ as tensor of effective masses, writing

$$\epsilon_{\vec{k}} = \epsilon_0 - \frac{\hbar^2}{2} \vec{k}^T \frac{1}{\underline{\underline{M}}^h} \vec{k} + \dots$$

for the valence band. The properties of carriers in these states are such that they react for example to an external electric field with an acceleration in the opposite direction,⁸ i.e. if one sticks to the interpretation that $q|\psi|^2$ represents the charge density they behave like positively particles with charge $q = +e$. The states near a parabolic maximum in the dispersion therefore behave similar to the holes already encountered for the free electron gas. Therefore, one has introduced the following *naming convention*:

Electronic states in the vicinity of a parabolic minimum of the dispersion are called *electron or particle states*, their dispersion is represented as

$$\epsilon_{\vec{k}} \approx \epsilon_0 + \frac{\hbar^2}{2} \vec{k}^T \frac{1}{\underline{\underline{M}}} \vec{k} . \quad (5.3)$$

Electronic states near a maximum in the dispersion are called *hole states*, with a dispersion

$$\epsilon_{\vec{k}} \approx \epsilon_0 - \frac{\hbar^2}{2} \vec{k}^T \frac{1}{\underline{\underline{M}}^h} \vec{k} . \quad (5.4)$$

The eigenvalues of $\underline{\underline{M}}$ are written as m_i and denoted as *effective masses*.

Note that these effective masses have to be distinguished from those appearing in Fermi liquid theory. Here, they are a measure of the noninteracting band structure, i.e. typically merely due to geometric properties like crystal structure, lattice constant and involved atomic orbitals. In contrast to interaction induced masses, which typically tend to enhance m^* , these *band masses* are typically

⁸Simply because $\vec{\nabla} \epsilon_{\vec{k}}$ has a negative sign.

found in the range $10^{-3} < m_i/m < 10^1$. Similarly, branches of the Fermi surface deriving from electron-like dispersions are called *electron Fermi surfaces*, those deriving from hole-like parts of the dispersion are called *hole Fermi surfaces*. An example can be found in Fig. 5.2 in the Fermi surface of Aluminum, where the violet parts represent electron Fermi surfaces and the amber branch a hole Fermi surface.⁹ The Fermi surface of copper, on the other hand, is electron-like. Let me emphasise that this effective description is more than just a convenient way of rewriting the dispersion. In particular in semiconductor physics one is often interested in spatially slowly varying electric fields. Similar to the arguments used in the discussion of the Thomas-Fermi screening, one can then derive an effective equation for the behavior of the electrons on these large length scales¹⁰ and arrives at a description in terms of a free Fermi gas with the electron mass replaced by the mass tensor defined above.

⁹This can also be deduced from the curvature, which for the amber branch quite obviously is negative.

¹⁰Large compared to the lattice constant, but small compared to the system size.

5.4. EFFECTIVE MASS AND ELECTRONS AND HOLES

Chapter 6

Lattice dynamics

6.1 The harmonic approximation

Up to now we have treated the ions as static objects sitting at the points of a crystal lattice, which we can identify with the equilibrium positions $\vec{R}_\alpha^{(0)}$. However, because of finite temperature or quantum mechanics (zero-point motion) the ions will move, i.e. in the course of time t the ions will occupy positions $\vec{R}_\alpha(t) = \vec{R}_\alpha^{(0)} + \vec{u}_\alpha(t)$. As discussed in section 1.2, both the core and valence electrons will modify the bare Coulomb interaction between the ions in a hitherto unknown way. But we know from experiment that the solid is stable, i.e. the total energy is minimal with respect to the equilibrium positions $\vec{R}_\alpha^{(0)}$. Further, as starting point we may assume that the displacements $\vec{u}_\alpha(t)$ are small. Consequently, we can expand¹

$$E \approx E_0 + \frac{1}{2} \sum_{\alpha \neq \beta} \sum_{i,j=1}^d \sqrt{M_\alpha} u_\alpha^i F_{\alpha\beta}^{ij} \sqrt{M_\beta} u_\beta^j, \quad F_{\alpha\beta}^{ij} := \frac{1}{\sqrt{M_\alpha M_\beta}} \left. \frac{\partial^2 E}{\partial u_\alpha^i \partial u_\beta^j} \right|_{\vec{u}=0},$$

with E_0 the energy of the equilibrium configuration. The quantity $F_{\alpha\beta}^{ij}$ is called *force-constant matrix*. An important fact is, that due to the translational symmetry of the lattice the force-constant matrix cannot depend on the individual equilibrium positions of the ions, but must be of the form $F^{ij}(\vec{R}_\alpha - \vec{R}_\beta)$. As you have learned in *Analytical Mechanics*, one needs the eigenvalues and -vectors of the force-constant matrix, which describe the so-called *normal modes* of the oscillations of the atoms in a crystal.

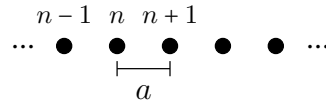
6.2 Ionic motion in solids

6.2.1 Repetitorium: Normal modes of the 1d Bravais lattice

The problem of a linear chain of masses coupled by harmonic springs has been discussed extensively in *Analytical Mechanics*. Therefore, I will just give a brief review of the important concepts.

The simplest case is a chain of N equal masses

m with an equilibrium distance between two masses a , as depicted to the right. Two neighboring masses interact via a harmonic potential



$V(R_n) = \frac{K}{2} [u_n - u_{n+1}]^2$, where $u_n = R_n - na$ is

the displacement from the equilibrium position. Note that the displacement is along the chain, which one calls *longitudinal* motion. A displacement perpendicular to the chain would be a *transverse* motion.

With periodic boundary conditions we can use as ansatz

$$u_n(t) \sim e^{i(kna - \omega t)}$$

¹The way the ionic masses enter seems a bit weird. However, in this manner the force-constant matrix contains direct information about the oscillation frequencies.

for the displacements. As usual, the boundary conditions then lead to

$$u_{N+1}(t) = u_1(t) \Leftrightarrow e^{ik(N+1)a} = e^{ika} \Leftrightarrow e^{ikNa} = 1 \Leftrightarrow k = \frac{2\pi}{a} \frac{i}{N}, \quad i \in \mathbb{Z},$$

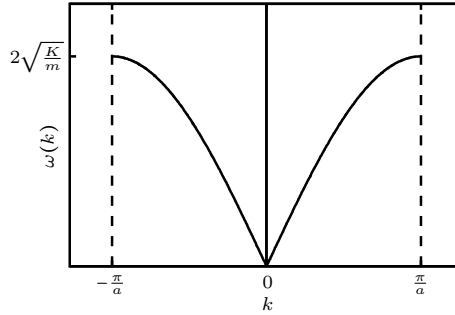
and, as for electrons in a periodic potential, there exist only N nonequivalent values for k , which we may choose from the *first Brillouin zone* $[-\frac{\pi}{a}, \frac{\pi}{a}]$. From a mathematical point of view, the fact that only N nonequivalent k values appear is connected with the structure of the equations of motion, which take the form of an eigenvalue problem for an $N \times N$ matrix.

Finally, the relation between ω and k ,

the *dispersion relation*, is determined

from the equation of motion as $\omega(k) = 2\sqrt{\frac{K}{m}} \left| \sin\left(\frac{1}{2}ka\right) \right|$. This dispersion relation is shown in the figure on the right.

It has some interesting features: First, it starts off linearly as $k \rightarrow 0$, and second it hits the Brillouin zone boundary with horizontal slope. We will see that these properties are not

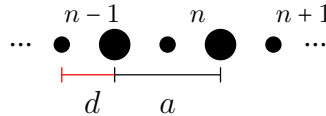


restricted to the one dimensional case considered here, but are general features

of the dispersion relations for any crystal. In particular, the behavior $\omega(k) \propto k$ for longitudinal waves like the ones discussed here is related to sound propagation. Our “theory” even gives an expression for the sound velocity, namely

$$c_s = \sqrt{\frac{K}{m}} a.$$

A slightly more complicated situation arises when one replaces every second mass by a larger one, say $M > m$, as shown to the right. Now we have something like in e.g. CsCl and consequently our crystal is a lattice with a basis.



Again, the lattice constant is a , and the distance between the small and the large mass we call d . For simplicity we assume $d = \frac{a}{2}$. The displacements are now

$u_n^{(1)}(t)$ for the mass m at $R_n = na$ and $u_n^{(2)}(t)$ for mass M at $R_n + d$. The harmonic potential in this case reads $V(R_n) = \frac{K}{2} \left\{ \left[u_n^{(1)} - u_n^{(2)} \right]^2 + \left[u_n^{(2)} - u_{n+1}^{(1)} \right]^2 \right\}$.

We again employ the periodic boundary conditions and use the ansatz

$$u_n^{(i)}(t) = \epsilon_i e^{i(kna - \omega t)}, \quad i = 1, 2,$$

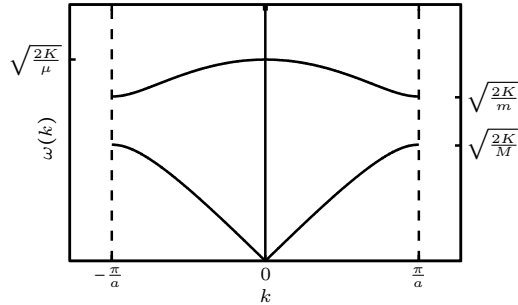
with $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$. Note that the first Brillouin zone is defined with respect to the lattice constant a and not the atomic spacing d . The prefactor ϵ_i describes the

relative amplitude and phase between the oscillations of the two masses within one unit cell. Inserting this ansatz into the equations of motion one obtains

$$\omega_{\pm}(k)^2 = \frac{K}{\mu} \left[1 \pm \sqrt{1 - 4 \frac{\mu}{m+M} \sin^2 \left(\frac{ka}{2} \right)} \right], \quad \mu = \frac{mM}{m+M}$$

for the dispersion relation. As $0 \leq \mu/(m+M) \leq 1/4$ we have $\omega(k)^2 \geq 0$ for all k and hence there exist two solutions $\omega_A(k) \equiv \omega_-(k)$ and $\omega_O(k) \equiv \omega_+(k)$.

The resulting dispersion for $M > m$ is shown to the right. Again one finds a branch (ω_A) with $\omega_A(k) \sim k$ as $k \rightarrow 0$. Analyzing the “polarization” ϵ_- in this case one finds that both masses oscillate in phase, i.e. the system behaves like the chain with a single mass. The slope, i.e. the sound velocity, consequently is $\sqrt{\frac{2K}{m+M}}$. Since this branch is connected with sound propagation²



along the chain it is also called *acoustic branch* (hence the A as subscript).

The second branch has a finite frequency even for $k = 0$. Analyzing the “polarization” ϵ_+ shows that here the two masses in a unit cell move with the opposite phase. For an ionic crystal, both constituents can also have opposite charge. In this case, such an oscillation will lead to a periodically varying dipole moment within the unit cell, which can couple to the electric field of electromagnetic waves. Therefore, this mode can couple to light, and is called the *optical mode*.

6.2.2 Normal modes of a crystal

Within the harmonic approximation, the force-constant matrix is defined as

$$F_{\alpha\beta}^{ij} := \frac{1}{\sqrt{M_\alpha M_\beta}} \left. \frac{\partial^2 E}{\partial u_\alpha^i \partial u_\beta^j} \right|_{\underline{u}=0} \quad (6.1)$$

From this definition one can deduce several properties of the force-constant matrix:

1. $F_{\alpha\beta}^{ij} = F_{\beta\alpha}^{ji}$
2. $F_{\alpha\beta}^{ij}$ is real, because the potential and displacements are.
3. $F_{\alpha\beta}^{ij}$ is invariant under transformations from the space group of the crystal, because the potential energy is independent of the “point of view”.

²More precisely: Propagation of elastic waves.

4. Let us study a homogeneous displacement of the whole crystal by a fixed vector \vec{R}_0 . As such a displacement does not change the relative positions of the atoms, the energy does not change either. Therefore,

$$0 = \sum_{i,j} \sum_{\alpha\beta} R_{0,i} F_{\alpha\beta}^{ij} R_{0,j} = \sum_{i,j} R_{0,i} R_{0,j} \sum_{\alpha\beta} F_{\alpha\beta}^{ij} .$$

Since \vec{R}_0 was arbitrary,

$$0 = \sum_{\alpha,\beta} F_{\alpha\beta}^{ij} = \sum_{\alpha,\beta} F^{ij} (\vec{R}_\alpha - \vec{R}_\beta) .$$

Furthermore, already the sum on \vec{R}_α already exhausts all possible vectors, hence

$$\sum_{\alpha} F_{\alpha\beta}^{ij} = 0 .$$

The first two points tell us, that the force-constant matrix is real-symmetric, i.e. it has $3Np$ real eigenvalues, where N is the number of unit cells and p is the number of atoms per unit cell. Furthermore, the eigenvectors $\vec{e}(\vec{R}_\alpha)$ of F form a complete orthonormal system. As F is invariant under transformations from the space group, which means $[F, T_g] = 0$ for all elements T_g of the symmetry group, the eigenvectors can be chosen to be simultaneously eigenvectors of the translation group, since this is a proper subgroup of the full space group. Thus, for all vectors \vec{R} from the Bravais lattice, Bloch's theorem (4.2) tells us

$$T(\vec{R})\vec{e}(\vec{R}_\alpha) = \vec{e}(\vec{R}_\alpha + \vec{R}) = e^{-i\vec{k}\cdot\vec{R}}\vec{e}(\vec{R}_\alpha) .$$

Let us now write the vector $\vec{R}_\alpha =: \vec{R} + \vec{\kappa}_\alpha$, where \vec{R} is as above a vector from the Bravais lattice and $\vec{\kappa}_\alpha$ points to the desired atom α in the unit cell pointed to by \vec{R} . The eigenvector can therefore be written as

$$\vec{e}(\vec{R}_\alpha) = \vec{e}(\vec{k}; \vec{R} + \vec{\kappa}_\alpha) = e^{i\vec{k}\cdot\vec{R}}\vec{e}(\vec{k}; \vec{\kappa}_\alpha) .$$

The vectors $\vec{e}_\alpha(\vec{k}) := \vec{e}(\vec{k}; \vec{\kappa}_\alpha)$ are called *polarization vectors* of the normal mode with wave vector \vec{k} .

By construction we know that the vectors $\vec{e}_\alpha(\vec{k})$ are eigenvectors of F , i.e.

$$\begin{aligned} \sum_{j\beta} F_{\alpha\beta}^{ij} e_j(\vec{R}_\beta) &= \omega(\vec{k})^2 e_i(\vec{R}_\alpha) \\ &= \sum_j \sum_{\vec{R},\beta} F^{ij} (\vec{R}_\alpha - \vec{R} - \vec{\kappa}_\beta) e^{i\vec{k}\cdot\vec{R}} e_{\beta,j}(\vec{k}) \\ &= \omega(\vec{k})^2 e^{i\vec{k}\cdot\vec{R}'} e_{\alpha,i}(\vec{k}) . \end{aligned}$$

This can be cast into the form

$$\sum_{\beta} \underline{D}_{\alpha\beta}(\vec{k}) \vec{e}_\beta(\vec{k}) = \omega(\vec{k})^2 \vec{e}_\alpha(\vec{k})$$

with

$$\begin{aligned} \underline{\underline{D}}_{\alpha\beta}(\vec{k}) &:= \sum_{\vec{R}} \underline{\underline{F}}(\vec{R}' + \vec{\kappa}_\alpha - \vec{R} - \vec{\kappa}_\beta) e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \\ &= \sum_{\vec{R}} \underline{\underline{F}}(\vec{R} + \vec{\kappa}_\alpha - \vec{\kappa}_\beta) e^{-i\vec{k}\cdot\vec{R}} . \end{aligned}$$

The matrix $\underline{\underline{D}}_{\alpha\beta}(\vec{k})$ is called *dynamical matrix*. It is hermitian, because $\underline{\underline{F}}$ is real-symmetric. Since for any vector \vec{G} from the reciprocal lattice $e^{-i\vec{G}\cdot\vec{R}} = 1$, the dynamical matrix has the property $\underline{\underline{D}}_{\alpha\beta}(\vec{k} + \vec{G}) = \underline{\underline{D}}_{\alpha\beta}(\vec{k})$. Therefore, as for electrons, also the eigenvectors and eigenvalues must be periodic with respect to the reciprocal lattice, and all nonequivalent vectors \vec{k} can be chosen to lie inside the first Brillouin zone. Furthermore, because the energy has a minimum, the eigenvalues must fulfill $\omega_k^2 \geq 0$. In other words, both $\underline{\underline{F}}$ and $\underline{\underline{D}}$ are positive semi-definite.

Collecting all these observations, we arrive at the following result:

There exist N nonequivalent wave vectors \vec{k} in the first Brillouin zone, which serve as label for the normal modes of the ionic oscillations obtained from the eigenvalue equation

$$\sum_{\alpha} \underline{\underline{D}}_{\beta\alpha}(\vec{k}) \vec{e}_{\alpha}(\vec{k}) = \omega(\vec{k})^2 \vec{e}_{\beta}(\vec{k}) .$$

For each \vec{k} , this eigenvalue equation has $3p$ eigenvalues and -vectors.

The $3p$ eigenvectors we will denote with $\vec{e}_{\alpha}^{(m)}(\vec{k})$, where $\alpha = 1, \dots, p$ denotes the atom in the unit cell, and $m = 1, \dots, 3$ is called *polarization index*. As usual, the eigenvectors form a complete orthonormal set, i.e.

$$\begin{aligned} \sum_{\alpha} [\vec{e}_{\alpha}^{(m)}(\vec{k})]^* \cdot \vec{e}_{\alpha}^{(n)}(\vec{k}) &= \delta_{nm} \\ \sum_m [e_{\alpha,i}^{(m)}(\vec{k})]^* e_{\beta,j}^{(m)}(\vec{k}) &= \delta_{ij} \delta_{\alpha\beta} . \end{aligned}$$

Inspection of the definition of the dynamical matrix shows that the \vec{k} dependence comes only from the factor $e^{-i\vec{k}\cdot\vec{R}}$. This means, that $\underline{\underline{D}}(\vec{k})$ is a continuous function of \vec{k} , a property which then is inherited by the eigenvalues and -vectors. A further property can be deduced from the fact that F is real-symmetric, which means that $D_{\alpha\beta}^{ij}(\vec{k}) = D_{\beta\alpha}^{ji}(-\vec{k})$. Combining this property with the hermiticity of D , one can follow that $\omega_m(\vec{k})^2 = \omega_m(-\vec{k})^2$ and $\vec{e}_{\kappa}^{(m)}(-\vec{k}) = \vec{e}_{\kappa}^{(m)}(\vec{k})^*$. Therefore, the dispersion of the normal modes of a crystal is always symmetric under inversion, even if the crystal does not have this symmetry! Note that this is

different from the electronic bandstructure, which only has this symmetry if the crystal is invariant with respect to inversion about a lattice point.

Let us now turn to point 4 of our initial enumeration, i.e.

$$\sum_{\alpha} F_{\alpha\beta}^{ij} = 0 .$$

Thus for any fixed vector \vec{R}_0

$$\sum_{\alpha} \underline{\underline{F}}_{\alpha\beta} \vec{R}_0 = 0$$

holds, which means that there always exists eigenvalues $\omega_m(\vec{k})^2 = 0$ with eigenvector \vec{R}_0 arbitrary. As \vec{R}_0 is an eigenvector, the relation $T_{\vec{R}} \vec{R}_0 = e^{i\vec{k} \cdot \vec{R}} \vec{R}_0 \stackrel{!}{=} \vec{R}_0$ must be fulfilled, which means that these eigenvalues must belong to $\vec{k} = 0$. Finally, as we have three independent directions in \mathbb{R}^3 , the eigenvalue $\omega = 0$ must be at least threefold degenerate. Due to the continuity of the dispersion as function of \vec{k} , we can make the following statement:

There exist three branches of the dispersion $\omega_m^A(\vec{k})$, $m = 1, 2, 3$, with $\omega_m^A(\vec{k} \rightarrow 0) \rightarrow 0$. These are called *acoustic branches*. The remaining $3(p-1)$ branches are called *optical*.

How do the acoustic branches depend on \vec{k} for $\vec{k} \rightarrow 0$. To this end we study $\underline{\underline{D}}_{\alpha\beta}(\vec{k} \rightarrow 0)$:

$$\underline{\underline{D}}_{\alpha\beta}(\vec{k}) \approx \sum_{\vec{R}} \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) \left[1 - i\vec{k} \cdot \vec{R} - \frac{1}{2}(\vec{k} \cdot \vec{R})^2 \right] .$$

As the dispersion must have inversion symmetry with respect to \vec{k} and also must be continuous, the term linear in \vec{k} must vanish and we obtain

$$\underline{\underline{D}}_{\alpha\beta} \approx \sum_{\vec{R}} \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) - \frac{1}{2} \sum_{ij} k_i \left[\sum_{\vec{R}} R_i \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) R_j \right] k_j .$$

For the acoustic branches and for $\vec{k} \rightarrow 0$ the eigenvectors are homogeneous displacements independent of the atom in the unit cell, i.e. $\vec{e}_{\beta}(\vec{k} \rightarrow 0) \approx \vec{e}(\vec{k})$. In this case we can make use of

$$\sum_{\beta} \sum_{\vec{R}} \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) \vec{e}_{\beta}(\vec{k}) \approx \sum_{\beta} \sum_{\vec{R}} \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) \vec{e}(\vec{k}) = \underbrace{\sum_{\vec{R}_i} \underline{\underline{F}}(\vec{R}_i)}_{=0} \vec{e}(\vec{k}) = 0$$

and the eigenvalue equation reads

$$\sum_{\beta} \underline{\underline{D}}_{\alpha\beta} \vec{e}(\vec{k}) = \sum_{\beta} \left\{ -\frac{1}{2} \sum_{ij} k_i \left[\sum_{\vec{R}} R_i \underline{\underline{F}}(\vec{R} + \vec{\kappa}_{\alpha} - \vec{\kappa}_{\beta}) R_j \right] k_j \right\} \vec{e}(\vec{k}) = \omega(\vec{k})^2 \vec{e}(\vec{k})$$

which enforces that the eigenvalues must be of the form

$$\omega_m^A(\vec{k})^2 = \vec{k}^T \underline{\underline{c}}_m \vec{k} \propto k^2 .$$

Therefore, the frequencies $\omega_m^A(\vec{k})$ of the acoustic branches vanish linearly with $\vec{k} \rightarrow 0$. The tensors $\underline{\underline{c}}_m$ can be connected with the elastic constants of the crystal.

As important as the eigenfrequencies are the eigenvectors $\vec{e}_{\alpha}^{(m)}(\vec{k})$ of the normal modes, in particular their connection with the direction \vec{k} of wave propagation. The simplest case is an isotropic medium, where only two possibilities can exist: either $\vec{e} \parallel \vec{k}$, in which case one calls the mode *longitudinal*, or $\vec{e} \perp \vec{k}$, which is named *transverse mode*. For the latter, one in addition has two possibilities. In a crystal, such a clear distinction is possible only along certain high-symmetry directions in \vec{k} -space, for example along a n -fold rotation axis of the reciprocal lattice. One then has the classification into *longitudinal acoustic* (LA) and optical (LO) respectively *transverse acoustic* (TA) and optical (TO) modes. As the dispersions are continuous in \vec{k} , one keeps the notions for the different branches also off these high symmetry directions.

6.3 Quantum theory of the harmonic crystal

6.3.1 The Hamilton operator

In the adiabatic and harmonic approximation the Hamilton function of a crystal is given by

$$H_N = \sum_{\alpha,i} \frac{P_{i,\alpha}^2}{M_{\alpha}} + V_{Harm} , \quad V_{Harm} = \frac{1}{2} \sum_{\alpha\beta} \sum_{ij} \sqrt{M_{\alpha}} u_{\alpha}^i F_{\alpha\beta}^{ij} \sqrt{M_{\beta}} u_{\beta}^j$$

with $\underline{\underline{F}}$ given by equation (6.1). In the previous section we have solved the corresponding classical problem (at least formally). As the polarization vectors $\vec{e}_{\alpha}^{(m)}(\vec{k})$ corresponding to eigenvalue $\omega_m(\vec{k})$ of the dynamical matrix form a complete orthonormal set we can expand the displacements $\vec{u}_{\alpha} = \vec{u}(\vec{R}_{\alpha}) = \vec{u}(\vec{R} +$

$\vec{\kappa}$) and momenta $\vec{P}_\alpha = \vec{P}(\vec{R} + \vec{\kappa})$ according to³

$$\begin{aligned}\vec{u}(\vec{R} + \vec{\kappa}) &= \frac{1}{\sqrt{N}} \sum_m \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}} \vec{e}_\kappa^{(m)}(\vec{k}) R_m(\vec{k}) \\ \vec{P}(\vec{R} + \vec{\kappa}) &= \frac{\sqrt{M_\kappa}}{\sqrt{N}} \sum_m \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}} \vec{e}_\kappa^{(m)}(\vec{k}) P_m(\vec{k}) ,\end{aligned}$$

where N is the number of unit cells in the Bravais lattice of the crystal and \vec{R} a lattice vector. As before, \vec{k} takes on all N nonequivalent values from the first BZ and the polarization index runs from $m = 1, \dots, 3p$ with p being the number of atoms per unit cell. Inserting these relations into the Hamiltonian, we arrive at

$$H_N = \sum_m \sum_{\vec{k}} \left[\frac{1}{2} P_m(\vec{k})^2 + \frac{1}{2} \omega_m(\vec{k})^2 R_m(\vec{k})^2 \right] .$$

Thus, H_N is the sum of $3Np$ decoupled harmonic oscillators. The quantization is now done along the standard lines: For the operators $\hat{R}_m(\vec{k})$ and $\hat{P}_m(\vec{k})$ we introduce the canonical commutation relations⁴ $[\hat{R}_m(\vec{k}), P_l(\vec{k}')] = i\hbar \delta_{ml} \delta_{\vec{k}, \vec{k}'}$. Note that due to the properties for $\vec{k} \rightarrow -\vec{k}$ we have $R_m(\vec{k})^\dagger = R_m(-\vec{k})$ and similar for $P_m(\vec{k})$. Finally, we can define ladder operators

$$\hat{b}_m(\vec{k})^{(\dagger)} = \sqrt{\frac{\omega_m(\vec{k})}{2\hbar}} \hat{R}_m(\vec{k})^{(\dagger)} \quad \begin{matrix} (+) \\ (-) \end{matrix} \quad \frac{i}{\sqrt{2\omega_m(\vec{k})\hbar}} \hat{P}_m(\vec{k})^{(\dagger)}$$

which obey the commutation relations

$$[\hat{b}_m(\vec{k}), \hat{b}_l(\vec{k}')^\dagger] = \delta_{ml} \delta_{\vec{k}, \vec{k}'} .$$

The Hamilton operator then takes on the form

$$\hat{H}_N = \sum_m \sum_{\vec{k}} \hbar \omega_m(\vec{k}) \left[\hat{b}_m(\vec{k})^\dagger \hat{b}_m(\vec{k}) + \frac{1}{2} \right] \quad (6.2)$$

The thus quantized modes of the lattice vibrations one calls *phonons* and the dispersion $\omega_m(\vec{k})$ the *phonon dispersion*. The operators \hat{b} and \hat{b}^\dagger are also called *annihilation* and *creation* operators for phonons.

Finally, taking into account $\hat{R}_m(\vec{k})^\dagger = \hat{R}_m(-\vec{k})$,

$$\hat{u}(\vec{R} + \vec{\kappa}) = \frac{1}{\sqrt{N}} \sum_m \sum_{\vec{k}} \sqrt{\frac{\hbar}{2\omega_m(\vec{k})}} e^{i\vec{k}\cdot\vec{R}} \vec{e}_\kappa^{(m)}(\vec{k}) [\hat{b}_m(\vec{k}) + \hat{b}_m(-\vec{k})^\dagger] \quad (6.3a)$$

$$\hat{P}(\vec{R} + \vec{\kappa}) = \frac{\sqrt{M_\kappa}}{\sqrt{N}} \sum_m \sum_{\vec{k}} \sqrt{\frac{\hbar \omega_m(\vec{k})}{2}} e^{i\vec{k}\cdot\vec{R}} \vec{e}_\kappa^{(m)}(\vec{k}) [\hat{b}_m(\vec{k}) - \hat{b}_m(-\vec{k})^\dagger] \quad (6.3b)$$

³The masses M_κ are included in the dynamical matrix and thus implicitly contained in the polarization vectors $|\vec{e}_\kappa^{(m)}(\vec{k})| \propto \sqrt{M_\kappa}^{-1}$.

⁴We may as well do this for \hat{u} and \hat{P} and then perform the unitary transformation to the normal modes.

The last two relations are needed for calculations of properties involving the actual ionic positions, such as x-ray or neutron scattering from the crystal. Furthermore, theories beyond the harmonic approximations use this expansion to rewrite the anharmonicities in terms of the ladder operators.

6.3.2 Thermodynamic properties of the crystal

Using the concepts of statistical physics, we can write the free energy of the quantum system “crystal” as

$$F = -k_B T \ln \mathcal{Z} ,$$

where the *partition function* \mathcal{Z} is defined as

$$\mathcal{Z} = \text{Tr} e^{-\hat{H}_N/k_B T} .$$

In the harmonic approximation, the Hamiltonian is given by (6.2), hence with $\beta^{-1} = k_B T$ and using the eigenstates $|n_m(\vec{k})\rangle$ defined as $\hat{b}_m(\vec{k})^\dagger \hat{b}_m(\vec{k})|n_m(\vec{k})\rangle = n_m(\vec{k})|n_m(\vec{k})\rangle$ with $n_m(\vec{k}) \in \mathbb{N}_0$,

$$\mathcal{Z} = \prod_{m, \vec{k}} \sum_n e^{-\beta(n+\frac{1}{2})\hbar\omega_m(\vec{k})} = \prod_{m, \vec{k}} \frac{e^{-\beta\hbar\omega_m(\vec{k})/2}}{1 - e^{-\beta\hbar\omega_m(\vec{k})}} = \prod_{m, \vec{k}} \frac{e^{\beta\hbar\omega_m(\vec{k})/2}}{e^{\beta\hbar\omega_m(\vec{k})} - 1} .$$

From thermodynamics, we know the relations

$$\begin{aligned} F(T, V) &= U(T, V) - TS(T, V) \\ S(T, V) &= -\frac{\partial F(T, V)}{\partial T} \\ C_V(t) &= \frac{\partial U(T, V)}{\partial T} . \end{aligned}$$

With some simple manipulations one finds

$$U(T, V) = \frac{1}{2} \sum_m \sum_{\vec{k}} \hbar\omega_m(\vec{k}) + \sum_m \sum_{\vec{k}} \frac{\hbar\omega_m(\vec{k})}{e^{\beta\hbar\omega_m(\vec{k})} - 1} ,$$

where the first term is the *zero point energy* we will denote with U_0 .

As the dispersion is bounded, we can distinguish two limiting cases:

- (i) $k_B T \gg$ typical phonon frequencies. Then we may expand with $x = \beta\hbar\omega_m(\vec{k}) \ll 1$

$$\frac{1}{e^x - 1} \approx \frac{1}{x + \frac{1}{2}x^2 + \dots} \approx \frac{1}{x} \left[1 - \frac{x}{2} \pm \dots \right]$$

to find

$$U(T, V) \approx U_0 + \sum_m \sum_{\vec{k}} k_B T = U_0 + 3Np k_B T$$

respectively for the specific heat

$$C_V = 3Npk_B ,$$

which is just the law of Dulong-Petit.

- (ii) $k_B T \rightarrow 0$, i.e. $x \gg 1$. Here only modes with $\omega_m(\vec{k}) \rightarrow 0$ can contribute, the other modes are damped exponentially. Typically, the relevant modes are just the acoustic modes $\omega_i^A(\vec{k}) \approx c_i k$. We thus have to evaluate

$$U(T, V) = U_0 + \sum_{i=1}^3 \sum_{\vec{k}} \frac{\hbar c_i k}{e^{\beta c_i k} - 1} .$$

Consequently, in the *thermodynamic limit* $N \rightarrow \infty$, $V \rightarrow \infty$, $n = \frac{N}{V} = \text{const.}$,

$$\frac{1}{V} U(T, V) = u_0 + \sum_{i=1}^3 \int_{\Omega_{BZ}} \frac{d^3 k}{(2\pi)^3} \frac{\hbar c_i k}{e^{\beta c_i k} - 1} .$$

For low enough T one can safely integrate over all \vec{k} as for finite k $\beta c_i k \gg 1$ and hence those contributions will be suppressed exponentially. With the further replacement $x = \beta \hbar c_i k$ we find

$$\begin{aligned} \frac{1}{V} U(T, V) &= u_0 + \sum_{i=1}^3 \int_0^\infty k^2 dk \int \frac{d\Omega_{\vec{k}}}{(2\pi)^3} \frac{\hbar c_i k}{e^{\beta c_i k} - 1} \\ &= u_0 + \sum_{i=1}^3 \underbrace{\int \frac{d\Omega_{\vec{k}}}{4\pi} \frac{1}{c_i^3}}_{=: \frac{3}{c_s^3}} \frac{(k_B T)^4}{2\pi^2 \hbar^3} \underbrace{\int_0^\infty \frac{x^3}{e^x - 1}}_{= \frac{\pi^4}{15}} \\ &= u_0 + \frac{\pi^2}{10} \frac{(k_B T)^4}{(\hbar c_s)^3} . \end{aligned}$$

The quantity c_s introduced is an measure of the sound velocity in the crystal. For the specific heat we finally find

$$\frac{1}{V} C_V = \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar c_s} \right)^3 .$$

Note that this shows the experimentally observed behavior $C_V(T) \rightarrow 0$ for $T \rightarrow 0$, which cannot be explained by classical physics.

- (iii) $\beta \hbar \omega_m(\vec{k}) \approx 1$, where one in principle has to perform a full calculation. As the full dispersion is usually not known, a typical approach is to use certain models. These are

- the Debye model – One assumes $\omega(\vec{k}) = ck$ everywhere up to a certain value k_D (*Debye wave vector*), where k_D is determined from the requirement that one has exactly $3N$ acoustic modes. This is achieved by equating the volume occupied by N wave vectors, $N \frac{(2\pi)^3}{V} = n \cdot (2\pi)^3$ with the volume of a sphere of radius k_D ,

$$= n \cdot (2\pi)^3 = \frac{4\pi}{3} k_D^3 \Leftrightarrow k_D^3 = 6\pi^2 \cdot n .$$

The quantity $\Theta_D = \frac{\hbar c}{k_B} k_D$ is called *Debye temperature*. Under these assumptions the contribution of the acoustic branches to the specific heat becomes

$$\frac{1}{V} C_V^{(A)} = 9nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4}{(e^x - 1)^2} . \quad (6.4)$$

- the Einstein model – The $3(p-1)$ optical branches are approximated by $\omega_m(\vec{k}) \approx \omega_E = \text{const.}$ within the Brillouin zone. For the specific heat we then find

$$\frac{1}{V} C_V^{(O)} = 3(p-1)nk_B \frac{(\beta\hbar\omega_E)^2 e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2} . \quad (6.5)$$

It is straightforward to show that for $C_V^{(A)} + C_V^{(O)} \xrightarrow{T \rightarrow \infty} 3pNk_B$ (Dulong-Petit), while for $T \rightarrow 0$ one finds

$$C_V \approx N \frac{3\pi^4}{5} k_B \left(\frac{T}{\Theta_D} \right)^3 + Nk_B(p-1) \left(\frac{\hbar\omega_E}{k_B T} \right)^2 e^{-\beta\hbar\omega_E} .$$

6.4 Beyond the harmonic approximation

How good is the harmonic approximation for the ionic motion? While at first glance the results from the previous section suggest that it is rather accurate, there are a large class of directly measurable physical quantities that show that anharmonic effects in crystals are actually very important. One class is transport, in particular thermal conductivity, which for a harmonic crystal would be infinite.

Another effect which must be attributed to anharmonic effects is the thermal expansion of a crystal. To see this let us play with the thermodynamic relations. We first observe that the pressure is given through the free energy as

$$p = - \left(\frac{\partial F}{\partial V} \right)_T .$$

From the Maxwell relations we further know that

$$T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = c_V(T)$$

and hence with $F = U - T \cdot S$ and $S(T = 0) = 0$

$$p = -\frac{\partial}{\partial V} \left[U - T \int_0^T \frac{dT'}{T'} \frac{\partial U(T', V)}{\partial T'} \right].$$

In the harmonic approximation, the internal energy is given by

$$U(T, V) = U_0 + \frac{1}{2} \sum_{\vec{k}} \hbar \omega_m(\vec{k}) + \sum_{\vec{k}} \frac{\hbar \omega_m(\vec{k})}{e^{\beta \hbar \omega_m(\vec{k})} - 1}.$$

As you will show in the exercises, inserting this formula into the expression for the pressure results in

$$p = -\frac{\partial}{\partial V} \left[U_0 + \frac{1}{2} \sum_{\vec{k}} \hbar \omega_m(\vec{k}) \right] + \sum_{\vec{k}} \left(-\frac{\partial \hbar \omega_m(\vec{k})}{\partial V} \right) \frac{1}{e^{\beta \hbar \omega_m(\vec{k})} - 1}.$$

The first term is the volume dependence of the ground state energy. The whole temperature dependence however comes from the second term, i.e. solely from the volume dependence of the oscillation frequencies. In the harmonic approximation, however, the frequencies do not explicitly depend on the displacements $\bar{u}_\alpha(t)$, hence the derivatives of the $\omega_m(\vec{k})$ with respect to the volume are identically zero.

How is this, at first maybe not so disturbing observation, related to thermal expansion? To this end we can use the relation

$$\left(\frac{\partial V}{\partial T} \right)_p = -\frac{\left(\frac{\partial p}{\partial T} \right)_V}{\left(\frac{\partial p}{\partial V} \right)_T}$$

and the definition of the bulk modulus

$$B = -V \left(\frac{\partial p}{\partial V} \right)_T$$

to obtain for a simple solid which is completely isotropic for the thermal expansion

$$\alpha := \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_p \stackrel{L = \sqrt[3]{V}}{=} \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{3B} \left(\frac{\partial p}{\partial T} \right)_V.$$

According to our previous discussion, $\alpha \equiv 0$ for a strictly harmonic crystal, which obviously contradicts the experimental observation that any solid has a sizable $\alpha > 0$ for all temperatures $T > 0$.

6.4. BEYOND THE HARMONIC APPROXIMATION

The explicit form of the volume dependence can be used to derive another rather important relation, the so-called *Grüneisen relation*

$$\alpha = \frac{\gamma c_V}{3B} .$$

Here, γ is the *Grüneisen parameter*. To deduce this relation let us note that from the form for p we find

$$\alpha = \frac{1}{3B} \sum_{m\vec{k}} \left(-\frac{\partial \hbar\omega_m(\vec{k})}{\partial V} \right) \frac{\partial n_{m\vec{k}}}{\partial T} ,$$

where $n_{m\vec{k}} = [e^{\beta\hbar\omega_m(\vec{k})} - 1]^{-1}$. On the other hand, the specific heat is given by

$$c_V = \sum_{m\vec{k}} \frac{\hbar\omega_m(\vec{k})}{V} \frac{\partial n_{m\vec{k}}}{\partial T} .$$

Let us now define a “specific heat per mode”

$$c_V(m, \vec{k}) := \frac{\hbar\omega_m(\vec{k})}{V} \frac{\partial n_{m\vec{k}}}{\partial T}$$

and a parameter

$$\gamma(m, \vec{k}) := -\frac{V}{\omega_m(\vec{k})} \frac{\partial \omega_m(\vec{k})}{\partial V} = -\frac{\partial (\ln \omega_m(\vec{k}))}{\partial (\ln V)} .$$

The latter is the logarithmic derivative of the dispersion with respect to the volume. Finally, we define

$$\gamma := \frac{\sum_{m\vec{k}} \gamma(m, \vec{k}) c_V(m, \vec{k})}{\sum_{m\vec{k}} c_V(m, \vec{k})}$$

to obtain the desired result.

Chapter 7

Electron Dynamics

7.1. SEMICLASSICAL APPROXIMATION

	free electrons	Bloch electrons
Quantum numbers (without spin)	$\vec{k} = \vec{p}/\hbar$ momentum	\vec{k}, n crystal momentum, band index
Range	$\vec{k} \in \mathbb{R}^d$ compatible with Born-von Karman conditions	$\vec{k} \in 1. \text{ BZ}$ compatible with Born-von Karman conditions
Energy	$\epsilon_{\vec{k}} = \hbar^2 \vec{k}^2 / 2m$	$\epsilon_{n, \vec{k}}$ from the solution of the periodic scattering problem. General properties: $\epsilon_{n, \vec{k} + \vec{G}} = \epsilon_{n, \vec{k}}$ for $\vec{G} \in \text{RG}$, gaps at boundaries of Brillouin zones
Group velocity	$\vec{v}_{\vec{k}}^{(g)} = \hbar \vec{k} / m$	$\vec{v}_{n, \vec{k}}^{(g)} = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon_{n, \vec{k}}$
Wave function	$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$	$\psi_{n, \vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n, \vec{k}}(\vec{r}),$ $u_{n, \vec{k}}(\vec{r} + \vec{R}) = u_{n, \vec{k}}(\vec{r})$

The starting point of our analysis are Bloch electrons, that is electrons in a periodic crystal. We want to address questions like what is their behavior in an external electrical field (electrical conductivity), in an external magnetic field, etc.

7.1 Semiclassical approximation

Both free electrons and Bloch electrons are solutions of the corresponding time-independent Schrödinger equation. We contrast their properties in table 7.1. The *semiclassical model for electrons* deals with Bloch electrons with well defined momenta in the Brillouin zone, that is $\Delta k \ll a^{-1}$. This automatically implies that the corresponding wave packets are spread out over many primitive unit cells in real space, $\Delta r \gg a$. The second assumption is that external fields (like electrical or magnetic fields) only vary very slowly on the scale set by the spatial size of the wave packets. If we denote the wavelength of their variation with \bar{q} , the previous statement means $|\bar{q}| \ll (\Delta r)^{-1}$. We therefore have a sequence of length scales $a \ll (\Delta k)^{-1}, \Delta r \ll |\bar{q}|^{-1}$. Under these conditions one can show the validity of the *semiclassical approximation*,¹ which treats aver-

¹The proof of this assertion is complex and nontrivial. For example, only recently one has realized that another condition needs to be met, namely that one has a topologically trivial

age position \vec{r} and average crystal momentum \vec{p}_{cr} as classical variables in the classical Hamilton's function

$$\mathcal{H}(\vec{r}, \vec{p}_{cr}) = \epsilon_n \left(\frac{\vec{p}_{cr}}{\hbar} \right) + V_{pot}(\vec{r}) \quad (7.1)$$

This yields the equations of motion

$$\dot{\vec{r}} = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \mathcal{H} = v_{n,\vec{k}}^{(g)} \quad (7.2)$$

$$\dot{\vec{p}}_{cr} = -\vec{\nabla}_{\vec{r}} V_{pot}(\vec{r}) \quad (7.3)$$

From the point of view of the external classical fields one is therefore dealing with a classical pointlike particle. The quantum mechanical description comes in at the level of the band structure $\epsilon_n(\vec{k})$, i.e. the quantum mechanical treatment of the periodic lattice.

In an electromagnetic field the semiclassical approximation then leads to the following behavior:

1. Equations of motion:

$$\dot{\vec{r}} = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon_n(\vec{k}) \quad (7.4)$$

$$\dot{\vec{k}} = -\frac{e}{\hbar} \left[\vec{E}(\vec{r}, t) + \frac{1}{c} \dot{\vec{r}} \times \vec{B}(\vec{r}, t) \right] \quad (7.5)$$

2. There are no transitions between different bands, the band index n is conserved.
3. In equilibrium, the occupation of a Bloch state is determined by the Fermi-Dirac distribution

$$f(\epsilon_{n,\vec{k}}) = \frac{1}{e^{\beta(\epsilon_{n,\vec{k}} - \mu)} + 1} \quad (7.6)$$

One obvious limitation of the semiclassical approximation becomes apparent in the limit crystal potential $U(\vec{r}) \rightarrow 0$ for fixed homogeneous electrical field. For free electrons the kinetic energy will grow unbounded, while in the semiclassical model the kinetic energy remains bounded within one energy band. The resolution of this contradiction is simply that for given external fields the band gaps must not be too small, otherwise there will be transitions to other bands violating rule 2 above. One can show the following criterion for the validity of having no band transitions

$$\left. \begin{array}{l} e E a \\ \hbar \omega_c \end{array} \right\} \ll \frac{(\Delta \epsilon_{n,\vec{k}})^2}{\epsilon_F} \quad (7.7)$$

phase in the sense of a vanishing Cherns number.

where $\Delta\epsilon_{n,\vec{k}}$ is the band gap. In metals this condition is usually fulfilled (i.e. there are no band transitions) since the largest electrical fields are of order 10^{-2}Vcm^{-1} . This gives $\Delta\epsilon_{n,\vec{k}} \gg 10^{-5}\text{eV}$, which is generically true. In insulators one can apply much larger fields and thereby induce a dielectric breakdown, which is due to band transitions. On the other hand, notice that in metals in magnetic fields of order 1T band transitions become possible already for $\Delta\epsilon_{n,\vec{k}} = O(10^{-2}\text{eV})$ (leading to so called magnetic tunneling). As expected the semiclassical approximation conserves the total energy of an electron

$$E_{tot} = \epsilon_n(\vec{k}(t)) - e\phi(\vec{r}(t)) \quad (7.8)$$

where $\phi(\vec{r})$ is the scalar potential corresponding to the electrical field. Now

$$\begin{aligned} \frac{dE_{tot}(t)}{dt} &= \sum_i \frac{\partial \epsilon_n}{\partial k_i} \dot{k}_i - e \vec{\nabla} \phi \cdot \dot{\vec{r}} \\ &= \vec{v}_n^{(g)}(\vec{k}(t)) \cdot (\hbar \dot{\vec{k}} - e \vec{\nabla} \phi) \end{aligned} \quad (7.9)$$

$$= 0 \quad (7.10)$$

since the term in parantheses is nothing but the equation of motion (7.5)

$$\hbar \dot{\vec{k}} = e \vec{\nabla} \phi \quad (7.11)$$

One important consequence of the semiclassical model is that filled bands are inert, i.e. they do not contribute to transport. One can see this from the explicit expression for the electrical current in the semiclassical approximation

$$\vec{j}_e = \langle (-e) \vec{v}_{n,\vec{k}}^{(g)} \rangle \quad (7.12)$$

$$= -\frac{e}{\hbar} 2 \int_{\text{occupied}} \frac{d^3 \vec{k}}{(2\pi)^3} \vec{\nabla}_{\vec{k}} \epsilon_{n,\vec{k}} \quad (7.13)$$

where the integration goes over all occupied states. Now in a filled band this region of integration is time-independent and always identical to the first Brillouin zone. In order to show that the above integral vanishes we first state a small useful theorem: Let $f(\vec{r})$ be a lattice periodic function. Then for all \vec{r}'

$$\int_{\text{unit cell}} d^3 \vec{r} \vec{\nabla}_{\vec{r}} f(\vec{r} + \vec{r}') = 0 \quad (7.14)$$

This is simply a consequence of

$$I(\vec{r}') \stackrel{\text{def}}{=} \int_{\text{unit cell}} d^3 \vec{r} f(\vec{r} + \vec{r}') \quad (7.15)$$

being independent of \vec{r}' due to the lattice periodicity of f . Hence

$$\vec{\nabla}_{\vec{r}'} I(\vec{r}') = 0 \quad (7.16)$$

$$\begin{aligned} &= \int_{\text{unit cell}} d^3 \vec{r} \vec{\nabla}_{\vec{r}'} f(\vec{r} + \vec{r}') \\ &= \int_{\text{unit cell}} d^3 \vec{r} \vec{\nabla}_{\vec{r}} f(\vec{r} + \vec{r}') \end{aligned} \quad (7.17)$$

Especially

$$\int_{\text{unit cell}} d^3\vec{r} \vec{\nabla}_{\vec{r}} f(\vec{r}) = 0 \quad (7.18)$$

Completely analogous one makes use of the periodicity of the dispersion relation in reciprocal space, $\epsilon_n(\vec{k} + \vec{K}) = \epsilon_n(\vec{k})$, and finds

$$\int_{\text{1. BZ}} \frac{d^3\vec{k}}{(2\pi)^3} \vec{\nabla}_{\vec{k}} \epsilon_{n,\vec{k}} = 0 \quad (7.19)$$

$$\Rightarrow \vec{j}_e = 0 \quad (7.20)$$

for filled bands: Electrons in filled bands do not contribute to transport. Electrical conductivity comes from only partially filled bands, hence the terminology conduction electrons and conduction band. Also notice that the above observation provides an a posteriori justification for our previous definition of insulators in Chapter 5.

Electron vs. hole conductivity

The above theorem states completely generally (for all fillings)

$$\begin{aligned} 0 &= -e \int_{\text{1. BZ}} \frac{d^3\vec{k}}{4\pi^3} v_{n,\vec{k}}^{(g)} \\ &= -e \int_{\text{occupied}} \frac{d^3\vec{k}}{4\pi^3} v_{n,\vec{k}}^{(g)} + (-e) \int_{\text{unoccupied}} \frac{d^3\vec{k}}{4\pi^3} v_{n,\vec{k}}^{(g)} \end{aligned} \quad (7.21)$$

therefore

$$\vec{j}_e = -e \int_{\text{occupied}} \frac{d^3\vec{k}}{4\pi^3} v_{n,\vec{k}}^{(g)} \quad (7.22)$$

$$= +e \int_{\text{unoccupied}} \frac{d^3\vec{k}}{4\pi^3} v_{n,\vec{k}}^{(g)} \quad (7.23)$$

From this simple equality one can deduce that the electrical current can either be interpreted as a current of electrons (occupied states) with charge -e, or completely equivalently as a current of holes (unoccupied states) with charge +e. The interpretation as a hole current is particularly useful for nearly filled bands, like the valence band in a doped semiconductor: there the current contribution of the valence band is set by the concentration of the holes, and not by the total number of electrons in the valence band.

7.2 Electrical conductivity in metals

Bloch electrons (that is wave packets made of Bloch eigenfunctions) propagate through the crystal without dissipation, i.e. ideally do not show any resistivity. This contradicts the experimental observation that every induced current decays as a function of time if it is not driven by an external electrical field. The reason

for this contradiction is that within the assumption of a perfect, static crystal one ignores several scattering mechanisms which lead to a decay of the current, and therefore contributing to a nonvanishing resistance. The most important scattering mechanisms are:

1. Scattering from impurities and lattice defects, that is *extrinsic* deviations from the perfect lattice periodicity. These effects are nearly temperature independent and therefore dominate the resistivity for low temperatures $T \rightarrow 0$. This is denoted residual resistivity.
2. Scattering from deviations from perfect lattice periodicity due to lattice vibrations, that is electron-phonon scattering. This is the most important temperature dependent contribution to the resistivity and dominates at higher temperatures.
3. Electron-electron scattering is relatively unimportant as compared to the above contributions since crystal momentum conservation only allows for a less efficient decay channel (since the current is related to the group velocity).

7.2.1 Boltzmann equation

The key theoretical tool in transport theory is the *Boltzmann equation* (or kinetic equation). It was first introduced by Boltzmann to model dilute gases: Let the *distribution function* $f(t, \vec{x}, \vec{p})$ describe the particle density at a given phase space point (\vec{x}, \vec{p}) at time t . If the particles do not talk to each other, it is reasonable to assume that the density obeys some sort of continuity equation. If there are scattering processes among the particles, they will lead to some kind of “source term” Ignoring external forces for the time being, i.e. setting $\dot{\vec{p}} = 0$, one therefore obtains as differential equation governing the time evolution of $f(t, \vec{x}, \vec{p})$ (Boltzmann equation)

$$\frac{d}{dt}f(t, \vec{x}, \vec{p}) = \frac{\partial f(t, \vec{x}, \vec{p})}{\partial t} + \left(\frac{\vec{p}}{m} \cdot \vec{\nabla} \right) f(t, \vec{x}, \vec{p}) = I[f](t, \vec{x}, \vec{p}) \quad (7.24)$$

The gradient term on the left hand side is the corresponding current-density for particles entering and leaving the phase space region around (\vec{x}, \vec{p}) . The functional $I[f]$ is the so called *Stossterm*, modeling collisions of gas particles. For example for local elastic 2-particle collisions one can write it as

$$\begin{aligned} I[f](t, \vec{x}, \vec{p}) &= \int d\vec{p}_2 d\vec{p}_3 d\vec{p}_4 W(p, p_2; p_3, p_4) \\ &\quad \times \delta(\epsilon(\vec{p}) + \epsilon(\vec{p}_2) - \epsilon(\vec{p}_3) - \epsilon(\vec{p}_4)) \delta(\vec{p} + \vec{p}_2 - \vec{p}_3 - \vec{p}_4) \\ &\quad \times [f(t, \vec{x}_3, \vec{p}_3) f(t, \vec{x}_4, \vec{p}_4) - f(t, \vec{x}, \vec{p}) f(t, \vec{x}_2, \vec{p}_2)] \end{aligned} \quad (7.25)$$

$W(\vec{p}_1, \vec{p}_2; \vec{p}_3, \vec{p}_4) = W(\vec{p}_3, \vec{p}_4; \vec{p}_1, \vec{p}_2)$ describes the scattering of two particles with incoming momenta \vec{p}_3 and \vec{p}_4 to momenta \vec{p}_1 and \vec{p}_2 , and vice versa. The terms in square brackets are gain and loss terms due to such scattering processes. Some remarks:

- In spite of microscopic reversibility $W(\vec{p}_1, \vec{p}_2; \vec{p}_3, \vec{p}_4) = W(\vec{p}_3, \vec{p}_4; \vec{p}_1, \vec{p}_2)$ Boltzmann showed that the entropy

$$S[f] = -H[f] = - \int d\vec{x} d\vec{p} f(t, \vec{x}, \vec{p}) \ln f(t, \vec{x}, \vec{p}) \quad (7.26)$$

can only increase as a function of time (Boltzmann's H -theorem)

$$\frac{dS[f]}{dt} \geq 0 \quad (7.27)$$

There is a whole body of literature devoted to understanding how irreversibility enters in the derivation of the Boltzmann equation. The key observation is that the derivation relies on the assumption that the particles are uncorrelated before the collision (while they certainly become correlated after the collision). For dilute gases this assumption seems plausible since it is unlikely for particles to scatter repeatedly. Under certain conditions this can even be established with mathematical rigor.

- One can show (problem set 10) that the only fixed point/equilibrium for an isotropic system is a Maxwell distribution

$$\frac{dS[f]}{dt} = 0 \quad \Leftrightarrow \quad f(\vec{x}, \vec{v}) \propto T^{-3/2} e^{-\vec{v}^2/k_B T} \quad (7.28)$$

Likewise one can show that the only fixed point (i.e. no entropy production) for a non-isotropic system with $\langle \vec{v} \rangle = 0$ is a local Maxwell distribution

$$f(\vec{x}, \vec{v}) \propto T(\vec{x})^{-3/2} e^{-\vec{v}^2/k_B T(\vec{x})} \quad (7.29)$$

7.2.2 Boltzmann equation for electrons

Applying the Boltzmann equation to quantum transport involves some additional approximations. In particular one is neglecting interference effects, i.e. one is effectively relying on a semiclassical picture. The validity of this picture needs to be verified for a specific setup. However, it is mandatory to properly take into account the exchange statistics of quantum particles. For example for the distribution function for electrons $n(\vec{r}, \vec{k}, t)$ in phase space (probability of finding a semiclassical electron in a volume \hbar^3 around (\vec{r}, \vec{k})) one has the constraint from the Pauli principle: $0 \leq n(\vec{r}, \vec{k}, t) \leq 1$. As we want to consider

the effect of scattering from defects (extrinsic or phonons), we can restrict the collision integral to single-particle scattering, i.e. it reads²

$$I[n] = \int \frac{d^3k'}{(2\pi)^3} \left[W_{\vec{k}'\vec{k}} n(\vec{k}') (1 - n(\vec{k})) - W_{\vec{k}\vec{k}'} n(\vec{k}) (1 - n(\vec{k}')) \right] \quad (7.30)$$

where the gain and loss terms incorporate the condition that the scattering has to go into empty states.

Using the relation $\dot{\vec{r}} = \vec{v}^{(g)}(\vec{k})$, the Boltzmann equation for electrons experiencing the Lorentz force

$$\hbar \dot{\vec{k}} = \vec{F}(\vec{r}, \vec{k}, t) = -e \left(\vec{E}(\vec{r}, t) + \frac{1}{c} \vec{v}^{(g)}(\vec{k}) \times \vec{B}(\vec{r}, t) \right) \quad (7.31)$$

then reads

$$\frac{d}{dt} n(t, \vec{r}, \vec{k}) = \frac{\partial n}{\partial t} + \vec{v}^{(g)}(\vec{k}) \cdot \vec{\nabla}_{\vec{r}} n + \vec{F}(\vec{r}, \vec{k}, t) \cdot \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} n = I[n](t, \vec{r}, \vec{k}) \quad (7.32)$$

The collision term can be split up in (elastic) scattering from lattice impurities V_{imp} and electron-phonon scattering W_{ph}

$$W(\vec{k}', \vec{k}) = V_{imp}(\vec{k}', \vec{k}) + W_{ph}(\vec{k}', \vec{k}) \quad (7.33)$$

Assuming an equilibrium distribution of the phonons with a temperature profile $T(\vec{r})$ one can show by analyzing the scattering matrix elements³

$$W_{ph}(\vec{k}', \vec{k}) e^{\epsilon_{\vec{k}}/k_B T(\vec{r})} = W_{ph}(\vec{k}, \vec{k}') e^{\epsilon_{\vec{k}'}/k_B T(\vec{r})} \quad (7.34)$$

Elastic scattering from (dilute) random impurities with concentration n_{imp} described by a potential $U_{sc}(\vec{r})$ for an impurity at the origin yields within 1. Born approximation

$$V_{imp}(\vec{k}', \vec{k}) = \frac{2\pi}{\hbar} n_{imp} \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}) |\langle k | U_{sc} | k' \rangle|^2 \quad (7.35)$$

with the matrix element evaluated between Bloch eigenfunctions

$$\langle k | U_{sc} | k' \rangle = \int d\vec{r} \psi_{nk'}^*(r) U_{sc}(r) \psi_{nk}(r) \quad (7.36)$$

Clearly $V_{imp}(\vec{k}', \vec{k}) = V_{imp}(\vec{k}, \vec{k}')$.

Eq. (7.34) yields a *unique* fixed point for the collision term (7.30) given by the local equilibrium distribution⁴

$$n^{(0)}(\vec{r}, \vec{k}) = \frac{1}{e^{(\epsilon_{\vec{k}} - \mu(\vec{r}))/k_B T(\vec{r})} + 1} \quad (7.37)$$

²One should at this stage also include band index and spin as further quantum numbers. We will omit this here to keep the notation simple.

³For details see Madelung, Solid-State Theory, Ch. 4.2.

⁴Strictly speaking the chemical potential profile $\mu(\vec{r})$ must also be determined by coupling to suitable baths to make this unique.

Therefore it makes sense to linearize the functional $I[n]$ around this distribution by defining

$$n(\vec{r}, \vec{k}, t) = n^{(0)}(\vec{r}, \vec{k}) + \delta n(\vec{r}, \vec{k}, t) \quad (7.38)$$

Inserting this definition into (7.30) and keeping only terms linear in δn yields after some straightforward algebra⁵

$$I[n] = \int \frac{d^3 k'}{(2\pi)^3} \left[V_{imp}(\vec{k}', \vec{k}) (\delta n(\vec{k}') - \delta n(\vec{k})) \right. \\ \left. + (V_{ph}(\vec{k}', \vec{k}) \delta n(\vec{k}') - V_{ph}(\vec{k}, \vec{k}') \delta n(\vec{k})) \right] \quad (7.39)$$

where we have defined

$$V_{ph}(\vec{k}', \vec{k}) = W_{ph}(\vec{k}', \vec{k}) \frac{1 - n^{(0)}(\vec{r}, \vec{k})}{1 - n^{(0)}(\vec{r}, \vec{k}')} \quad (7.40)$$

With the new definition

$$V(\vec{k}', \vec{k}) \stackrel{\text{def}}{=} V_{imp}(\vec{k}', \vec{k}) + V_{ph}(\vec{k}', \vec{k}) \quad (7.41)$$

one ends up with

$$I[n](t, \vec{r}, \vec{k}) = \int \frac{d^3 k'}{(2\pi)^3} \left(V(\vec{k}', \vec{k}) \delta n(\vec{r}, \vec{k}', t) - V(\vec{k}, \vec{k}') \delta n(\vec{r}, \vec{k}, t) \right) \quad (7.42)$$

This structure of the Stossterm motivates the so called *relaxation time approximation*

$$I[n](t, \vec{r}, \vec{k}) = -\frac{\delta n(\vec{r}, \vec{k}, t)}{\tau(\vec{k})} = -\frac{n(\vec{r}, \vec{k}, t) - n^{(0)}(\vec{r}, \vec{k})}{\tau(\vec{k})} \quad (7.43)$$

with the relaxation time

$$\tau^{-1}(\vec{k}) \stackrel{\text{def}}{=} \int \frac{d^3 k'}{(2\pi)^3} V(\vec{k}, \vec{k}') \quad (7.44)$$

Under certain conditions one can explicitly show the equivalence of (7.42) and (7.43). Details of this derivation can be found in Madelung, Ch. 4.2. At this point it should be mentioned that the relaxation time approximation (7.43) is employed quite generally to describe a Stossterm in the Boltzmann equation, even if the above conditions are not fulfilled. Essentially the idea is to model exponential relaxation to some equilibrium, which is strictly enforced in the limit of vanishing relaxation time $\tau \rightarrow 0$. Via this reasoning one also (often using intuitive arguments) identifies the equilibrium/fixed point distribution $n^{(0)}(\vec{r}, \vec{k})$.

⁵I skip all arguments which do not enter explicitly.

Armed with this knowledge we can now solve the Boltzmann equation (7.32) in the relaxation time approximation for small τ starting from e.g. $n(\vec{r}, \vec{k}, t = 0) = n^{(0)}(\vec{r}, \vec{k})$.⁶ To this end we use

$$\begin{aligned} \frac{\partial n(\vec{r}, \vec{k}, t)}{\partial t} &= \frac{\partial \delta n(\vec{r}, \vec{k}, t)}{\partial t} \\ \vec{\nabla}_{\vec{r}} n(\vec{r}, \vec{k}, t) &\approx - \left(-\frac{\partial f}{\partial x} \right)_{x=\frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})}} \vec{\nabla} \left(\frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})} \right) \\ &= -\frac{1}{k_{\text{B}}T(\vec{r})} \left(-\frac{\partial f}{\partial x} \right)_{x=\frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})}} \left[-\vec{\nabla}_{\vec{r}} \mu(\vec{r}) - \frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})} \vec{\nabla}_{\vec{r}} T(\vec{r}) \right] \\ \vec{\nabla}_{\vec{k}} n(\vec{r}, \vec{k}, t) &\approx -\frac{1}{k_{\text{B}}T(\vec{r})} \left(-\frac{\partial f}{\partial x} \right)_{x=\frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})}} \vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}} \end{aligned}$$

where

$$f(x) = \frac{1}{e^x + 1}$$

We now insert these expressions into the Boltzmann equation (7.32) together with the relaxation time approximation for the collision term, and solve for the explicit time dependence using the standard expression for an ordinary linear first order differential equation to obtain as solution

$$\begin{aligned} n(\vec{r}, \vec{k}, t) &= n^{(0)}(\vec{r}, \vec{k}) \\ &+ \int_0^t dt' e^{-(t-t')/\tau(\vec{k})} \left(-\frac{\partial f}{\partial x} \right)_{x=\frac{\epsilon(\vec{k})-\mu(\vec{r})}{k_{\text{B}}T(\vec{r})}} \\ &\quad \times \frac{\vec{v}^{(g)}(\vec{k})}{k_{\text{B}}T(\vec{r})} \cdot \left[-e \vec{E}(\vec{r}, t') - \vec{\nabla} \mu(\vec{r}) - \frac{\epsilon(\vec{k})-\mu(\vec{r})}{T(\vec{r})} \vec{\nabla} T(\vec{r}) \right] \end{aligned} \quad (7.45)$$

One can verify the solution (7.45) by explicit insertion into (7.32), which shows that corrections are higher order in τ . Also notice that the magnetic field does not appear in (7.45) since $\vec{v}^{(g)} \cdot [\vec{v}^{(g)} \times \vec{B}] = 0$.

We now assume that the electric field $\vec{E}(\vec{r}, t)$ is time-independent. In this case we can introduce

$$\begin{aligned} \tau(\vec{k}, t) &:= \int_0^t dt' e^{-(t-t')/\tau(\vec{k})} \\ &= \tau(\vec{k}) \left(1 - e^{-t/\tau(\vec{k})} \right) \end{aligned} \quad (7.46)$$

and rewrite (7.45) in leading order in τ as⁷

$$n(\vec{r}, \vec{k}, t) = n^{(0)} \left(\vec{r} - \tau(\vec{k}, t) \vec{v}^{(g)}(\vec{k}), \vec{k} + e \frac{\tau(\vec{k}, t)}{\hbar} \vec{E}(\vec{r}) \right) \quad (7.47)$$

⁶The asymptotic time-invariant distribution $n(\vec{r}, \vec{k}, t = \infty)$ is independent of the initial value as can be verified easily.

⁷Because (7.45) has the form of a Taylor expansion.

One sees that a stationary state

$$n^{(\infty)}(\vec{r}, \vec{k}) = \lim_{t \rightarrow \infty} n(\vec{r}, \vec{k}, t) = n^{(0)}\left(\vec{r} - \tau(\vec{k}) \vec{v}^{(g)}(\vec{k}), \vec{k} + \frac{\tau(\vec{k})}{\hbar} e \vec{E}(\vec{r})\right) \quad (7.48)$$

is approached exponentially fast.

7.2.3 dc-conductivity

We calculate the dc-conductivity, that is \vec{E} time-independent and uniform, $\vec{B} = 0$ and $\mu(\vec{r}) = \mu$, $T(\vec{r}) = T$. From (7.48) we read off the stationary state

$$n^{(\infty)}(\vec{k}) = \left[e^{(\epsilon_{\vec{k} + \tau(\vec{k})} e \vec{E} / \hbar - \mu) / k_B T} + 1 \right]^{-1} \quad (7.49)$$

The electrical field effectively shifts the Fermi surface by $\tau(\vec{k}) e \vec{E} / \hbar$. This amounts to an electrical current density

$$\begin{aligned} \vec{j} &= -e \int \frac{d\vec{k}}{4\pi^3} \vec{v}^{(g)}(\vec{k}) n^{(\infty)}(\vec{k}) \\ &= -e \int \frac{d\vec{k}}{4\pi^3} \vec{v}^{(g)}(\vec{k}) n^{(0)}(\vec{k}) \\ &\quad + e^2 \int \frac{d\vec{k}}{4\pi^3} \vec{v}^{(g)}(\vec{k}) \tau(\vec{k}) \left(-\frac{\partial n^{(0)}}{\partial \epsilon_{\vec{k}}} \right) \vec{E} \cdot \vec{v}^{(g)}(\vec{k}) \end{aligned} \quad (7.50)$$

The first integral vanishes since it is a product of an antisymmetric with a symmetric function. The second integral is of the form

$$\vec{j} = \underline{\underline{\sigma}} \vec{E} \quad (7.51)$$

where we introduced the *conductivity tensor*

$$\sigma_{ij} = e^2 \int \frac{d\vec{k}}{4\pi^3} \tau(\vec{k}) v_i^{(g)}(\vec{k}) v_j^{(g)}(\vec{k}) \left(-\frac{\partial n^{(0)}}{\partial \epsilon_{\vec{k}}} \right) \quad (7.52)$$

If more than one band contributes to transport we need to additionally sum over the various bands. Notice that the derivative of the Fermi function in (7.52) is only nonvanishing for energies within $k_B T$ of the Fermi energy ϵ_F . Hence the contribution of filled bands vanishes as already shown before.

From the fact that the derivative of the Fermi function only leads to contributions in the vicinity of the Fermi surface one can also verify that (7.52) can be approximated in order $(k_B T / \epsilon_F)^2$ by its $T = 0$ value. Therefore the relaxation time can be evaluated at the Fermi surface and taken out of the integral. Also from the chain rule

$$v_j^{(g)}(\vec{k}) \left(-\frac{\partial n^{(0)}}{\partial \epsilon_{\vec{k}}} \right) = -\frac{1}{\hbar} \frac{\partial}{\partial k_j} n^{(0)}(\vec{k}) \quad (7.53)$$

This allows integration by parts⁸

$$\sigma_{ij} = e^2 \tau(\epsilon_F) \int \frac{d\vec{k}}{4\pi^3} n^{(0)}(\vec{k}) \frac{1}{\hbar} \frac{\partial}{\partial k_j} v_i^{(g)}(\vec{k}) \quad (7.54)$$

$$= e^2 \tau(\epsilon_F) \int_{\text{occ.}} \frac{d\vec{k}}{4\pi^3} [\underline{\underline{M}}(\vec{k})^{-1}]_{ij} \quad (7.55)$$

where the integral runs over all occupied levels. M_{ij} is the tensor of effective masses already introduced for semiconductors in (5.3) respectively (5.4)

$$[\underline{\underline{M}}(\vec{k})^{-1}]_{ij} := \frac{1}{\hbar^2} \frac{\partial^2 \epsilon(\vec{k})}{\partial k_j \partial k_j} \quad (7.56)$$

Notice that the relaxation time $\tau(\epsilon_F)$ will in general still have a strong temperature dependence.

Some additional remarks:

1. The dc-conductivity vanishes in the limit of very short relaxation time as intuitively expected.
2. In a general crystal structure the conductivity tensor is not diagonal, i.e. an electrical field can induce a current which is not parallel to it. However, for cubic crystals one finds $\sigma_{ij} = \sigma \delta_{ij}$ since clearly $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ for symmetry reasons and all off diagonal matrix elements must vanish (if a field in x -direction would induce a current in y -direction, that current would actually vanish since symmetry makes both y -directions equivalent).
3. Since the effective mass (7.56) is the derivative of a periodic function, its integral over the Brillouin zone vanishes similar to the discussion following (7.14). Hence we can alternatively express the conductivity as an integral over the unoccupied states

$$\sigma_{ij} = -e^2 \tau(\epsilon_F) \int_{\text{unocc.}} \frac{d\vec{k}}{4\pi^3} [\underline{\underline{M}}(\vec{k})^{-1}]_{ij} \quad (7.57)$$

thereby again showing the equivalence of particle and hole picture.

4. For free electrons the expression for the conductivity takes the Drude form

$$M_{ij}^{-1} = \frac{\delta_{ij}}{m} \Rightarrow \sigma_{ij} = \delta_{ij} \frac{ne^2\tau}{m} \quad (7.58)$$

It is actually “surprising” that the Drude picture gives a reasonable answer.

⁸Boundary terms vanish by making use of the fact that $\vec{\nabla}_{\vec{k}} \epsilon_{\vec{k}} = 0$ on the boundary of the BZ.

7.2.4 Thermal conductivity

We are interested in the thermal current $\vec{j}^{(q)}$ transported by electrons, which is the most important contribution in metals under normal conditions. Because of $\delta Q = T dS$ one has (consider a small volume)

$$\vec{j}^{(q)} = T \vec{j}^{(s)} \quad (7.59)$$

with the entropy current $\vec{j}^{(s)}$. Then because of $T dS = dU - \mu dN$ one concludes

$$T \vec{j}^{(s)} = \vec{j}^{(\epsilon)} - \mu \vec{j}^{(n)} \quad (7.60)$$

with the energy current

$$\vec{j}^{(\epsilon)} = \int \frac{d^3k}{4\pi^3} \epsilon_{\vec{k}} \vec{v}^{(g)}(\vec{k}) n^{(\infty)}(\vec{r}, \vec{k}) \quad (7.61)$$

and particle current

$$\vec{j}^{(n)} = \int \frac{d^3k}{4\pi^3} \vec{v}^{(g)}(\vec{k}) n^{(\infty)}(\vec{r}, \vec{k}) \quad (7.62)$$

$$\Rightarrow \vec{j}^{(q)} = \int \frac{d^3k}{4\pi^3} (\epsilon_{\vec{k}} - \mu) \vec{v}^{(g)}(\vec{k}) n^{(\infty)}(\vec{r}, \vec{k}) \quad (7.63)$$

We already calculated the stationary distribution function for $\vec{B} = 0$ and time independent fields (7.45)

$$n^{(\infty)}(\vec{r}, \vec{k}) \approx n^{(0)}(\vec{k}) + \tau(\vec{k}) \left(-\frac{\partial f}{\partial \epsilon} \right) \vec{v}^{(g)}(\vec{k}) \cdot \left[-e \vec{\mathcal{E}} + \frac{\epsilon(\vec{k}) - \mu}{T} (-\vec{\nabla}_{\vec{r}} T) \right] \quad (7.64)$$

where we have defined

$$\vec{\mathcal{E}} \stackrel{\text{def}}{=} \vec{E} + \frac{1}{e} \vec{\nabla}_{\vec{r}} \mu \quad (7.65)$$

One can read of that electrical and thermal current are related to the external fields via four 3x3 matrices

$$\vec{j}^{(e)} = \underline{\underline{L}}^{11} \vec{\mathcal{E}} + \underline{\underline{L}}^{12} (-\vec{\nabla} T) \quad (7.66)$$

$$\vec{j}^{(q)} = \underline{\underline{L}}^{21} \vec{\mathcal{E}} + \underline{\underline{L}}^{22} (-\vec{\nabla} T) \quad (7.67)$$

This is a typical “linear response” result. We define

$$\mathcal{L}_{ij}^{(m)} = e^2 \int \frac{d^3k}{4\pi^3} \left(-\frac{\partial n^{(0)}}{\partial \epsilon_{\vec{k}}} \right) \tau(\vec{k}) v_i^{(g)}(\vec{k}) v_j^{(g)}(\vec{k}) (\epsilon_{\vec{k}} - \mu)^m \quad (7.68)$$

for $m = 0, 1, 2$. Then the linear response coefficients can be expressed as

$$\underline{\underline{L}}^{11} = \underline{\underline{\mathcal{L}}}^{(0)} \quad (7.69)$$

$$\underline{\underline{L}}^{21} = -\frac{1}{e} \underline{\underline{\mathcal{L}}}^{(1)} = T \underline{\underline{L}}^{12} \quad (7.70)$$

$$\underline{\underline{L}}^{22} = \frac{1}{e^2 T} \underline{\underline{\mathcal{L}}}^{(2)} \quad (7.71)$$

Assuming a relaxation rate that only depends on energy, $\tau(\vec{k}) \approx \tau(\epsilon_{\vec{k}})$, we can define

$$\sigma_{ij}(\epsilon) := e^2 \tau(\epsilon) \int \frac{d^3k}{4\pi^3} \delta(\epsilon - \epsilon_{\vec{k}}) v_i^{(g)}(\vec{k}) v_j^{(g)}(\vec{k}) \quad (7.72)$$

$$\Rightarrow \underline{\underline{\mathcal{L}}}^{(m)} = \int d\epsilon \left(-\frac{\partial f}{\partial \epsilon} \right) (\epsilon - \mu)^m \underline{\underline{\sigma}}(\epsilon) \quad (7.73)$$

Employing the Sommerfeld expansion (see exercises) one arrives at

$$\begin{aligned} \underline{\underline{\mathcal{L}}}^{(m)} &= \int d\epsilon f(\epsilon) \frac{\partial}{\partial \epsilon} [(\epsilon - \mu)^m \underline{\underline{\sigma}}(\epsilon)] \\ &= \int_{-\infty}^{\mu} d\epsilon \frac{\partial}{\partial \epsilon} [(\epsilon - \mu)^m \underline{\underline{\sigma}}(\epsilon)] \\ &\quad + \frac{\pi^2}{6} (k_B T)^2 \left. \frac{\partial^2}{\partial \epsilon^2} \right|_{\epsilon_{\mu}} [(\epsilon - \mu)^m \underline{\underline{\sigma}}(\epsilon)] \\ &\quad + O((T/\mu)^4) \end{aligned} \quad (7.74)$$

One can read off

$$\underline{\underline{\mathcal{L}}}^{(0)} = \underline{\underline{\sigma}}(\mu) \quad (7.75)$$

$$\underline{\underline{\mathcal{L}}}^{(1)} = \frac{\pi^2}{6} (k_B T)^2 2 \underline{\underline{\sigma}}'(\mu) \quad (7.76)$$

$$\underline{\underline{\mathcal{L}}}^{(2)} = \frac{\pi^2}{6} (k_B T)^2 2 \underline{\underline{\sigma}}(\mu) \quad (7.77)$$

plus terms that are smaller factors $(T/\epsilon_F)^2$. This constitutes the central result for the linear response coefficients, which now read

$$\underline{\underline{L}}^{11} = \underline{\underline{\sigma}}(\epsilon_F) = \underline{\underline{\sigma}} \quad (7.78)$$

$$\underline{\underline{L}}^{21} = T \underline{\underline{L}}^{12} = -\frac{\pi^2}{3e} (k_B T)^2 \underline{\underline{\sigma}}'(\epsilon_F) \quad (7.79)$$

$$\underline{\underline{L}}^{22} = \frac{\pi^2}{3} \frac{k_B^2 T}{e^2} \underline{\underline{\sigma}} \quad (7.80)$$

where σ is just the (electrical) conductivity tensor (7.52). The thermal conductivity tensor K relates a temperature gradient to the induced thermal current

$$\vec{j}^{(q)} = \underline{\underline{K}} (-\vec{\nabla} T) \quad (7.81)$$

under the condition that the electrical current vanishes $\vec{j}^{(e)} = 0$. This implies from (7.66)

$$\vec{\mathcal{E}} = -(\underline{\underline{L}}^{11})^{-1} \underline{\underline{L}}^{12} (-\vec{\nabla} T) \quad (7.82)$$

$$\Rightarrow \underline{\underline{K}} = \underline{\underline{L}}^{22} - \underline{\underline{L}}^{21} (\underline{\underline{L}}^{11})^{-1} \underline{\underline{L}}^{12} \quad (7.83)$$

Since the conductivity σ only varies on the energy scale ϵ_F , the second term in the expression for K is of order $(T/\epsilon_F)^2$ and can be neglected. $K = L^{22}$ is just the Wiedemann-Franz law

$$K = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \sigma \quad (7.84)$$

relating the electrical conductivity tensor to the thermal conductivity tensor. At this point it is worth emphasizing that we have used the relaxation time approximation in writing down the stationary solution, especially implying the condition that the electrons only scatter elastically. This is not strictly true for scattering off phonons, which can lead to deviations from the Wiedemann-Franz law (since inelastic scattering affects thermal and electrical currents differently). Also notice that the other linear response coefficients derived above contain information about other interesting physical effects like the Seebeck effect: A temperature gradient induces an electrical field for vanishing current, $\vec{E} = Q \vec{\nabla} T$.

7.2. ELECTRICAL CONDUCTIVITY IN METALS

Chapter 8

Magnetism

8.1 Absence of magnetism in a classical theory

One of the fundamental problems of physics is the origin of solid-state magnetism in for example iron or nickel. The phenomenon of magnetism is well-known to mankind since more than 3000 years, and one of the longest known materials is magnetite, Fe_3O_4 , but there are many others as can be seen from the table to the right. Moreover, the “simple” ferromagnet of our daily life with a net magnetization is by far not the only magnetic structure appearing in nature. There are antiferromagnets, where no such net magnetization is visible to the outside, ferrimagnets, which partially compensated magnetic moment, magnetic spirals and many more. Since the days of Ørsted and Maxwell we also know that magnetic phenomena are intimately connected to varying electric fields and currents, so a first attempt may be to try to understand magnetism in terms of classical fields. In a classical description, a magnetic field would enter the Hamilton function of an electron as (see sec. 3.1.5)

Material	Curie temperature (K)
Fe	1043
Co	1388
Ni	627
Gd	293
Dy	85
CrBr_3	37
Au_2MnAl	200
Cu_2MnAl	630
Cu_2MnIn	500
Fe_3O_4	852
EuO	77
EuS	16.5
MnAs	318
MnBi	670
GdCl_3	2.2
Fe_2B	1015
MnB	578

Table 8.1: Curie temperatures for various materials

$$H = \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A}(\vec{r}, t) \right)^2 + V(\vec{r}, t)$$

with the magnetic field given as $\vec{B}(\vec{r}, t) = \vec{\nabla} \times \vec{A}(\vec{r}, t)$. For a classical many-particle system, one would need to add interactions (e.g. the Coulomb interaction), which however typically depend on the particle positions but not on their momenta. The thermodynamics of the system are then described by the partition function

$$\mathcal{Z} \propto \int d^{3N}r d^{3N}p e^{-\beta H} .$$

In particular the momentum integrals extend over all \mathbb{R}^{3N} (we ignore relativistic effects here) and as the vector potential depends only on the positions and time, it can be absorbed into a redefinition of the momentum integration and hence

vanishes exactly from the partition function. Consequently, \mathcal{Z} will not depend on \vec{B} and the classical model will not respond at all to an external magnetic field. This rather unexpected and disturbing result is called *Bohr-van Leeuwen theorem*. Hence, magnetism appearing in solids is a purely quantum-mechanical effect.

8.2 Basics of magnetism

We have already learned that magnetic properties of solids can be best characterized by inspecting the response to an external magnetic field, i.e. the magnetization \vec{M} and the magnetic susceptibility

$$\chi(T) = \frac{\partial M}{\partial B} \stackrel{B \rightarrow 0}{\approx} \frac{M}{B} ,$$

where B is a homogeneous external field and M the component of the magnetization in the direction of the field. For non-interacting electrons the latter is typically paramagnetic, i.e. $M(B) \rightarrow 0$ as $B \rightarrow 0$, and a general theorem by Lieb and Matthis tells us, that without interaction one will not find anything else.

Magnets we know from daily life are systems which undergo something called *phase transition*, i.e. their physical properties change abruptly below a certain *critical temperature* T_c . In the case of magnets the phase below T_c (for ferromagnets called *Curie temperature*) is characterized by a magnetization $M(B) \rightarrow M_0 \neq 0$ as $B \rightarrow 0$, i.e. a *spontaneous magnetization*; while for temperatures $T > T_C$ we as usual find $M(B) \rightarrow 0$ as $B \rightarrow 0$.

For a ferromagnet the magnetization is uniform across the material. In terms of a Fourier analysis a uniform quantity is connected to a wave vector $\vec{q} = 0$, and the above statement can be rephrased as

$$\lim_{B \rightarrow 0} M(\vec{q} = 0, B) = M_0 \neq 0 .$$

The extension is now obvious. One generally speaks of a *spontaneous magnetic order* or *long-ranged magnetic order* if there exists some wave vector \vec{q} for which

$$\lim_{\vec{B}(\vec{q}) \rightarrow 0} \vec{M}(\vec{q}, \vec{B}(\vec{q})) = \vec{M}_0 \neq 0 .$$

Here, $\vec{B}(\vec{q})$ and $\vec{M}(\vec{q})$ are the Fourier components of the magnetic field and the magnetization for the wave vector \vec{q} . In many materials one can find a wave vector \vec{Q} such that for a vector $\vec{R} = k \cdot \vec{a}_1 + l \cdot \vec{a}_2 + m \cdot \vec{a}_3$ from the Bravais lattice $\vec{R} \cdot \vec{Q} = \pi(k + l + m)$. For this wave vector the Fourier components alternates in sign from lattice site to lattice site. If in addition $\vec{M}_o(\vec{Q}) \neq 0$ one speaks

of *antiferromagnetism*, and \vec{M}_0 is called *staggered magnetization*. The critical temperature, where this long-range order appears, is called *Néel temperature*, denoted as T_N . Note that the net magnetization, i.e. the sum over all local magnetic moments, vanishes. A slightly more complicated structure is realized if the magnetization not only alternates in sign, but also the magnitudes are different. Here one speaks about *ferrimagnetism*.

Magnetic structures like ferro-, ferri- or antiferromagnetism are commensurable with the lattice structure and consequently called *commensurable structures*. For arbitrary \vec{q} this is in general not the case, and one speaks of *incommensurable magnetic structures*.

Another characteristic feature is that as $T \searrow T_C$ the susceptibility $\chi(T)$ diverges in a characteristic fashion as $\chi(T \searrow T_C)^{-1} \propto (T - T_C)^\gamma$, with some $\gamma > 0$. For the special value $\gamma = 1$ one speaks of *Curie-Weiss behavior*.

How can one detect a magnetic order which is not accompanied by a net magnetization? The answer is by elastic neutron scattering. Because neutrons have a magnetic moment, one can observe Bragg reflections coming from the regular arrangement of spins. Comparing the different spin directions of the neutrons, these reflexes can be discriminated from the ions, which have a spin-independent scattering pattern.

8.3 The Heisenberg model

As you have learned in quantum mechanics, electrons have an internal degree of freedom, called spin, which is connected to a magnetic moment as $\vec{M} = -g \frac{\mu_B}{\hbar} \vec{s}$, where μ_B is Bohr's magneton. Together with the orbital moments it determines the response of the electrons to an external field, and as we have seen in section 3.1.5 it is usually the more important player in the game. It is therefore reasonable to ask if the spins can be made responsible for the phenomenon of magnetism.

8.3.1 Free spins on a lattice

In the simplest approach one may wonder if already an isolated ensemble of spins sitting on a lattice is sufficient to produce the observed phenomena. In that case we may use a Hamilton operator

$$\hat{H} = \sum_i \frac{g\mu_B}{\hbar} \hat{s}_i \cdot \vec{B}_i ,$$

where \hat{s}_i is the operator of a spin located at site \vec{R}_i , and \vec{B}_i the magnetic field at this site. To keep things simple, we furthermore assume a homogeneous field

$\vec{B}_i = B\vec{e}_z$. Since the eigenvalues of $\hat{s}_{i,z}$ are $\pm\hbar/2$, we can immediately calculate the partition function as

$$\mathcal{Z} = \text{Tr} e^{-\beta\hat{H}} = \prod_i \sum_{\sigma=\pm 1} e^{-\beta \frac{g\mu_B B}{2} \sigma} = \left[2 \cosh \frac{g\mu_B B}{2k_B T} \right]^N$$

where N is the number of lattice sites in our volume. The free energy finally is obtained as

$$F = -k_B T \ln \mathcal{Z} = -Nk_B T \left[2 + \ln \cosh \frac{g\mu_B B}{2k_B T} \right]$$

We are interested in the magnetic response, i.e. the magnetization

$$m = -\frac{\partial F}{\partial B} = \frac{g\mu_B}{2} \tanh \frac{g\mu_B B}{2k_B T} \xrightarrow{B \rightarrow 0} \frac{\left(\frac{g\mu_B}{2}\right)^2}{k_B T} B + O(B^3)$$

and susceptibility

$$\chi = \frac{\partial m}{\partial B} = \frac{\left(\frac{g\mu_B}{2}\right)^2}{k_B T \cdot \cosh^2 \frac{g\mu_B B}{2k_B T}} \xrightarrow{B \rightarrow 0} \frac{\left(\frac{g\mu_B}{2}\right)^2}{k_B T} + O(B^2) .$$

This particular form $\chi(T) \propto 1/T$ is called *Curie behavior* and its occurrence a sign for the existence of free spins in the system. Unfortunately, it is not the form $\chi(T)^{-1} \propto (T - T_C)^\gamma$ expected for magnetic material.

8.3.2 Effects of the Coulomb interaction

Quite obviously, we have been missing something important, and of course this “something” are interactions. As you have learned in the basic physics courses, the lowest order interaction in magnetism is the dipole interaction, so one is tempted to use this here, too. However, choosing typical parameters for atoms and a classical theory for magnetism, one arrives at interaction energies $E_{dipole} \sim 10^{-3} \text{eV}$, while the transition temperatures are $T_C \sim 1000 \text{K} \sim 0.1 \text{eV}$. These two energies simply do not fit together. Thus, where do magnetic moments and the interaction between them come from?

The answer is surprising and simple: Magnetism is a result of the Coulomb interaction and Pauli’s principle. To understand this statement let us consider an oversimplified situation. We assume that we have a regular lattice, where at each lattice site we have exactly one immobile electron in a $1s$ configuration. Thus the only relevant quantum numbers are the lattice site n and the spin quantum number σ . In the Fock space of variable particle number the Coulomb

interaction now reads

$$\begin{aligned}\hat{H}_C &= \frac{1}{2} \sum_{\substack{n_1\sigma_1 \\ n_2\sigma_2}} \sum_{\substack{n'_1\sigma'_1 \\ n'_2\sigma'_2}} \hat{a}_{n_1\sigma_1}^\dagger \hat{a}_{n_2\sigma_2}^\dagger \underbrace{W(\dots)}_{\sim \delta_{\sigma_1\sigma'_1} \delta_{\sigma_2\sigma'_2}} \hat{a}_{n'_2\sigma'_2} \hat{a}_{n_1\sigma'_1} \\ &= \frac{1}{2} \sum_{\substack{n_1n'_1 \\ n_2n'_2}} \sum_{\sigma_1\sigma_2} \hat{a}_{n_1\sigma_1}^\dagger \hat{a}_{n_2\sigma_2}^\dagger W(\dots) \hat{a}_{n'_2\sigma_2} \hat{a}_{n_1\sigma_1} ,\end{aligned}$$

where we have used the fact the the Coulomb interaction does not depend on spin explicitly.

Of course we have to take into account a constraint, namely that we have one electron per site, i.e. $N_n = N_{n\uparrow} + N_{n\downarrow} = 1$. This leaves us with two possibilities for the quantum numbers n_i and n'_i : (i) $n'_1 = n_1 \wedge n'_2 = n_2$ or (ii) $n'_1 = n_2 \wedge n'_2 = n_1$. All other combinations will violate the constraint (check it out!). The two possibilities lead to a Hamiltonian

$$\begin{aligned}\hat{H}_C &= \hat{H}_{(i)} + \hat{H}_{(ii)} \\ \hat{H}_{(i)} &= \frac{1}{2} \sum_{\substack{n_1n_2 \\ \sigma_1\sigma_2}} \hat{a}_{n_1\sigma_1}^\dagger \hat{a}_{n_2\sigma_2}^\dagger K_{n_1n_2} \hat{a}_{n_2\sigma_2} \hat{a}_{n_1\sigma_1} , \\ K_{ij} &:= \langle v_i^{(1)} v_j^{(2)} | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | v_j^{(2)} v_i^{(1)} \rangle\end{aligned}\tag{8.1a}$$

$$\begin{aligned}\hat{H}_{(ii)} &= \frac{1}{2} \sum_{\substack{n_1n_2 \\ \sigma_1\sigma_2}} \hat{a}_{n_1\sigma_1}^\dagger \hat{a}_{n_2\sigma_2}^\dagger J_{n_1n_2} \hat{a}_{n_1\sigma_2} \hat{a}_{n_2\sigma_1} , \\ J_{ij} &:= \langle v_i^{(1)} v_j^{(2)} | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | v_i^{(2)} v_j^{(1)} \rangle .\end{aligned}\tag{8.1b}$$

The quantities K_{ij} are called (*direct*) *Coulomb integrals*, and the J_{ij} are the *exchange integrals*. We can use now once more the constraint

$$\sum_{\sigma} \hat{a}_{n\sigma}^\dagger \hat{a}_{n\sigma} = 1$$

to find the simplification

$$\hat{H}_{(i)} = \frac{1}{2} \sum_{n_1 \neq n_2} K_{n_1 n_2} \mathbb{1} .$$

Furthermore, we can introduce operators $\hat{s}_n^+ := \hbar \hat{a}_{n\uparrow}^\dagger \hat{a}_{n\downarrow}$, $\hat{s}_n^- := \hbar \hat{a}_{n\downarrow}^\dagger \hat{a}_{n\uparrow}$ and $\hat{s}_n^z := \frac{\hbar}{2} (\hat{a}_{n\uparrow}^\dagger \hat{a}_{n\uparrow} - \hat{a}_{n\downarrow}^\dagger \hat{a}_{n\downarrow})$. It is now easy to show (do it!) that these operators fulfill the commutation relations of angular momentum and furthermore that \hat{s}_n^z has the eigenvalues $\pm \hbar/2$. Thus, the operators \hat{s}_n^α represent the spin operators for the site n . Inserting these definitions into the Hamiltonian we arrive at

$$\hat{H}_C = -\frac{1}{\hbar^2} \sum_{i \neq j} J_{ij} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j + \frac{1}{4} \sum_{i \neq j} (2K_{ij} + J_{ij}) \mathbb{1} .$$

This is the famous *Heisenberg model* for magnetism. The magnetic moments are formed by the spin of the electrons – *not* the orbital moment – and their interaction is a consequence of Pauli’s principle manifesting itself in the exchange interaction J . Note that as J comes from the strong Coulomb interaction, it easily takes on values $J \sim 1/20 \dots 1\text{eV}$, yielding transition temperatures $T_C = O(1000)\text{K}$ very naturally.

Although Heisenberg’s model has been proposed in the early thirties of the last century, it is still a model at the heart of current solid state research. First, it cannot be solved analytically except in one spatial dimension (by the so-called Bethe ansatz).

8.3.3 Mean-field solution of the Heisenberg model

To keep things simple we restrict the discussion to a simple-cubic lattice and an exchange constant

$$J_{ij} = \begin{cases} J & \text{for } i \text{ and } j \text{ nearest neighbors} \\ 0 & \text{else} \end{cases}$$

in the following. To proceed we write $\hat{\mathbf{s}} = \langle \hat{\mathbf{s}} \rangle + \delta \hat{\mathbf{s}}$, where $\delta \hat{\mathbf{s}} = \hat{\mathbf{s}} - \langle \hat{\mathbf{s}} \rangle$. We insert this expression into the Hamiltonian and obtain¹

$$\begin{aligned} \hat{H} &= -\frac{J}{\hbar^2} \sum_{\langle i,j \rangle} \{ \langle \hat{\mathbf{s}}_i \rangle \langle \hat{\mathbf{s}}_j \rangle + \langle \hat{\mathbf{s}}_i \rangle \delta \hat{\mathbf{s}}_j + \delta \hat{\mathbf{s}}_i \delta \hat{\mathbf{s}}_j + \delta \hat{\mathbf{s}}_i \delta \hat{\mathbf{s}}_j \} \\ &= -\frac{J}{\hbar^2} \sum_{\langle i,j \rangle} \{ \hat{\mathbf{s}}_i \cdot \langle \hat{\mathbf{s}}_j \rangle + \langle \hat{\mathbf{s}}_i \rangle \cdot \hat{\mathbf{s}}_j \} + \frac{J}{\hbar^2} \sum_{\langle i,j \rangle} \langle \hat{\mathbf{s}}_i \rangle \langle \hat{\mathbf{s}}_j \rangle + O(\delta \hat{\mathbf{s}}^2) \\ &\approx -\sum_i \frac{g\mu_B \vec{B}_i^{\text{eff}}}{\hbar} \cdot \vec{\hat{s}}_i + E_0 \end{aligned} \quad (8.2)$$

with

$$\begin{aligned} \vec{B}_i^{\text{eff}} &:= \frac{2J}{\hbar g\mu_B} \sum_{\text{nn } i} \langle \hat{\mathbf{s}}_j \rangle \\ E_0 &:= \frac{J}{\hbar^2} \sum_{\langle i,j \rangle} \langle \hat{\mathbf{s}}_i \rangle \langle \hat{\mathbf{s}}_j \rangle \end{aligned} \quad (8.3)$$

The effective Hamiltonian (8.2) describes a set of decoupled spins in an effective magnetic field \vec{B}_i^{eff} , which by virtue of equation (8.3) is determined by the

¹With $\langle i, j \rangle$ I denote nearest-neighbors.

expectation value of the spins at the neighboring sites. One calls such a theory an *effective field theory* or *mean-field theory*. For the Heisenberg model in particular, it is called *Weiss mean-field theory* and \vec{B}_i^{eff} the *Weiss field*.

The relation (8.3) furthermore tells us, that the effective field at site i points into the direction of the averaged spins from the neighboring sites. Therefore, the average of the spin at site i will be pointing in the same direction, averages of components perpendicular to the effective field are zero.² Choosing this direction as z -axis, we can express the expectation value $\langle \hat{s}_i \rangle = \langle \hat{s}_{i,z} \rangle$ as

$$\langle \hat{s}_{i,z} \rangle = \frac{\hbar}{2} \tanh \frac{g\mu_B B_{i,z}^{\text{eff}}}{2k_B T} = \frac{\hbar}{2} \tanh \left[\frac{J}{\hbar^2 k_B T} \sum_{j \text{ nn } i} \langle \hat{s}_{j,z} \rangle \right]. \quad (8.4)$$

Equation (8.4) constitutes a *self-consistency equation*. It always has the trivial solution $\langle \hat{s}_{i,z} \rangle = 0$ for all i . The more interesting situation of course is when the expectation value is non-zero. We must distinguish two cases:³

- (i) $J > 0$: If we assume $\langle \hat{s}_{j,z} \rangle > 0$, then $B_{i,z}^{\text{eff}} > 0$ and (8.2) together with (8.3) means that also $\langle \hat{s}_{j,z} \rangle > 0$. Together with translational invariance we can deduce $\langle \hat{s}_{j,z} \rangle = \langle \hat{s}_{i,z} \rangle = s > 0$. If we denote with \mathcal{K} the number of nearest neighbors, the so-called *coordination number*, we have

$$\sum_{j \text{ nn } i} \langle \hat{s}_{j,z} \rangle = \mathcal{K}s$$

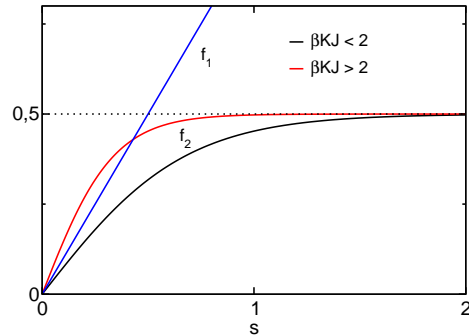
and hence

$$s = \frac{1}{2} \tanh \frac{\mathcal{K}Js}{T}. \quad (8.5)$$

As we have a homogeneous solution s , and the magnetization is given by $M_z = Ngs \neq 0$, we just have found a ferromagnet, provided there exists a solution $s \neq 0$.

Whether such an equation has a non-trivial solution, can best be discussed graphically. Let us define $f_1 = s$ and $f_2 = \tanh \mathcal{K}\beta Js$.

The figure to the right shows f_1 (blue curve) and f_2 for two values of $\mathcal{K}\beta J$, namely $\mathcal{K}\beta J < 2$ (black curve) and $\mathcal{K}\beta J > 2$ (red curve). In the first case, f_1 does not cross f_2 , i.e. we only have the trivial solution $s = 0$. In the second case, f_1 and f_2 cross at a finite value of s .



²This is a property of the present assumption of a cubic lattice and nearest-neighbor exchange. For other lattice structures or longer-ranged exchange, more complex situations can occur.

³To keep the notation simple, I use $k_B = \hbar = \mu_B = 1$ in the following.

Therefore, there exists a nontrivial solution $s > 0$. A closer inspection of equation (8.5) shows that the latter solution only exists for $\mathcal{K}\beta_c J > 2$, i.e. $\mathcal{K}\beta J = 2$ denotes the critical value, which yields a critical temperature (*Curie temperature*)

$$T_C = \frac{\mathcal{K}J}{2} . \quad (8.6)$$

The mere existence of a solution $s \neq 0$ does of course not imply that it is also the thermodynamically stable one. To ensure this, one needs to inspect the free energy. To this end we insert (8.2) into the formula for the partition function and obtain after some manipulation and using (8.6)

$$\frac{F}{Nk_B T_C} = 2s^2 - \frac{T}{T_C} \ln 2 - \frac{T}{T_C} \ln \cosh\left(2s \frac{T_C}{T}\right) .$$

Note that the term E_0 in (8.2) is essential, as it leads to the first part. Let us discuss this result at fixed T for $s \rightarrow 0$. In this case we can expand

$$\cosh\left(2s \frac{T_C}{T}\right) \approx 1 + \frac{1}{2} \left(\frac{2sT_C}{T}\right)^2$$

and

$$\ln(1+x) \approx x$$

to obtain

$$\frac{F}{Nk_B T_C} \approx \frac{1}{2} (2s)^2 - \frac{T}{T_C} \ln 2 - \frac{1}{2} \frac{T}{T_C} \left(\frac{2sT_C}{T}\right)^2 = \frac{1}{2} \frac{T - T_C}{T} (2s)^2 - \frac{T}{T_C} \ln 2 .$$

Thus, for $T > T_C$, the prefactor of the first term is positive, i.e. we have a minimum of F at $s = 0$. As for large S , the term involving \cosh behaves at most proportional to s , the contribution s^2 always wins, i.e. the minimum for $s = 0$ is the only one. On the other hand, for $T < T_C$, the initial slope is negative, i.e. at $s = 0$ we now have a maximum.

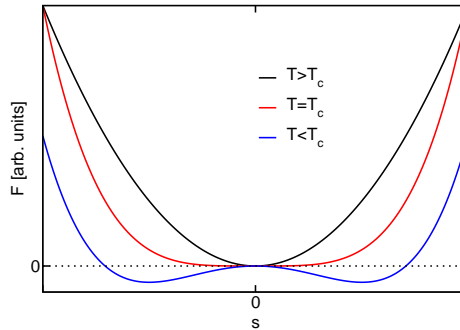


Figure 8.1: Schematic behavior of the mean-field free energy.

Since the previous argument for large s is still valid, we must have an additional minimum for finite $|s_m|$ (more precisely two for $\pm s_m$), which no is the

absolute minimum and consequently describes the stable thermodynamical equilibrium state. This structure of the free energy is schematically shown in Fig. 8.1.

Note that as function of temperature T the change from one single minimum at $s = 0$ to an ordered state with two minima at $|s| > 0$ and a maximum at $s = 0$ happens continuously. In this case one speaks of a *continuous* or *second order phase transition*.

How does the susceptibility behave as $T \searrow T_C$? To this end let us add a small *external* field B_0 . The expectation for the spin then becomes

$$\langle \hat{s}_{i,z} \rangle = \frac{1}{2} \tanh \frac{gB_{i,z}^{\text{eff}} + gB_0}{2T} .$$

Using $B_{i,z}^{\text{eff}} = \mathcal{K}Js = 2T_C s$ and $M/N =: m = gs$, we can rewrite this as

$$m = \frac{g}{2} \tanh \left[\frac{2T_C}{gT} m + \frac{gB_0}{2T} \right] . \quad (8.7)$$

As $T > T_C$, i.e. $s(B_0 \rightarrow 0) \sim B_0 \rightarrow 0$

$$\chi = \left. \frac{\partial m}{\partial B_0} \right|_{B_0=0} = \frac{g^2}{2} \left. \frac{d \tanh x}{dx} \right|_{x=\frac{2T_C}{T} s(B_0=0)=0} \left[\frac{1}{2T} + \frac{2T_C}{g^2 T} \left. \frac{\partial m}{\partial (B_0)} \right|_{B_0=0} \right] .$$

Therefore, we arrive at

$$\chi = \frac{g^2}{2} \left[\frac{1}{2T} + \frac{2T_C}{g^2 T} \chi \right] .$$

This equation can be re-expressed as

$$\chi \left(1 - \frac{T_C}{T} \right) = \frac{g^2}{4T}$$

and finally with

$$\chi = \frac{g^2}{4} \frac{1}{T - T_C} \quad (8.8)$$

we arrive at the expected Curie-Weiss behavior of the susceptibility.

Inserting all factors \hbar , k_B and μ_B , we can rewrite the prefactor for $s = 1/2$ as

$$C = \frac{g^2 s(s+1) \mu_B^2}{3k_B} =: \frac{\mu_{\text{eff}}^2}{k_B} .$$

The quantity μ_{eff} is called *effective moment* and the constant C *Curie constant*.

We can also look at the behavior of s as function of T for $T \nearrow T_C$ and $B_0 = 0$. To this end we expand the equation (8.7) for $s \ll 1$ and obtain in leading order

$$s \approx \frac{1}{2} \left[\frac{gT_C}{T} s - \frac{1}{3} \left(\frac{gT_C}{T} \right)^3 s^3 \right]$$

which can be solved to give (with $g = 2$)

$$s(T) \approx \frac{1}{2} \frac{T}{T_C} \sqrt{3 \left(1 - \frac{T}{T_C} \right)} .$$

Since we are close to T_C , we can safely set $T \approx T_C$ in front of the root to find for the magnetization $m = g\mu_B s$

$$m(T) \approx \sqrt{3} \mu_B \sqrt{\left(1 - \frac{T}{T_C} \right)} \Theta(T_C - T) \quad (8.9)$$

for temperatures close to T_C .

For $T \rightarrow 0$, on the other hand, we know that $s = 1/2$, and the limiting behavior can be investigated by looking at

$$x := \frac{1}{2} - s = \frac{1}{2} - \frac{1}{2} \tanh \left[\frac{2T_C}{T} \left(\frac{1}{2} - x \right) \right] .$$

Rewriting the hyperbolic tangent with exponentials, we find with $t := T/T_C$

$$x = \frac{1}{1 + e^{2(1-2x)/t}} \approx e^{-2(1-2x)/t} \approx e^{-2/t} \left(1 - \frac{4x}{t} \right) ,$$

where we implicitly assumed that x goes to zero much faster than t .⁴ This last equation has the solution

$$x = e^{-2T_C/T} \left(1 - \frac{4T_C}{T} e^{-2T_C/T} \right)$$

or for the magnetization

$$m(T \rightarrow 0) \approx \mu_B \left[1 - 2e^{-2T_C/T} \left(1 - \frac{4T_C}{T} e^{-2T_C/T} \right) \right] . \quad (8.10)$$

- (ii) $J < 0$: Due to the negative sign of J , equation (8.4) cannot have a homogeneous solution $\langle \hat{s}_{i,z} \rangle = s > 0$. However, if we assume that for a given

⁴The equation indeed suggests that $x \propto e^{-2/t}$, which is definitely fast enough.

spin at site \vec{R}_i we have a expectation value $\langle \hat{s}_{i,z} \rangle = s$, while all surrounding nearest neighbors \vec{R}_j have expectation values $\langle \hat{s}_{j,z} \rangle = -s$, we arrive at

$$s = \frac{1}{2} \tanh \frac{-\mathcal{K}Js}{T} = \frac{1}{2} \tanh \frac{\mathcal{K}|J|s}{T} . \quad (8.11)$$

This is the same equation as for the ferromagnet $J > 0$, only that the magnetization switches sign from site to site, i.e. we have an antiferromagnet. The system exhibits such a *staggered magnetization* below the *Néel temperature*

$$T_N = \frac{\mathcal{K}|J|}{2} .$$

If we try to calculate for $T > T_N$ the susceptibility for a homogeneous field B_0 , we arrive at

$$\chi(T) = \frac{C}{T - \Theta} , \quad \Theta = -T_N . \quad (8.12)$$

This does obviously not diverge when we approach T_N . You will have however noticed, that we need to use a magnetic field consistent with the magnetic structure, i.e. a so-called *staggered magnetic field* $B_{i,0}$ which changes sign from site to site. Using such a field, we arrive at

$$\chi(\vec{q} = \vec{Q}, T) = \frac{C}{T - T_N} \quad (8.13)$$

and a behavior equivalent to (8.9) as $T \nearrow T_N$ respectively (8.10) as $T \rightarrow 0$ for the staggered magnetization.

The behavior (8.12) is actually also important, because we cannot apply a staggered field. Thus, measuring for high enough temperatures $\chi(T)$ for a homogeneous field the observation of such a behavior indicates that the system exhibits antiferromagnetic spin correlations and that one may expect antiferromagnetic order with a Néel temperature of the order of Θ .

We thus have indeed found that the Heisenberg model, at least in the mean-field solution, fosters the anticipated magnetic solutions. For the simple situation used here, only ferro- and antiferromagnetic solutions appear, but for more complicated lattices and longer-ranged exchange one can also obtain other, even incommensurate solutions. Within the mean-field theory, we even could identify the critical exponents, for example we find that $\gamma = 1$. In practice, one observes different values, which indicate that the mean-field solution is not the correct one. The *theory of critical phenomena*, which is tightly connected to so-called

renormalization concepts and *universality* uses the critical exponents to classify the types of phase transitions. However, really calculating these exponents for a given model is a huge challenge and involves large-scale computations even today.

8.4 Delocalizing the spins

8.4.1 The Hubbard model

The results of the preceding section were quite nice, but had one serious flaw.

- Where do these localized moments actually come from?
We have learned up to now, that insulators are typically obtained for completely filled bands, i.e. an even number of electrons per unit cell. These will quite likely have a total spin $S = 0$, hence the spin is gone.
- How can we understand metallic magnets?
Several well-known examples of magnets like iron are nice conductors. Within our model these cannot be understood at all.

In order to gain at least a feeling how these questions can find an answer let us go back to the tight-binding approximation for a single s -like band on a simple-cubic lattice (5.2)

$$\begin{aligned}\hat{H}_{\text{tb}} &= \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} \\ \epsilon_{\vec{k}} &= -2t \sum_{i=1}^3 \cos(k_i a) \ .\end{aligned}$$

I did already mention the Lieb-Matthis theorem, which tells us that we will not obtain magnetism without interactions, i.e. we need to supplement the kinetic energy by some interaction term. Within the spirit of the tight-binding approximation – well-localized orbitals with only weak overlap to neighboring site – plus the screening of the Coulomb interaction by other electronic states in the system we can assume that the only relevant Coulomb matrix elements are those where all four site indices belong to the same site. Since we furthermore have an s -band, we can only accommodate two electrons at the same site if their spins are opposite. Together, this argument leads to a rather simple model

$$\begin{aligned}\hat{H}_{\text{tb}} &= \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} + U \sum_i \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} \quad (8.14) \\ \epsilon_{\vec{k}} &= -2t \sum_{i=1}^3 \cos(k_i a) \ .\end{aligned}$$

called *Hubbard model*. The new parameter U characterizes the strength of the Coulomb repulsion between to electrons with opposite spin at the same site. This model, first proposed in 1963 independently by Hubbard, Gutzwiller and Kanamori, looks rather dull at first sight. It is however a model still used for cutting-edge research in solid-state theory. That it is highly nontrivial can be understood from a simple quantum mechanical argument: The Hamiltonian has two terms, the kinetic energy built from *delocalized* states and the interaction written in a localized basis. This is what quantum mechanics calls *complementary* operators and there does not exist a simple basis where both terms can simultaneously be diagonalized.

8.4.2 Mean-field solution of the Hubbard model

Let us try to approximately solve for magnetic properties by using our mean-field ansatz

$$\hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} \approx \langle \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \rangle \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} + \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \langle \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} \rangle$$

with which we obtain

$$\hat{H} \approx \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma} + U \sum_{i\sigma} \langle \hat{c}_{i,-\sigma}^\dagger \hat{c}_{i,-\sigma} \rangle \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} .$$

To proceed we have several possibilities. The simplest is the case of a homogeneous system, and if we find a finite magnetization we have a ferromagnet. For a homogeneous system

$$\langle \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma} \rangle = \langle \hat{c}_\sigma^\dagger \hat{c}_\sigma \rangle = n + \sigma m$$

must hold, where

$$\begin{aligned} n &:= \sum_{\sigma} \langle \hat{c}_\sigma^\dagger \hat{c}_\sigma \rangle \\ m &:= \sum_{\sigma} \sigma \cdot \langle \hat{c}_\sigma^\dagger \hat{c}_\sigma \rangle . \end{aligned}$$

In this case we can write

$$\hat{H} \approx \sum_{\vec{k}\sigma} [\epsilon_{\vec{k}} - \sigma U m] \hat{c}_{\vec{k}\sigma}^\dagger \hat{c}_{\vec{k}\sigma}$$

and use our results for noninteracting electrons

$$\langle \hat{c}_\sigma^\dagger \hat{c}_\sigma \rangle = \frac{1}{N} \sum_{\vec{k}} f(\epsilon_{\vec{k}} - \sigma U m) \stackrel{T=0}{=} \int_{-\infty}^{E_F + \sigma U m} d\epsilon \mathcal{N}(\epsilon) .$$

For m we then obtain from the definition

$$m = \int_{-Um}^{Um} d\epsilon \mathcal{N}(E_F + \epsilon) \stackrel{Um \gg 0}{\approx} 2Um \mathcal{N}(E_F) .$$

If we require $m \neq 0$, this can only be true if

$$1 = 2UN(E_F) \text{ Stoner criterion.} \quad (8.15)$$

Note that in literature sometimes the factor 2 is missing. This is because the density of states is then defined with this spin factor included!

The Stoner criterion gives a rough estimate if one has to expect a ferromagnetic transition. Note that one can rephrase it as $2UN(E_F) > 1$, as one can then always find a temperature $T > 0$, where

$$m = \frac{1}{N} \sum_{\vec{k}} f(\epsilon_{\vec{k}} - \sigma Um) - \frac{1}{N} \sum_{\vec{k}} f(\epsilon_{\vec{k}} + \sigma Um) > 0$$

can be fulfilled.

The second interesting case is the antiferromagnet. Here, we cannot assume a homogeneous phase any more, but need at least a dependence of m on the lattice site. One consequently introduces

$$\begin{aligned} \langle \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma} \rangle &= n + \sigma m_i \\ n &:= \sum_{\sigma} \langle \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \rangle \\ m_i &:= \sum_{\sigma} \sigma \cdot \langle \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \rangle . \end{aligned}$$

Note that we still assume a homogeneous state with respect to the average occupation per site, n , but allow for a dependence of m_i .

The calculation now is not as straightforward any more. The standard trick is to divide the lattice into two sublattices, called A and B , and assign all spin up sites to the sublattice A and all spin down to B . This is shown in the figure to the right. For our next-nearest neighbor dispersion one only connects A sites to B sites in the hopping process. One now defines new operators

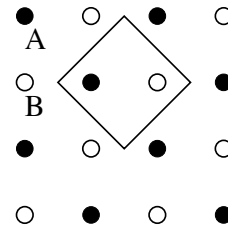


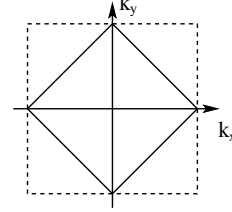
Figure 8.2: AB lattice for the Néel state.

$$\hat{\Psi}_{i\sigma} := \begin{pmatrix} \hat{c}_{i_A,\sigma} \\ \hat{c}_{i_B,\sigma} \end{pmatrix} ,$$

where $i_{A/B}$ means Bravais lattice site i , and sublattice site A respectively B . It is easy to show that these operators obey standard Fermi anticommutation rules if one reads the anticommutators in a tensor-product fashion. With these operators we obtain

$$\hat{H} = \sum_{\langle i,j \rangle, \sigma} \hat{\Psi}_{j\sigma}^\dagger \begin{pmatrix} \sigma Um & -t \\ -t & -\sigma Um \end{pmatrix} \hat{\Psi}_{i\sigma} = \sum_{\vec{k}\sigma} \hat{\Psi}_{\vec{k}\sigma}^\dagger \begin{pmatrix} \sigma Um & \epsilon_{\vec{k}} \\ \epsilon_{\vec{k}} & -\sigma Um \end{pmatrix} \hat{\Psi}_{\vec{k}\sigma}$$

After the second equal sign, we reintroduced the Fourier transform. However, because the AB lattice has a larger unit cell containing two atoms, see Fig. 8.2. The corresponding first Brillouin zone of the reciprocal lattice is therefore smaller, and the \vec{k} sum runs only over this reduced portion called *magnetic Brillouin zone* of the original Brillouin zone. Its form and position relative to the original first Brillouin zone (dashed line) is shown as full line in Fig. 8.3.



As there appears a matrix in the Hamiltonian, a natural path is to diagonalize it, which leads to the eigenvalue equation

Figure 8.3: 1st Brillouin zone for the AB lattice.

$$\begin{vmatrix} (\sigma m U - E_{\vec{k}}) & \epsilon_{\vec{k}} \\ \epsilon_{\vec{k}} & (-\sigma m U - E_{\vec{k}}) \end{vmatrix} = -[U^2 m^2 - E_{\vec{k}}^2] - \epsilon_{\vec{k}}^2 = 0 ,$$

which has the solutions

$$\begin{aligned} E_{1,\vec{k}} &= -\sqrt{\epsilon_{\vec{k}}^2 + (Um)^2} \\ E_{2,\vec{k}} &= \sqrt{\epsilon_{\vec{k}}^2 + (Um)^2} \end{aligned}$$

In the following, we assume that we have an average occupancy $n = 1$ (*half-filling*).

As before, the magnetization m appears in the formula for the dispersion $E_{n,\vec{k}}$, i.e. we again have a self-consistency problem. Since only $|m|$ enters, we can restrict our calculations to the A lattice (the B lattice has just the opposite sign), i.e. use

$$m = \langle \hat{c}_{iA\uparrow}^\dagger \hat{c}_{iA\uparrow} \rangle - \langle \hat{c}_{iA\downarrow}^\dagger \hat{c}_{iA\downarrow} \rangle .$$

However, this is not just the sum over the corresponding Fermi function using dispersion $E_{n,\vec{k}}$, because the diagonalization also mixes the operators through a unitary transformation

$$\begin{pmatrix} \hat{\gamma}_{1,\vec{k},\sigma} \\ \hat{\gamma}_{2,\vec{k},\sigma} \end{pmatrix} = \begin{pmatrix} -\frac{\epsilon_{\vec{k}}}{\sqrt{\epsilon_{\vec{k}}^2 + (E_{\vec{k}} + \sigma U|m|)^2}} & \frac{E_{\vec{k}} + \sigma U|m|}{\sqrt{\epsilon_{\vec{k}}^2 + (E_{\vec{k}} + \sigma U|m|)^2}} \\ \frac{E_{\vec{k}} - \sigma U|m|}{\sqrt{\epsilon_{\vec{k}}^2 + (E_{\vec{k}} - \sigma U|m|)^2}} & \frac{\epsilon_{\vec{k}}}{\sqrt{\epsilon_{\vec{k}}^2 + (E_{\vec{k}} - \sigma U|m|)^2}} \end{pmatrix} \begin{pmatrix} \hat{c}_{A,\vec{k},\sigma} \\ \hat{c}_{B,\vec{k},\sigma} \end{pmatrix}$$

into the new basis, where the Hamilton operator becomes

$$\hat{H} = \sum_{\vec{k}\sigma} (-E_{\vec{k}}) \hat{\gamma}_{1,\vec{k},\sigma}^\dagger \hat{\gamma}_{1,\vec{k},\sigma} + \sum_{\vec{k}\sigma} (+E_{\vec{k}}) \hat{\gamma}_{2,\vec{k},\sigma}^\dagger \hat{\gamma}_{2,\vec{k},\sigma} . \quad (8.16)$$

The operator $\hat{c}_{A,\bar{k},\sigma}$ is then obtained by applying the transpose to the $\hat{\gamma}$ vector, yielding

$$\hat{c}_{A,\bar{k},\sigma} = -\frac{\epsilon_{\bar{k}}}{\sqrt{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} + \sigma U|m|)^2}} \hat{\gamma}_{1,\bar{k},\sigma} + \frac{E_{\bar{k}} - \sigma U|m|}{\sqrt{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} - \sigma U|m|)^2}} \hat{\gamma}_{2,\bar{k},\sigma}$$

and hence

$$\begin{aligned} \hat{c}_{A,\bar{k},\sigma}^\dagger \hat{c}_{A,\bar{k},\sigma} &= \frac{\epsilon_{\bar{k}}^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} + \sigma U|m|)^2} \hat{\gamma}_{1,\bar{k},\sigma}^\dagger \hat{\gamma}_{1,\bar{k},\sigma} + \frac{(E_{\bar{k}} - \sigma U|m|)^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} - \sigma U|m|)^2} \hat{\gamma}_{2,\bar{k},\sigma}^\dagger \hat{\gamma}_{2,\bar{k},\sigma} \\ &\quad + \text{terms involving } \hat{\gamma}_{1,\bar{k},\sigma}^\dagger \hat{\gamma}_{2,\bar{k},\sigma} \text{ and } \hat{\gamma}_{2,\bar{k},\sigma}^\dagger \hat{\gamma}_{1,\bar{k},\sigma}. \end{aligned}$$

When we calculate the expectation value $\langle \hat{c}_{A,\bar{k},\sigma}^\dagger \hat{c}_{A,\bar{k},\sigma} \rangle$ the structure of the mean-field Hamiltonian (8.16) ensures that $\langle \hat{\gamma}_{1,\bar{k},\sigma}^\dagger \hat{\gamma}_{2,\bar{k},\sigma} \rangle = 0$. Thus,

$$\langle \hat{c}_{A,\bar{k},\sigma}^\dagger \hat{c}_{A,\bar{k},\sigma} \rangle = \frac{1}{N} \sum_{\bar{k}} \frac{\epsilon_{\bar{k}}^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} + \sigma U|m|)^2} f(-E_{\bar{k}}) + \frac{(E_{\bar{k}} - \sigma U|m|)^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} - \sigma U|m|)^2} f(+E_{\bar{k}}),$$

and for the difference we get

$$\begin{aligned} m &= \frac{1}{N} \sum_{\bar{k}} \left[\langle \hat{c}_{A,\bar{k},\uparrow}^\dagger \hat{c}_{A,\bar{k},\uparrow} \rangle - \langle \hat{c}_{A,\bar{k},\downarrow}^\dagger \hat{c}_{A,\bar{k},\downarrow} \rangle \right] \\ &= \frac{1}{N} \sum_{\bar{k}} \left[\frac{\epsilon_{\bar{k}}^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} + U|m|)^2} - \frac{\epsilon_{\bar{k}}^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} - U|m|)^2} \right] f(-E_{\bar{k}}) \\ &\quad + \frac{1}{N} \sum_{\bar{k}} \left[\frac{(E_{\bar{k}} - U|m|)^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} - U|m|)^2} - \frac{(E_{\bar{k}} + U|m|)^2}{\epsilon_{\bar{k}}^2 + (E_{\bar{k}} + U|m|)^2} \right] f(+E_{\bar{k}}) \\ &= \frac{1}{N} \sum_{\bar{k}} \frac{|m|U}{E_{\bar{k}}} [f(-E_{\bar{k}}) - f(+E_{\bar{k}})] \\ &= \frac{1}{N} \sum_{\bar{k}} \frac{|m|U}{E_{\bar{k}}} \tanh \frac{E_{\bar{k}}}{2k_{\text{B}}T}. \end{aligned}$$

Remember, that the \bar{k} -sum runs over the magnetic Brillouin zone and N here denotes the number of unit cells in the AB lattice.

As before, we obtain a self-consistency equation for m . With the help of the density of states it can be rewritten as

$$m = mU \int_{-\infty}^0 d\epsilon \mathcal{N}(\epsilon) \frac{\tanh\left(\frac{\sqrt{\epsilon^2 + m^2 U^2}}{2k_{\text{B}}T}\right)}{\sqrt{\epsilon^2 + m^2 U^2}}.$$

In particular, the critical temperature T_N can be obtained by assuming an infinitesimal $m > 0$, which then leads to

$$\frac{1}{U} = \int_{-\infty}^0 d\epsilon \mathcal{N}(\epsilon) \frac{\tanh \frac{\epsilon}{2k_B T_N}}{\epsilon} \quad (8.17)$$

in the limits $T \nearrow T_N$.

Equation (8.17) can be evaluated numerically. For a further analytical treatment we need an additional simplification, namely we assume $\mathcal{N}(\epsilon) = N_F \cdot \Theta(W/2 - \epsilon)$, i.e. a featureless density of states of width W and weight N_F . Then, equation (8.17) becomes

$$\frac{1}{N_F U} = \int_{-W/2}^0 d\epsilon \frac{\tanh \frac{\epsilon}{2k_B T_N}}{\epsilon} = \int_0^{W/2} d\epsilon \frac{\tanh \frac{\epsilon}{2k_B T_N}}{\epsilon} .$$

This integral can be evaluated in the limit $w/k_B T_N \gg 1$ with the result

$$\frac{1}{N_F U} = \ln \left(\frac{2\gamma}{\pi} \frac{W}{2k_B T_N} \right) ,$$

where $\gamma = 1.78$ denotes Euler's constant, respectively

$$k_B T_N = W \cdot \frac{\gamma}{\pi} e^{-1/(N_F \cdot U)} \approx 0.565 W e^{-1/(N_F \cdot U)} \quad (8.18)$$

Note that this result depends nonanalytically on U , and that we have a finite Néel temperature for any $U > 0$. This also means that the antiferromagnet wins over the ferromagnet at $n = 1$, as there a finite U is needed.

8.4.3 The limit $U \rightarrow \infty$

Let us again stick to the special case $n = 1$, i.e. we accommodate one electron per lattice site. We already have learned, that in such a situation we have a half-filled band (that's why we call this half-filling), and for small values of the interaction U , we expect the Hubbard model (8.14) to describe a Fermi liquid, i.e. a metal.⁵ Let us now increase U in a gedankenexperiment. At some point, it will become rather unfavorable for the electrons to move, as each site is populated by one electron, and to put a second on the same site one has to pay the high price U . Consequently, we can expect the electrons to *localize* for some critical U_c , avoiding the cost of U on the expense of the kinetic energy. As the latter is characterized by the bandwidth W , a good guess is that this will happen for $U_c/W \gtrsim 1$. For any $U > U_c$ the electrons refuse to move, and

⁵Actually, this has to be proven, but for small U it does not seem unreasonable.

we have an novel type of insulator a so-called *correlation induced* or *Mott-Hubbard* insulator. Note that we now have precisely the situation anticipated when motivating the Heisenberg model, i.e. immobile fermions with spin $s = 1/2$ sitting on a nice lattice. Unfortunately, we do not have the Coulomb repulsion between neighboring sites at our disposal, only the local U .

Nevertheless, we have localized spins, and we may ask the question how these communicate. With the help of the connection between fermionic creation and annihilation operators and the spin operators for $s = 1/2$, we can rewrite the interaction term in the Hubbard model (8.14) as

$$\hat{H}_I = -\frac{2}{3}U \sum_i \hat{S}_i^2 .$$

If we now pick the extreme limit and set $t/U = 0$, then the lowest energy for the half-filled case $n = 1$ is obviously realized, when at *each* lattice site the spin is maximized. If we denote by $|\sigma_i\rangle$ a state of a spin at site \vec{R}_i with quantum number $s_i = \sigma_i \hbar/2$, then

$$|\Psi\rangle = \prod_i |\sigma_i\rangle$$

is an eigenstate of \hat{H}_i , and since for each site the spin is maximal, it also represents a ground state. Quite obviously, the ground state of the system with $t = 0$ is 2^N fold degenerate (I can choose freely the direction of the spin at each of the N sites). Any finite t will lift this degeneracy.

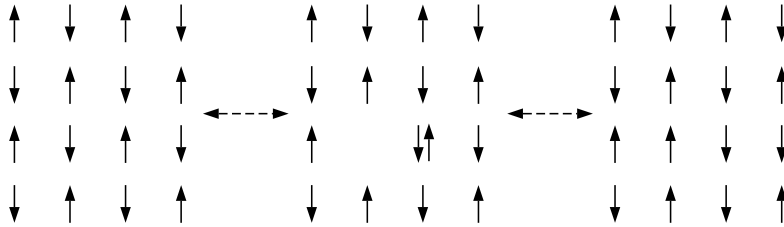


Figure 8.4: Processes contributing to perturbation theory for small t

How this precisely happens can be deduced with the help of Fig. 8.4, where the left- and rightmost configurations represent to possible ground state configurations, which have the energy E_0 . When the hopping t is finite, both can be transformed into the middle configuration, which now has one empty and one doubly occupied site. Inserting numbers you will easily check that this state has an energy $E_0 + U$. Note further, that the hopping is only active when the neighboring spins are antiparallel, otherwise it is forbidden by Pauli's principle. To apply perturbation theory, we need to return to the original ground state, which makes a second hopping process necessary. You should now remember

from QM I, that (i) second order perturbation theory always leads to a reduction of the ground state energy and (ii) its contribution is given by the square of the matrix element driving the process, here t , divided by the energy difference between excited state and ground state, here $E_0 + U - E_0 = U$. Therefore, the whole process will give an energy reduction with respect to the degenerate ground state at $t = 0$

$$\Delta E \propto -\frac{t^2}{U}$$

for *antiparallel spins*. Analyzing the perturbation theory using second quantization, applying the constraint that we are in the half-filled sector and rearranging the operators to form spin operators, one can show that

$$H_{\text{Hubbard}} \xrightarrow{U \rightarrow \infty} \hat{H} = \frac{2t^2}{U} \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j$$

which again is the Heisenberg model, this time as limit of a model describing itinerant electrons. Note that quite naturally we obtain an antiferromagnetic coupling here. This type of transformation is called *Schrieffer-Wolf* transformation, and the type of exchange occurring *super exchange*. It plays an important role in all transition metal oxides.

We are now in the position to actually draw a rough magnetic phase diagram of the Hubbard model at half filling. For small U we expect our previous mean-field theory to be at least qualitatively correct, at large U we know from the mean-field treatment of the Heisenberg model how T_N must look like. The result is shown in Fig. 8.5. You will not

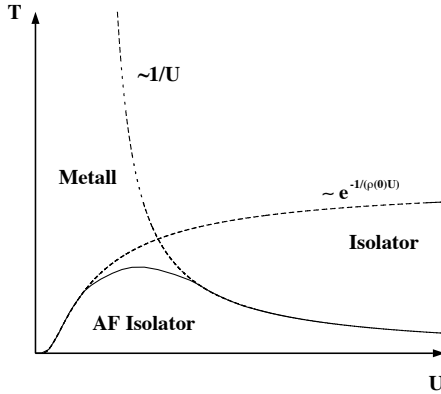


Figure 8.5: Qualitative phase diagram of the Hubbard model at half-filling calculating this phase diagram is a very hard task.

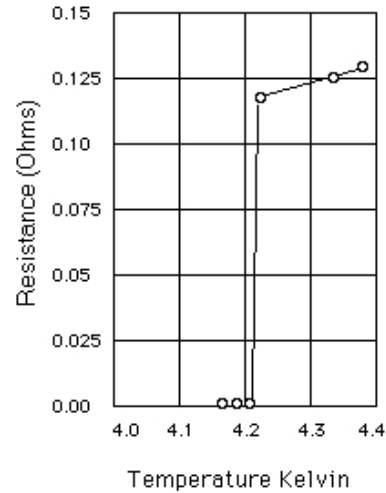
be surprised to learn that actually Like the Heisenberg model, the Hubbard model cannot be solved analytically except in one spatial dimension (again with the Bethe ansatz), and even the statement that it is ordering antiferromagnetically is a conjecture, although a rather plausible one.

Chapter 9

Superconductivity

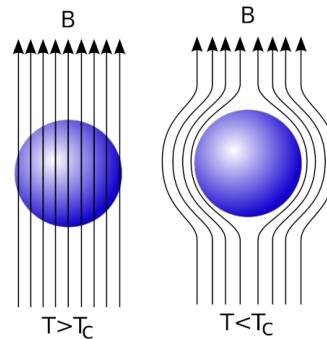
9.1 Phenomenology

The fundamental property of superconductivity appearing in solids was discovered by Heike Kammerlingh Onnes in Leiden (Netherlands). He has just before successfully liquified ^4He and studied the properties of liquid mercury. He observed that at a certain critical temperature $T_c \approx 4.2\text{K}$ the metallic resistivity went abruptly¹ to zero, i.e. mercury at low enough temperatures behaves as a perfect conductor. The graph produced by his group is shown on the right. Similar results were soon found for other metals like lead and tin.



At first sight the phenomenon thus leads to a perfect conductor, which is in principle possible in view of Bloch's theorem: In a perfect periodic crystal the "momentum" \vec{k} is conserved (modulo a reciprocal lattice vector), i.e. a electron subject to an electric field will accelerate without scattering and hence the system will conduct perfectly.² Therefore one might think that at low enough temperature when phonons or deviations from the perfect crystal structure are "frozen out" that a clean enough metal will behave as perfect conductor.

The situation is however more complicated. In 1933 Meißner and Ochsenfeld showed that such a *superconductor* expels any external magnetic field, as shown schematically in the figure to the right. For a perfect conductor, this would happen if one switches on the field in the perfect conducting phase (*zero-field cooled*) due to the eddy currents induced by the law of induction, while for a field present when the material enters into the perfect conducting state (*field cooled*) nothing should happen. Meißner and



Ochsenfeld however showed that the state is the same, namely with field expelled, in both cases. Thus, the state at a certain temperature T is unique and hence the material is in a different thermodynamic phase: *The transition between the normal metal and the superconductor is a true macroscopic phase transition.*

As expelling the field from the volume of the volume of the superconductor

¹More precisely: In a rather narrow temperature window.

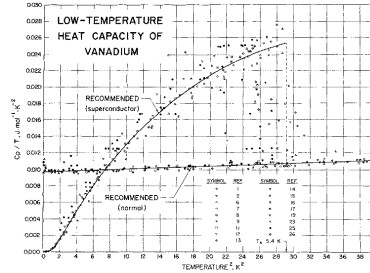
²Interactions do not change this property, as they must be compatible with the lattice periodicity and hence do not destroy Bloch's theorem.

costs a certain energy $H^2/8\pi$ and the superconducting state will only have a finite lower free energy as compared to the normal metal, there will exist a finite *critical field* H_c , which eventually destroys superconductivity. Knowing this field at a temperature $T < T_c$ tells us about the gain in free energy via the relation

$$-\frac{H_c(T)^2}{8\pi V} = F_{sc}(T,V) - F_n(T,V) ,$$

where V is the volume.³ Experimentally, one finds $H_c(T) \approx H_c(0) [1 - (T/T_c)^2]$ as very good approximation for most cases.

Further evidence that the transition to superconductivity is a macroscopic phase transition comes from the specific heat. A series of measurements of $C(T)/T$ versus T^2 is shown in the figure for different vanadium samples ($T_c \approx 5.4\text{K}$). For a normal metal, one finds a nice linear behavior due to phonons and a finite value as $T \rightarrow 0$ characteristic for a Fermi liquid.



In the superconducting state the specific heat jumps due to the drop in free energy, and the form also shows that the transition is not accompanied by a latent heat, i.e. is a second order transition. Furthermore, at low temperatures, $C(T)$ decreases exponentially like $e^{-\beta\Delta}$. Therefore, one has to expect that the excitation spectrum is gapped in a superconductor. There are many other phenomenological properties. A rather comprehensive and complete overview can be found in the book by M. Tinkham [?]. Here we only note that the electrodynamics of a superconductor are governed by two characteristic length scales: The *penetration depth* usually designated as λ , which is a measure of the extent to which an external magnetic field can enter into the superconductor, and the *coherence length* written as ξ , which measures the length scale over which the superconducting charge density typically varies. It is quite amusing to note that the Meißner effect of the existence of a finite λ can be interpreted in the sense that the boson mediating the electromagnetic interactions has become massive in a superconductor. As we will learn later, superconductivity can be understood as spontaneous breaking of global gauge invariance, and the mass generation of a phonon mass thus similar to the famous Higgs mechanism in the standard model of particle physics. Indeed did the solid-state theorist P.W. Anderson propose that a mechanism similar to superconductivity could be responsible for the otherwise incomprehensible existence of finite masses and, together with work by Nambu and the Ginzburg-Landau theory of phase transitions, inspired R. Brout and Francois Englert, and

³We do not care for geometrical factors here.

independently P. Higgs as well as G. Guralnik, C.R. Hagen, and T. Kibble in 1964 to propose the mechanism later coined Higgs mechanism by t'Hooft.

9.2 The BCS theory

Nearly 50 years the phenomenon of superconductivity was not understood theoretically. Over the years several successful phenomenological descriptions have been put forward, for example the London theory of electrodynamics of a superconductor, later extended by Pippard and Ginzburg and Landau. However, an understanding of the microscopic basis of superconductivity and the reason for the success of the phenomenological theories was lacking.

9.2.1 The Cooper instability

In 1956 Cooper has shown 1956 that the ground state of an electron gas with arbitrarily weak *attractive* interaction cannot be described by a Fermi-Dirac distribution with sharp Fermi edge. This observation is the basis of the BCS theory, the first valid microscopic theory of superconductivity. This *Cooper instability* can most conveniently be understood within a rather artificial model: One considers an interaction which is attractive and constant within a shell of width $\hbar\omega_c$ above the Fermi energy, and zero everywhere else. The Hamilton operator thus reads

$$\begin{aligned} H &= \sum_{\vec{k}\sigma} \epsilon_k c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + \frac{1}{2} \sum_{\vec{k}_1, \vec{k}_2} \sum_{\sigma_1, \sigma_2} \langle \vec{k}_1 + \vec{q}, \vec{k}_2 - \vec{q} | V | \vec{k}_2, \vec{k}_1 \rangle c_{\vec{k}_1 + \vec{q}\sigma_1}^\dagger c_{\vec{k}_2 - \vec{q}\sigma_2}^\dagger c_{\vec{k}_2\sigma_2} c_{\vec{k}_1\sigma_1} \\ &=: H_0 + H_I \end{aligned}$$

with

$$\langle \vec{k}_1 + \vec{q}, \vec{k}_2 - \vec{q} | V | \vec{k}_2, \vec{k}_1 \rangle = \begin{cases} v < 0 & \text{for } E_F < \epsilon_{k_1}, \dots < E_F + \hbar\omega_c \\ 0 & \text{else} \end{cases}$$

Proof: Let

$$|F\rangle = \prod_{\substack{\vec{k}\sigma \\ \epsilon_k \leq E_F}} c_{\vec{k}\sigma}^\dagger |0\rangle$$

be the Fermi sea ground state. Then

$$H|F\rangle = H_0|F\rangle = E_0|F\rangle, \quad E_0 = \sum_{\substack{\vec{k}\sigma \\ \epsilon_k \leq E_F}} \epsilon_k$$

We now add two electrons with opposite momenta and spin and define

$$|-\vec{k} \downarrow, \vec{k} \uparrow\rangle := c_{-\vec{k}\downarrow}^\dagger c_{\vec{k}\uparrow}^\dagger |F\rangle,$$

to obtain

$$H|-\vec{k}\downarrow, \vec{k}\uparrow\rangle = (2\epsilon_k + E_0)|-\vec{k}\downarrow, \vec{k}\uparrow\rangle + v \sum'_{\vec{k}'} |-\vec{k}'\downarrow, \vec{k}'\uparrow\rangle$$

with

$$\sum'_{\vec{k}} = \sum_{\substack{\vec{k} \\ E_F < \epsilon_k \leq E_F + \hbar\omega_c}} .$$

Due to the interaction the pair $|-\vec{k}\downarrow, \vec{k}\uparrow\rangle$ will be scattered into the pair $|-\vec{k}'\downarrow, \vec{k}'\uparrow\rangle$, i.e. such a state is not an eigenstate of H . To obtain an eigenstate we make an ansatz

$$|\downarrow, \uparrow\rangle := \sum'_{\vec{k}} g(\vec{k}) |-\vec{k}\downarrow, \vec{k}\uparrow\rangle$$

with a function $g(\vec{k})$ to be determined. We seek a solution of $H|\downarrow, \uparrow\rangle = E|\downarrow, \uparrow\rangle$, i.e.

$$\begin{aligned} \sum'_{\vec{k}_1} g(\vec{k}_1) (2\epsilon_{k_1} + E_0) |-\vec{k}_1\downarrow, \vec{k}_1\uparrow\rangle + v \sum'_{k_1} g(\vec{k}_1) \sum'_{k_2} |-\vec{k}_2\downarrow, \vec{k}_2\uparrow\rangle \\ = E \sum'_{k_3} g(\vec{k}_3) |-\vec{k}_3\downarrow, \vec{k}_3\uparrow\rangle \end{aligned}$$

Using the orthonormality of the states $|-\vec{k}\downarrow, \vec{k}\uparrow\rangle$ one finds

$$g(\vec{k})(2\epsilon_k + E_0) + v \sum'_{\vec{k}_1} g(\vec{k}_1) = E g(\vec{k}) .$$

For a constant interaction v this integral equation can be solved easily: Define

$$C = -v \sum'_{k_1} g(\vec{k}_1) ,$$

then

$$g(\vec{k}) = \frac{C}{2\epsilon_k + E_0 - E}, \quad C = -v \sum'_{\vec{k}} \frac{C}{2\epsilon_k + E_0 - E} ,$$

and for $C \neq 0$ we find

$$1 = -v \sum'_{\vec{k}} \frac{1}{2\epsilon_k + E_0 - E}$$

For a discrete energy spectrum this eigenvalue equation has many solutions, which in general correspond to slightly shifted particle-hole excitations. We are looking for a solution $E < E_0 + 2E_F$, which is the minimal energy of two additional Fermions at the Fermi energy. If such an energy exists, the pair state will be preferred to the Fermi sea. Let us define $\xi = \epsilon_k - E_F$ and $\Delta E =$

$E - (E_0 + 2E_F)$. Transforming the \vec{k} -sum into an energy integral with $N(E_F)$ the density of states at the Fermi energy

$$\begin{aligned} 1 &= -vN(E_F) \int_0^{\hbar\omega_c} d\xi \frac{1}{2\xi - \Delta E} = -vN(E_F) \frac{1}{2} \ln \frac{\hbar\omega_c - \Delta E/2}{-\Delta E/2} \\ &\approx -vN(E_F) \frac{1}{2} \ln \frac{\hbar\omega_c}{-\Delta E/2}, \quad \hbar\omega_c \gg |\Delta E| \end{aligned}$$

It becomes now clear that a solution exists only for $v < 0$. Solving for $\Delta E < 0$ yields

$$\Delta E = -2\hbar\omega_c e^{-2/\lambda}, \quad E = E_0 + 2E_F - 2\hbar\omega_c e^{-2/\lambda} \quad (9.1)$$

i.e. a pair state formed from electronic states above the Fermi energy has in the case of an attractive interaction a lower energy than a Fermi sea with two additional electrons at the Fermi energy. Thus, putting two electrons from states just below the Fermi energy into a pair state just above the Fermi energy lowers the total energy of the system, i.e. the Fermi body is unstable. Note, however, that up to now we did not show what happens if multiple pair states are occupied.

Since $\exp(-2/\lambda)$ is not an analytic function of λ for $\lambda = 0$, this result cannot be obtained within some kind of perturbation expansion in v . This quite likely is one of the reasons why it took 50 years after the discovery of superconductivity to formulate a theory.

Besides the general question how, given the strong and repulsive Coulomb interaction, an attractive interaction between electrons can occur at all, two further points must be discussed: Firstly, why does one form pairs of states with opposite momentum and secondly, why does one pair states with opposite spin? The first question is quite easy to answer. For electronic states with a net momentum $\vec{q} \neq 0$ one can show that the net energy gain is smaller. Furthermore, for a specimen at rest conservation of total momentum actually implies $\vec{q} = 0$. The answer to the second point is more subtle. In fact, there is no apparent reason why one cannot construct a pair state $|\uparrow, \uparrow\rangle$. However, for a constant interaction Pauli's principle actually forbids such a pair, because for a state

$$|\uparrow, \uparrow\rangle := \sum_{\vec{k}}' \tilde{g}(\vec{k}) |-\vec{k} \uparrow, \vec{k} \uparrow\rangle$$

one obtains the same formula for the function $\tilde{g}(\vec{k})$ as before. In particular, for a constant interaction it immediately follows $\tilde{g}(-\vec{k}) = \tilde{g}(\vec{k})$. On the other hand, antisymmetrization requires $|-\vec{k} \uparrow, \vec{k} \uparrow\rangle = -|+\vec{k} \uparrow, -\vec{k} \uparrow\rangle$, and consequently $\tilde{g}(\vec{k}) = 0$. Note that this argument is valid only for a \vec{k} independent interaction.⁴

⁴More precisely for an interaction which has no nodes in \vec{k} space.

For an interaction of the form $v(\vec{k}, \vec{k}')$ with $v(-\vec{k}, -\vec{k}') = -v(\vec{k}, \vec{k}')$ one can also have $\tilde{g}(-\vec{k}) = -\tilde{g}(\vec{k})$, and a pairing with total spin $S = 1$ would become possible. This situation is for example realised in supra fluid ${}^3\text{He}$ or in Sr_2RuO_4 .

9.2.2 BCS-Theorie

Let us now extend Cooper's argument to a more realistic case, also allowing a finite density of pairs. First, we extend the artificial interaction in the Hamiltonian introduced for the proof of the Cooper instability. As before, the Hamiltonian reads

$$H = \sum_{\vec{k}\sigma} \epsilon_k c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + \frac{1}{2} \sum_{\vec{k}_1 \vec{k}_2} \sum_{\sigma_1 \sigma_2} \langle \vec{k}_1 + \vec{q}, \vec{k}_2 - \vec{q} | V | \vec{k}_2 \vec{k}_1 \rangle c_{\vec{k}_1 + \vec{q}\sigma_1}^\dagger c_{\vec{k}_2 - \vec{q}\sigma_2}^\dagger c_{\vec{k}_2\sigma_2} c_{\vec{k}_1\sigma_1}$$

with an attractive and constant two-particle interaction for all states within a shell $|\epsilon_k - E_F| \leq \hbar\omega_c$ of the Fermi energy. From the Cooper instability one can infer that the Fermi body will be unstable against the formation of *Cooper pairs* $\vec{k} \uparrow, -\vec{k} \downarrow$. We can therefore expect that ground state expectation values of the form $\langle G | c_{\vec{k}_2\sigma_2} c_{\vec{k}_1\sigma_1} | G \rangle$ will become macroscopically large for the combination $\vec{k}_2 = -\vec{k}_1$ and $\sigma_2 = -\sigma_1$. Note that this type of expectation value explicitly breaks the global gauge invariance, i.e. the invariance of a transformation $c_{\vec{k}\sigma} \rightarrow e^{i\varphi} c_{\vec{k}\sigma}$, of the Hamiltonian. From fundamental quantum mechanics you know, on the other hand, that this type of gauge invariance is connected to the electromagnetic potentials. Thus, breaking of gauge invariance also implies the breaking of gauge invariance for an electromagnetic field, which can shown to have the form of a mass term. This is the connection between Higgs' mechanism for mass generation in particle physics and the similar phenomenon in superconductivity. It is, however, inconvenient to study such effects within the framework of wave functions for fixed particle number directly. A more suited approach is using the grand canonical ensemble of quantum statistics, as there particle number is not fixed anyway and such matrix elements can be written as conventional expectation values. Formally, we need to study the operator $H - \mu N$ instead only H . For simplicity, we will call the former "Hamiltonian", although strictly speaking the Hamiltonian is only the first part.

As we cannot solve the problem exactly, we need a further approximation, which will be again the Hartee-Fock approximation discussed extensively in section 3.2.1. There, however, only expectation values of the form $\langle c^\dagger c \rangle$ have been taken into account in the construction of the effective Hamiltonian. These lead to modifications of the dispersion, but otherwise do not change the character of the ground state. Here, we however also allow for expectation values of the

form $\langle c_{\vec{k}\uparrow} c_{-\vec{k}\downarrow} \rangle$. With the above Hamiltonian, this leads to

$$c_{\vec{k}_1+\vec{q}\sigma_1}^\dagger c_{\vec{k}_2-\vec{q}\sigma_2}^\dagger c_{\vec{k}_2\sigma_2} c_{\vec{k}_1\sigma_1} \rightarrow c_{\vec{k}_1+\vec{q}\sigma_1}^\dagger c_{-\vec{k}_1-\vec{q}\sigma_1}^\dagger \langle c_{-\vec{k}_1\sigma_1} c_{\vec{k}_1\sigma_1} \rangle \delta_{\sigma_2, \bar{\sigma}_1} \delta_{\vec{k}_2, -\vec{k}_1} + \text{h.c.}$$

and by replacing the sum over \vec{q} by a sum over $\vec{k}' = \vec{q} + \vec{k}_1$ we obtain a Hartree-Fock Hamiltonian

$$H_{\text{HF}} = \sum_{\vec{k}\sigma} \xi_k c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + \sum_{\vec{k}} \left(\Delta_{\vec{k}} c_{-\vec{k}\downarrow}^\dagger c_{\vec{k}\uparrow}^\dagger + \Delta_{\vec{k}}^* c_{\vec{k}\uparrow} c_{-k\downarrow} \right) \quad (9.2)$$

with $\xi_k := \epsilon_k - \mu$,

$$\Delta_k = \sum_{\vec{k}'} \mathcal{V}(\vec{k}, \vec{k}') \langle c_{\vec{k}'\uparrow} c_{-\vec{k}'\downarrow} \rangle \quad (9.3)$$

and

$$\mathcal{V}(\vec{k}, \vec{k}') = \langle -\vec{k}, \vec{k} | V | -\vec{k}', \vec{k}' \rangle .$$

In order to discuss the structure of the ground state and the excitations of our theory, we need to diagonalise H_{HF} , i.e. we seek a set of operators $\gamma_{\vec{k}\sigma}^{(\dagger)}$ with

$$H_{\text{HF}} = \sum_{\vec{k}\sigma} E_{k\sigma} \gamma_{\vec{k}\sigma}^\dagger \gamma_{\vec{k}\sigma} .$$

The operators $\gamma_{\vec{k}\sigma}$ are as usual linear combinations of the original electronic operators $c_{\vec{k}\sigma}$ and will therefore also obey fermionic anticommutation rules. A rather elegant way to diagonalise H_{HF} is via studying the equations of motion. In the diagonalised form we simply have

$$[H_{\text{HF}}, \gamma_{\vec{k}\sigma}] = -E_{k\sigma} \gamma_{\vec{k}\sigma}$$

In this sense we can interpret now $E_{k\sigma}$ as quasiparticle energy and $\gamma_{\vec{k}\sigma}^\dagger$ as creation operator of such a quasiparticle. For the original operators we on the other hand obtain for example for $c_{\vec{k}\uparrow}$:

$$[H_{\text{HF}}, c_{\vec{k}\uparrow}] = -\xi_k c_{\vec{k}\uparrow} + \Delta_{\vec{k}} c_{-\vec{k}\downarrow}^\dagger$$

Here operators with opposite spin and momentum are mixed. Similarly we obtain for $c_{-\vec{k}\downarrow}^\dagger$

$$[H_{\text{HF}}, c_{-\vec{k}\downarrow}^\dagger] = \xi_k c_{-\vec{k}\downarrow}^\dagger + \Delta_{\vec{k}}^* c_{\vec{k}\uparrow} .$$

An obviously sensible ansatz now is

$$\gamma_{\vec{k}\sigma} = x c_{\vec{k}\sigma} + y c_{-\vec{k}\bar{\sigma}}^\dagger$$

and require

$$[H_{\text{HF}}, \gamma] = -\lambda \gamma .$$

With this ansatz we find

$$\begin{aligned} [H_{\text{HF}}, \gamma] &= x \left(-\xi_k c_{\bar{k}\sigma} + \Delta_{\bar{k}} c_{-\bar{k}\bar{\sigma}}^\dagger \right) + y \left(\xi_k c_{-\bar{k}\bar{\sigma}}^\dagger + \Delta_{\bar{k}}^* c_{\bar{k}\sigma} \right) \\ &\stackrel{!}{=} -\lambda \left(x c_{\bar{k}\sigma} + y c_{-\bar{k}\bar{\sigma}}^\dagger \right) \end{aligned}$$

Comparing the coefficients one arrives at the system of equations

$$\begin{aligned} (\lambda - \xi_k)x + \Delta_{\bar{k}}^* y &= 0 \\ \Delta_{\bar{k}} x + (\lambda + \xi_k)y &= 0 . \end{aligned}$$

Its eigenvalues are

$$\lambda = \pm E_k, \quad E_k = +\sqrt{\xi_k^2 + |\Delta_{\bar{k}}|^2}$$

and the two solutions for the quasiparticle operators are

$$\begin{aligned} \lambda_1 = +E_k &: \gamma_{\bar{k}\uparrow} = u_{\bar{k}} c_{\bar{k}\uparrow} - v_{\bar{k}} c_{-\bar{k}\downarrow}^\dagger \\ \lambda_2 = -E_k &: \gamma_{-k\downarrow}^\dagger = v_k^* c_{\bar{k}\uparrow} + u_k^* c_{-\bar{k}\downarrow}^\dagger \end{aligned}$$

where

$$\begin{aligned} |u_{\bar{k}}|^2 &= \frac{1}{2} \left(1 + \frac{\xi_k}{E_k} \right) \\ |v_k|^2 &= \frac{1}{2} \left(1 - \frac{\xi_k}{E_k} \right) \\ u_k v_k &= \frac{\Delta_{\bar{k}}}{2E_k} . \end{aligned}$$

The quantities $u_{\bar{k}}$ and $v_{\bar{k}}$ are often called *coherence factors*. For values $\epsilon_k \ll E_F$ we have $u_{\bar{k}} \rightarrow 0$ and $v_{\bar{k}} \rightarrow 1$, i.e. $\gamma_{-k\downarrow}^\dagger \rightarrow c_{\bar{k}\uparrow}$, while for $\epsilon_k \gg E_F$ we have $u_{\bar{k}} \rightarrow 1$ and $v_{\bar{k}} \rightarrow 0$ with $\gamma_{-k\downarrow}^\dagger \rightarrow c_{-\bar{k}\downarrow}^\dagger$. The above convention in introducing annihilator and creator is thus based on the sign of the quasiparticle energy and such that for energies far away from the Fermi energy they approach the proper electronic operators: For energies below the Fermi energy “creation” of a quasiparticle means annihilation of an time-reversal related electron, while above the Fermi energy “creation” of a quasiparticle does the usual thing.

The absolute values of the coefficients u_k , v_k are determined by requiring the anticommutator relations

$$\begin{aligned} \gamma_{\bar{k}\sigma}^\dagger \gamma_{\bar{k}'\sigma'} + \gamma_{\bar{k}'\sigma'}^\dagger \gamma_{\bar{k}\sigma} &= \delta_{\bar{k}\bar{k}'} \delta_{\sigma\sigma'} \\ \gamma_{\bar{k}\sigma} \gamma_{\bar{k}'\sigma'} + \gamma_{\bar{k}'\sigma'} \gamma_{\bar{k}\sigma} &= 0 \end{aligned}$$

These relations imply

$$|u_{\bar{k}}|^2 + |v_{\bar{k}}|^2 = 1$$

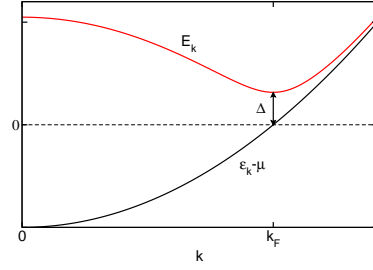
Without loss of generality we can choose $u_{\vec{k}}$ real and positive. The phase of $v_{\vec{k}}$ is then determined by the phase of $\Delta_{\vec{k}} = |\Delta_{\vec{k}}|e^{i\varphi_{\vec{k}}}$. It is important to note that through the self-consistency equation (9.3) the phases $\varphi_{\vec{k}}$ for different \vec{k} are coupled. In the simplest case one can assume all phases to be equal and can set them to 0. However, there are cases where these phases are actually important, for example for the Josephson effect.

The Hartree-Fock Hamiltonian has the form

$$H_{\text{HF}} = \sum_{\vec{k}\sigma} E_k \gamma_{\vec{k}\sigma}^\dagger \gamma_{\vec{k}\sigma}$$

i.e. only positive energies E_k appear. As these are the energies of the quasiparticles in the system, the ground state is a state without any quasiparticles present! The quasiparticle excitation spectrum for a constant

Δ is shown schematically in the figure to the right. The interesting feature is the appearance of an *energy gap* of size Δ at the Fermi momentum. This means that there exists a minimal energy necessary to create excitations above the ground state. For a conventional Fermi liquid the excitation spectrum is gapless.



9.2.3 The gap function $\Delta_{\vec{k}}$

The gap function Δ_k , also called *order parameter*, is obtained from the self-consistency equation (9.3). In the following we assume that there is no external magnetic field present. The expectation value of the right-hand side is calculated using the Hartree-Fock Hamiltonian (9.2). When expressed with the quasiparticle operators, it is diagonal and as these operators obey conventional fermionic statistics we know that

$$\begin{aligned} \langle \gamma_{\vec{k}\sigma}^\dagger \gamma_{\vec{k}'\sigma'} \rangle &= \delta_{\vec{k},\vec{k}'} \delta_{\sigma\sigma'} f(E_k), & f(E_k) &= \frac{1}{e^{\beta E_k} + 1} \\ \langle \gamma_{k\sigma} \gamma_{k'\sigma'} \rangle &= 0 \end{aligned}$$

and, expressing the normal Fermion operators by quasiparticle operators,⁵ one finds

$$\langle c_{\vec{k}\uparrow}^\dagger c_{-\vec{k}\downarrow} \rangle = -u_{\vec{k}} v_{\vec{k}} \langle \gamma_{\vec{k}\uparrow}^\dagger \gamma_{\vec{k}\uparrow} \rangle + u_{\vec{k}} v_{\vec{k}} \langle \gamma_{-\vec{k}\downarrow}^\dagger \gamma_{-\vec{k}\downarrow} \rangle = -u_{\vec{k}} v_{\vec{k}} [1 - 2f(E_k)]$$

or

$$\langle c_{\vec{k}\uparrow}^\dagger c_{-\vec{k}\downarrow} \rangle = -\frac{\Delta_{\vec{k}}}{2E_k} \tanh \frac{\beta E_k}{2}$$

⁵We concentrate on real Δ_k , u_k , v_k

The equation for the gap then reads

$$\Delta_{\vec{k}} = - \sum_{\vec{k}'} \mathcal{V}(\vec{k}, \vec{k}') \frac{\Delta_{\vec{k}'}}{2E_{k'}} \tanh \frac{\beta E_{k'}}{2} . \quad (9.4)$$

As usual, this equation always has the trivial solution $\Delta_{\vec{k}} = 0$, which corresponds to the normal Fermi liquid state. Non-trivial solutions potentially appear for low temperatures, but only if the interaction $\mathcal{V}(\vec{k}, \vec{k}') < 0$ close to the Fermi energy. Depending on the actual form of this interaction and its symmetries regarding \vec{k} one can generate very different pair states. They are usually characterised by the type of nodes of the resulting $\Delta_{\vec{k}}$. Without any nodes, one speaks of *s*-wave, with one node of *p*-wave, with two nodes of *d*-wave pairing and so on. Note that *p*-wave pairing implies $\Delta_{-k} = -\Delta_{\vec{k}}$ and in such a case one must have $S = 1$ pairs (triplet superconductor), while for *s*- and *d*-wave pairing the total spin is $S = 0$ (singlet superconductor).

The simplest model is obtained for an attractive constant interaction in a shell $\pm\hbar\omega_c$ about the Fermi energy, i.e.

$$\mathcal{V}(\vec{k}, \vec{k}') = \begin{cases} g < 0 & \text{for } |\epsilon_{k_i} - \mu| < \hbar\omega_c \\ 0 & \text{else} \end{cases}$$

In such a case the self-consistency reduces to

$$\Delta = -g \sum'_{\vec{k}'} \frac{\Delta}{2E_{k'}} \tanh \frac{\beta E_{k'}}{2} .$$

The prime at the sum indicates that it has to be cut off for energies outside the shell $\pm\hbar\omega_c$. Inside this shell Δ is independent of k , and zero outside. Nontrivial solutions exist again only for $g < 0$.

We now assume that $\hbar\omega_c$ is much smaller than the Fermi energy, and that we can approximate the density of states in the interval $[E_F - \hbar\omega_c, E_F + \hbar\omega_c]$ by a constant $N(E_F)$. We then can again convert the \vec{k} -sum into an energy integral

$$1 = \lambda \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{1}{2E(\xi)} \tanh \frac{\beta E(\xi)}{2} d\xi = \lambda \int_0^{\hbar\omega_c} \frac{1}{E(\xi)} \tanh \frac{\beta E(\xi)}{2} d\xi \quad (9.5)$$

with $E(\xi) = \sqrt{\xi^2 + \Delta^2}$ and $\lambda = N(E_F)|g|$. This equation determines Δ as function of T . Analytical solutions can be found in two limiting cases:

(i) For $T = 0$, denoting $\Delta(T = 0) = \Delta_0$, we obtain

$$1 = \lambda \int_0^{\hbar\omega_c} \frac{1}{\sqrt{\xi^2 + \Delta_0^2}} d\xi = \lambda \ln \left(\xi + \sqrt{\xi^2 + \Delta_0^2} \right) \Big|_0^{\hbar\omega_c}$$

Usually the cut-off energy is large compared to Δ_0 . Then

$$1 = \lambda \ln \left(\frac{2\hbar\omega_c}{\Delta_0} \right)$$

which results in

$$\Delta_0 = 2\hbar\omega_c \exp(-1/\lambda) \quad (9.6)$$

for the gap at $T = 0$.

(ii) In the limit $T \rightarrow T_c$, where $\Delta \rightarrow 0$, one has

$$1 = \lambda \int_0^{\hbar\omega_c} \frac{1}{\xi} \tanh \frac{\beta_c \xi}{2} d\xi$$

with $\beta_c = 1/(k_B T_c)$. As we already learned from equation (8.18), the result for $\hbar\omega_c \gg k_B T_c$ is

$$1 = \lambda \ln \left(\frac{2\gamma}{\pi} \frac{\hbar\omega_c}{k_B T_c} \right)$$

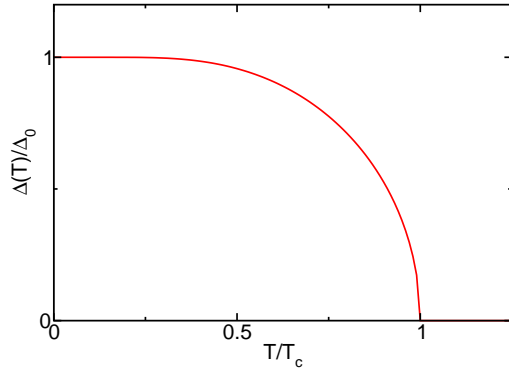
with Euler's constant $\gamma = 1.78$. This yields

$$k_B T_c = 1.13 \hbar\omega_c \exp\left(-\frac{1}{\lambda}\right) \quad (9.7)$$

for the value of the critical temperature T_c .

Note that in BCS theory the ratio $2\Delta_0/k_B T_c = 3.54$ is universal and independent of all material parameters. Again, both Δ_0 and T_c cannot be obtained from perturbation theory in g , as the results are nonanalytical in g . For an arbitrary temperature $0 < T < T_c$, the function $\Delta(T)$ has to be determined by numerically solving the integral equation (9.5). Again, for

$\hbar\omega_c \gg k_B T_c$ a universal curve is obtained, which is shown in the figure.



A first idea that this theory may indeed be connected to the phenomenon of superconductivity can be obtained by calculating the specific heat. As usual, this quantity can be obtained from the temperature derivative of the entropy as

$$c = \frac{T}{V} \frac{\partial S}{\partial T},$$

where the entropy of a noninteracting Fermi gas is given by

$$S = -2k_B \sum_{\vec{k}} \left[(1 - f_{\vec{k}}) \ln(1 - f_{\vec{k}}) + f_{\vec{k}} \ln f_{\vec{k}} \right]$$

and $f_{\vec{k}} := f(E_k)$ denotes the Fermi function. For c we then find

$$\begin{aligned} c &= 2\beta k_B \sum_{\vec{k}} \frac{\partial f_{\vec{k}}}{\partial \beta} \ln \frac{f_{\vec{k}}}{1 - f_{\vec{k}}} = \dots \\ &= \frac{2}{T} \sum_{\vec{k}} \left(-\frac{\partial f_{\vec{k}}}{\partial E_k} \right) \left[E_k^2 + \frac{\beta}{2} \frac{d\Delta(T)^2}{d\beta} \right]; \end{aligned}$$

For $T \rightarrow 0$, the existence of the gap $\Delta_0 \gg k_B T$ in the excitation spectrum leads to a behavior

$$c(T \rightarrow 0) \propto e^{-\frac{\Delta_0}{k_B T}}$$

for the specific heat, as also observed experimentally. Close to T_c , $\Delta(T) \rightarrow 0$. Here it is interesting to study the difference to the specific heat in the normal state, $c_n(T_c) = \frac{2\pi}{3} k_B^2 T_c \mathcal{N}(E_F)$. As the first term in the expression for c corresponds to the normal state contribution in the limit $\Delta \rightarrow 0$, the normalized difference $(c_s - c_n)/c_n$ for the difference of the specific heat in the superconducting respectively normal state is given by the expression

$$\frac{c_s - c_n}{c_n} = \frac{1}{c_n} \int d\epsilon \mathcal{N}(\epsilon) \left(-\frac{\partial f(E_k)}{\partial E_k} \right) \left(-\frac{\partial \Delta(T)^2}{\partial T} \right)_{T=T_c} = \frac{1}{c_n} \left(-\frac{\partial \Delta(T)^2}{\partial T} \right)_{T=T_c},$$

where we made use of

$$\int d\epsilon \mathcal{N}(\epsilon) \left(-\frac{\partial f(E_k)}{\partial E_k} \right) \Big|_{T=T_c} = \int d\epsilon \mathcal{N}(\epsilon) \left(-\frac{\partial f(\epsilon)}{\partial \epsilon} \right) = \mathcal{N}(\mu) .$$

Careful analysis of the gap equation near T_c yields

$$\Delta(T \nearrow T_c) = k_B T_c \pi \sqrt{\frac{8}{7\zeta(3)}} \sqrt{1 - \frac{T}{T_c}}$$

resulting in

$$\left(-\frac{\partial \Delta(T)^2}{\partial T} \right)_{T=T_c} = \frac{8\pi^2 k_B^2}{7\zeta(3)} T_c .$$

Together with the expression for $c_n(T_c)$ one finally gets

$$\frac{c_s - c_n}{c_n} = \frac{12}{7\zeta(3)} \approx 1.43 . \quad (9.8)$$

At T_c , the specific heat actually jumps, and the height of the jump relative to the normal state value is again a universal value. Indeed is this behavior found in all superconductors, and also the relative value is in fair to good agreement with the predicted value for a large number of different superconductors.

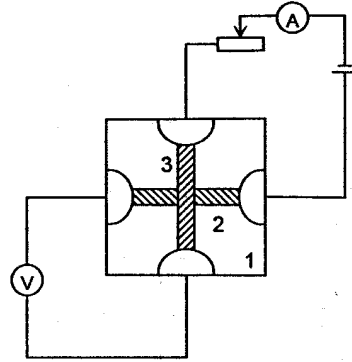
9.2.4 Density of states and tunneling experiments

We have already learned that the density of states is an interesting quantity. Here we obtain for a given temperature $T < T_c$ where $\Delta > 0$

$$\begin{aligned}
 \mathcal{N}_s(\epsilon) &= \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon - E_{\vec{k}}) \\
 &= \int d\eta \mathcal{N}(\eta + \mu) \delta(\epsilon - \sqrt{\eta^2 + \Delta^2}) \\
 &= \int \frac{E dE}{\sqrt{E^2 - \Delta^2}} \Theta(|E| - \Delta) \mathcal{N}(\mu + \sqrt{E^2 - \Delta^2}) \delta(\epsilon - E) \\
 &= \frac{\epsilon}{\sqrt{\epsilon^2 - \Delta^2}} \mathcal{N}(\mu + \sqrt{\epsilon^2 - \Delta^2}) \Theta(|\epsilon| - \Delta) \\
 &\approx \mathcal{N}(\mu) \frac{\epsilon}{\sqrt{\epsilon^2 - \Delta^2}} \Theta(|\epsilon| - \Delta) .
 \end{aligned}$$

In the last step we have used $\mu \gg \sqrt{\epsilon^2 - \Delta^2}$. The density of states thus shows a gap of width 2Δ around the Fermi energy, with characteristic square-root singularities at the gap edges.

Can such a structure be observed experimentally? The answer is yes, namely in a tunneling experiment. The schematic setup is shown in the figure. The two metallic strips are separated by a very thin insulating barrier. One of them is a material, which becomes superconducting, the other stays a normal metal at low T . Without external voltage, the system will have a common chemical potential, which for the superconductor will be in the middle of the gap. Therefore, a situation shown in Fig. 9.1a will occur. As in the superconductor no



states are available at the chemical potential, no current will flow. Increasing the applied voltage V will shift the chemical potential and eventually the gap edge of the superconductor is hit. Now a current will start to flow. At even larger V the gap structure becomes unimportant and the current will approach its behavior in a metal-insulator-metal junction. The resulting current-voltage profile is shown in Fig. 9.1b.

Therefore, performing such an experiment for temperatures $T < T_c$ one can extract the value $\Delta_{\text{exp}}(T)$ and compare it to $\Delta_{\text{BCS}}(T)$. The data obtained for In, Sn and Pb are collected in the Fig. 9.2 together with the curve from (9.5). It is amazing how accurate the agreement is.

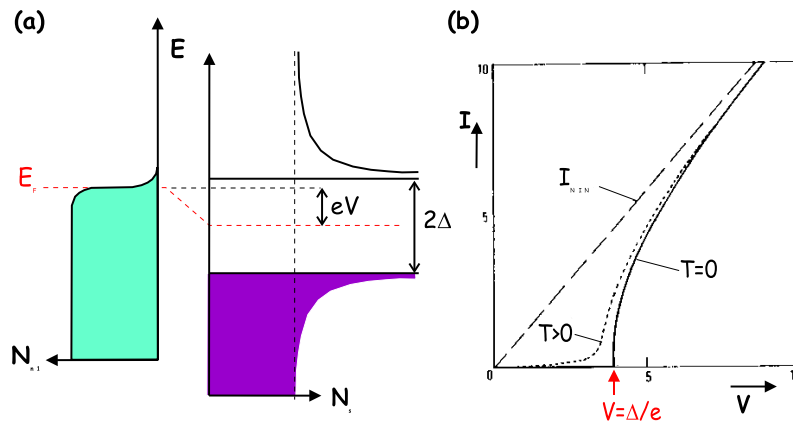


Figure 9.1: Tunneling experiment in a normal-insulator-superconductor setup

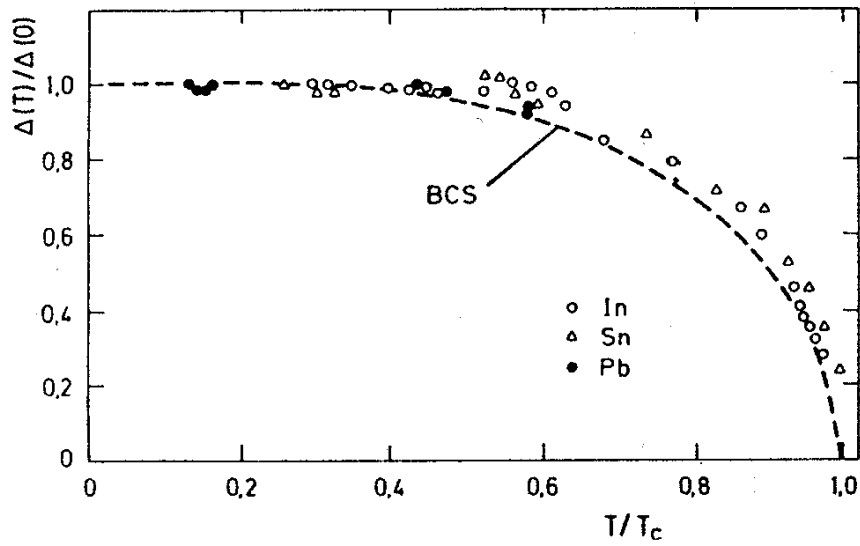


Figure 9.2: Gap obtained from tunneling experiments compared to the BCS curve.

9.2.5 Meißner effect

For an electric field of the form

$$\vec{E}(\vec{r}, t) = \vec{E} e^{i\vec{q}\cdot\vec{r} - i\omega t}$$

the conductivity is defined by the response of the current to the electric field

$$\langle J_\alpha(\vec{r}, t) \rangle = \sum_\beta \sigma_{\alpha\beta}(\vec{q}, \omega) E_\beta(\vec{r}, t) .$$

For isotropic systems the *conductivity tensor* $\sigma_{\alpha\beta}$ is diagonal. The electric field does not occur explicitly in the Hamiltonian, only the potentials do. We therefore rewrite the above equation in terms of the potentials as

$$\vec{E}(\vec{r}, t) = -\vec{\nabla}\Phi(\vec{r}, t) - \frac{\partial}{\partial t}\vec{A}(\vec{r}, t) .$$

In the Coulomb gauge $\vec{\nabla}\vec{A} = 0$ the first term describes the longitudinal response and the second the transverse response with respect to the direction of the wave vector \vec{q} . Consequently one distinguishes between a longitudinal and a transverse conductivity. Let $\vec{q}\|\vec{e}_z$, then

$$\langle J_x(\vec{r}, t) \rangle = \sigma_T(\vec{q}, \omega) E_x(\vec{r}, t) =: -K(\vec{q}, \omega) A_x(\vec{q}, t)$$

with $K(\vec{q}, \omega) = -i\omega\sigma_T(\vec{q}, \omega)$. For the present purpose it is sufficient to discuss the longitudinal conductivity as for $\vec{q} \rightarrow 0$ it describes the response to a magnetic field and thus the Meißner effect.

In a normal metal one observes for $\vec{q} \rightarrow 0$ a so-called Drude behavior

$$\sigma(0, \omega) = \frac{ne^2}{m} \frac{\tau}{1 - i\omega\tau}$$

for the conductivity, where τ is a characteristic time for the scattering of charge carriers from e.g. defects. With this form we immediately see that

$$\lim_{\omega \rightarrow 0} K_n(0, \omega) = 0 .$$

In a superconductor, on the other hand,

$$\lim_{\omega \rightarrow 0} K(0, \omega) \neq 0$$

and one obtains

$$\vec{J}(\vec{r}, t) = K(0, 0)\vec{A}(\vec{r}, t) =: -\frac{c}{4\pi\lambda^2}\vec{A}(\vec{x}, t) \quad (9.9)$$

which is called *London equation*.

As the London equation is in particular valid for a constant field, it directly leads to the Meißner effect. With the Maxwell equation

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{J}$$

one gets from the London equation

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{B}) = -\frac{1}{\lambda^2} \vec{B} .$$

For a field in x direction varying in z direction, one finds

$$\frac{\partial^2}{\partial z^2} B_x(z) = \frac{1}{\lambda^2} B_x(z)$$

which in the superconductor region $z > 0$ has the solution

$$\vec{B}(\vec{r}) = B_0 \vec{e}_x e^{-z/\lambda} .$$

Thus, λ denotes the *penetration depth* of the magnetic field into the superconductor. Connected to the field are screening currents

$$\vec{J} = -\frac{c}{4\pi\lambda} \vec{e}_y B_0 e^{-z/\lambda} .$$

Note that this expelling of the magnetic field from the superconducting is an *intrinsic property* of the system for $T < T_c$, i.e. is realized for both zero-field cooling and field cooling, as also found experimentally.

The preceding discussion has shown that it is important to study the response function $K(0, \omega)$. To this end we must try to obtain an expression relating current and external field. Let us start from the Hamiltonian of electrons in a magnetic field, which reads

$$H = \frac{1}{2m} \sum_{\sigma} \int d^3r \Psi_{\sigma}(\vec{r})^{\dagger} (-i\hbar\vec{\nabla} + e\vec{A}(\vec{r}, t))^2 \Psi_{\sigma}(\vec{r}) .$$

For the current operator we can use the quantum mechanical expression transformed into the operator language giving

$$\begin{aligned} \vec{J}(\vec{r}) &= \frac{-e}{2m} \sum_{\sigma} \Psi_{\sigma}(\vec{r})^{\dagger} (-i\hbar\vec{\nabla} + e\vec{A}(\vec{r}, t)) \Psi_{\sigma}(\vec{r}) \\ &= \vec{j}_p(\vec{x}) + \vec{j}_d(\vec{x}) \end{aligned}$$

with the *paramagnetic current density*

$$\vec{j}_p(\vec{r}) = \frac{ei\hbar}{2m} \sum_{\sigma} (\Psi_{\sigma}(\vec{r})^{\dagger} \vec{\nabla} \Psi_{\sigma}(\vec{r}) - \vec{\nabla} \Psi_{\sigma}(\vec{r})^{\dagger} \Psi_{\sigma}(\vec{r}))$$

and the *diamagnetic current density*

$$\vec{j}_d(\vec{r}) = -\frac{e^2}{m} \vec{A}(\vec{r}, t) \sum_{\sigma} \Psi_{\sigma}(\vec{r})^{\dagger} \Psi_{\sigma}(\vec{r}) = -\frac{e^2}{m} \vec{A}(\vec{r}, t) \hat{n}(\vec{r})$$

If we restrict the calculation to terms linear in the field \vec{A} one finds⁶

$$\langle J_{\alpha}(\vec{q}, t) \rangle = \sum_{\beta} \left(\chi_{\alpha\beta}(\vec{q}, \omega) - \frac{e^2 n}{m} \delta_{\alpha\beta} \right) A_{\beta}(\vec{r}, t)$$

with

$$\chi_{\alpha\beta}(\vec{q}, \omega) = \frac{i}{\hbar} \int_0^{\infty} dt e^{i(\omega+in)t} \frac{1}{Vol} \langle [j_{p,\alpha}(\vec{q}, t), j_{p,\beta}(-\vec{q}, 0)] \rangle .$$

Evaluation of this expression is rather lengthy and requires knowledge of advanced many-body tools. I therefore just quote the result:

⁶This is called “linear response theory” and the result “Kubo formula”. You should have seen this in statistical physics.

1. Evaluation in the normal state yields

$$K(0, \omega) = \frac{e^2 n}{m} \frac{\omega}{\omega + i/\tau}, \quad \sigma(0, \omega) = \frac{ne^2 \tau}{m} \frac{1}{1 - i\omega\tau}$$

and thus $K(0, 0) = 0$ as anticipated.

2. Evaluation in the superconducting state yields for $K(0, 0)$

$$\begin{aligned} K(0, 0) &= \frac{e^2 n}{m} \left[1 + \int d\xi \frac{\partial f(E)}{\partial E} \right] \\ &= \frac{e^2 n}{m} \left[1 - 2 \int_{\Delta}^{\infty} dE \frac{E}{\sqrt{E^2 - \Delta^2}} \left(-\frac{\partial f(E)}{\partial E} \right) \right] \end{aligned}$$

expressed through the density of states of the superconductor. For $T = 0$ only the second term vanishes while for $T \rightarrow T_c$ the whole expression vanishes. Usually one interprets the combination

$$n_s(T) := n \cdot \left[1 - 2 \int_{\Delta}^{\infty} dE \frac{E}{\sqrt{E^2 - \Delta^2}} \left(-\frac{\partial f(E)}{\partial E} \right) \right]$$

as the *superconducting condensate density* and writes

$$K(0, 0) = \frac{e^2 n_s(T)}{m} =: \frac{c}{4\pi\lambda^2(T)}$$

which also provides an explicit expression for the temperature dependence of the penetration depth. Again, the experimental findings agree very nicely with the BCS prediction.

The result that $K(0, 0) \neq 0$ has a further consequence. Namely, from the result we can obtain the expression

$$\sigma(\omega) = -i \frac{K(0, \omega)}{\omega} \approx -i \frac{K(0, 0)}{\omega} .$$

for the conductivity. This means that the conductivity is purely imaginary. On the other hand, the analytical structure of the conductivity implies, that such a purely imaginary conductivity with a decay $\propto 1/\omega$ must be accompanied by a delta function in the real part, i.e.

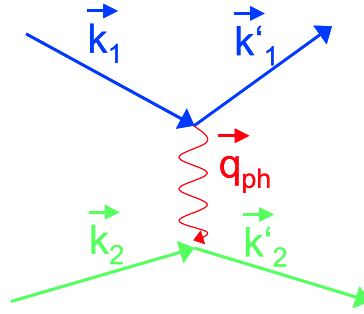
$$\sigma(\omega) = K(0, 0)\delta(\omega) - i \frac{K(0, 0)}{\omega}$$

Therefore $\Re\sigma(\omega = 0) = \infty$ and hence the system behaves as perfect conductor.

9.3 Origin of attractive interaction

All these considerations tell us that the BCS theory provides a rather accurate description of the superconducting state. The only missing part is where the attractive interaction actually comes from and why it is restricted to some restricted region around the Fermi surface and what physical interpretation the cutoff $\hbar\omega_c$ has.

Actually, the possibility of an effective attractive interaction was already well known when BCS proposed their theory. In 1950, Fröhlich and Bardeen suggested that the electron-phonon coupling can in fact result in such an interaction. If one analyzes the effect of this electron-phonon coupling, one is lead to processes depicted on the right, where two electrons scatter from a phonon exchanging momentum and energy. While the momentum transfer is restricted only by momentum conservation, the energy a phonon can carry is limited by the support of the phonon spectrum, which is typically of the order of $\hbar\omega_D$, where ω_D is the Debye frequency.



While it is a rather demanding task to properly evaluate the effective interaction described by the above sketch, we can use physical intuition to at least obtain an idea what will go on. The first electron will excite a phonon, i.e. will create a distortion of the lattice and thus locally disturb charge neutrality, leaving a net positive background. Of course this imbalance will relax pretty fast, but on lattice time scales. As we have already learned, electrons are much faster than the lattice motions and hence a second electron may pass the region with charge imbalance before it has relaxed and hence can gain energy. The effect will be maximal when the phase of the ionic oscillation is the same as at the time when the first electron initiated it.

It is important to note that this interaction cannot be static, but is inherently dynamic. Further, the point (or microscopic region) in space with the charge imbalance will not move significantly before the second electron “arrives” due to the same reasons. Thus, the resulting effective interaction will be retarded, i.e. nonlocal in time, but more or less localized in space.

We now have explained that phonons can lead to a reduction of the Coulomb interaction between electrons. To this end we note again that the maximal gain in energy by the second electron will occur if it finds the local environment almost in the state the first electron left it. This means that the second electron

should appear at the location at a time $2\pi/\omega_D =: T_D$. At this time the first electron has moved a distance $R = v_F \cdot T_D$, which for typical metals is of the order of 100nm. On the other hand, the mobility of electrons in metals leads to the phenomenon of screening, i.e. the Coulomb interaction is cut off after a few lattice constants, i.e. in the range of 1nm. Consequently, the two electrons will “feel” the retarded attraction, but not the Coulomb repulsion.

Let us summarize the arguments:

- Phonons lead to an effective attractive contribution to the interaction of two electrons.
- The attraction is strongly retarded, i.e. nonlocal in time, but comparatively local in space. The latter means that it is only weakly momentum dependent.
- Due to screening, the Coulomb repulsion does not play a role on the time scales the effective attraction is active. Thus, in the low-frequency limit the phonon-mediated attraction can in fact overcompensate the Coulomb repulsion, but it becomes unfavorable for larger energies. A reasonable estimate of the “cross-over” is given by the Debye energy $\hbar\omega_D$.

Therefore, the “bare-bones” interaction consistent with these points is

$$\langle \vec{k}_1 + \vec{q}, \vec{k}_2 - \vec{q} | V | \vec{k}_2 \vec{k}_1 \rangle = \begin{cases} g < 0 & \text{for } |E_F - \epsilon_{k_i}| < \hbar\omega_D \\ 0 & \text{else} \end{cases}$$

which is precisely the interaction used in our BCS theory.

Remains to be clarified why Hartree-Fock theory is so accurate. This is again to some extent a miracle and connected to the average distance of the two constituents of a Cooper pair, which we estimated to be of the order of 100nm. It is quite clear that within this region a huge number of other Cooper pairs will exist, i.e. one Cooper pair has a large number of neighbors. This is a situation where, as statistical physics tells us, a mean-field theory like Hartree-Fock works excellently.

Chapter 10

Theory of scattering from crystals

10.1 Experimental setup and dynamical structure factor

Investigation of the properties of a crystal with thermodynamic quantities (specific heat, thermal expansion, etc.) or elastic constants (sound velocity etc.) gives an averaged picture, but does not allow a direct access to the crystal structure or phonon dispersion. This is however possible with scattering experiments, where one shoots light or particles on the crystal and determines how the light or particles are reflected and how they exchange energy with the ions. By far the most important experiments are those involving x-ray, because the wave length is small enough to resolve the lattice constant, and neutrons with low enough energy (*thermal neutrons*) because they again have a de Broglie wave length small enough to resolve the lattice structure but do not have a charge. The latter property means that they do not disturb the crystal by changing the local electric and magnetic fields. Another interesting feature of neutrons is that they possess a spin and can thus be used to study magnetic properties.

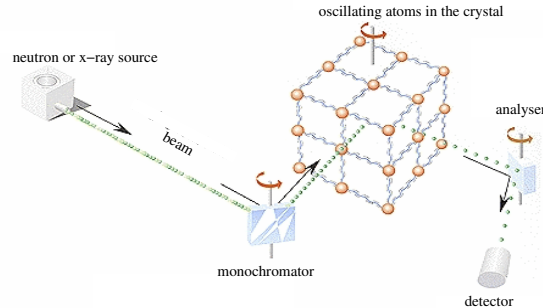


Figure 10.1: Sketch of a scattering experiment

The schematic setup of a scattering experiment from a crystal of oscillating ions is shown in Fig. 10.1. The basic concepts of scattering theory you already know from classical mechanics. The main aspects are that (i) far away from the target the neutrons may be described by “free” particles carrying a momentum $\hbar\vec{k}$ and an energy $\epsilon_{\vec{k}} = \frac{\hbar k^2}{2m}$. After the scattering process and far enough away from the target the neutron will be again a free particle, however now with momentum $\hbar\vec{k}'$ and energy $\epsilon_{\vec{k}'}$. Of course, we must obey momentum and energy conservation, i.e. the crystal must absorb a momentum $\hbar\vec{q}$ with $\vec{q} = \vec{k}' - \vec{k}$, we call *scattering vector*, and the energy $\hbar\omega = \epsilon_{\vec{k}'} - \epsilon_{\vec{k}}$. The actual quantities measured is the number of particles found in a certain solid angle range $\delta\Omega$ in the direction of \vec{k}' and a energy interval $d\hbar\omega$ normalized to the total number of incident

particles per unit area and unit time. This quantity is called *differential cross section* and denoted as

$$\frac{d^2\sigma}{d\Omega d\hbar\omega} .$$

The quantum mechanical description of the scattering process will be discussed in detail in Quantum Mechanics II. Here I just quote the result in lowest order in the scattering interaction (*first Born approximation*), using in addition Fermi's Golden Rule for the calculation of transition rates. It reads

$$\frac{d^2\sigma}{d\Omega d\hbar\omega} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2} \right)^2 \sum_{i,f} p_i |\langle \vec{k}', f | \hat{H}_I | \vec{k}, i \rangle|^2 \delta(\hbar\omega - (E_f - E_i)) . \quad (10.1)$$

The symbols have the following meaning: The “quantum numbers” i and f denote the initial state of the target prior to scattering with energy E_i and the final state after scattering with energy E_f . The change of energy $\Delta E = E_f - E_i$ is transferred to the neutrons as $\hbar\omega = \epsilon_{\vec{k}'} - \epsilon_{\vec{k}}$, and the interaction between neutrons and crystal is described by \hat{H}_I . The probability to find the target in the initial state i is p_i . As we do not care for the state of the target, we have to sum over all possible initial and final states.

To proceed we use some¹ “standard tricks”: First, we insert a decomposition of the unity in the Hilbert space

$$\mathbb{1} = \int d^3r |\vec{r}\rangle \langle \vec{r}| ,$$

use

$$\langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{(2\pi)^3}} e^{-i\vec{k}\cdot\vec{r}} ,$$

write $\hat{H}_I |\vec{r}\rangle = |\vec{r}\rangle \hat{H}_I(\vec{r})$ and obtain for the matrix element

$$\begin{aligned} \langle \vec{k}', f | \hat{H}_I | \vec{k}, i \rangle &= \langle f | \langle \vec{k}' | \int d^3r |\vec{r}\rangle \langle \vec{r} | \vec{k} \rangle \hat{H}_I(\vec{r}) | i \rangle \\ &= \frac{1}{(2\pi)^3} \int d^3r e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} \langle f | \hat{H}_I(\vec{r}) | i \rangle \\ &= \langle f | \hat{H}_I(-\vec{q}) | i \rangle . \end{aligned}$$

Furthermore,

$$\delta(\hbar\omega) = \frac{1}{\hbar} \delta(\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} .$$

If we denote the Hamilton operator of the target as \hat{H}_T , with $\hat{H}_T |i(f)\rangle = E_{i(f)} |i(f)\rangle$, and write

$$\hat{H}_I(\vec{q}, t) = e^{\frac{i}{\hbar} \hat{H}_T t} \hat{H}_I(\vec{q}) e^{-\frac{i}{\hbar} \hat{H}_T t}$$

¹Again: One can do this very accurate using the notion of distributions, but I will be sloppy here.

for the time evolution (note that this is the Dirac picture). After inserting all those things into (10.1) we end up with²

$$\frac{d^2\sigma}{d\Omega d\hbar\omega} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2} \right)^2 \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_i p_i \langle i | \hat{H}_I(-\vec{q}, t)^\dagger \hat{H}_I(-\vec{q}, 0) | i \rangle .$$

Note that one also has to make use of the completeness of the target states,

$$\mathbb{1}_T = \sum_f |f\rangle\langle f| .$$

To proceed we have to specify what \hat{H}_I actually is. As neutrons interact with the nuclei via strong interaction, we of course do not know this interaction. However, as we usually are not interested in absolute values of the cross section, we may assume a reasonable form and leave the actual strength as parameter of the theory. Quite generally, we can write the interaction as

$$\hat{H}_I(\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_{\alpha} V(\vec{r} - \hat{R}_{\alpha}) ,$$

where the prefactor is for convenience and the operator character is due to the positions of the ions. With this ansatz

$$\begin{aligned} \hat{H}_I(\vec{q}) &= \frac{1}{(2\pi)^3} \int d^3r e^{-i\vec{q}\cdot\vec{r}} \hat{H}_I(\vec{r}) \\ &= \frac{1}{(2\pi)^3} \int d^3r e^{-i\vec{q}\cdot\vec{r}} \sum_{\alpha} \frac{2\pi\hbar^2}{m} V(\vec{r} - \hat{R}_{\alpha}) \\ &= \frac{2\pi\hbar^2}{m} \sum_{\alpha} e^{-i\vec{q}\cdot\hat{R}_{\alpha}} \frac{1}{(2\pi)^3} \int d^3r e^{-i\vec{q}\cdot(\vec{r}-\hat{R}_{\alpha})} V(\vec{r} - \hat{R}_{\alpha}) \\ &= \frac{2\pi\hbar^2}{m} \sum_{\alpha} e^{-i\vec{q}\cdot\hat{R}_{\alpha}} V(\vec{q}) . \end{aligned}$$

Finally,

$$\frac{d^2\sigma}{d\Omega d\hbar\omega} = \frac{k'}{k} \frac{|V(\vec{q})|^2}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{\alpha,\beta} \sum_i p_i \langle i | e^{-i\vec{q}\cdot\hat{R}_{\alpha}(t)} e^{i\vec{q}\cdot\hat{R}_{\beta}(0)} | i \rangle .$$

Conventionally, one writes the above result as

$$\frac{d^2\sigma}{d\Omega d\hbar\omega} = \frac{k'}{k} \frac{|V(\vec{q})|^2}{\hbar} S(\vec{q}, \omega) ,$$

with the *dynamical structure factor*

$$S(\vec{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{\alpha,\beta} \sum_i p_i \langle i | e^{-i\vec{q}\cdot\hat{R}_{\alpha}(t)} e^{i\vec{q}\cdot\hat{R}_{\beta}(0)} | i \rangle .$$

²It is a little bit of straightforward algebra, which you surely want to do yourself!

10.2 Evaluation of $S(\vec{q}, \omega)$ in the harmonic approximation

In the following we again write $\vec{R}_\alpha = \vec{R}_i + \vec{\kappa} + \vec{u}_{i,\kappa}(t)$, where \vec{R}_i is a vector from the Bravais lattice. With this notation and $\alpha = (j, \kappa)$, $\beta = (l, \lambda)$ one obtains

$$\sum_i p_i \langle i | e^{-i\vec{q}\cdot\hat{R}_\alpha(t)} e^{i\vec{q}\cdot\hat{R}_\beta(0)} | i \rangle = e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_j)} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})} \sum_i p_i \langle i | e^{-i\vec{q}\cdot\hat{u}_{j,\kappa}(t)} e^{i\vec{q}\cdot\hat{u}_{l,\lambda}(0)} | i \rangle .$$

In the harmonic approximation,

$$\hat{u}_{j,\kappa} = \sum_{m,\vec{k}} \sqrt{\frac{\hbar}{2N\omega_m(\vec{k})}} e^{i\vec{k}\cdot\vec{R}_j} \vec{\epsilon}_\kappa^{(m)}(\vec{k}) (\hat{b}_m(\vec{k}) + \hat{b}_m(-\vec{k})^\dagger) ,$$

and to determine $\hat{u}_{j,\kappa}(t)$ we need $\hat{b}_m(\vec{k}, t)$ calculated with the Hamiltonian (6.2). This task has been performed already in Quantum Mechanics I with the result

$$\hat{b}_m(\vec{k}, t) = e^{\frac{i}{\hbar}\hat{H}_N t} \hat{b}_m(\vec{k}) e^{-\frac{i}{\hbar}\hat{H}_N t} = e^{-i\omega_m(\vec{k})t} \hat{b}_m(\vec{k}) .$$

Similarly, together with $\omega_m(-\vec{k}) = \omega_m(\vec{k})$,

$$\hat{b}_m(-\vec{k}, t)^\dagger = e^{\frac{i}{\hbar}\hat{H}_N t} \hat{b}_m(-\vec{k})^\dagger e^{-\frac{i}{\hbar}\hat{H}_N t} = e^{i\omega_m(\vec{k})t} \hat{b}_m(-\vec{k})^\dagger .$$

As next step we need to calculate something of the form $e^{\hat{A}} e^{\hat{B}} \neq e^{\hat{A}+\hat{B}}$. There is however one exception, namely when $[\hat{A}, \hat{B}] \in \mathbb{C}$. In this case the equality

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{A}+\hat{B}} e^{\frac{1}{2}[\hat{A}, \hat{B}]}$$

holds. Using the commutation relation $[b_m(\vec{k}), b_l(\vec{q})^\dagger] = \delta_{ml}\delta_{\vec{k},\vec{q}}$ it is straightforward to show

$$\begin{aligned} [-i\vec{q}\cdot\hat{u}_{j,\kappa}(t), i\vec{q}\cdot\hat{u}_{l,\lambda}(0)] &= \frac{1}{N} \sum_{m,\vec{k}} \frac{\hbar}{2\omega_m(\vec{k})} e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_l)} \times \\ &\quad (\vec{q}\cdot\vec{\epsilon}_\kappa^{(m)}(\vec{k})) (\vec{q}\cdot\vec{\epsilon}_\lambda^{(m)}(\vec{k})) [e^{-i\omega_m(\vec{k})t} - e^{i\omega_m(\vec{k})t}] \\ &\in \mathbb{C} \\ &\Rightarrow e^{-i\vec{q}\cdot\hat{u}_{j,\kappa}(t)} e^{i\vec{q}\cdot\hat{u}_{l,\lambda}(0)} = e^{i\vec{q}\cdot(\hat{u}_{l,\lambda}(0) - \hat{u}_{j,\kappa}(t))} e^{\frac{1}{2}[\dots]} . \end{aligned}$$

We thus have to calculate

$$\begin{aligned} \langle e^{i\vec{q}\cdot(\hat{u}_{l,\lambda}(0) - \hat{u}_{j,\kappa}(t))} \rangle &= \langle \exp\left\{ \sum_{m\vec{k}} \sqrt{\frac{\hbar}{2N\omega_m(\vec{k})}} \right. \\ &\quad \left[\left\{ (\vec{q}\cdot\vec{e}_\lambda^{(m)}) e^{i\vec{k}\cdot\vec{R}_l} - (\vec{q}\cdot\vec{e}_\kappa^{(m)}) e^{i(\vec{k}\cdot\vec{R}_j - \omega_m(\vec{k})t)} \right\} \hat{b}_m(\vec{k}) + \right. \\ &\quad \left. \left. \left\{ (\vec{q}\cdot\vec{e}_\lambda^{(m)}) e^{i\vec{k}\cdot\vec{R}_l} - (\vec{q}\cdot\vec{e}_\kappa^{(m)}) e^{i(\vec{k}\cdot\vec{R}_j + \omega_m(\vec{k})t)} \right\} \hat{b}_m(-\vec{k})^\dagger \right] \right\} \rangle , \end{aligned}$$

where I have introduced the short hand notation

$$\langle \dots \rangle = \sum_i p_i \dots .$$

For the actual calculation we need some results from statistical physics:

10.2. EVALUATION OF $S(\vec{Q}, \omega)$ IN THE HARMONIC APPROXIMATION

- The probabilities p_i can be related to the Hamiltonian as

$$p_i = \frac{e^{-\beta E_i}}{\mathcal{Z}} , \quad \mathcal{Z} = \text{Tr} e^{-\beta \hat{H}} .$$

The expectation value can then be written equivalently as

$$\langle \dots \rangle = \text{Tr} \frac{e^{-\beta \hat{H}}}{\mathcal{Z}} \dots$$

- For a Hamiltonian

$$\hat{H} = \sum_k \hbar \omega_k \hat{b}_k^\dagger \hat{b}_k$$

bilinear in the ladder operators one can prove *Wick's theorem*

$$\begin{aligned} \langle \hat{b}_1 \hat{b}_2 \dots \hat{b}_n \hat{b}_{n+1}^\dagger \dots \hat{b}_{2n}^\dagger \rangle &= \langle \hat{b}_1 \hat{b}_{n+1}^\dagger \rangle \langle \hat{b}_2 \dots \hat{b}_n \hat{b}_{n+2}^\dagger \dots \hat{b}_{2n}^\dagger \rangle \\ &+ \langle \hat{b}_1 \hat{b}_{n+2}^\dagger \rangle \langle \hat{b}_2 \dots \hat{b}_n \hat{b}_{n+1}^\dagger \dots \hat{b}_{2n}^\dagger \rangle \\ &+ \dots \\ &+ \langle \hat{b}_1 \hat{b}_{2n}^\dagger \rangle \langle \hat{b}_2 \dots \hat{b}_n \hat{b}_{n+1} \dots \hat{b}_{2n-1}^\dagger \rangle . \end{aligned}$$

Note that $\langle \hat{b}_i \hat{b}_j \rangle = \langle \hat{b}_i^\dagger \hat{b}_j^\dagger \rangle = 0$.

For an operator $\hat{C} = \sum (u_k \hat{b}_k + v_k \hat{b}_k^\dagger)$ one then finds

$$\begin{aligned} \langle e^{\hat{C}} \rangle &= \sum_{n=0}^{\infty} \frac{1}{n!} \langle \hat{C}^n \rangle = \sum_{n=0}^{\infty} \frac{1}{(2n)!} \langle \hat{C}^{2n} \rangle = \sum_{n=0}^{\infty} \frac{1}{(2n)!} \underbrace{\langle \hat{C} \dots \hat{C} \rangle}_{2n} \\ &= \sum_{n=0}^{\infty} \frac{1}{(2n)!} \frac{(2n)!}{n! 2^n} \underbrace{\langle \hat{C}^2 \rangle \dots \langle \hat{C}^2 \rangle}_{2n} \end{aligned}$$

The combinatorial factor counts possibilities to combine $2n$ objects ($(2n)!$ permutations) into n pairs ($n!$ permutations) with two possible realizations for each pair (2^n). Thus

$$\langle e^{\hat{C}} \rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{1}{2} \langle \hat{C}^2 \rangle \right)^n = e^{\frac{1}{2} \langle \hat{C}^2 \rangle} .$$

Please keep in mind that this result like Wick's theorem is valid only for a Hamiltonian bilinear in the ladder operators!

With this knowledge we can now write down an expression for the needed expectation value as

$$\begin{aligned} \langle e^{-i\vec{q} \cdot \hat{u}_{j,\kappa}(t)} e^{i\vec{q} \cdot \hat{u}_{l,\lambda}(0)} \rangle &= \\ \exp \left\{ \frac{1}{2} \langle [i\vec{q} \cdot (\hat{u}_{l,\lambda}(0) - \hat{u}_{j,\kappa}(t))]^2 + [\vec{q} \cdot \hat{u}_{l,\lambda}(0), \vec{q} \cdot \hat{u}_{j,\kappa}(t)] \rangle \right\} &= \\ \exp \left\{ -\frac{1}{2} \langle (\vec{q} \cdot \hat{u}_{l,\lambda}(0))^2 + (\vec{q} \cdot \hat{u}_{j,\kappa}(t))^2 - (\vec{q} \cdot \hat{u}_{l,\lambda}(0)) (\vec{q} \cdot \hat{u}_{j,\kappa}(t)) \rangle \right\} \end{aligned}$$

Let us evaluate the different terms in the exponent. To this end we need the relations

$$\begin{aligned}\langle \hat{b}_m(-\vec{k})^\dagger \hat{b}_{m'}(\vec{k}') \rangle &= N_m(\vec{k}) \delta_{mm'} \delta_{-\vec{k}, \vec{k}'} \\ \langle \hat{b}_m(\vec{k}) \hat{b}_{m'}(-\vec{k}')^\dagger \rangle &= [N_m(\vec{k}) + 1] \delta_{mm'} \delta_{\vec{k}, -\vec{k}'} \\ N_m(\vec{k}) &:= \left[e^{\beta \hbar \omega_m(\vec{k})} - 1 \right]^{-1}, \quad \beta = \frac{1}{k_B T}\end{aligned}$$

together with $\omega_m(-\vec{k}) = \omega_m(\vec{k})$ and obtain

$$\begin{aligned}\langle (\vec{q} \cdot \hat{u}_{j,\kappa}(t))^2 \rangle &= \frac{\hbar}{2N} \sum_{\substack{kk' \\ mm'}} \frac{(\vec{q} \cdot \vec{e}_\kappa^{(m)}(\vec{k})) (\vec{q} \cdot \vec{e}_\kappa^{(m')}(\vec{k}'))}{\sqrt{\omega_m(\vec{k}) \omega_{m'}(\vec{k}')}} e^{i(\vec{k} + \vec{k}') \cdot \vec{R}_j} \\ &\quad \times \langle (e^{-i\omega_m(\vec{k})t} \hat{b}_m(\vec{k}) + e^{i\omega_m(\vec{k})t} \hat{b}_m(-\vec{k})^\dagger) \\ &\quad (e^{-i\omega_{m'}(\vec{k}')t} \hat{b}_{m'}(\vec{k}') + e^{i\omega_{m'}(\vec{k}')t} \hat{b}_{m'}(-\vec{k}')^\dagger) \rangle \\ &= \frac{2\hbar}{N} \sum_{\vec{k}m} \frac{|\vec{q} \cdot \vec{e}_\kappa^{(m)}(\vec{k})|^2}{2\omega_m(\vec{k})} \left[N_m(\vec{k}) + \frac{1}{2} \right] \\ \langle (\vec{q} \cdot \hat{u}_{l,\lambda})^2 \rangle &= \frac{2\hbar}{N} \sum_{\vec{k}m} \frac{|\vec{q} \cdot \vec{e}_\lambda^{(m)}(\vec{k})|^2}{2\omega_m(\vec{k})} \left[N_m(\vec{k}) + \frac{1}{2} \right]\end{aligned}$$

respectively

$$\begin{aligned}\langle (\vec{q} \cdot \hat{u}_{l,\lambda}) (\vec{q} \cdot \hat{u}_{j,\kappa}(t)) \rangle &= \frac{\hbar}{2N} \sum_{\substack{kk' \\ mm'}} \frac{(\vec{q} \cdot \vec{e}_\lambda^{(m)}(\vec{k})) (\vec{q} \cdot \vec{e}_\kappa^{(m')}(\vec{k}'))}{\sqrt{\omega_m(\vec{k}) \omega_{m'}(\vec{k}')}} e^{i(\vec{k} \cdot \vec{R}_l + \vec{k}' \cdot \vec{R}_j)} \\ &\quad \times \langle (\hat{b}_m(\vec{k}) + \hat{b}_m(-\vec{k})^\dagger) \\ &\quad (e^{-i\omega_{m'}(\vec{k}')t} \hat{b}_{m'}(\vec{k}') + e^{i\omega_{m'}(\vec{k}')t} \hat{b}_{m'}(-\vec{k}')^\dagger) \rangle \\ &= \frac{\hbar}{N} \sum_{\vec{k}m} \frac{e^{i\vec{k} \cdot (\vec{R}_l - \vec{R}_j)} (\vec{q} \cdot \vec{e}_\lambda^{(m)}(\vec{k})) (\vec{q} \cdot \vec{e}_\kappa^{(m)}(\vec{k}))^*}{2\omega_m(\vec{k})} \\ &\quad \left\{ e^{i\omega_m(\vec{k})t} [N_m(\vec{k}) + 1] + e^{-i\omega_m(\vec{k})t} N_m(\vec{k}) \right\}\end{aligned}$$

The final result then is

10.3. BRAGG SCATTERING AND EXPERIMENTAL
DETERMINATION PHONON BRANCHES

$$S(\vec{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j,l} \sum_{\kappa\lambda} e^{-2w_{\kappa\lambda}(\vec{q})} e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_j)} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})} e^{F_{j\kappa,l\lambda}(t)} \quad (10.2)$$

$$w_{\kappa\lambda}(\vec{q}) = \frac{\hbar}{N} \sum_{\vec{k}m} \frac{1}{2} \left(\left| \vec{q} \cdot \vec{e}_{\kappa}^{(m)}(\vec{k}) \right|^2 + \left| \vec{q} \cdot \vec{e}_{\lambda}^{(m)}(\vec{k}) \right|^2 \right) \frac{N_m(\vec{k}) + \frac{1}{2}}{2\omega_m(\vec{k})} \quad (10.3)$$

$$F_{j\kappa,l\lambda}(t) = \frac{\hbar}{N} \sum_{\vec{k}m} \frac{e^{i\vec{k}\cdot(\vec{R}_l - \vec{R}_j)} \left(\vec{q} \cdot \vec{e}_{\lambda}^{(m)}(\vec{k}) \right) \left(\vec{q} \cdot \vec{e}_{\kappa}^{(m)}(\vec{k}) \right)^*}{2\omega_m(\vec{k})} \left\{ e^{i\omega_m(\vec{k})t} [N_m(\vec{k}) + 1] + e^{-i\omega_m(\vec{k})t} N_m(\vec{k}) \right\}$$

The term $e^{-2w_{\kappa\lambda}(\vec{q})}$ is called *Debye-Waller factor*. As all terms in (10.3) are positive, this factor always leads to a suppression of the intensity. Furthermore, $w_{\kappa\lambda}(\vec{q}) \propto \langle \hat{u}_{j,\kappa}^2 + \hat{u}_{l,\lambda}^2 \rangle$, i.e. is determined by the *fluctuations* of the displacements. As even for $T = 0$ these are always finite (*zero-point motion*), $w(\vec{q}) > 0$. Furthermore, for acoustic branches, $w(\vec{q}) \propto q^2$. Thus, the Debye-Waller factor is particularly efficient in suppressing the intensity for (i) high temperatures and (ii) large momentum transfers.

10.3 Bragg scattering and experimental determination phonon branches

Further evaluation is possible through an expansion of the exponential $e^{F_{j\kappa,l\lambda}(t)}$.

(i) 0. order:

$$S^{(0)}(\vec{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j,l} \sum_{\kappa\lambda} e^{-2w_{\kappa\lambda}(\vec{q})} e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_j)} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})}$$

Using

$$\int_{-\infty}^{\infty} dt e^{i\omega t} = 2\pi\delta(\omega)$$

$$\sum_{j,l} e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_j)} = N^2 \sum_{\vec{G} \in \text{RG}} \delta_{\vec{q}, \vec{G}}$$

we find

$$S^{(0)}(\vec{q}, \omega) = N^2 \delta(\omega) \sum_{\vec{G} \in \text{RG}} \delta_{\vec{q}, \vec{G}} \underbrace{\sum_{\kappa\lambda} e^{-2w_{\kappa\lambda}(\vec{q})} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})}}_{\text{form-factor } \mathcal{F}(\vec{q})}$$

$$= N^2 \delta(\omega) \sum_{\vec{G} \in \text{RG}} \delta_{\vec{q}, \vec{G}} \mathcal{F}(\vec{q}) .$$

Due to the prefactor $\delta(\omega)$, the part $S^{(0)}(\vec{q}, \omega)$ describes *elastic* scattering with $\epsilon_{\vec{k}} = \epsilon_{\vec{k}'}$, which is possible only for $\vec{q} = \vec{k} - \vec{k}' = \vec{G} \in \text{RG}$. This is the well-known *Bragg condition* for elastic scattering from a regular lattice, the basis of structure analysis using x-ray or neutron scattering. . Due to the Debye-Waller factor scattering is drastically suppressed for large $\vec{G} \neq 0$. Note that the above result is exact only for an infinite crystal, finite crystals lead to a broadening of the Bragg peaks.

(ii) 1. order:

$$\begin{aligned}
 S^{(1)}(\vec{q}, \omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{j,l} \sum_{\kappa\lambda} e^{-2w_{\kappa\lambda}(\vec{q})} e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_j)} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})} \\
 &\quad \times \frac{\hbar}{N} \sum_{\vec{k}m} \frac{e^{i\vec{k}\cdot(\vec{R}_l - \vec{R}_j)} \left(\vec{q} \cdot \vec{e}_{\lambda}^{(m)}(\vec{k}) \right) \left(\vec{q} \cdot \vec{e}_{\kappa}^{(m)}(\vec{k}) \right)^*}{2\omega_m(\vec{k})} \\
 &\quad \left\{ e^{i\omega_m(\vec{k})t} [N_m(\vec{k}) + 1] + e^{-i\omega_m(\vec{k})t} N_m(\vec{k}) \right\} \\
 &= \hbar N \sum_{\kappa\lambda} e^{-2w_{\kappa\lambda}(\vec{q})} e^{i\vec{q}\cdot(\vec{\lambda} - \vec{\kappa})} \\
 &\quad \sum_{\vec{k}m} \sum_{\vec{G}} \frac{\left(\vec{q} \cdot \vec{e}_{\lambda}^{(m)}(\vec{k}) \right) \left(\vec{q} \cdot \vec{e}_{\kappa}^{(m)}(-\vec{k}) \right)}{2\omega_m(\vec{k})} \delta_{\vec{k} + \vec{q}, \vec{G}} \\
 &\quad \times \left\{ [N_m(\vec{k}) + 1] \delta(\omega + \omega_m(\vec{k})) + N_m(\vec{k}) \delta(\omega - \omega_m(\vec{k})) \right\}
 \end{aligned}$$

describes *inelastic* scattering processes, where *exactly one* phonon with frequency $\omega_m(\vec{k})$ is involved. Momentum conservation tells us that $\vec{k}_i - \vec{k}_f + \vec{k} = \vec{G}$ or equivalently $\vec{k}_f = \vec{k}_i + \vec{k}$ modulo \vec{G} , while energy conservation leads to $\epsilon_{\vec{k}_f} = \epsilon_{\vec{k}_i} \mp \hbar\omega_m(\vec{k})$, where the upper sign refers to the first term in curly brackets (scattering with *emission* of a phonon to the lattice) and the lower to the second (scattering with *absorption* of a phonon from the lattice). In particular we have

$$\frac{\text{prob. for emission}}{\text{prob. for absorption}} = \frac{N_m(\vec{k}) + 1}{N_m(\vec{k})} = e^{\beta\hbar\omega_m(\vec{k})},$$

i.e. processes with emission of phonons (Stokes processes) are exponentially enhanced over those with absorption of phonons (anti-Stokes processes).

(iii) Higher orders $n > 1$ are so-called multi-phonon processes.

10.3. BRAGG SCATTERING AND EXPERIMENTAL DETERMINATION PHONON BRANCHES

From the information provided by the first order term $S^{(1)}(\vec{q}, \omega)$ we can at least in principle extract the dispersion $\omega_m(\vec{k})$. As the theory we developed is valid both for photons and neutrons one may wonder which of the two is more appropriate for such a job.

As photons are nothing but light, their dispersion reads $\epsilon_{\vec{k}} = \hbar c k$. Therefore $\hbar\omega_m(\vec{k}) = |\epsilon_{\vec{k}_i} - \epsilon_{\vec{k}_f}| = \hbar c |k_i - k_f|$.

$$\begin{aligned}
 |\vec{k} + \vec{G}| &= |\vec{k}_i - \vec{k}_f| = [k_i^2 + k_f^2 - 2k_i k_f \cos \vartheta]^{1/2} \\
 &= \left[k_i^2 + k_f^2 - 2k_i k_f + 4k_i k_f \sin^2 \frac{\vartheta}{2} \right]^{1/2} \\
 &= \left[(k_i - k_f)^2 + 4k_i k_f \sin^2 \frac{\vartheta}{2} \right]^{1/2} \\
 &= \frac{1}{c} \left[\omega_m(\vec{k})^2 + 4c^2 k_i k_f \sin^2 \frac{\vartheta}{2} \right]^{1/2} \\
 &= \frac{1}{c} \left[\omega_m(\vec{k})^2 + 4 \frac{\epsilon_{\vec{k}_i} \epsilon_{\vec{k}_f}}{\hbar^2} \sin^2 \frac{\vartheta}{2} \right]^{1/2} \\
 &= \frac{1}{c} \left[\omega_m(\vec{k})^2 + 4 \frac{\epsilon_{\vec{k}_i}}{\hbar} \left(\frac{\epsilon_{\vec{k}_i}}{\hbar} \pm \omega_m(\vec{k}) \right) \sin^2 \frac{\vartheta}{2} \right]^{1/2}
 \end{aligned}$$

For electromagnetic radiation of the near infrared region and beyond we have $\hbar\omega = \epsilon_{\vec{k}_i} \gg \hbar\omega_m(\vec{k})$, i.e.

$$|\vec{k} + \vec{G}| \approx \frac{2\epsilon_{\vec{k}_i}}{\hbar c} \left| \sin \frac{\vartheta}{2} \right| = 2 \frac{\omega}{c} \left| \sin \frac{\vartheta}{2} \right| = \frac{4\pi}{\lambda} \left| \sin \frac{\vartheta}{2} \right| ,$$

where λ is the wavelength of the electromagnetic radiation. Preferably, one would like to use light with wavelength of the order of the lattice spacing, i.e. some Å. Such a wavelength can be realized with x-rays, which however have an energy of some keV. As phonons typically have energies of up to a few 100meV, one would have to resolve energy differences in the scattered x-rays of relative magnitude 10^{-5} , i.e. way below any reasonable experimental resolution. From the order of magnitude of the energy, near infrared or visible light would thus be more appropriate. However, in that case the wavelength $\lambda = O(10^4 \text{Å}) \gg a$ and hence

$$|\vec{k} + \vec{G}| \leq \frac{4\pi}{\lambda} \ll a^{-1} .$$

Thus, with visible light, only a small regime with $\vec{k} \approx \vec{G}$ can be resolved, i.e. $\omega_m(\vec{k}) \approx \omega_m(\vec{G}) = \omega_m(0)$.

Furthermore, for the same reasons as above, only branches with $\omega_m(0) > 0$ can possibly be resolved, i.e. scattering with light – so-called *Raman scattering* – usually probes the optical branches at $\vec{k} \rightarrow 0$ (the Γ point of the Brillouin zone). Under certain conditions scattering from acoustic phonons is possible, too, which then is called *Brillouin scattering*.

In the case of neutrons the de Brogli relation

$$E = \frac{m_N}{2}v^2 = \frac{4\pi^2\hbar^2}{2m_N\lambda^2}$$

connects a certain energy with a wavelength λ . The important aspect is that for energies in the meV range – so-called *thermal neutrons* – this wave length is of the order of lattice constants. Neutrons thus are the perfect tool to study

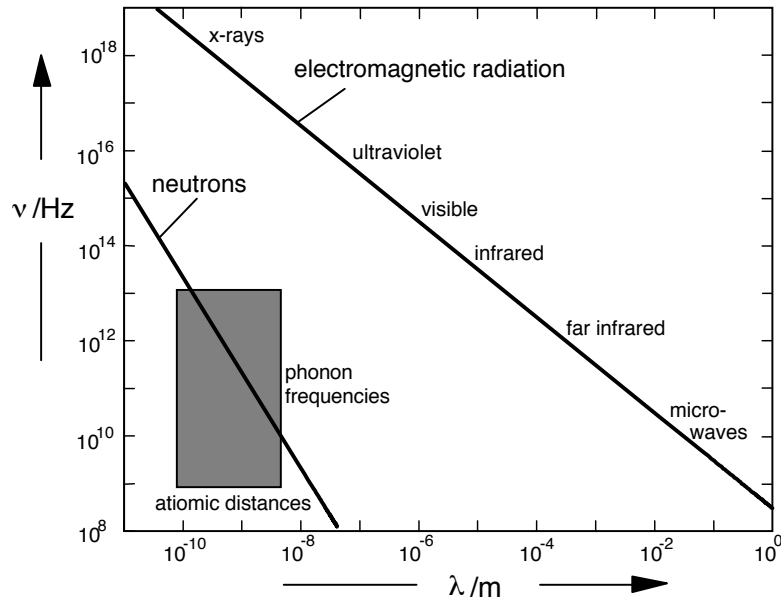


Figure 10.2: Energy versus wavelength for photons and neutrons.

spatial structures on the scale of \AA , while at the same time they allow to probe energetics in the meV range typical for phonons. Most importantly, apart from possible selection rules, all \vec{k} vectors and all phonon branches are accessible by neutrons. Furthermore, choosing scattering with finite \vec{G} , one can circumvent selection rules in the first Brillouin zone, of course on the expense of a stronger reduction by the Debye-Waller factor. A typical spectrum obtained in a neutron scattering experiment is shown in Fig. 10.3 on the left hand side. Note the strong increase in intensity for $\omega \rightarrow 0$, which is the elastic Bragg peak. On the wings of this strong signal the interesting inelastic structures can be identified as peaks. Performing a series of such experiments for different momentum transfers one can obtain pictures like the phonon dispersions of quartz on the right side of Fig. 10.3. Note that only certain special directions in the first Brillouin zone are shown.

10.3. BRAGG SCATTERING AND EXPERIMENTAL DETERMINATION PHONON BRANCHES

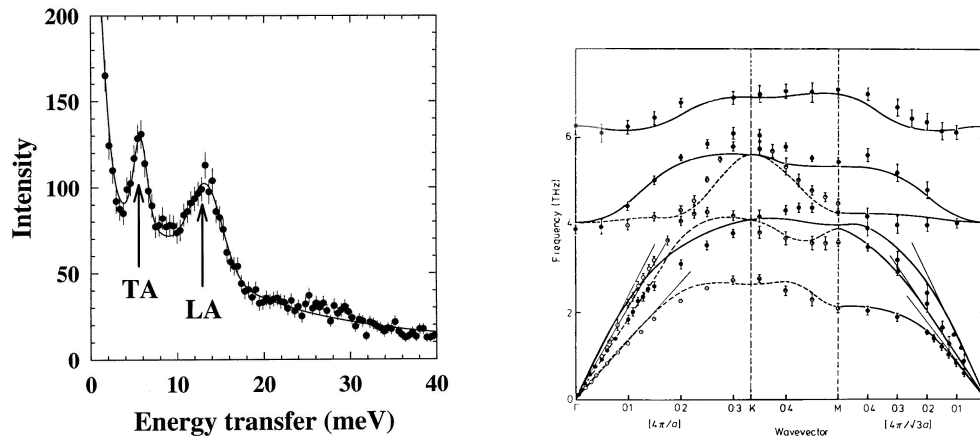


Figure 10.3: Typical neutron spectrum and measured phonons of quartz.

Appendix A

Sommerfeld expansion

Appendix B

Hartree-Fock approximation

B.1 Hartree-Fock equations for finite temperature

We want to set up an approximate treatment of a Hamilton operator

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_W \\ \hat{H}_0 &= \sum_{\alpha} \epsilon_{\alpha} \hat{c}_{\alpha}^{\dagger} \hat{c}_{\alpha} \\ \hat{H}_W &= \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \hat{c}_{\alpha}^{\dagger} \hat{c}_{\gamma}^{\dagger} \hat{c}_{\delta} \hat{c}_{\beta} \ ,\end{aligned}$$

where α collects a set of quantum numbers, by seeking an effective Hamiltonian

$$\hat{H}_{\text{eff}} = \sum_{\alpha\beta} X_{\alpha\beta} \hat{c}_{\alpha}^{\dagger} \hat{c}_{\beta}$$

such that the *free energy*

$$F[\hat{\rho}_{\text{eff}}] := \langle \hat{H} \rangle_{\text{eff}} - TS_{\text{eff}}$$

becomes minimal. The operator $\hat{\rho}_{\text{eff}}$ is the statistical operator

$$\hat{\rho}_{\text{eff}} = \frac{1}{\mathcal{Z}_{\text{eff}}} e^{-\beta \hat{H}_{\text{eff}}}$$

obtained from the effective Hamiltonian and \mathcal{Z}_{eff} the corresponding partition function. The entropy is obtained via $S_{\text{eff}} = -k_{\text{B}} \text{Tr} \hat{\rho}_{\text{eff}} \ln \hat{\rho}_{\text{eff}}$. Note that in general $F[\hat{\rho}_{\text{eff}}] \neq F_{\text{eff}} = -k_{\text{B}} T \ln \mathcal{Z}_{\text{eff}}$, but

$$\begin{aligned}F[\hat{\rho}_{\text{eff}}] &= \langle \hat{H} \rangle_{\text{eff}} - TS_{\text{eff}} \\ &= \langle \hat{H} \rangle_{\text{eff}} - \langle \hat{H}_{\text{eff}} \rangle_{\text{eff}} - k_{\text{B}} T \ln \mathcal{Z}_{\text{eff}} \\ &= F_{\text{eff}} + \langle \hat{H} - \hat{H}_{\text{eff}} \rangle_{\text{eff}}\end{aligned}$$

instead. Let us define $V_{\alpha\beta}^{\text{eff}} := X_{\alpha\beta} - \delta_{\alpha\beta} \epsilon_{\alpha}$. Then

$$\langle \hat{H} - \hat{H}_{\text{eff}} \rangle_{\text{eff}} = - \sum_{\alpha\beta} V_{\alpha\beta}^{\text{eff}} \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}} + \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\gamma}^{\dagger} \hat{c}_{\delta} \hat{c}_{\beta} \rangle_{\text{eff}} \ .$$

It is an easy exercise to show that¹

$$\langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\gamma}^{\dagger} \hat{c}_{\delta} \hat{c}_{\beta} \rangle_{\text{eff}} = \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}} \langle \hat{c}_{\gamma}^{\dagger} \hat{c}_{\delta} \rangle_{\text{eff}} - \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\delta} \rangle_{\text{eff}} \langle \hat{c}_{\gamma}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}}$$

which then leads to

$$\begin{aligned}F[\hat{\rho}_{\text{eff}}] &= F_{\text{eff}} - \sum_{\alpha\beta} V_{\alpha\beta}^{\text{eff}} \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}} + \\ &\quad \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}} \langle \hat{c}_{\gamma}^{\dagger} \hat{c}_{\delta} \rangle_{\text{eff}} - \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \langle \hat{c}_{\alpha}^{\dagger} \hat{c}_{\delta} \rangle_{\text{eff}} \langle \hat{c}_{\gamma}^{\dagger} \hat{c}_{\beta} \rangle_{\text{eff}}\end{aligned}$$

¹This relation is called *Wick's theorem*. You can prove it very easily by direct evaluation.

This expression must be minimized with respect to $X_{\alpha\beta}$, i.e. we have to find the roots of the derivative

$$\begin{aligned} \frac{\partial F[\hat{\rho}_{\text{eff}}]}{\partial X_{\mu\nu}} &= \frac{\partial F_{\text{eff}}}{\partial X_{\mu\nu}} - \sum_{\alpha\beta} \frac{\partial V_{\alpha\beta}^{\text{eff}}}{\partial X_{\mu\nu}} \langle \hat{c}_\alpha^\dagger \hat{c}_\beta \rangle_{\text{eff}} - \sum_{\alpha\beta} V_{\alpha\beta}^{\text{eff}} \frac{\partial \langle \hat{c}_\alpha^\dagger \hat{c}_\beta \rangle_{\text{eff}}}{\partial X_{\mu\nu}} + \\ &\quad \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \langle \hat{c}_\alpha^\dagger \hat{c}_\beta \rangle_{\text{eff}} \frac{\partial \langle \hat{c}_\gamma^\dagger \hat{c}_\delta \rangle_{\text{eff}}}{\partial X_{\mu\nu}} - \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} V_{\alpha\beta}^{\gamma\delta} \langle \hat{c}_\alpha^\dagger \hat{c}_\delta \rangle_{\text{eff}} \frac{\partial \langle \hat{c}_\gamma^\dagger \hat{c}_\beta \rangle_{\text{eff}}}{\partial X_{\mu\nu}} \end{aligned}$$

where the prefactor 1/2 in the last two terms was cancelled by the two, after renaming of indexes identical, contributions. From the definitions we have

$$\begin{aligned} \frac{\partial F_{\text{eff}}}{\partial X_{\mu\nu}} &= \langle \hat{c}_\mu^\dagger \hat{c}_\nu \rangle_{\text{eff}} \\ \frac{\partial V_{\alpha\beta}^{\text{eff}}}{\partial X_{\mu\nu}} &= \delta_{\alpha\mu} \delta_{\beta\nu} \quad , \end{aligned}$$

and therefore, after suitably renaming the indexes in the last term, we arrive at the conditions

$$V_{\alpha\beta}^{\text{eff}} = \sum_{\gamma\delta} \left(V_{\alpha\beta}^{\gamma\delta} - V_{\alpha\delta}^{\gamma\beta} \right) \langle \hat{c}_\gamma^\dagger \hat{c}_\delta \rangle_{\text{eff}} \quad (\text{B.1})$$

to determine the $X_{\alpha\beta}$. Note that through the expectation value the $X_{\alpha\beta}$ appear also implicitly on the right hand side, which means that these equations in general constitute a rather complicated, nonlinear set of coupled equations.

Finally, one can write down an expression for the free energy as

$$F = F_{\text{eff}} - \frac{1}{2} \sum_{\substack{\alpha\beta \\ \gamma\delta}} \left(V_{\alpha\beta}^{\gamma\delta} - V_{\alpha\delta}^{\gamma\beta} \right) \langle \hat{c}_\alpha^\dagger \hat{c}_\beta \rangle_{\text{eff}} \langle \hat{c}_\gamma^\dagger \hat{c}_\delta \rangle_{\text{eff}} \quad (\text{B.2})$$

which is very important if one needs to actually obtain results for F , for example to determine phase boundaries.

B.2 Application to the Jellium model

Let us discuss as specific example the Jellium model (3.19) of the electron gas. The quantum numbers are here $\alpha = (\vec{k}, \sigma)$. Without magnetic field, the quantities do not explicitly depend on the spin quantum number, and we find

$$\begin{aligned} X_{\vec{k}\sigma, \vec{k}'\sigma'} &= \delta_{\vec{k}, \vec{k}'} \delta_{\sigma, \sigma'} \epsilon_k + \\ &\quad \sum_{\vec{q}} \sum_{\substack{\vec{k}_2, \vec{k}'_2 \\ \sigma_2, \sigma'_2}} V_{\vec{q}} \left(\delta_{\vec{k}, \vec{k}'+\vec{q}} \delta_{\vec{k}_2, \vec{k}'_2-\vec{q}} \delta_{\sigma, \sigma'} \delta_{\sigma_2, \sigma'_2} - \right. \\ &\quad \left. \delta_{\vec{k}, \vec{k}'-\vec{q}} \delta_{\vec{k}_2, \vec{k}'+\vec{q}} \delta_{\sigma, \sigma_2} \delta_{\sigma', \sigma'_2} \right) \langle \hat{c}_{\vec{k}_2 \sigma_2}^\dagger \hat{c}_{\vec{k}'_2 \sigma'_2} \rangle_{\text{eff}} \end{aligned}$$

APPENDIX B. HARTREE-FOCK APPROXIMATION

As the first term on the right-hand side is diagonal in \vec{k} and σ , we may try this as ansatz to obtain

$$\langle \hat{c}_{\vec{k}_2\sigma_2}^\dagger \hat{c}_{\vec{k}'_2\sigma'_2} \rangle_{\text{eff}} = \delta_{\vec{k}_2, \vec{k}'_2} \delta_{\sigma_2, \sigma'_2} f(X_{\vec{k}, \vec{k}}) ,$$

where $f(\epsilon)$ is the Fermi function. Observing furthermore

$$\begin{aligned} \delta_{\vec{k}_2, \vec{k}'_2 - \vec{q}} \delta_{\vec{k}_2, \vec{k}'_2} &= \delta_{\vec{q}, 0} \\ \delta_{\vec{k}, \vec{k}_2 - \vec{q}} \delta_{\vec{k}_2, \vec{k}' + \vec{q}} &= \delta_{\vec{k}, \vec{k}'} \end{aligned}$$

we arrive at (N_e is number of electrons in the system)

$$X_{\vec{k}\sigma, \vec{k}'\sigma'} = \delta_{\vec{k}, \vec{k}'} \left[\epsilon_k + V_{\vec{q}=0} N_e - \sum_{\vec{q}} V_{\vec{q}} f(X_{\vec{k}+\vec{q}, \vec{k}+\vec{q}}) \right] .$$

As discussed in section 3.2.1, the term with $\vec{q} = 0$, also called the *direct* or *Hartree term* on the right-hand side is cancelled by the positive background, leaving the second so-called *Fock* or *exchange term*

$$E_k = \epsilon_k - \sum_{\vec{q}} V_{\vec{q}} f(E_{\vec{k}+\vec{q}}) \quad (\text{B.3})$$

to determine the Hartree-Fock energies. The self-consistent nature of the Hartree-Fock procedure is now apparent, as E_k appears in the Fermi function on the right-hand side of equation (B.3). It is by the way not trivial to solve the fully self-consistent equations, as they in addition couple different \vec{k} vectors in a non-linear fashion. A rather common (and quite good) approximation is to replace $E_{\vec{k}+\vec{q}} \approx \epsilon_{\vec{k}+\vec{q}}$ in the Fermi function.

At $T = 0$ such an approximation is not necessary. As the Hartree-Fock Hamiltonian is a single-particle Hamiltonian, the ground state is uniquely determined by the corresponding Fermi sphere. Furthermore, the radius k_F is a function of the electron density only, and hence $f(E_k) = f(\epsilon_k) = \Theta(k_F - k)$.