Condensed Matter Physics

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1.1 Introduction

In everyday life matter can be observed in three different states of aggregation: solid, liquid, and gaseous. Let us take as an example water (H_2O) at a pressure of one atmosphere. For temperatures below 0° C, H₂O molecules condense into crystals. This solid form of water is known as ice. In the temperature range between 0° C and 100° C, water is a liquid while for temperatures above 100° C, water can be found in the gaseous phase (water vapor).



Figure 1.1: Water in its three state of aggregation encountered in everyday live: Ice, liquid water, water vapour. (Images taken from Wikipedia.)

Within this course, we will investigate properties of the solid state of aggregation. It is characterized by structural rigidity, i.e., a solid object keeps its shape without support. This property results from the strong binding of the atoms in a solid object due to the electromagnetic interaction of the electrons and the nuclei. A measure of the binding strength of a solid is the cohesive energy. It is defined as the energy that must be added to the solid to separate it into atoms at rest, at infinite separation, and with the same electronic configuration. The cohesive energy strongly depends on the type of bonding. It ranges between some 10 meV and several eV per atom.

In this chapter, we will discuss the five principal types of bonding in solids: Van der Waals bonding, ionic bonding, covalent bonding, metallic bonding, and hydrogen bonds. Please note, however, that in many solid materials bonding results from a mixture of these types.



Figure 1.2: Schematic representation of the five principal types of bonding in crystals. The blue shaded areas correspond to regions with negative charge density while the red regions correspond to positive charge density. Hydrogen bonds are represented by dashed black lines.

1.2 Van der Waals bonding

We will start the discussion with Van der Waals bonding. A prototypical realization of this type of bonding can be found in crystals made from noble gas atoms. These atoms exhibit a stable closed-shell electronic configuration with spherical symmetry. At very low temperatures, the attractive dipole-dipole interaction (Van der Waals interaction) of the atoms overcomes their thermal motion and they form crystals. On this occasion, the face center cubic (fcc) lattice (see section 2.4) is preferred since this lattice type maximizes the atomic packaging density.

The dipole-dipole interaction results in an attractive potential which varies as the inverse sixth power of the inter-atomic separation r (proof: exercise). For small inter-atomic separations, the wave functions of the electrons start to overlap and the Pauli principle results in a strong repulsion. A phenomenological ansatz for the potential energy of two

noble gas atoms that incorporates these two effects is the Lennard-Jones potential:

$$\phi(r) = 4\mathcal{E}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right].$$
(1.2.1)

Here, \mathcal{E} and σ characterize the strength of attraction and the radius of the repulsive core, respectively. The latter quantity is defined by the condition $\phi(\sigma) = 0$.



Figure 1.3: Lennard-Jones potential.

In the following, we consider a crystal containing N noble gas atoms. The potential energy of the m-th atom in the presence of the other atoms is given by

$$U_m = \sum_{m \neq n} \phi(r_{mn}), \tag{1.2.2}$$

where r_{mn} is the separation between the *m*-th atom and the *n*-th atom. The binding energy of the whole crystal can be calculated as:

$$U_B = \frac{1}{2} \sum_m U_m = \frac{N}{2} U_m = 2N \mathcal{E} \sum_{m \neq n} \left[\left(\frac{\sigma}{r_{mn}} \right)^{12} - \left(\frac{\sigma}{r_{mn}} \right)^6 \right].$$
(1.2.3)

Here, the factor 1/2 has to be taken into account in order to avoid double-counting of each pair of atoms. Next, we express the atomic separation as

$$r_{mn} = \alpha_{mn} R, \tag{1.2.4}$$

where R is the nearest-neighbor separation and α_{mn} is a dimensionless number. With this definition, the binding energy of the crystal can be written as

$$U_B = 2N\mathcal{E}\left[A_{12}\left(\frac{\sigma}{R}\right)^{12} - A_6\left(\frac{\sigma}{R}\right)^6\right],\tag{1.2.5}$$

3

with the lattice sums

$$A_j = \sum_{m \neq n} \frac{1}{\alpha_{mn}^j}.$$
(1.2.6)

The nearest neighbor separation in equilibrium R_0 follows from $\partial U_B / \partial R = 0$. For a fcc-lattice with lattice sums $A_{12} = 12.13$ and $A_6 = 14.45$, one finds:

$$R_0 = 1.09\sigma.$$
 (1.2.7)

This value is in good agreement with the experimental data (see table 1.1).

	Ne	Ar	Kr	Xe
$\mathcal{E}(eV)$	0.0031	0.0104	0.014	0.02
$\sigma(\AA)$	2.74	3.40	3.65	3.98
Exp. $R_0(\mathring{A})$	3.13	3.75	3.99	4.33
$R_0 = 1.09\sigma(\mathring{A})$	2.99	3.71	3.98	4.34

Table 1.1: Lennard Jones parameters and nearest-neighbor distances for solid noble gases. Source: Ashcroft/Mermin, Solid State Physics.

Van der Waals bonding also plays an important role in many layered materials. These socalled Van der Walls materials are composed of stacks of atomically thin, two-dimensional (2D) layers that are weakly bound by dipole-dipole interaction. In contrast, the atoms within each layer are bound by strong covalent bonds (see section 1.4). A prominent example of this class of materials is graphite (see Fig. 1.4)). It consist of monoatomar thick graphene layers, in which carbon atoms are arranged in a two-dimensional honeycomb configuration.



Figure 1.4: Ball-and-stick model of graphite.

The anisotropy in bonding strength allows for the preparation of 2D crystalline materials by mechanical exfoliation. For instance, an adhesive tape can be used to peel off graphene flakes from a piece of graphite. This so-called Scotch-tape method is also suitable for the preparation of other 2D materials. Figure 1.5 exemplifies an optical micrograph of a layered Molybdenum diselenide (MoSe₂) sample.



Figure 1.5: Optical micrograph of a piece of MoSe₂ prepared by the Scotch-tape method.

1.3 Ionic bonding

Ionic crystals contain positively and negatively charged ions and are predominantly bound by electrostatic forces. A well known example of an ionic crystal is salt (sodium chloride) which comprises positively charged Na⁺ ions and negatively charged Cl⁻ ions. Since the ions usually exhibit closed shell electronic configurations (e.g., Na⁺: $1s^22s^22p^6$, Cl⁻: $1s^22s^22p^63s^23p^6$), their charge distributions are (in good approximation) spherical. This favors a crystal structure with dense packaging of the ions.

Ionic crystals form if the electrostatic attraction between the positive and negative ions is strong enough to overcome the energetic cost to form the ions from the neutral atoms. Hence, ionic bonding is preferred if one sort of atom has a low ionization potential while the other type has a high electron affinity. This is for instance the case for ionic crystals composed of cations from the groups I and II of the periodic table and anions from the groups VI or VII. For these ionic crystals, the cohesive energy is typically in the order of several eV per atom.

In the following, we calculate the reduction of energy due to the electrostatic interaction of the ions. The potential energy of the m-th ion in the presence of the other ions is given



Figure 1.6: Left: Image of some sodium-chloride crystals. Right: Spatial arrangement of the ions in sodium chloride. (Images provided by Wikipedia.)

by:

$$U_m = \sum_{n \neq m} \left[\frac{C}{r_{mn}^{12}} \mp \frac{e^2}{4\pi\epsilon_0 r_{mn}} \right].$$
 (1.3.1)

The first term describes the short-range repulsive interaction of the ions due to the overlap of the electronic wave functions at small distances while the second term results from the long-range electrostatic interaction of two ions. With $r_{mn} = \alpha_{mn}R$, we can rewrite equation (1.3.1) as

$$U_m = \sum_{n \neq m} \left[\frac{C}{\left[\alpha_{mn}R\right]^{12}} \mp \frac{e^2}{4\pi\epsilon_0 \alpha_{mn}R} \right]$$

$$\approx z \frac{C}{R^{12}} - A \frac{e^2}{4\pi\epsilon_0 R}.$$
(1.3.2)

Here, z is the number of nearest neighbors and A is the Madelung constant defined as the lattice sum

$$A \equiv \sum_{n \neq m} \frac{\pm 1}{\alpha_{mn}}.$$
(1.3.3)

This sum is mathematically not well-behaved as its value depends critically on the order in which the summation is performed. This property results from the fact that the energy of a finite collection of charged particle is strongly influenced by the actual configuration of its surface. Each order of summation corresponds to constructing the infinite crystal as a particular limiting form of successively larger finite crystals. Hence, we can have arbitrary distributions of surface charges at all stages. In order to evaluate the Madelung constant, we must thus guarantee that there are no appreciable contributions to the energy from charges at the surface at all stages of the summation.

Crystal structure	Madelung constant A
Cesium chloride	1.7627
Sodium chloride	1.7476
Zincblende	1.6381

Table 1.2: Madelung constant A for some cubic crystal structures. Source: Ashcroft/Mermin, Solid State Physics.

The total lattice energy of the crystal containing 2N ions is given by

$$U_{\text{lattice}} = N \left(z \frac{C}{R^{12}} - A \frac{e^2}{4\pi\epsilon_0 R} \right). \tag{1.3.4}$$

The equilibrium separation R_0 can again be derived from the condition $\partial U/\partial R = 0$.

1.4 Covalent bonding

Covalent crystals such as, for example, diamond or silicon are hard materials with a high melting point. They typically feature a cohesive energy of a few electron volts per atom. These properties result from a network of covalent bonds extending throughout the crystal. In a single covalent bond, two neighboring atoms share two electrons, one from each atom participating in the bond. The electrons are partially localized in the region between the two atoms resulting in a reduction of the total electronic energy. Because of this electron configuration, covalent bonds are of short range and directional.

Many properties of covalent crystals can be already understood by investigating a single covalent bond. For this purpose, we start by considering a single electron system, i.e., the hydrogen molecule-ion H_2^+ . Subsequently, we will add a second electron and investigate the H_2 molecule.

1.4.1 The hydrogen molecule-ion H⁺₂

In this section, we will calculate the energy expectation value of the hydrogen molecule-ion H_2^+ . The Hamiltonian of this one-electron system is given by

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}.$$
 (1.4.1)

The geometrical parameters r_a , r_b , and R_{ab} are defined in Fig. 1.7. The first term describes the kinetic energy of the electron, the next two terms are due to the electrostatic

interaction of the electron with the two protons, and the last term takes the repulsion of the two protons into account.



Figure 1.7: Geometry of the hydrogen molecule-ion H_2^+ .

We consider the following ansatz for the electronic wave function of the hydrogen moleculeion H_2^+ :

$$\psi = c_1 \varphi_a + c_2 \varphi_b. \tag{1.4.2}$$

Here, φ_a and φ_b are ground state wave functions of isolated hydrogen atoms at positions A and B, respectively. c_1 and c_2 are real constants. The expectation value of the energy can be calculated as

$$E = \frac{\int \psi^* H \psi dV}{\int \psi^* \psi dV} = \frac{c_1^2 H_{aa} + c_2^2 H_{bb} + 2c_1 c_2 H_{ab}}{c_1^2 + c_2^2 + 2c_1 c_2 S}$$
(1.4.3)

with

$$H_{aa} = \int \varphi_a^* H \varphi_a dV, \qquad (1.4.4)$$

$$H_{bb} = \int \varphi_b^* H \varphi_b dV, \qquad (1.4.5)$$

$$H_{ab} = \int \varphi_a^* H \varphi_b dV = \int \varphi_b^* H \varphi_a dV \qquad (1.4.6)$$

$$S = \Re \int \varphi_a^* \varphi_b dV. \tag{1.4.7}$$

The so-called overlap integral S is a measure for the spatial overlap of the two wave functions φ_a and φ_b .

The energy expectation value of the exact wave function is always smaller than the corresponding expectation value of an approximate solution. We choose the constants c_1 and c_2 such that the energy expectation value becomes as small as possible for our ansatz. With $\partial E/\partial c_1 = 0$ and $\partial E/\partial c_2 = 0$, we find:

$$c_1(H_{aa} - E) + c_2(H_{ab} - ES) = 0,$$

$$c_1(H_{ab} - ES) + c_2(H_{bb} - E) = 0.$$
(1.4.8)

After a short calculation, we obtain

$$E_{+,-} = \frac{H_{aa} \pm H_{ab}}{1 \pm S} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}.$$
(1.4.9)

The corresponding wavefunctions are given by

$$\psi_+ = c(\varphi_a + \varphi_b), \tag{1.4.10}$$

$$\psi_{-} = c(\varphi_a - \varphi_b). \tag{1.4.11}$$

The reduction of the energy for the symmetric wave function ψ_+ results from an increase of the electron density between the two atoms (bonding state). The antisymmetric wave function ψ_- is connected with a low electron density between the two atoms which increases the energy of this state (anti-bonding state).



Figure 1.8: Symmetric and anti-symmetric wave functions.

1.4.2 The hydrogen molecule H_2

Following the preliminary considerations of the previous section, we now turn to the hydrogen molecule H_2 as a model system for a covalent bond (see Fig. 1.9). Its Hamiltonian is given by

$$H = H_0 + H_1 \tag{1.4.12}$$

$$H_0 = -\frac{\hbar^2}{2m} \nabla_{e1}^2 - \frac{\hbar^2}{2m} \nabla_{e2}^2 - \frac{e^2}{4\pi\epsilon_0 r_{1a}} - \frac{e^2}{4\pi\epsilon_0 r_{2b}}$$
(1.4.13)

$$H_1 = \frac{e^2}{4\pi\epsilon_0 R_{ab}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{e^2}{4\pi\epsilon_0 r_{1b}} - \frac{e^2}{4\pi\epsilon_0 r_{2a}}.$$
 (1.4.14)



Figure 1.9: Geometry of the hydrogen molecule H₂.

Due to the their repulsive interaction, it is unlikely that both electrons are simultaneously located near one of the atoms. The so-called Heitler-London-ansatz for the two-particle wave function takes this aspect into account:

$$\psi_{+,-}(\mathbf{r}_1, \mathbf{r}_2) = c_{+,-} \left[\varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) \pm \varphi_b(\mathbf{r}_1) \varphi_a(\mathbf{r}_2) \right].$$
(1.4.15)

Here, $c_{+,-}$ are normalization coefficients, \mathbf{r}_1 and \mathbf{r}_2 are the coordinates of electron 1 and 2, respectively, and $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$ are the ground state single-electron wave functions of the isolated $(R_{ab} \to \infty)$ hydrogen atoms A and B, respectively. In order to fulfill the Pauli-principle, $\psi_+(\mathbf{r}_1, \mathbf{r}_2)$ requires an anti-parallel orientation of the two electron spins (singlet state) while $\psi_-(\mathbf{r}_1, \mathbf{r}_2)$ is connected with a parallel orientation of the spins (triplet state).

We assume that $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$ are normalized. The normalization coefficients are thus given by

$$c_{+,-} = \frac{1}{\sqrt{2 \pm 2S}} \tag{1.4.16}$$

with the overlapp integral

$$S = \int \varphi_a^*(\mathbf{r}_1)\varphi_b^*(\mathbf{r}_2)\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)dV_1dV_2 \qquad (1.4.17)$$

$$= \int \varphi_a^*(\mathbf{r}_2) \varphi_b^*(\mathbf{r}_1) \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) dV_1 dV_2.$$
(1.4.18)

The energy expectation value for the singulet and triplet state are given by

$$E_{+} = 2E_{0} + \frac{V + A}{1 + S}, \qquad (1.4.19)$$

$$E_{-} = 2E_{0} + \frac{V - A}{1 - S}, \qquad (1.4.20)$$

respectively. Here, E_0 is the ground state energy of an isolated hydrogen atom, V is the Coulomb integral, and A is the so-called exchange integral. The latter two are given by

$$V = \int \varphi_a^*(\mathbf{r}_1) \varphi_b^*(\mathbf{r}_2) H_1 \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) dV_1 dV_2$$
(1.4.21)

$$= \int \varphi_a^*(\mathbf{r}_2)\varphi_b^*(\mathbf{r}_1)H_1\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)dV_1dV_2 \qquad (1.4.22)$$

and

$$A = \int \varphi_a^*(\mathbf{r}_1) \varphi_b^*(\mathbf{r}_2) H_1 \varphi_a(\mathbf{r}_2) \varphi_b(\mathbf{r}_1) dV_1 dV_2 \qquad (1.4.23)$$

$$= \int \varphi_a^*(\mathbf{r}_2) \varphi_b^*(\mathbf{r}_1) H_1 \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) dV_1 dV_2, \qquad (1.4.24)$$

respectively. Upon evaluation of the integrals one finds that the singulet state is a bound state with $E_+ < 2E_0$ for a proton-proton separation R_{ab} of approximately $1\mathring{A}$. In contrast, the energy of the triplet state E_- is larger than $2E_0$ for all values of R_{ab} .



Figure 1.10: Scheme of the energy levels of the singlet- and triplet-state of the hydrogen molecule.

Hybrid orbitals in carbon compounds

The ground state electronic configuration of carbon is $(1s^2)(2s^2)(2p_x)(2p_y)$. Hence, one would anticipate that the two unpaired *p*-electrons give rise of two covalent bonds in carbon compounds. Since the *p*-wave functions are oriented, the angle between the two bonds is expected to be 90°. Contrary to this expectation, one finds carbon compounds with bond angles of 180°, 120°, and 109.5°. The reason for this is that the electronic wave functions of carbon usually mix before they form molecular bonds. Through the formation of these so-called hybrid orbitals, the overlap of the wave functions of neighboring atoms is maximized and, consequently, the energy is minimized.

sp-Hybridization

In the case of *sp*-hybridization, the 2*s* orbital mixes with one of the 2*p* orbitals, e.g., $2p_z$. The other two 2*p*-orbitals are unchanged. The normalized *sp*-hybrid orbitals are given by

$$\phi_1^{sp} = \frac{1}{\sqrt{2}} \left[\phi(s) + \phi(p_z) \right], \qquad (1.4.25)$$

$$\phi_2^{sp} = \frac{1}{\sqrt{2}} \left[\phi(s) - \phi(p_z) \right]. \tag{1.4.26}$$

The two *sp*-orbitals are oriented in opposite directions. The bond angle is thus 180° .

*sp*²-Hybridization

Mixing of the 2s orbital with two the 2p orbitals leads to sp^2 -hybridization. The corresponding sp^2 -hybrid orbitals can be written as

$$\phi_1^{sp^2} = \frac{1}{\sqrt{3}} \left[\phi(s) + \sqrt{2}\phi(p_x) \right], \qquad (1.4.27)$$

$$\phi_2^{sp^2} = \frac{1}{\sqrt{3}} \left[\phi(s) - \frac{1}{\sqrt{2}} \phi(p_x) + \frac{\sqrt{3}}{\sqrt{2}} \phi(p_y) \right], \qquad (1.4.28)$$

$$\phi_3^{sp^2} = \frac{1}{\sqrt{3}} \left[\phi(s) - \frac{1}{\sqrt{2}} \phi(p_x) - \frac{\sqrt{3}}{\sqrt{2}} \phi(p_y) \right].$$
(1.4.29)

This type of hybridization can be found, e.g., in graphene. The corresponding bond angle is 120°.

sp^3 -Hybridization

 sp^3 -hybridization results from mixing of the 2s orbital with all three 2p orbitals. The corresponding sp^3 -hybrid orbitals are given by:

$$\phi_1^{sp^3} = \frac{1}{2} \left[\phi(s) + \sqrt{3}\phi(p_z) \right], \qquad (1.4.30)$$

$$\phi_2^{sp^3} = \frac{1}{2} \left| \phi(s) + \sqrt{\frac{8}{3}} \phi(p_x) - \sqrt{\frac{1}{3}} \phi(p_z) \right|, \qquad (1.4.31)$$

$$\phi_3^{sp^3} = \frac{1}{2} \left[\phi(s) - \sqrt{\frac{2}{3}} \phi(p_x) + \sqrt{2} \phi(p_y) - \sqrt{\frac{1}{3}} \phi(p_z) \right], \qquad (1.4.32)$$

$$\phi_4^{sp^3} = \frac{1}{2} \left[\phi(s) - \sqrt{\frac{2}{3}} \phi(p_x) - \sqrt{2} \phi(p_y) - \sqrt{\frac{1}{3}} \phi(p_z) \right].$$
(1.4.33)

This type of hybridization can be found, e.g., in diamond. The corresponding bond angle is 109.5° .

Schematic representations of the three different hybrid orbitals can be found below.



1.5 Metallic bonding

Metallic bonding can be qualitatively understood in terms of a simple electron-gas model. Here, we assume that the outermost electrons are detached from the metal atoms and are free to move throughout the whole crystal. The remaining atoms are positively charged and are usually referred to as ion cores. In the following, we assume that the charge of a single conduction electron is homogeneously smeared over a sphere with radius r_a . This so

called Wigner-Seitz radius corresponds to one-half of the distance between two adjacent metal atoms. With this assumption, the electron density in a monovalent metal can be calculated as

$$n = \frac{3}{4\pi r_a^3}.$$
 (1.5.1)

The average kinetic energy of a conduction electron is given by (see section 6.1)

$$E_{\rm av} = \frac{3}{5} E_F^0 = \frac{3}{5} \left(\frac{9\pi}{4}\right)^{2/3} \frac{\hbar^2}{2m} \frac{1}{r_a^2}.$$
(1.5.2)

Next, we calculate the potential energy per conduction electron. On this occasion, we have to take into account that the positive charge of the ion-cores is partially screened by the homogeneous negative charge distribution $\rho = -en$ of the conduction electrons. In a distance r from a given ion-core, the screened Coulomb potential reads

$$\phi(r) = \frac{e - e\left(\frac{r}{r_a}\right)^3}{4\pi\epsilon_0 r}.$$
(1.5.3)

The negative charge contained in a shell centered around the ion-core with radius r and thickness dr provides the following contribution to the potential energy:

$$dE_{\rm Pot} = \phi(r)\rho 4\pi r^2 dr = -\frac{3e^2}{4\pi\epsilon_0} \left(\frac{r}{r_a^3} - \frac{r^4}{r_a^6}\right) dr.$$
 (1.5.4)

The total potential energy per conduction electron can be calculated as

$$E_{\rm Pot} = \int_0^{r_a} dE_{\rm Pot} = -\frac{9e^2}{40\pi\epsilon_0} \frac{1}{r_a}.$$
(1.5.5)

With the Bohr radius $a_0 = 4\pi\epsilon_0\hbar^2/me^2$, the last equation can be rewritten as

$$E_{\rm Pot} = -\frac{9}{5} \frac{\hbar^2}{2ma_B^2} \frac{a_0}{r_a}.$$
 (1.5.6)

The total energy per conduction electron is thus given by

$$E_{\text{total}} = \frac{\hbar^2}{2ma_0^2} \left[\frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} \left(\frac{a_0}{r_a} \right)^2 - \frac{9}{5} \left(\frac{a_0}{r_a} \right) \right].$$
(1.5.7)

Its minimum value is reached at

$$\frac{r_a}{a_0} = \frac{2}{3} \left(\frac{9\pi}{4}\right)^{2/3},\tag{1.5.8}$$

which corresponds to a separation between two ion-cores of approximately 2.6 Å. Given the extreme simplicity of the model, this value is in reasonable agreement with the experimental data (see Table 1.3).

Metal	Nearest neighbor distance (Å)	Binding energy (eV/atom)
Li	3.02	1.63
Na	3.66	1.11
Κ	4.52	0.93
\mathbf{Cs}	5.24	0.8

Table 1.3: Nearest neighbor distance and binding energy of alkali metals. Source: Hunklinger, Festkörperphysik.

1.6 Hydrogen bonds

A hydrogen atom has a single electron and hence can form only a single covalent bond with another atom. It is thus surprising, that in some materials, e.g. ice, hydrogen can cause the binding of two atoms.

We can qualitatively understand the formation of a hydrogen bond in a two-step process. If hydrogen is covalently bond to an electronegative atom like oxygen, nitrogen, or fluorine, the electron is partially detached from the proton and transferred to the other atom (step 1). Thus, the hydrogen atom can be effectively treated as a positively charged ion ("proton") even though complete ionization of hydrogen is unlikely because of the large ionization energy (13.6 eV). The "proton" has an attractive effect on a second nearby electronegative atom (step 2). Because of its small size, the "proton" can mediate an attractive effect only between two electronegative atoms.

2 Crystal structure

2.1 Introduction

Solid materials can be categorized according to the spatial arrangement of the constituting atoms:

- Crystalline solids (or, for short, crystals) are characterized by a strictly periodic arrangement of the constituting atoms in all three spatial dimensions. Crystals exhibit long-range order, i.e., the positions of the atoms in different parts of the crystal are correlated.
- Polycrystalline solids are composed of crystallites (small crystals) with varying size and orientation. Within each crystallite, the positions of the atoms are correlated. However, there is no long-range order between different crystallites.
- Amorphous solids are solids which do not possess long-range order.

In this course, we will concentrate on crystalline solids.



Figure 2.1: Schematic representation of a crystalline solid, a polycrystalline solid, and an amorphous solid. Images taken from Wikipedia.

2.2 Ideal crystals

An ideal crystal is composed of identical groups of atoms which are arranged in an infinite, periodic array (see Fig. 2.2 for a schematic representation). A set of equivalent points in

2 Crystal structure

the array defines the lattice of the crystal. A group of atoms that is attached to every point of the lattice is called a basis.



Figure 2.2: An ideal crystal can be constructed by attaching the basis to every lattice point.

For instance, graphene consits of a single layer of carbon atoms. Each atom has three nearest neighbors with 120° bond angles resulting from sp² hybridization (see Fig. 2.3). This honeycomb structure can be described by a triangular lattice with a two-atom basis.



Figure 2.3: In graphene, the carbon atoms are arranged in a triangular lattice (marked by the blue dots) with a two-atom basis (marked by the red dashed line).

2.2.1 Translation vectors

A given three-dimensional lattice can be characterized by a set of three primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . Two arbitrary points of the lattice, \mathbf{R} and \mathbf{R}' , are connected through translation by suitable integer multiples m_i of the vectors \mathbf{a}_i :

$$\mathbf{R}' = \mathbf{R} + \sum_{j=1}^{3} m_j \mathbf{a}_j. \tag{2.2.1}$$

For a given lattice, there is more than one set of primitive translation vectors. Moreover, not every set of vectors that connects a lattice point with three other lattice points defines

a set of primitive translation vectors. These aspects are exemplified in Fig. 2.4 for the analogous situation in two dimensions.



Figure 2.4: The red and blue arrows represent in each case a set of primitive translation vectors. In contrast, the two greens arrows do not represent a set of primitive translation vectors because we cannot construct the complete lattice through translation by integer multiples of these two vectors.

2.2.2 Unit cells

A unit cell is a volume that fills all space without overlap or leaving voids when translated through a set of lattice vectors. If this set contains all lattice vectors, the unit cell is called a primitive cell or primitive unit cell. For a given lattice, there is no unique way of choosing a primitive cell. Each primitive cell contains one lattice point. Lattice points at the edges of the primitive cell are equally shared among the adjacent primitive cells.

The parallelepiped spanned by three primitive translation vectors is a primitive cell. Its volume (and that of every other primitive cell) is given by

$$V_u = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|. \tag{2.2.2}$$

The Wigner-Seitz cell is the region of space that is closer to a given lattice point than to any other lattice point. By construction, it is a primitive unit cell with the full symmetry of the lattice.

It is often useful to choose a unit cell which is a parallelepiped with edges parallel to a suitable set of translation vectors and which displays the full symmetry of the lattice. This so-called conventional unit cell can contain more than one lattice point.

2 Crystal structure



Figure 2.5: Primitive unit cell (red), conventional unit cell (blue), and Wigner-Seitz cell (green) of a 2D lattice. The conventional unit cell contains two lattice points.

2.3 Point groups and space groups

Next, we consider the symmetry operations that transform the crystal structure into itself while leaving at least one point fixed. These operations form the so-called crystallographic point groups. In three dimensions, there are 32 distinct crystallographic point-groups. Possible symmetry operations of a point group are:

- Rotations through multiples of $2\pi/n$ about some axis: The axis is called a *n*-fold axis. A Bravais lattice (see next section) can contain only 2-, 3-, 4-, or 6-fold axes.
- Reflections: Reflection in a plane that takes every point into its mirror image.
- Inversions: Every point \mathbf{r} is taken into $-\mathbf{r}$. The origin is the inversion center.
- Rotation-reflection: Rotation through $2\pi/n$ followed by a reflection in a plane perpendicular to the rotation axis.
- Rotation-inversion: Rotation through $2\pi/n$ followed by an inversion in a point lying on the rotation axes.

The combination of these symmetry operations with translational symmetries forms the so-called space group. In three dimensions, there are 230 different space groups.

2.4 Bravais lattices

Often, one is only interested in the symmetry properties of the lattice of a crystal, i.e., translations, rotations, reflections, and inversions, that take the lattice into itself. In three dimensions, there are 14 distinct types of lattices, the so-called Bravais lattices, that can be grouped in 7 crystal systems. The conventional unit cells of the 14 Bravais lattices are depicted in Fig. 2.6.



Figure 2.6: Conventional unit cells of the 14 Bravais lattices (adopted from Wikipedia).

2.5 Lattice planes and Miller indices

A lattice plane of a Bravais lattice is defined by three noncollinear lattice points. Because of the translational symmetry of the Bravais lattice, the lattice plane will contain infinitely many lattice points. A family of lattice planes is a set of parallel and equally spaced lattice planes which together contain all lattice points of the Bravais lattice.

A family of lattice planes can be characterized by a set of three numbers (hkl). The so-called Miller indices h,k,l are determined in the following way:

- The translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 define three crystal axes.
- Determine the intercepts $S_1 = s_1 |\mathbf{a}_1|$, $S_2 = s_2 |\mathbf{a}_2|$, $S_3 = s_3 |\mathbf{a}_3|$ of one of the lattice planes with the axes (see Fig. 2.7).
- The Miller indices are the smallest three integers h, k, l with no common factor that satisfy

$$h:k:l = \frac{1}{s_1}:\frac{1}{s_2}:\frac{1}{s_3}.$$
(2.5.1)

- The Miller index is set to 0 if the lattice plane is parallel to the corresponding axis.
- A negative Miller index is denoted by an overbar, e.g., $(h, -k, l) \rightarrow (h, \bar{k}, l)$.

Note that the set of Miller indices depends on the choice of translation vectors.



Figure 2.7: Lattice plane.

The notation $\{hkl\}$ represents all families of planes that are equivalent to (hkl) by the symmetry of the lattice. For example, in a cubic crystal $\{100\}$ denotes the three families of planes (100),(010), and (001). Directions in a lattice are denoted by square brackets. The [hkl]-direction is parallel to the vector $h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3$.

In the case of hexagonal and rhombohedrical lattice systems one often uses the Miller-Bravais system with four indices (hkil) to characterize family of planes. Here, h, k and l are the corresponding Miller indices and the index i obeys the constraint h + k + i = 0. The advantage of the Miller-Bravais indices is that they make permutation symmetries apparent which are not obvious in the case of the Miller indices.



Figure 2.8: Miller indices and Miller-Bravais indices of two selected planes of the hexagonal lattice.

3 Structural analysis

3.1 Introduction

Knowledge of the spatial arrangement of the atoms in a crystal is the key for understanding many of its physical properties. Scattering techniques such as x-ray scattering and neutron scattering allow to analyze the crystal structure in a non-destructive way. In this chapter, we introduce the concept of the reciprocal lattice and discuss a simple classical theory to analyze the diffraction of a wave by the crystal.

3.2 The reciprocal lattice and Fourier expansion of periodic functions

Consider a Bravais lattice with primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 and lattice vectors

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, n_j \in \mathbb{Z}.$$
(3.2.1)

In the following, we will call this lattice the direct lattice. The primitive translation vectors of the corresponding reciprocal lattice are defined by:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \tag{3.2.2}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \tag{3.2.3}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{3.2.4}$$

A short calculation shows that the \mathbf{b}_i satisfy the condition

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}.\tag{3.2.5}$$

An arbitrary lattice point **G** of the reciprocal lattice can be written as a linear combination of the \mathbf{b}_i with integral coefficients v_i :

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3. \tag{3.2.6}$$

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If \mathbf{R} and \mathbf{G} are arbitrary lattice vectors of the direct lattice and the reciprocal lattice, respectively, it follows from equation (3.2.5) that

$$\mathbf{R} \cdot \mathbf{G} = 2\pi \underbrace{\left(n_1 v_1 + n_2 v_2 + n_3 v_3\right)}_{\in \mathbb{Z}}.$$
(3.2.7)

One can easily verify that the reciprocal lattice of the reciprocal lattice is the direct lattice.

The reciprocal lattice vector $\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is normal to the lattice plane with Miller indices (hkl). The separation d_{hkl} between two adjacent lattice planes of this family is given by

$$d_{hkl} = \frac{2\pi}{|\mathbf{G}_{hkl}|}.$$
(3.2.8)

Proof: Exercise.

The first Brillouin zone is defined as the Wigner-Seitz cell of the reciprocal lattice centered at the origin. We will see in the following chapters, that it plays an important role in condensed matter physics.

Examples

1D lattice

Consider a 1D lattice with lattice constant a. According to equation (3.2.5), the lattice constant b of the reciprocal lattice is

$$b = \frac{2\pi}{a}.\tag{3.2.9}$$

2D square lattice

For a 2D square lattice with lattice spacing a, a set of primitive translation vectors is given by

$$\mathbf{a}_1 = a \, \hat{\mathbf{e}}_x, \tag{3.2.10}$$
$$\mathbf{a}_2 = a \, \hat{\mathbf{e}}_y. \tag{3.2.11}$$

The corresponding primitive translation vectors of the reciprocal lattice are

$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{e}}_x, \tag{3.2.12}$$

$$\mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{e}}_y. \tag{3.2.13}$$

2D triangular lattice

Next, we consider a 2D triangular lattice with primitive translation vectors

$$\mathbf{a}_1 = \frac{a}{2} \left(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y \sqrt{3} \right), \tag{3.2.14}$$

$$\mathbf{a}_2 = \frac{a}{2} \left(\hat{\mathbf{e}}_x - \hat{\mathbf{e}}_y \sqrt{3} \right). \tag{3.2.15}$$

With the help of equation (3.2.5), we find the primitive translation vectors of the reciprocal lattice:

$$\mathbf{b}_1 = \frac{2\pi}{a} \left(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y / \sqrt{3} \right), \qquad (3.2.16)$$

$$\mathbf{b}_2 = \frac{2\pi}{a} \left(\hat{\mathbf{e}}_x - \hat{\mathbf{e}}_y / \sqrt{3} \right). \tag{3.2.17}$$

3D simple cubic lattice

A set of primitive translation vectors of the simple cubic lattice is given by

\mathbf{a}_1	=	$a\hat{\mathbf{e}}_x,$	(3.2.18)
\mathbf{a}_2	=	$a \hat{\mathbf{e}}_{u},$	(3.2.19)

$$\mathbf{a}_3 = a \, \hat{\mathbf{e}}_z. \tag{3.2.20}$$

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Applying equations (3.2.2)-(3.2.4), we obtain the primitive translation vectors of the reciprocal lattice:

$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{e}}_x, \tag{3.2.22}$$

$$\mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{e}}_y, \tag{3.2.23}$$

$$\mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{e}}_z. \tag{3.2.24}$$

We will now consider a periodic function $\rho(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{R})$ that is invariant under translation by any lattice vector **R**. The Fourier expansion of $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}},\tag{3.2.25}$$

with the expansion coefficients

$$\rho_{\mathbf{G}} = \frac{1}{V_u} \int_{V_u} \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV.$$
(3.2.26)

The sum in equation (3.2.25) runs over all reciprocal lattice vectors **G**. The domain of integration in equation (3.2.26) is the primitive unit cell of the direct lattice and V_u is its volume (Proof: Exercise).

3.3 Scattering of waves by crystals

In the following, we present a classical theory to analyze the scattering of a wave by a crystal. Originally, this theory was developed to explain x-ray diffraction patterns from crystals. Since the theory is not specific to the nature of the wave, it can be also applied to neutron- or electron-scattering.

3.3.1 Wave diffraction

Let us consider a monochromatic plane wave impinging on a crystal. The field of the incident wave is given by

$$A(\mathbf{r},t) = A_0 e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)}$$
(3.3.1)

with frequency ω_0 , wave vector \mathbf{k}_0 , and amplitude A_0 . The incident wave interacts with the atoms of the crystal and creates secondary, spherical waves. The field of a secondary, spherical waves will vary as $e^{i\mathbf{k}\cdot\mathbf{R}}/|\mathbf{R}|$, where R is the distance from the scattering center. The distribution of scattering centers in the crystal is characterized by a function $\rho(\mathbf{r})$. It depends both on the material and the nature of the incident wave. For example, x-rays are scattered for the most part from the electrons in the crystal while neutrons predominately interact with the atomic nuclei. In our discussion, we consider only elastic scattering and assume that the scattered waves do not undergo a second scattering event in the crystal.



Figure 3.1: Scheme of the scattering geometry.

The total scattered field at the detector results from the coherent superposition of the scattered waves emitted from all scattering centers. The contribution dA_s of a small volume dV around the point **r** is given by

$$dA_{s}(\mathbf{R}_{0},t) = \rho(\mathbf{r}) A(\mathbf{r},t) \frac{e^{i\mathbf{k}\cdot\mathbf{R}_{1}}}{|\mathbf{R}_{1}|} dV$$

$$= \rho(\mathbf{r}) A_{0} e^{i(\mathbf{k}_{0}\cdot\mathbf{r}-\omega_{0}t)} \frac{e^{i\mathbf{k}\cdot\mathbf{R}_{1}}}{|\mathbf{R}_{1}|} dV. \qquad (3.3.2)$$

 \mathbf{R}_0 , \mathbf{R}_1 , and \mathbf{r} are defined according to Fig. (3.1). Integration over the volume of the crystal V_c yields the total scattered field:

$$A_s(\mathbf{R}_0, t) = \frac{A_0 e^{i(\mathbf{k} \cdot \mathbf{R}_0 - \omega_0 t)}}{|\mathbf{R}_0|} \int_{V_c} \rho(\mathbf{r}) e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}} dV.$$
(3.3.3)

Here, we have used the condition $|\mathbf{R}_0| \approx |\mathbf{R}_1|$. The factor in front of the integral does not depend on **r**. Hence, the spatial arrangement of the atoms is encoded in the scattering amplitude:

$$A(\mathbf{K}) = \int_{V_c} \rho(\mathbf{r}) \, e^{-i\mathbf{K}\cdot\mathbf{r}} \, dV. \tag{3.3.4}$$

Here, we have introduced the scattering vector

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_0. \tag{3.3.5}$$

The detector signal is proportional to the intensity of the scattered wave:

$$I(\mathbf{K}) \propto |A(\mathbf{K})|^2 = \left| \int_{V_c} \rho(\mathbf{r}) \, e^{-\imath \mathbf{K} \cdot \mathbf{r}} \, dV \right|^2.$$
(3.3.6)

For a crystal, the distribution of scattering centers $\rho(\mathbf{r})$ is a periodic function and can be expanded according to equation (3.2.25). The intensity of the scattered wave can thus be written as

$$I(\mathbf{K}) \propto |A(\mathbf{K})|^2 = \left| \sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_{V_c} e^{i(\mathbf{G} - \mathbf{K}) \cdot \mathbf{r}} dV \right|^2.$$
(3.3.7)

For sufficiently large volumes, the integral is a representation of the δ -function:

$$\int_{V_c} e^{i(\mathbf{G}-\mathbf{K})\cdot\mathbf{r}} dV \simeq \begin{cases} V_c & \text{for } \mathbf{G} = \mathbf{K} \\ 0 & \text{for } \mathbf{G} \neq \mathbf{K} \end{cases}$$
(3.3.8)

According to equation (3.3.8), we can only observe a signal at the detector if the diffraction condition

$$\mathbf{G} = \mathbf{K} \tag{3.3.9}$$

is fulfilled. In this case, the scattered waves from different unit cells are in phase and interfere constructively. In contrast, destructive interference results in a negligible signal at the position of the detector if the diffraction condition is not met.

3.3.2 Ewald construction

The Ewald construction is an elegant geometrical approach to find solutions of the diffraction condition (see Fig. 3.2). We start with the reciprocal lattice and fix the tip of the incident wave vector \mathbf{k}_0 at the origin of the reciprocal lattice. Next, we draw a sphere (in 2D a circle) with radius $|\mathbf{k}_0|$ about the tail of \mathbf{k}_0 . This sphere is usually referred to as the Ewald sphere. The diffraction condition is fulfilled if a reciprocal lattice point **G** lies on the the Ewald sphere. The wave vector of the diffracted wave \mathbf{k} is constructed by connecting the tail of \mathbf{k}_0 with the lattice point **G**.


Figure 3.2: Ewald construction. (Figure adapted from Wikipedia).

3.3.3 Bragg's law

An intuitive explanation for the occurrence of diffracted beams from a crystal was introduced by William Lawrence Bragg. He assumed, that a crystal is composed of parallel planes of atoms and that an incident beam is specularly reflected from these planes. The path difference of two rays reflected from adjacent planes is $2d\sin(\theta)$ (see. Fig. 3.3). A diffracted beam occurs if the reflections interfere constructively, i.e., the path difference is an integral multiple n of the wavelength λ . This condition leads to Bragg's law:

$$2d\sin(\theta) = n\lambda. \tag{3.3.10}$$



Figure 3.3: Bragg reflection from a particular family of lattice planes.

It can be easily shown that Bragg's law and the diffraction condition are equivalent. We start by noting that the diffraction condition requires that the three vectors \mathbf{k}_0 , \mathbf{k} , \mathbf{G} can

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be arranged in a triangle. We find from inspection of Fig. 3.4

$$\sin(\theta) = \frac{1}{2} \frac{\lambda}{2\pi} |\mathbf{G}|. \tag{3.3.11}$$

Here, we have used that

$$|\mathbf{k}_0| = |\mathbf{k}| = \frac{2\pi}{\lambda}.\tag{3.3.12}$$

The reciprocal lattice vector \mathbf{G} can always be written as

$$\mathbf{G} = n\mathbf{G}_{hkl},\tag{3.3.13}$$

where \mathbf{G}_{hkl} is the shortest reciprocal lattice vector parallel to \mathbf{G} and n is an integer. \mathbf{G}_{hkl} is normal to the family of lattice planes characterized by the Miller indices (hkl) (see last section). Next, we identify Bragg's planes of atoms with this family of lattice plane and obtain together with equation (3.2.8) again Bragg's law

$$2d_{hkl}\sin(\theta) = n\lambda. \tag{3.3.14}$$



Figure 3.4: Scattering condition.

3.3.4 Structure factor of the basis and atomic form factor

In the previous sections, we have seen that the reciprocal lattice of a given crystal determines the directions of the diffracted signals. The intensities of these signals are proportional to $|\rho_{\mathbf{G}}|^2$ and hence depend on the spatial distribution of scattering centers in a unit cell. To further investigate this point, we start with equation (3.2.26)

$$\rho_{\mathbf{G}} = \frac{1}{V_u} \int_{V_u} \rho(\mathbf{r}) e^{-\imath \mathbf{G} \cdot \mathbf{r}} dV.$$
(3.3.15)

Next, we write the distribution function $\rho(\mathbf{r})$ as the sum of the distribution functions $\rho_j(\mathbf{r} - \mathbf{r}_j)$ of the atoms contained in the unit cell:

$$\rho(\mathbf{r}) = \sum_{j} \rho_j (\mathbf{r} - \mathbf{r}_j). \tag{3.3.16}$$

Here, \mathbf{r}_j is the vector to the center of the *j*-th atom. Inserting equation(3.3.16) into equation (3.3.15) yields

$$\rho_{\mathbf{G}} = \frac{1}{V_{u}} \int_{V_{u}} \rho(\mathbf{r}) e^{-\imath \mathbf{G} \cdot \mathbf{r}} dV$$

$$= \frac{1}{V_{u}} \sum_{j} e^{-\imath \mathbf{G} \cdot \mathbf{r}_{j}} \int_{V_{j}} \rho_{j}(\mathbf{r}') e^{-\imath \mathbf{G} \cdot \mathbf{r}'} dV'$$

$$= \frac{1}{V_{u}} \sum_{j} f_{j}(\mathbf{G}) e^{-\imath \mathbf{G} \cdot \mathbf{r}_{j}},$$
(3.3.17)

where $\mathbf{r}' = \mathbf{r} - \mathbf{r}_j$.

The function $f_j(\mathbf{G}) = \int_{V_j} \rho_j(\mathbf{r}') e^{-i\mathbf{G}\cdot\mathbf{r}'} dV'$ characterizes the scattering power of the *j*-th atom and is called the atomic form factor of this atom. Furthermore, we define the structure factor of the basis by

$$S_{\mathbf{G}} = \rho_{\mathbf{G}} V_u = \sum_j f_j(\mathbf{G}) \, e^{-\imath \mathbf{G} \cdot \mathbf{r}_j}.$$
(3.3.18)

For further analysis, it is useful to express the position vector of the atom j in terms of the translation vectors of the lattice

$$\mathbf{r}_j = u_j \mathbf{a}_1 + v_j \mathbf{a}_2 + w_j \mathbf{a}_3. \tag{3.3.19}$$

Note that u_j , v_j , and w_j are no integers. With $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, we obtain

$$S_{\mathbf{G}} = \sum_{j} f_{j}(\mathbf{G}) e^{-2\pi i (hu_{j} + kv_{j} + lw_{j})}.$$
(3.3.20)

The following example shows that the interference of waves scattered from different atoms within one unit cell can have a strong influence on the intensity of the diffracted wave.

Example: Structure factor of the bcc lattice

A bcc lattice can be regarded as a simple cubic lattice with a unit cell containing two atoms located at $\mathbf{r}_1 = \mathbf{0}$ and $\mathbf{r}_2 = \frac{a}{2} (\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z)$, respectively. The corresponding structure factor is given by

$$S_{\mathbf{G}} = f(\mathbf{G}) \left[1 + e^{-\imath \pi (h+k+l)} \right]$$

=
$$\begin{cases} 2f(\mathbf{G}) & \text{for } h+k+l & \text{even} \\ 0 & \text{for } h+k+l & \text{odd} \end{cases}$$
(3.3.21)

Since the structure factor vanishes for odd h + k + l, there is, e.g., no Bragg reflex from the (100)-plane of a bcc crystal.

3.4 X-ray scattering: Experimental methods

3.4.1 Laue method

The Laue method (see Fig. 3.5) uses a collimated x-ray beam with a continuous spectrum to illuminate a single crystal of fixed orientation. The diffracted beams are recorded with a photo plate. A Bragg peak can be observed if the diffraction condition is fulfilled by a wavelength component of the incident spectrum. If the incident beam is parallel to a symmetry axis of the crystal, the Laue diffraction pattern has the same symmetry. Hence, the Laue method is often used to determine the orientation of single crystals whose structure is known.



Figure 3.5: Scheme of the Laue method.

3.4.2 Rotating crystal method

In the rotating crystal method (see Fig. 3.6), a single crystal is illuminated with a monochromatic x-ray beam. The crystal is oriented with one crystal axis perpendicular to the beam and rotated around this axis. As the crystal rotates, the reciprocal lattice also rotates by the same amount around this axis. Hence, the reciprocal lattice points move on circles around the axis and a Bragg reflex occurs whenever a circle intersects the Ewald sphere. The diffracted beams are recorded with a cylindrical photo plate. The rotating crystal method can be used to determine the crystal structure of unknown materials.



Figure 3.6: Scheme of the rotating crystal method.

3.4.3 Powder or Debye-Scherrer method

The powder or Debye-Scherrer method uses instead of a single crystal a sample which contains many randomly oriented crystallites. As the sample is illuminated with a monochromatic x-ray beam, one will always find crystallites with proper orientation to satisfy the Bragg condition for a given family of lattice planes. The corresponding diffracted beams all lie on a cone with full opening angle 4θ around the incident beam direction.



Figure 3.7: Scheme of the powder or Debye-Scherrer method.

4 Lattice dynamics

4.1 Introduction

Most physical properties of solid materials can be attributed to either the vibration of atoms about their equilibrium positions or to the dynamics of the electrons. Because of the large ratio of nuclear and electronic masses, we can address these two issues separately. We assume in the so-called Born-Oppenheimer approximation that the light electrons "instantaneously" adapt themselves to the respective positions of the nuclei. The resulting electron distribution in combination with the position of the nuclei determines the potential that is responsible for the the comparatively slow dynamics of the crystal lattice.

4.2 Lattice with monoatomic basis

In this section, we will consider the lattice vibrations of a crystal with a monoatomic unit cell. For the sake of mathematical simplicity, we pick a family of lattice planes which is oriented normal to a high symmetry direction of the crystal, e.g., the the [100] direction of a simple cubic lattice. We assume that the planes of atoms are displaced either parallel or perpendicular to the surface normal. The displacement of the *s*-th plane from its equilibrium position will be denoted by u_s . We will see below, that the displacement of the planes parallel to the surface normal gives rise to longitudinal waves while the displacement perpendicular to the surface normal creates transverse waves.

We choose an atom of the s-th plane and consider the force acting on this atom caused by all the atoms of the s + n-th plane. The components of the force normal to the relative displacement of the two planes cancel for symmetry reasons (see Fig. 4.1). The remaining parallel component of the force is proportional to $u_{s+n} - u_s$ in the case of small displacements. Both aspects can be combined in the so-called linear chain model, in which each plane of the lattice is represented by one atom of a one-dimensional linear chain (see Fig. 4.2). The forces between the planes are modeled by adding "springs" to the chain with effective force constants C_n . The total force acting on the s-th atom in the presence

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Figure 4.1: Displacement of atoms (dark blue) from their equilibrium positions (light blue) in longitudinal direction (left) and transverse direction (right). The red arrows indicate the force on an atom due to the relative displacement of the planes of atoms.

of all other atoms is given by:

$$F_s = \sum_n C_n \left[u_{s+n} - u_s \right].$$
(4.2.1)

The equation of motion for the s-th atom with mass M can hence be written as:

$$M\frac{d^2u_s}{dt^2} = \sum_n C_n \left[u_{s+n} - u_s \right].$$
(4.2.2)

In the following, we look for solutions of this equation of motion which have the form of a traveling wave:

$$u_s = \tilde{u} e^{i(qsa-\omega t)}.$$
(4.2.3)

Here, \tilde{u} is a constant, q is the wave vector, a is the equilibrium separation of atoms in the chain, and ω is the frequency of the wave. Inserting this ansatz in the equation of motion



Figure 4.2: Equivalent one-dimensional linear chain for longitudinal displacement.

(4.2.2) yields:

$$\omega^2 M = \sum_n C_n \left[1 - e^{iqna} \right].$$
(4.2.4)

For symmetry reasons, we have $C_n = C_{-n}$ and obtain:

$$\omega^{2} = \frac{1}{M} \sum_{n=1}^{\infty} C_{n} \left[2 - e^{iqna} - e^{-iqna} \right] = \frac{2}{M} \sum_{n=1}^{\infty} C_{n} \left[1 - \cos\left(qna\right) \right].$$
(4.2.5)

In most cases, the interaction between neighboring atoms dominates and we can set $C_n = 0$ for n > 1. This results in the following dispersion relation of the linear chain:

$$\omega^{2} = \frac{2C_{1}}{M} \left[1 - \cos\left(qa\right)\right] = \frac{4C_{1}}{M} \sin^{2}\left(\frac{qa}{2}\right), \qquad (4.2.6)$$

$$\omega = 2\sqrt{\frac{C_1}{M}} \left| \sin\left(\frac{qa}{2}\right) \right|. \tag{4.2.7}$$



Figure 4.3: Dispersion relation of the linear chain. The first Brillouin zone is highlighted in white.

Next, we calculate the phase difference between two neighboring atoms:

$$\frac{u_{s+1}}{u_s} = \frac{\tilde{u} \, e^{-\iota\omega t} e^{\iota q(s+1)a}}{\tilde{u} \, e^{-\iota\omega t} e^{\iota qsa}} = e^{\iota qa}.\tag{4.2.8}$$

Since the trigonometric functions have a modulus of periodicity of 2π , the range of the physical meaningful values of the wavevector is restricted to the first Brillouin zone:

$$-\frac{\pi}{a} < q \le \frac{\pi}{a}.\tag{4.2.9}$$

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Figure 4.4: Periodic displacement of atoms (black dots) in transverse direction. The wavevectors of the two waves depicted in red and blue differ by a reciprocal lattice vector $2\pi/a$.

An equivalent statement is that the wavelength λ has to be the same or greater than two times the lattice constant a. This is easy to understand since the amplitude of the wave between two neighboring atoms is without any physical significance (see Fig. 4.4).

A wavevector q' outside of the first Brillouin zone can always be transformed back into the first Brillouin zone by the addition of an appropriate reciprocal lattice vector G:

$$q = q' + G \tag{4.2.10}$$

with

$$-\frac{\pi}{a} < q \le \frac{\pi}{a}.\tag{4.2.11}$$

The velocity of a wave packet is given by the group velocity:

$$v_g = \frac{\partial \omega}{\partial q}.\tag{4.2.12}$$

With the dispersion relation (4.2.7), we find:

$$v_g = \sqrt{\frac{C_1 a^2}{M}} \cos\left(\frac{qa}{2}\right). \tag{4.2.13}$$

The group velocity vanishes for $q \to \pi/a$. This situation corresponds to a standing wave resulting from the superposition of a forward and a backward moving wave.

4.3 Lattice with diatomic basis

In the following, we consider a diatomic chain of atoms with masses M_1 and M_2 (see Fig. 4.5). The displacements of the atoms from their equilibrium positions are denoted by u_s and v_s , respectively. We assume that each atom interacts only with its nearest neighbors and that the force constants are identical between all pairs of atoms.



Figure 4.5: Diatomic chain of atoms with masses M_1 and M_2 .

The dynamics of the atomic motion is described by the coupled equations of motions:

$$M_{1} \frac{d^{2} u_{s}}{dt^{2}} = C \left[v_{s} + v_{s-1} - 2u_{s} \right],$$

$$M_{2} \frac{d^{2} v_{s}}{dt^{2}} = C \left[u_{s} + u_{s+1} - 2v_{s} \right].$$
(4.3.1)

Again, we look for solutions which have the form of a traveling wave:

$$u_s = U e^{i(qsa-\omega t)}, (4.3.2)$$

$$v_s = V e^{i(qsa-\omega t)}. ag{4.3.3}$$

Inserting equation (4.3.3) in equation (4.3.1) yields:

$$(2C - \omega^2 M_1) U - C (1 + e^{-iqa}) V = 0, -C (1 + e^{iqa}) U + (2C - \omega^2 M_2) V = 0.$$
(4.3.4)

A short calculation yields:

$$\omega_{\pm}^{2} = C\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right) \pm C\sqrt{\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right)^{2} - \frac{4}{M_{1}M_{2}}\sin^{2}\left(\frac{qa}{2}\right)}.$$
(4.3.5)

The dispersion relation of the diatomic linear chain exhibits two solutions, ω_{-} and ω_{+} , for every wavevector q. $\omega_{-}(q)$ and $\omega_{+}(q)$ are usually referred to as the acoustical branch

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Figure 4.6: Dispersion relation of the diatomic linear chain. The maximum frequency of the optical branch is given by $\omega_{max} = \sqrt{2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$.

and the optical branch, respectively. The two branches differ in the relative phase of the displacement of neighboring atoms. This can be best seen in the long wavelength limit, i.e., for $q \to 0$. A short calculation yields:

$$\omega_{-}^{2} \approx \frac{1}{2}q^{2}a^{2}\frac{C}{M_{1}+M_{2}} \quad \text{(acoustical branch)}, \tag{4.3.6}$$

$$\omega_{+}^{2} \approx 2C\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right) = \omega_{max}^{2} \quad \text{(optical branch)}.$$
(4.3.7)

Using equation (4.3.4), we can calculate the ratio of the amplitudes:

$$\frac{u}{v} \approx \frac{2C}{2C - \omega^2 M_1} \quad \text{for} \quad q \to 0.$$
(4.3.8)

For the acoustical branch ($\omega \approx 0$), we find $u \approx v$ in the long wavelength limit. Hence, the two sorts of atoms are oscillating in phase. This behavior corresponds to a sound wave propagating through the crystal. In contrast, the optical branch is characterized by $u/v \approx -M_2/M_1$ in the limit $q \to 0$. Thus, the two sorts of atoms vibrate against each other. If the two sorts of atoms carry opposite charges, e.g. in an ionic crystal, the optical branch is connected with an oscillating electric dipole moment. Hence, a light wave with the corresponding frequency can couple to this lattice vibration and is absorbed. This process typically happens to infrared light and such a crystal is thus called infrared active.



Figure 4.7: Diatomic linear chain: Acoustical branch and optical branch of a transverse wave in the long wavelength limit for $M_2 > M_1$.

4.4 Lattice with several atoms per unit cell

If we lift our restriction and consider arbitrary propagation directions, the lattice vibrations are in general not purely transverse or longitudinal waves but rather a mixture. Depending on which type of displacement dominates, these waves are called quasi-transverse modes or quasi-longitudinal modes, respectively.

It can be shown, that a crystal with p atoms per unit cell exhibits for every propagation direction 3 acoustical modes, namely 2 quasi-transverse modes (TA modes) and 1 quasilongitudinal mode (LA mode). In addition to the acoustical modes, there are 2(p-1)quasi-transverse optical modes (TO modes) and (p-1) quasi-longitudinal modes (LO modes). In general, all these modes will be non-degenerate.

4.5 Scattering from time-varying lattices

In the last chapter, we considered scattering of a wave from a static lattice. Here, we will investigate how lattice vibrations influence the scattering properties of a crystal.

For mathematical simplicity, we assume a lattice with a monoatomic basis and pointlike scatterers at the positions \mathbf{r}_m . With these assumptions, we obtain the scattering amplitude:

$$A(\mathbf{K}) \propto \sum_{m} e^{-i\mathbf{K}\cdot\mathbf{r}_{m}}.$$
(4.5.1)

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The corresponding amplitude of the scattered wave is then given by

$$A_s(t) \propto e^{-\imath \omega_0 t} A(\mathbf{K}) \propto e^{-\imath \omega_0 t} \sum_m e^{-\imath \mathbf{K} \cdot \mathbf{r}_m}.$$
(4.5.2)

We now account for the lattice vibrations and write:

$$\mathbf{r}_m(t) = \mathbf{R}_m + \mathbf{u}_m(\mathbf{R}_m, t). \tag{4.5.3}$$

Here, the lattice vector \mathbf{R}_m corresponds to the equilibrium position of the atom and $\mathbf{u}_m(\mathbf{R}_m, t)$ is its time-varying displacement.

Since the displacement amplitudes are small compared to the wavelength of the incident wave, we can make the expansion:

$$e^{-\imath \mathbf{K} \cdot \mathbf{u}_m(\mathbf{R}_m, t)} \approx 1 - \imath \mathbf{K} \cdot \mathbf{u}_m(\mathbf{R}_m, t).$$
 (4.5.4)

Next, we choose an ansatz for the displacement $\mathbf{u}_m(\mathbf{R}_m, t)$ in the form of a superposition of plane waves:

$$\mathbf{u}_m(\mathbf{R}_m, t) = \sum_{\mathbf{q}} \mathbf{U}_{\mathbf{q}} e^{\pm i (\mathbf{q} \cdot \mathbf{R}_m - \omega_q t)}.$$
(4.5.5)

Inserting (4.5.4) and (4.5.5) in (4.5.2) results in

$$A_{s}(t) \propto \underbrace{\sum_{m} e^{-i\mathbf{K}\cdot\mathbf{R}_{m}} e^{-i\omega_{0}t}}_{\text{elastic}} - \underbrace{\sum_{m} \sum_{\mathbf{q}} i\mathbf{K}\cdot\mathbf{U}_{\mathbf{q}} e^{-i(\mathbf{K}\mp\mathbf{q})\cdot\mathbf{R}_{m}} e^{-i(\omega_{0}\pm\omega_{\mathbf{q}})t}}_{\text{inelastic}}.$$
(4.5.6)

The scattered wave $A_s(t)$ has two components. The first term in (4.5.6) is due to elastic scattering as discussed in the previous chapter. The second term results from lattice vibrations and describes inelastic scattering. In the following, we will concentrate on the latter process. A diffracted signal can be only observed for a given scattering vector Kand a given frequency ω if all partial waves scattered from different parts of the crystal interfere constructively. Upon inspection of (4.5.6), we find that this condition is fulfilled for

$$\omega_0 \pm \omega_q = \omega, \tag{4.5.7}$$

$$\mathbf{K} \mp \mathbf{q} = \mathbf{G}. \tag{4.5.8}$$

In a quantum mechanical sense, lattice vibrations can be regarded as quasiparticles, the so called phonons, with energy $\hbar\omega_q$ and momentum $\hbar \mathbf{q}$. With this in mind, we can

interpret the last two equations as the conservation of energy (4.5.7) and the conservation of momentum (4.5.8) in an inelastic scattering process. For example, an incident neutron with energy $\hbar\omega_0$ and momentum $\hbar\mathbf{k}_0$ interacts with the lattice and creates (minus sign) or annihilates (plus sign) a phonon with energy $\hbar\omega_q$ and quasimomentum $\hbar\mathbf{q}$. This results in a scattered neutron with energy $\hbar\omega$ and momentum $\hbar\mathbf{k}$.

A phonon is not connected with the vibration of a single atom but rather a wave which is distributed over the whole crystal:

$$\mathbf{u}_{\mathbf{q}}(\mathbf{R},t) = \mathbf{U}_{\mathbf{q}} e^{i(\mathbf{q}\cdot\mathbf{R}-\omega_q t)}.$$
(4.5.9)

The phonon quasimomentum $\hbar \mathbf{q}$ is not a real physical momentum as the excitation of a phonon does not result is a net mass transport. Instead, the momentum $\hbar \mathbf{q} + \mathbf{G}$ necessary to fulfill momentum conservation in the scattering process is transferred to the whole crystal. Hence, a phonon is not an elementary particle like, e.g., an electron, but rather a convenient concept to interpret equations (4.5.7) and (4.5.8).

4.6 Inelastic neutron scattering

Thermal neutrons produced in a fission reactor have a typical energy of about $E_{\text{neutron}} = 0.1 \text{ eV}$. A typical phonon energy is $E_{\text{phonon}} = 0.01 \text{ eV}$. Hence, the relative energy change in an inelastic neutron scattering process is in the order of $E_{\text{phonon}}/E_{\text{neutron}} = 10^{-1}$. This energy resolution is easily attainable with a three axis neutron spectrometer (see below). In contrast, one would require a much better energy resolution of $E_{\text{phonon}}/E_{\text{x-ray}} = 10^{-6}$ in the corresponding inelastic x-ray scattering experiment. Hence, phonon dispersion curves are usually measured by inelastic neutron scattering.

The scheme of a triple axis neutron spectrometer is shown in Fig. 4.8. Neutrons with a defined energy are selected from the incident broad neutron spectrum by Bragg scattering from a single crystal monochromator (first axis). The energy of the diffracted neutrons depends on the orientation of the monochromator crystal and the monochromator material. The sample is then irradiated with the monochromaticed neutron beam. Rotation of the sample allows to change its orientation with respect to the incident beam (second axis). Those neutrons which are scattered under a certain scattering angle and which have a specified final energy are detected in the detector which is placed behind an analyzer crystal (third axis).

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Figure 4.8: Scheme of a triple-axis neutron spectrometer.

5 Thermal properties of the lattice

5.1 Thermal energy of a harmonic oscillator

In this chapter, we investigate the thermal properties of the lattice. For this purpose, we treat the lattice vibrations, i.e., the phonons, as a set of independent harmonic oscillators. In quantum mechanics, the energy eigenvalues E_n of a harmonic oscillator with angular frequency ω are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{5.1.1}$$

The occupation number n of the harmonic oscillator can take all positive integer numbers and zero. The smallest possible energy eigenvalue $E_0 = \frac{1}{2}\hbar\omega$ is the so-called zero-point energy.

We assume that the harmonic oscillator is in thermal equilibrium with a heat reservoir at temperature T. The probability P_n for finding the harmonic oscillator in the energy eigenstate E_n is then given by:

$$P_n = \frac{e^{-E_n/k_B T}}{Z}.$$
 (5.1.2)

Here, k_B is the Boltzmann constant. The normalizing constant Z can be found from the condition

$$\sum_{n=0}^{\infty} P_n \stackrel{!}{=} 1.$$
(5.1.3)

Inserting (5.1.1) and (5.1.2) in (5.1.3) results in

$$\frac{1}{Z} \sum_{n=0}^{\infty} e^{-E_n/k_B T} = \frac{1}{Z} e^{-\hbar\omega/2k_B T} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/k_B T} \right)^n \\ = \frac{1}{Z} \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} \stackrel{!}{=} 1.$$
(5.1.4)

Solving for Z, we find

$$Z = \frac{e^{-\hbar\omega/2k_BT}}{1 - e^{-\hbar\omega/k_BT}}$$
(5.1.5)

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and thus

$$P_n = e^{-n\hbar\omega/k_B T} \left(1 - e^{-\hbar\omega/k_B T}\right).$$
(5.1.6)

The average energy of the harmonic oscillator is given by

$$E(\omega,T) = \sum_{n=0}^{\infty} E_n P_n = \left(1 - e^{-\hbar\omega/k_B T}\right) \hbar\omega \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \left(e^{-\hbar\omega/k_B T}\right)^n.$$
(5.1.7)

With

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad \text{and} \quad \sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}$$
(5.1.8)

we obtain

$$E(\omega, T) = \hbar\omega \left(\frac{1}{2} + \langle n \rangle_T\right).$$
(5.1.9)

Here, the average occupation number is given by

$$\langle n \rangle_T = \frac{1}{e^{\hbar \omega/k_B T} - 1}.$$
(5.1.10)

Equation (5.1.10) is the Bose-Einstein distribution for the case of a vanishing chemical potential $\mu = 0$. This corresponds to a situation in which the total number of particles is not fixed. Based on our assignment of harmonic oscillators and phonons, we can treat phonons as Bose particles (bosons).

5.2 Density of states of phonons

So far, we have dealt with ideal crystals with infinite extension in all directions. In what follows, we consider a finite crystal with Volume V_c and $N_c = m^3$ unit cells. For large N_c , the bulk properties of the finite crystal will not depend on its actual size and we can neglect the influence of the surfaces on the bulk properties.

Consider the atomic displacement caused by the excitation of phonon with frequency ω and wavevector **q**:

$$u_{\mathbf{q}}(\mathbf{R},t) = U_{\mathbf{q}}e^{i(\mathbf{q}\cdot\mathbf{R}-\omega_{\mathbf{q}}t)}.$$
(5.2.1)

Since the interfaces have a negligible influence on the interior of a large crystal, we are free to choose the boundary conditions according to our convenience. In the following we assume periodic boundary conditions:

$$u_{\mathbf{q}}(\mathbf{R},t) = u_{\mathbf{q}}(\mathbf{R} + m\,\mathbf{a}_1, t) = u_{\mathbf{q}}(\mathbf{R} + m\,\mathbf{a}_2, t) = u_{\mathbf{q}}(\mathbf{R} + m\,\mathbf{a}_3, t), \tag{5.2.2}$$

where \mathbf{a}_i , \mathbf{a}_2 , and \mathbf{a}_3 are the primitive translation vectors of the lattice. By inserting (5.2.1) in (5.2.2), we find:

$$m \mathbf{q} \cdot \mathbf{a}_i = 2\pi h_i, \quad i = 1, 2, 3.$$
 (5.2.3)

This condition can be only fulfilled, if the wavevector \mathbf{q} satisfies the condition

$$\mathbf{q} = \frac{1}{m} \left(h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3 \right), \tag{5.2.4}$$

where \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 are the primitive translation vectors of the reciprocal lattice. Restriction of the wavevector \mathbf{q} to the first Brillouin-zone yields:

$$-\frac{m}{2} \le h_i \le \frac{m}{2}.\tag{5.2.5}$$

This result shows that the wavevector can only take a discrete number of equally spaced values in a finite crystal. The total number of allowed **q**-values equals the number of unit cells $N_c = m^3$. Since the allowed values of the wavevector are equally spaced, we can assign to each **q**-value a volume

$$\Delta^3 q = \frac{1}{m^3} \left(\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3 \right) = \frac{(2\pi)^3}{V_c}$$
(5.2.6)

of the reciprocal space.

The number of phonon states dN_{ω} per Volume V_c in a frequency interval $d\omega$ around the frequency ω can be written as

$$\frac{dN_{\omega}}{V_c} = \mathcal{D}(\omega)d\omega, \qquad (5.2.7)$$

where $\mathcal{D}(\omega)$ is the density of states of phonons. In order to calculate dN_{ω}/V_c , we have to sum over all phonon modes with frequencies $\omega(\mathbf{q})$ in the interval $[\omega, \omega + d\omega]$. For large N_c , the allowed values of the wavevector form a quasicontinuous distribution. Thus, we can replace the sum over **q**-values by an integral. In three dimensions, we obtain:

$$\frac{dN_{\omega}}{V_c} = \mathcal{D}(\omega)d\omega = \frac{1}{V_c}\sum_{\omega(\mathbf{q})}^{\omega(\mathbf{q})+d\omega(\mathbf{q})} = \frac{1}{V_c}\frac{1}{\Delta^3 q}\sum_{\omega(\mathbf{q})}^{\omega(\mathbf{q})+d\omega(\mathbf{q})}\Delta^3 q = \frac{1}{(2\pi)^3}\int_{\omega(\mathbf{q})}^{\omega(\mathbf{q})+d\omega(\mathbf{q})} d^3 q \quad (5.2.8)$$

To evaluate the integral, we express the volume element d^3q as

$$d^3q = dq_\perp dS_\omega,\tag{5.2.9}$$

where dS_{ω} is an element of the surface $S(\omega)$ defined by $\omega(\mathbf{q}) = \text{const}$ and dq_{\perp} is the perpendicular distance between the surfaces $S(\omega)$ and $S(\omega + d\omega)$ [see Fig. (5.1)].

5 Thermal properties of the lattice



Figure 5.1: Scheme to calculate the density of states.

With $d\omega = |\nabla_{\mathbf{q}}\omega(\mathbf{q})| dq_{\perp}$, we can write the density of states as

$$\mathcal{D}(\omega) = \frac{1}{(2\pi)^3} \int_{S(\omega)} \frac{dS_\omega}{|\nabla_{\mathbf{q}}\omega(\mathbf{q})|}.$$
(5.2.10)

The density of states $\mathcal{D}(\omega)$ becomes particularly large if the group velocity $|\nabla_{\mathbf{q}}\omega(\mathbf{q})|$ is small or even zero, e.g. at the boundary of the first Brillouin zone. For certain directions in reciprocal space, the integrand diverges while the integral over the whole surface still has a finite value. The corresponding peaks in the density of states $\mathcal{D}(\omega)$ are called van-Hove singularities.

Example

Consider an elastic isotropic medium with the following dispersion relations for longitudinal and transverse sound waves, respectively:

$$\omega_l(\mathbf{q}) = |\mathbf{q}|c_l, \tag{5.2.11}$$

$$\omega_t(\mathbf{q}) = |\mathbf{q}|c_t. \tag{5.2.12}$$

Here, c_l and c_t are the corresponding sound velocities of the modes.

The derivatives are given by:

$$|\nabla_{\mathbf{q}}\omega_j(\mathbf{q})| = c_j, \ j = l, t.$$
(5.2.13)

The density of states of branch j can be expressed as:

$$\mathcal{D}_{j}(\omega) = \frac{1}{(2\pi)^{3}} \int_{S(\omega)} \frac{dS_{\omega}}{|\nabla_{\mathbf{q}}\omega_{j}(\mathbf{q})|} = \frac{1}{(2\pi)^{3}} \int_{S(\omega)} \frac{dS_{\omega}}{c_{j}}$$
(5.2.14)

$$= \frac{1}{(2\pi)^3} \frac{4\pi q(\omega)^2}{c_j} = \frac{1}{2\pi^2} \frac{\omega^2}{c_j^3}.$$
 (5.2.15)

The total density of states is thus given by:

$$\mathcal{D}(\omega) = \mathcal{D}_l + 2\mathcal{D}_t = \frac{1}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \omega^2.$$
(5.2.16)

5.3 Specific heat capacity of the lattice

In the following we investigate the thermal properties of a lattice with a monoatomic unit cell. We assume that the lattice can be treated as an elastic isotropic medium (Debye approximation). For an elastic isotropic medium, the number of modes in the *j*-th branch with a frequency less than ω is given by:

$$N_{j}(\omega) = V_{c} \int_{0}^{\omega} \mathcal{D}_{j}(\omega') d\omega' = \frac{V_{c}}{2\pi^{2}} \frac{1}{c_{j}^{3}} \frac{\omega^{3}}{3}.$$
(5.3.1)

To account for the finite number of modes of a real crystal, we define for the *j*-th branch a cutoff frequency $\omega_{max,j}$ such that $N_j(\omega_{max,j})$ equals the number of unit cells N_c in the crystal (see previous section). Solving for $\omega_{max,j}$, we obtain:

$$\omega_{max,j} = \left(\frac{6\pi^2 c_j^3 N_c}{V_c}\right)^{\frac{1}{3}}.$$
(5.3.2)

The total density of states in the Debye approximation reads:

$$\mathcal{D}(\omega) = \frac{1}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \omega^2 = \frac{3}{2\pi^2} \frac{\omega^2}{c_D^3}.$$
(5.3.3)

Here, we have introduced in the second step the Debye velocity via

$$\frac{3}{c_D^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3}.$$
(5.3.4)

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In general, the cutoff frequency of the longitudinal branch differs from the cutoff frequency of the two degenerate transverse branches. However, in practice, one often uses a common cutoff frequency ω_D (Debye frequency) defined by

$$\omega_D = \left(\frac{6\pi^2 c_D^3 N_c}{V_c}\right)^{\frac{1}{3}}.$$
(5.3.5)

In the framework of the Debye approximation, the internal energy¹ $\mathcal{U}(T)$ of the lattice in thermal equilibrium can be expressed as:

$$\mathcal{U}(T) = V_c \int_{0}^{\omega_D} \mathcal{D}(\omega) E(\omega, T) \, d\omega = \frac{9N_c}{\omega_D^3} \int_{0}^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1} \, d\omega.$$
(5.3.6)

Here, ω_D is the only material-specific parameter. Next, we introduce the so-called Debye temperature:

$$k_B \Theta_D = \hbar \omega_D. \tag{5.3.7}$$

The heat capacity of a substance with constant volume is defined by

$$C_V = \left(\frac{\partial \mathcal{U}}{\partial T}\right)_V.$$
(5.3.8)

In the Debye approximation, we obtain with $x_D = \hbar \omega_D / k_B T$ the important result:

$$C_V = 9N_c k_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx.$$
(5.3.9)

For large temperatures $(T \gg \Theta_D)$, the integral can be approximated by

$$\int_{0}^{x_{D}} \frac{x^{4}e^{x}}{\left(e^{x}-1\right)^{2}} dx \stackrel{x \to 0}{\approx} \int_{0}^{x_{D}} \frac{x^{4} \cdot 1}{\left(1+x-1\right)^{2}} dx = \int_{0}^{x_{D}} x^{2} dx = \frac{1}{3} \left(\frac{\Theta_{D}}{T}\right)^{3}$$
(5.3.10)

¹We neglect in this calculation the zero-point energy.

Table 5.1: Debye temperature of selected elements. Source: Festkörperphysik, S. Hunklinger.

and the heat capacity reaches the classical value

$$C_V = 3N_c k_B. (5.3.11)$$

In the limit of small temperatures $(T \ll \Theta_D)$, we can set the upper limit of the integral to infinity and obtain with

$$\int_{0}^{\infty} \frac{x^4 e^x}{\left(e^x - 1\right)^2} \, dx = \frac{4\pi^4}{15}.\tag{5.3.12}$$

the famous T^3 -law for the heat capacity:

$$C_V = \frac{12\pi^4}{5} N_c k_B \left(\frac{T}{\Theta_D}\right)^3.$$
(5.3.13)



Figure 5.2: Heat capacity according to the Debye approximation.

5.4 Anharmonic effects

So far, we have considered the lattice dynamics in the so-called harmonic approximation. Here, the potential energy is assumed to depend quadratically on the displacement ρ of an atom from its equilibrium position:

$$U(\rho) = a\rho^2. \tag{5.4.1}$$

In what follows, we will go beyond the harmonic approximation and study several effects that result from an anharmonic contribution to the potential energy.

5.4.1 Thermal expansion

Consider that the potential $U(\rho)$ has the following form:

$$U(\rho) = a\rho^2 - b\rho^3$$
, with $a > 0, b > 0$ and $b \ll a$. (5.4.2)

The second term of the potential characterizes the asymmetry of the potential that arises due to the strong repulsion of two atoms for small separations. To calculate the average displacement $\langle \rho \rangle$, we weight each displacement with the corresponding Boltzmann factor and integrate over all displacements:

$$\langle \rho \rangle = \frac{\int\limits_{-\infty}^{\infty} \rho \, e^{-U(\rho)/k_B T} \, d\rho}{\int\limits_{-\infty}^{\infty} e^{-U(\rho)/k_B T} \, d\rho}.$$
(5.4.3)

For a small anharmonic contribution to the potential $(b \ll a)$, we can expand the integrands as

$$\int_{-\infty}^{\infty} \rho \, e^{-U(\rho)/k_B T} \, d\rho = \int_{-\infty}^{\infty} e^{-a\rho^2/k_B T} \left(\rho + \frac{b\rho^4}{k_B T}\right) \, d\rho$$
$$= \frac{b \, (k_B T)^{3/2}}{a^{5/2}} \int_{-\infty}^{\infty} e^{-x^2} x^4 \, dx = \frac{b \, (k_B T)^{3/2}}{a^{5/2}} \frac{3}{4} \sqrt{\pi}$$
(5.4.4)

and

$$\int_{-\infty}^{\infty} e^{-U(\rho)/k_B T} d\rho = \int_{-\infty}^{\infty} e^{-a\rho^2/k_B T} \left(1 + \frac{b\rho^3}{k_B T}\right) d\rho$$
$$= \frac{(k_B T)^{1/2}}{a^{1/2}} \int_{-\infty}^{\infty} e^{-x^2} dx = \frac{(k_B T)^{1/2}}{a^{1/2}} \sqrt{\pi}.$$
(5.4.5)

Hence, the average displacement $\langle \rho \rangle$ is given by

$$\langle \rho \rangle = \frac{\frac{b(k_B T)^{3/2}}{a^{5/2}} \frac{3}{4} \sqrt{\pi}}{\frac{(k_B T)^{1/2}}{a^{1/2}} \sqrt{\pi}} = \frac{3bk_B}{4a^2} T.$$
(5.4.6)

Note, that a nonvanishing value of $\langle \rho \rangle$ corresponds to an expansion of crystal upon heating.

Next, we define the coefficient of thermal expansion as

$$\alpha = \frac{d}{dT} \frac{\langle \rho \rangle}{r_0}.$$
(5.4.7)

With equation (5.4.6), we obtain

$$\alpha = \frac{3bk_B}{4a^2r_0}.\tag{5.4.8}$$

Thermal expansion is obviously an effect of the anharmonicity of the potential.

5.4.2 Phonon-Phonon interaction

In the harmonic approximation, the equation of motion (4.2.2) which governs the displacement of the atoms is a linear differential equation. The corresponding solutions are plane waves. Because of the linearity of (4.2.2), the superposition of two waves is another solution. Hence, within the framework of the harmonic approximation, phonons do not interact with each other and a phonon distribution once created persists unchanged for all times. In other words, the phonons will not reach a thermal distribution as discussed in section 5.1.

In contrast, if we include a small anharmonicity of the potential [see, e.g., equation (5.4.2)], plane waves are no longer exact solutions of the equation of motion but rather an approximate solution. As a consequence, the lattice waves are no longer independent from each other and start to mix. We can interpret this effect as the interaction of phonons. The physics behind this process can be understood as follows: A phonon produces a temporal and spatial periodic elastic strain which modulates through the anharmonicity of the potential the elastic properties of the crystal. A second phonon is scattered from this modulation and thereby produces a third phonon.

It can be shown, that in a three phonon scattering process energy and quasi-momentum are conserved:

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3. \tag{5.4.9}$$

$$\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}_3 + \mathbf{G}. \tag{5.4.10}$$

At first, we will consider the case that no reciprocal lattice vector ($\mathbf{G} = 0$) is required for the conservation of the quasi-momentum (see Fig. 5.3, left handside). These processes are called normal processes or N-process and dominate at low temperatures ($T \ll \Theta_D$).

5 Thermal properties of the lattice

N-processes do not help to establish thermal equilibrium. To understand this point, we consider a distribution of phonons with total momentum

$$\mathbf{J} = \sum_{\mathbf{q}} n_{\mathbf{q}} \hbar \mathbf{q}. \tag{5.4.11}$$

Obviously, \mathbf{J} is conserved if we only consider N-processes and the phonon distribution will propagate through the crystal with no thermal resistance (see next section).

The situation is different, if we also include scattering processes which require reciprocal lattice vectors $\mathbf{G} \neq 0$ to fulfill quasi-momentum conservation (see Fig. 5.3, right hand-side). These processes are called umklapp processes or U-processes and are connected with a large net change in phonon momentum. U-processes result in a rapid decay of an initial phonon flux and are thus responsible for the thermal resistance.



Figure 5.3: Three phonon processes. Left: N-process. Right: U-process.

5.4.3 Thermal conductivity

In the previous sections we have assumed that the whole crystal is characterized by a uniform temperature T. We will now consider the effect of a temperature gradient. At this, we will assume that the spatial variation of T is sufficiently small such that all the relevant quantities, e.g., the phonon occupation number, can be locally defined.

We know from thermodynamics that the thermal current density \mathbf{j}_t is proportional to the temperature gradient:

$$\mathbf{j}_t = -K\nabla T,\tag{5.4.12}$$

where, K is the thermal conductivity.

Next, we express the thermal current density in terms of properties of the phonons. The energy density of a phonon-mode with wavevector \mathbf{q} in branch j is given by

$$\frac{E(\omega,T)}{V} = \frac{\hbar\omega_{\mathbf{q},j}\langle n_{\mathbf{q},j}\rangle}{V},\tag{5.4.13}$$

where $\langle n_{\mathbf{q},j} \rangle$ is the local phonon occupation number. The corresponding energy transport velocity is the group velocity

$$\mathbf{v}_{\mathbf{q},j}^g = \nabla_{\mathbf{q}}\omega_{\mathbf{q},j}.\tag{5.4.14}$$

Thus, the x-component of the thermal current density² is given by

$$j_{t,x} = \frac{1}{V} \sum_{\mathbf{q},j} \hbar \omega_{\mathbf{q},j} \langle n_{\mathbf{q},j} \rangle \underbrace{\mathbf{v}_{\mathbf{q},j}^g \cdot \hat{\mathbf{e}}_x}_{v_x}.$$
(5.4.15)

In thermal equilibrium, the thermal current density vanishes because the fluxes in positive and negative direction cancel each other. For isotropic materials, this is a result of the symmetry of the dispersion relation $[v_x(\mathbf{q}) = -v_x(-\mathbf{q})]$ and the fact that the equilibrium phonon occupation number $\langle n_{\mathbf{q},j} \rangle_0$ does not depend on the orientation of \mathbf{q} . Hence, we can rewrite³ equation (5.4.15) as:

$$j_{t,x} = \frac{1}{V} \sum_{\mathbf{q},j} \hbar \omega \left(\langle n \rangle - \langle n \rangle_0 \right) v_x.$$
(5.4.16)

A temporal change of the phonon occupation number of a certain phonon mode in a certain region of the crystal can result either from phonon diffusion or from phonon decay:

$$\frac{d\langle n\rangle}{dt} = \left.\frac{\partial\langle n\rangle}{\partial t}\right|_{\text{diff}} + \left.\frac{\partial\langle n\rangle}{\partial t}\right|_{\text{decay}}.$$
(5.4.17)

The diffusive term is related to the gradient of the temperature:

$$\frac{\partial \langle n \rangle}{\partial t} \Big|_{\text{diff}} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[\langle n(x - v_x \Delta t) \rangle - \langle n(x) \rangle \right] \\
= -v_x \frac{\partial \langle n \rangle}{\partial x} = -v_x \frac{\partial \langle n \rangle_0}{\partial T} \frac{\partial T}{\partial x}.$$
(5.4.18)

Here, we have assumed in the last step, that the phonons are in *l*ocal thermal equilibrium.

For the second term, we introduce a relaxation time ansatz:

$$\left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{decay}} = -\frac{\langle n \rangle - \langle n \rangle_0}{\tau}.$$
(5.4.19)

 2 Every current density can be written as density times the corresponding transport velocity. 3 Here, we drop the indices for the sake of brevity.

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In what follows, we consider a steady-state situation with $d\langle n \rangle/dt = 0$ in which the diffusive term exactly balances the decay term. Hence, we obtain:

$$j_{t,x} = -\frac{1}{V} \sum_{\mathbf{q},j} \hbar \omega_{\mathbf{q},j} \tau_{\mathbf{q},j} v_x^2 \frac{\partial \langle n_{\mathbf{q},j} \rangle}{\partial T} \frac{\partial T}{\partial x}.$$
(5.4.20)

For an isotropic material, we have

$$\langle v_x^2 \rangle = \frac{1}{3}v^2. \tag{5.4.21}$$

By comparison of (5.4.20) with (5.4.12), we can express the thermal conductivity of the lattice as

$$K = \frac{1}{3V} \sum_{\mathbf{q},j} v_{\mathbf{q},j} \Lambda_{\mathbf{q},j} \frac{\partial E(\omega_{\mathbf{q},j},T)}{\partial T}$$
(5.4.22)

with the phonon mean free path

$$\Lambda_{\mathbf{q},j} = v_{\mathbf{q},j} \,\tau_{\mathbf{q},j}.\tag{5.4.23}$$

Finally, we want to discuss the temperature dependence of the thermal conductivity. For this purpose, we assume that the group velocity as well as the phonon mean free path do not depend on the wave vector or the branch number:

$$v_{\mathbf{a}\,i} \approx \bar{v},$$
 (5.4.24)

$$\Lambda_{\mathbf{q},j} \approx \bar{\Lambda}. \tag{5.4.25}$$

With these assumptions, equation (5.4.22) simplifies to

$$K(T) = \frac{1}{3V} \bar{v} \bar{\Lambda}(T) C_V(T).$$
(5.4.26)

We can identify three different temperature regimes:

- Low temperature regime: U-processes are "frozen out" so that the mean free path becomes independent of temperature, $\bar{\Lambda} \neq \bar{\Lambda}(T)$. Hence, we expect that the thermal conductivity varies like the specific heat as $K \propto C_V(T) \propto T^3$.
- Intermediate temperature regime: Here, the temperature dependence of the thermal conductivity is governed by the onset of U-processes. The phonon-phonon scattering rate $1/\tau$ is proportional to the number of phonons with which a given phonon can interact,. For U-processes, the phonon energy must be larger than approximately $k_B\Theta_D/2$. Hence, we expect that the mean free path is proportional to $\Lambda \sim e^{\theta_d/2T} 1 \approx e^{\theta_d/2T}$.
- High temperature regime: For $T \gg \Theta_D$, the specific heat becomes constant and the thermal conductivity scales like the mean free path as $\Lambda(T) \propto 1/\langle n \rangle \propto 1/T$.

6 Free electrons in solids

In this chapter, we start with the the analysis of the electronic properties of solids. As a first step, we treat the conduction electrons in a metal as a gas of free electrons, which is confined to the solid by an infinite square well potential. The distribution of the electrons among the available one-electron states is governed by the so-called Fermi statistics.

6.1 Free electrons in a box

We initially consider the case of a single free electron in an infinite square well potential. The Schrödinger equation reads in that case:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) = E'\Psi(\mathbf{r}).$$
(6.1.1)

with

~

$$V(x, y, z) = \begin{cases} V_0 = \text{const} & \text{for} & 0 \le x, y, z, \le L \\ \infty & \text{otherwise} \end{cases}$$
(6.1.2)

With $E = E' - V_0$, equation (6.1.1) can be rewritten as:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \tag{6.1.3}$$

The infinite barriers at x, y, z = 0 and L confine the electron to the 'box':

$$\int_{\text{box}} |\Psi(x, y, z)|^2 \, dV = 1. \tag{6.1.4}$$

Furthermore, the infinite barriers give rise to the boundary condition $\Psi(\mathbf{r}) = 0$ for all points of the barrier. One can easily confirm, that the wave functions

$$\Psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z)$$
(6.1.5)

have all the required properties. The corresponding energy eigenvalues are, as expected, those of a free electron:

$$E = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right).$$
(6.1.6)

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Figure 6.1: First three wave functions of a free electron in a 1D square well potential of length L with infinite barrier height.

The boundary conditions restrict the components of the wave vector to the values:

$$k_j = \frac{\pi}{L} n_j, \ n_j = 1, 2, 3, \dots; j = x, x, z.$$
 (6.1.7)

Negative values of n_x, n_y, n_z can be discarded as they do not give rise to new solutions. Hence, we can assign to each state the k-space volume:

$$\Delta_k^3 = \left(\frac{\pi}{L}\right)^3. \tag{6.1.8}$$

Next, we calculate the density of electronic states. For this purpose, we proceed as in the case of phonons (see section 5.2). In three dimensions, the number of states with a wavevecor of magnitude between k and k + dk is given by:

$$dN_k = \frac{2}{8} \frac{4\pi k^2}{(\pi/L)^3} \, dk. \tag{6.1.9}$$

Here, a factor 2 has been introduced to account for the two possible orientations of the electron spin for each k-value and the factor 1/8 results from the fact that the components of the wavevector have to be positive [see equation (6.1.7)].

According to equation (6.1.6), the constant energy surface E(k) is a sphere. With

$$dE = \frac{\hbar^2 k}{m} dk \tag{6.1.10}$$

we find the number of states per volume $V = L^3$ with energy between E(k) and E(k)+dE:

$$\frac{dN_E}{V} = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} E^{1/2} dE.$$
(6.1.11)



Figure 6.2: Free electron gas in three dimensions at T = 0 K.

The density of states of a free electron gas in three dimensions is thus given by:

$$\mathcal{D}(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} E^{1/2}.$$
(6.1.12)

The electron density per unit volume can be calculated from

$$n = \int_{0}^{\infty} \mathcal{D}(E) f(E,T) dE.$$
(6.1.13)

Here, the distribution of the conduction electrons on the available states follows a temperature dependent distribution function f(E, T).

For the remainder of this section, we consider the case T = 0 K. In this case, the Pauli exclusion principle requires that f(E, T) is a step function with

$$f(E, T = 0 \,\mathrm{K}) = \begin{cases} 1 & \text{for } E \le E_F^0 \\ 0 & \text{for } E > E_F^0 \end{cases}$$
(6.1.14)

The energy E_F^0 , which separates at T = 0 K the occupied from the unoccupied states, is the so-called Fermi energy. Using equation (6.1.12) and (6.1.14), we can write the electron density per unit volume as

$$n = \int_{0}^{E_{F}^{0}} \frac{(2m)^{3/2}}{2\pi^{2}\hbar^{3}} E^{1/2} dE.$$
(6.1.15)

A simple calculation then yields:

$$E_F^0 = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{2/3}.$$
(6.1.16)

The Fermi wavevector k_F is the radius of the sphere of occupied states in **k**-space. According to equation (6.1.6), it is related to the Fermi energy by:

$$E_F^0 = \frac{\hbar^2 k_F^2}{2m}.$$
(6.1.17)

The comparison of the last two equations yields:

$$k_F = \left(3\pi^2 n\right)^{1/3}.$$
(6.1.18)

Next, we define the Fermi temperature T_F as:

$$T_F = \frac{E_F^0}{k_B}.$$
 (6.1.19)

For typical values of the electron density n in a metal, T_F is in the order of several 10^4 K. The total energy of the electron gas at T = 0 K in the 'box' with volume V is given by:

$$E_{\text{total}} = V \int_{0}^{E_{F}^{0}} \mathcal{D}(E) E \, dE = \frac{V(2m)^{3/2}}{2\pi^{2}\hbar^{3}} \int_{0}^{E_{F}^{0}} E^{3/2} \, dE = \frac{2}{5} \frac{V(2m)^{3/2}}{2\pi^{2}\hbar^{3}} (E_{F}^{0})^{5/2}. \quad (6.1.20)$$

Using equation (6.1.16), we can simplify the last equation to obtain

$$E_{\text{total}} = \frac{3}{5} N E_F^0, \tag{6.1.21}$$

where N = nV is the total number of electrons in the 'box'. The average kinetic energy of the electrons in the free electron gas is thus given by

$$E_{\rm av} = \frac{E_{\rm total}}{N} = \frac{3}{5} E_F^0. \tag{6.1.22}$$

6.2 Fermi surface of metals

The Fermi surface is the surface in **k**-space that separates the occupied from the unoccupied electronic states of a given crystal at T = 0 k. All the states at the Fermi surface are characterized by $E(\mathbf{k}) = E_F$. We will see later that the shape of the Fermi surface plays an import role in the context of transport phenomena. In this section, we investigate the Fermi surface of monovalent metals (alkali metals and noble metals). We start with the alkali metals, which crystallize in a body-centered cubic lattice. Many of the electronic properties of the alkalis can be traced back to the single electron in the outermost *s*-orbital. The other electrons form closed shells and are strongly bound to the nucleus. In a solid, each alkali atom contributes its one *s*-electron to the conduction band. Here, we treat these conduction electrons as a free electron gas with density

$$n = \frac{2}{a^3},\tag{6.2.1}$$

where a is the side of the conventional cubic unit cell of the bcc lattice¹.

The Fermi surface of a free electron gas has the form of a sphere with radius k_F . With the aid of equation (6.1.18), we find that

$$k_F = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \left(\frac{2\pi}{a}\right) = 0.620 \left(\frac{2\pi}{a}\right). \tag{6.2.2}$$

The reciprocal lattice of the bcc lattice is the fcc lattice. The shortest distance from the zone center to the border of the first Brillouin zone is the so-called ΓN direction with

$$|\Gamma N| = \frac{2\pi}{a} \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + 0^2} = 0.707 \left(\frac{2\pi}{a}\right).$$
(6.2.3)

Since the relation $k_F < |\Gamma N|$ holds, we see that the Fermi surface of the alkali metals is entirely contained within the first zone. Numerical calculations show that the Fermi surface of sodium is almost spherical and completely contained in the first zone (see Fig. 6.3, left hand side). This result justifies in retrospect our simplistic assumptions about the treatment of the conduction electrons as gas of free electrons.

In the case of the noble metals (copper, silver, gold), one has to take in addition to the electron in the outer s-orbital also the electrons in the lower-lying d-orbitals into account. Numerical calculations show that the Fermi surfaces of the noble metals are contained within the first zone and are in general closely related to the free electron case. However, exceptions can be found in the $\langle 111 \rangle$ directions, in which the Fermi surface touches the zone faces and forms necks (see Fig. 6.3, right hand side).

6.3 Fermi-Dirac statistics

In this section, we consider N electrons in thermal equilibrium at a finite temperature T. Our goal is to find the distribution function f(E, T) which governs the distribution of the electrons over the accessible states of the system.

¹The conventional cubic unit cell of the bcc lattice contains two lattice points.



Figure 6.3: Calculated Fermi surfaces of sodium (left hand side) and copper (right hand side). The black lines indicate the edges of the respective first Brillouin zone. Image source: http://www.phys.ufl.edu/fermisurface/.

The probability that the system is in a state with energy E is given by:

$$P_N(E) = \frac{e^{-E/k_B T}}{\sum_{\alpha} e^{-E_{\alpha}^N/k_B T}}.$$
(6.3.1)

Here, E_{α}^{N} is the energy of the α -th state of the N-electron system. The sum is over all possible states which are occupied with N-electrons and which are compatible with Pauli's exclusion principle².



Figure 6.4: Schematic representation of three different N-electron states (N=5). The red dots symbolize an occupied one-electron state.

The denominator is known as the partition function in statistical mechanics. It is related to the Helmholtz free energy, $F = \mathcal{U} - TS$ (where \mathcal{U} is the internal energy and S is the entropy) by

$$\sum_{\alpha} e^{-E_{\alpha}^{N}/k_{B}T} = e^{-F_{N}/k_{B}T} \tag{6.3.2}$$

²The N electrons must be filled in N different one-electron states.

Inserting (6.3.2) in (6.3.1) results in:

$$P_N(E) = e^{-(E - F_N)/k_B T} ag{6.3.3}$$

We can characterize a given N-electron state by listing the N one-electron levels which are occupied. The probability, that a particular one-electron state i is occupied, is denoted by f_i^N . We can calculate f_i^N by summing the probability of all N-electron states in which the *i*-th one-electron state is filled:

$$f_i^N = \sum_{\alpha} P_N(E_{\alpha}^N) \tag{6.3.4}$$

Since electrons obey Pauli's exclusion principle, we can write f_i^N also as one minus the probability that the *i*-th one electron state is empty:

$$f_i^N = 1 - \sum_{\gamma} P_N(E_{\gamma}^N).$$
 (6.3.5)

Here, the sum is over all N-electron states without an electron in the i-th one-electron state.

We can construct any N-electron state without an electron in the *i*-th one-electron state by starting with the corresponding N + 1-electron state in which all N one-electron states of the N-electron state plus the *i*-th one-electron state are filled and then remove the electron in the *i*-th one-electron state. The energy difference of the N-electron state and the N + 1-electron state which are related in that way is given by the energy of *i*-th one-electron state, \mathcal{E}_i . Based on this argument, we can rewrite equation (6.3.5) as:

$$f_i^N = 1 - \sum_{\alpha} P_N(E_{\alpha}^{N+1} - \mathcal{E}_i),$$
(6.3.6)

where the sum is over all N + 1-electron states in which the *i*-th one-electron state is occupied. With the help of equation (6.3.3), we can express the summand as

$$P_N(E_{\alpha}^{N+1} - \mathcal{E}_i) = e^{(\mathcal{E}_i - \mu)/k_B T} P_{N+1}(E_{\alpha}^{N+1}).$$
(6.3.7)

Here, we have introduced the chemical potential

$$\mu = F_{N+1} - F_N. \tag{6.3.8}$$

For T = 0 K, the chemical potential of the electrons equals the Fermi energy:

$$\mu(T = 0 \,\mathrm{K}) = E_F^0. \tag{6.3.9}$$

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For that reason, the notation "Fermi-level" and the symbol E_F are often used for the chemical potential of the conduction electrons. Substituting (6.3.7) into (6.3.6), we find:

$$f_{i}^{N} = 1 - e^{(\mathcal{E}_{i} - \mu)/k_{B}T} \sum_{\alpha} P_{N+1}(E_{\alpha}^{N+1}),$$

= $1 - e^{(\mathcal{E}_{i} - \mu)/k_{B}T} f_{i}^{N+1}.$ (6.3.10)

For large N, f_i^N and f_i^{N+1} are practically identical and we obtain the important result:

$$f_i^N = \frac{1}{e^{(\mathcal{E}_i - \mu)/k_B T} + 1}.$$
(6.3.11)

This function is known as the Fermi-Dirac distribution.



Figure 6.5: Fermi-Dirac distribution for three different temperatures.

The mean number of electrons in the *i*-th one-electron level is given by f_i^N . Thus, the total number of electrons N can be calculated as

$$N = \sum_{i} f_{i}^{N} = \sum_{i} \frac{1}{e^{(\mathcal{E}_{i} - \mu)/k_{B}T} + 1}.$$
(6.3.12)

We can use this relation to determine N as a function of temperature T and the chemical potential μ .

6.4 Sommerfeld expansion

In the following sections we will have to evaluate integrals of the form

$$I = \int_0^\infty H(E) \, f(E) \, dE,$$
(6.4.1)
where H(E) is a well behaved function of the energy E and f(E) is the Fermi-Dirac distribution

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}.$$
(6.4.2)

To evaluate these Integrals, we will use the so-called Sommerfeld expansion. By substituting

$$x = \frac{E - \mu}{k_B T},\tag{6.4.3}$$

we can rewrite I as

$$I = k_B T \int_{-\mu/k_B T}^{\infty} \frac{H(\mu + k_B T x)}{e^x + 1} \, dx.$$
(6.4.4)

Next, we divide the range of integration

$$I = I_1 + I_2 = k_B T \int_{-\mu/k_B T}^{0} \frac{H(\mu + k_B T x)}{e^x + 1} \, dx + k_B T \int_0^{\infty} \frac{H(\mu + k_B T x)}{e^x + 1} \, dx.$$
(6.4.5)

The first term can be rewritten as

$$I_1 = k_B T \int_{-\mu/k_B T}^{0} \frac{H(\mu + k_B T x)}{e^x + 1} \, dx = k_B T \int_{0}^{\mu/k_B T} \frac{H(\mu - k_B T x)}{e^{-x} + 1} \, dx. \tag{6.4.6}$$

With

$$\frac{1}{e^{-x}+1} = 1 - \frac{1}{e^x+1},\tag{6.4.7}$$

we obtain

$$I_1 = k_B T \int_0^{\mu/k_B T} H(\mu - k_B T x) \, dx - k_B T \int_0^{\mu/k_B T} \frac{H(\mu - k_B T x)}{e^x + 1} \, dx.$$
(6.4.8)

The integrand of the second term decreases rapidly with increasing x. We can thus set the upper limit of the second term to infinity. With this approximation the integral Ireads:

$$I \approx \int_0^{\mu} H(E) \, dE + k_B T \int_0^{\infty} \frac{H(\mu + k_B T x) - H(\mu - k_B T x)}{e^x + 1} \, dx.$$
(6.4.9)

The nominator in the second term can be approximated as

$$\Delta H(\mu) = H(\mu + k_B T x) - H(\mu - k_B T x) \approx 2k_B T x H'(\mu).$$
(6.4.10)

so that

$$I \approx \int_0^\mu H(E) \, dE + 2(k_B T)^2 H'(\mu) \int_0^\infty \frac{x}{e^x + 1} \, dx.$$
(6.4.11)

With

$$\int_0^\infty \frac{x}{e^x + 1} \, dx = \frac{\pi^2}{12} \tag{6.4.12}$$

we finally obtain

$$I \approx \int_0^{\mu} H(E) \, dE + \frac{\pi^2 (k_B T)^2}{6} H'(\mu). \tag{6.4.13}$$

6.5 Chemical potential of the free electron gas

The chemical potential is an important thermodynamic quantity that characterizes the energy required to add a particle of a certain species, e.g. an electron, to the system. It is related to the internal energy by the fundamental thermodynamic relation

$$d\mathcal{U} = TdS - pdV + \mu dN. \tag{6.5.1}$$

Here \mathcal{U} is the internal energy, T the temperature, S the entropy, μ the chemical potential, and N the particle number of the corresponding species.

At T = 0 K the chemical potential of the free electron gas is given by the Fermi energy E_F . To calculate the chemical potential for an arbitrary temperature T we use the fact that the electron number does not depended on T. The electron number N can be expressed as

$$N = V_c \int_0^\infty f(E,T) \mathcal{D}(E) dE.$$
(6.5.2)

Using the Sommerfeld expansion, we can rewrite this equation as

$$N \approx V_c \int_0^\mu \mathcal{D}(E) \, dE + V_c \left(k_B T\right)^2 \frac{\pi^2}{6} \left(\frac{d\mathcal{D}(E)}{dE}\right)_{E=\mu}.$$
(6.5.3)

With

$$\int_{0}^{\mu} \mathcal{D}(E) dE = \int_{0}^{E_F} \mathcal{D}(E) dE + \int_{E_F}^{\mu} \mathcal{D}(E) dE$$
$$\approx \int_{0}^{E_F} \mathcal{D}(E) dE + \mathcal{D}(E_F)(\mu - E_F), \qquad (6.5.4)$$

we obtain

$$N = V_c \int_{0}^{E_F} \mathcal{D}(E) dE + V_c \left[\mathcal{D}(E_F)(\mu - E_F) + (k_B T)^2 \frac{\pi^2}{6} \left(\frac{d\mathcal{D}(E)}{dE} \right)_{E=\mu} \right]$$

= $N(T = 0 \text{ K}) + \tilde{N}.$ (6.5.5)

The condition that the number of electrons is independent from the temperature implies that

$$\tilde{N} = 0 = \left[\mathcal{D}(E_F)(\mu - E_F) + (k_B T)^2 \frac{\pi^2}{6} \left(\frac{d\mathcal{D}(E)}{dE} \right)_{E=\mu} \right].$$
(6.5.6)

Solving for μ , we obtain

$$\mu(T) = E_F - (k_B T)^2 \frac{\pi^2}{6} \frac{\left(\frac{d\mathcal{D}(E)}{dE}\right)_{E=\mu}}{\mathcal{D}(E_F)}.$$
(6.5.7)

For a 3D electron gas with $\mathcal{D}(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} E^{1/2}$, the chemical potential reads

$$\mu(T) = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right].$$
(6.5.8)

As already stated above, the Fermi temperature T_F of a typical metal is several 10000 K. Hence, the ratio T/T_F is small under most experimental conditions and we can approximate the chemical potential by the Fermi energy (see Figure 6.6).



Figure 6.6: Chemical potential of the free electron gas as a function of temperature.

6.6 Specific heat capacity of metals

In this section we calculate the contribution of the conduction electrons to the specific heat capacity of a metal. For this purpose, we start with the internal energy of the conduction electrons:

$$\mathcal{U}(T) = V_c \int_0^\infty E f(E, T) \mathcal{D}(E) dE$$
(6.6.1)

with the Fermi-Dirac distribution

$$f(E,T) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$
(6.6.2)

6 Free electrons in solids

and the density of states of a 3D free electron gas

$$\mathcal{D}(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{E}.$$
(6.6.3)

Using the Sommerfeld expansion, we obtain

$$\mathcal{U}(T) \approx V_{c} \int_{0}^{\mu} E \mathcal{D}(E) dE + V_{c} (k_{B}T)^{2} \frac{\pi^{2}}{6} \left(\frac{d [E \mathcal{D}(E)]}{dE} \right)_{E=\mu} \\
\approx V_{c} \int_{0}^{E_{F}} E \mathcal{D}(E) dE + V_{c} \int_{E_{F}}^{\mu} E \mathcal{D}(E) dE + V_{c} (k_{B}T)^{2} \frac{\pi^{2}}{6} \left[E_{F} \frac{d \mathcal{D}(E_{F})}{dE} + \mathcal{D}(E_{F}) \right] \\
\approx \mathcal{U}(T=0) + V_{c} E_{F} \mathcal{D}(E_{F}) (\mu - E_{F}) + V_{c} (k_{B}T)^{2} \frac{\pi^{2}}{6} \left[E_{F} \frac{d \mathcal{D}(E_{F})}{dE} + \mathcal{D}(E_{F}) \right] \\
\approx \mathcal{U}(T=0) + V_{c} E_{F} \underbrace{\left[\mathcal{D}(E_{F}) (\mu - E_{F}) + (k_{B}T)^{2} \frac{\pi^{2}}{6} \frac{d \mathcal{D}(E_{F})}{dE} \right]}_{\tilde{N}=0} + V_{c} (k_{B}T)^{2} \frac{\pi^{2}}{6} \mathcal{D}(E_{F})} \\
\approx \mathcal{U}(T=0) + V_{c} (k_{B}T)^{2} \frac{\pi^{2}}{6} \mathcal{D}(E_{F}).$$
(6.6.4)

The specific heat capacity is defined as the derivative of the internal energy with respect to temperature:

$$C_V = \frac{\partial \mathcal{U}}{\partial T} = V_c k_B^2 T \frac{\pi^2}{3} \mathcal{D}(E_F).$$
(6.6.5)

In the limit $T \ll T_F$, the electron density of a 3D free electron gas is given by

$$\frac{N}{V_c} = \frac{2}{3}\mathcal{D}(E_F)E_F.$$
(6.6.6)

With this result, we can express the contribution of the conduction electrons to the specific heat capacity as:

$$C_V = \frac{\pi^2}{2} N k_B^2 \frac{T}{E_F} = \frac{\pi^2}{2} N k_B \frac{T}{T_F} = \gamma T.$$
(6.6.7)

At low temperatures $(T \ll \Theta_D, T_F)$, the total specific heat capacity of a metal can be expressed as the sum of the electron and lattice contribution:

$$c_V = \gamma T + \beta T^3. \tag{6.6.8}$$

Here, γ and β are material specific constants.

6.7 Electrostatic screening in a Fermi gas

Next, we address the effect of an additional electric point charge which is placed inside the metal. The point charge produces a potential $\delta U(\mathbf{r})$ which acts as a local perturbation of the otherwise constant potential V_0 inside of the metal. In thermodynamic equilibrium, the Fermi-level must be constant throughout the metal. To guarantee this property, the electron density in the vicinity of the point charge must change compared to case without the additional point charge by

$$\delta n(\mathbf{r}) = \mathcal{D}(E_F) |e| \delta U(\mathbf{r}). \tag{6.7.1}$$

Here, we have assumed that $|e\delta U| \ll E_F$.



Figure 6.7: Redistribution of electrons due to a local pertubation potential δU .

In vacuum, the potential of a point charge is given by the Coulomb potential. However, the redistribution of the electrons results in a screening of the potential $\delta U(\mathbf{r})$. The change in the local electron concentration $\delta n(\mathbf{r})$ causes a space charge density which is related to the perturbation potential $\delta U(\mathbf{r})$ via the Poisson equation:

$$\nabla^2(\delta U(\mathbf{r})) = \frac{e}{\epsilon_0} \delta n(\mathbf{r}) = \frac{e^2}{\epsilon_0} \mathcal{D}(E_F) \delta U(\mathbf{r}).$$
(6.7.2)

The Yukawa potential is a solution of this differential equation in spherical coordinates:

$$\delta U(r) = \frac{ae^{-\lambda r}}{r},\tag{6.7.3}$$

where

$$\lambda = \sqrt{e^2 \mathcal{D}(E_F)/\epsilon_0}.$$
(6.7.4)

The quantity $r_{\rm TF} = 1/\lambda$ is known as the Thomas-Fermi screening length:

$$r_{\rm TF} = \sqrt{\frac{\epsilon_0}{e^2 \mathcal{D}(E_F)}} \tag{6.7.5}$$

For a free electron gas with carrier density n, one obtains:

$$r_{\rm TF} \approx 0.5 \left(\frac{a_0^3}{n}\right)^{1/6} \tag{6.7.6}$$

with the Bohr radius $a_0 = 4\pi h^2 \epsilon_0 / (me^2)$.

Example - Screening in gold

- Density of conduction electrons in gold: $n = 5.9 \times 10^{28} / \text{m}^3$
- Bohr radius: $a_0 = 0.53 \times 10^{-10}$ m
- Thomas-Fermi screening length : $r_{\rm TF} = 0.58 \times 10^{-10} {\rm m}.$

Fig. 6.8 shows, that the screened potential $\delta U(r)$ falls off much faster than the bare Coulomb potential. Hence, the electric field of a defect is only "visible" within a distance in the order of the Thomas-Fermi screening length.

6.8 Low dimensional electron gases

In the following we consider the case that the motion of the electrons is tightly confined by a potential V in one or two dimensions. This so-called quantum confinement results in the formation of a set of sub bands for the electrons. Low dimensional electron gases play an important role in modern semiconductor physics and technology.

6.8.1 Two-dimensional electron gas

As a first example, we consider an electron gas whose motion is restricted in z-direction by infinitely high potential barriers at $z = \pm \frac{L}{2}$. The allowed electron states $\Psi(\mathbf{r})$ are



Figure 6.8: Unscreened (red) and screened (blue) Coulomb potential for a positive unit charge in a gas of free electrons.

solutions of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(z)\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$
(6.8.1)

with the potential

$$V(z) = \begin{cases} 0 & \text{for } -\frac{L}{2} \le z \le \frac{L}{2} \\ \infty & \text{for } |z| > \frac{L}{2} \end{cases}$$
(6.8.2)

Substitution of the ansatz

$$\Psi(\mathbf{r}) = \phi_n(z) e^{i(k_x x + k_y y)} = \phi_n(z) e^{i\mathbf{k}_{||} \cdot \mathbf{r}}$$
(6.8.3)

into the Schrödinger equation (6.8.1) leads to two independent equations:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right]e^{i\mathbf{k}_{||}\cdot\mathbf{r}} = E_{||}e^{i\mathbf{k}_{||}\cdot\mathbf{r}}, \qquad (6.8.4)$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V(z)\right]\phi_n(z) = e_n\phi_n(z).$$
(6.8.5)

Equation (6.8.4) describes the free motion of the electron in the xy-plane. The corresponding energy eigenvalues are

$$E_{||}(\mathbf{k}_{||}) = \frac{\hbar^2 |\mathbf{k}_{||}|^2}{2m}.$$
(6.8.6)

The one-dimensional Schrödinger equation (6.8.5) is that of a particle in a box. The known eigenfunctions have the form

$$\phi_n(z) = \sqrt{\frac{2}{L}} \sin\left[\frac{\pi n}{L}\left(z + \frac{L}{2}\right)\right] \tag{6.8.7}$$

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and the corresponding energy eigenvalues are

$$e_n = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} n^2. \tag{6.8.8}$$

The total energy of the electron is thus given by

$$E(\mathbf{k}_{||},n) = E_{||}(\mathbf{k}_{||}) + e_n = \frac{\hbar^2 |\mathbf{k}_{||}|^2}{2m} + \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} n^2.$$
(6.8.9)

For further analysis, it is convenient to group these energy levels into 2D sub bands, which exhibit a parabolic behavior as a function of the in-plane wave number $|\mathbf{k}_{||}|$. Each sub band is characterized by a designated value of the quantum number n and attains the minimum value $E(0, n) = e_n$ for $\mathbf{k}_{||} = 0$.

The density of states of the n-th sub band is given by:

$$\mathcal{D}_{n}^{(2D)}(E) = \begin{cases} 0 & \text{for } E < e_{n} \\ \frac{1}{2\pi} \frac{2m}{\hbar^{2}} = \text{const} & \text{for } E \ge e_{n} \end{cases}$$
(6.8.10)

Proof: Exercise.

The total density of states is calculated as the sum of the densities of states of all sub bands:

$$\mathcal{D}(E) = \sum_{n} \mathcal{D}_{n}^{(2D)}(E). \tag{6.8.11}$$



Figure 6.9: Left: Sub bands of a two dimensional electron gas. Right: Density of states.

6.8.2 One-dimensional electron gas

Next, we consider the case that the motion of the electrons is tightly confined in two dimensions, e.g., the y-direction and the z-direction. In this way we retain a so-called quantum wire. The corresponding energy eigenvalues are given by:

$$E(k_x, n_y, n_z) = \frac{\hbar^2 k_x^2}{2m} + e_{n_y, n_z} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2}{2m} \frac{\pi^2}{L_y^2} n_y^2 + \frac{\hbar^2}{2m} \frac{\pi^2}{L_z^2} n_z^2, \qquad (6.8.12)$$

where L_y and L_z are the separations of the potential barriers in y- and z-direction, respectively. The energy levels can be grouped into 1D sub bands with parabolic profile. Each sub band is characterized by the two quantum numbers n_y and n_z .

The density of states of a 1D sub band can be calculated to be

$$\mathcal{D}_{n_{y},n_{z}}^{(1D)}(E) = \begin{cases} 0 & \text{for } E < e_{n_{y},n_{z}} \\ \frac{1}{2\pi} \left(\frac{2m}{\hbar^{2}}\right)^{\frac{1}{2}} \left(E - e_{n_{y},n_{z}}\right)^{-\frac{1}{2}} & \text{for } E \ge e_{n_{y},n_{z}} \end{cases}$$
(6.8.13)

Proof: Exercise.

The total density of states is given by the sum of the densities of states of all sub bands:

$$\mathcal{D}(E) = \sum_{n_y, n_z} \mathcal{D}_{n_y, n_z}^{(1D)}(E).$$
(6.8.14)



Figure 6.10: Left: Sub bands of a one dimensional electron gas. Right: Density of states.

7 Electronic band structure

In the previous chapter, we considered the properties of free electrons in a square-well potential. Despite of its extreme simplicity, the model allowed us to derive a number of important features of metals, e.g., the specific heat capacity of the electron gas. In this chapter, we will investigate the effect of a periodic potential on the electrons in a crystal. We will again restrict ourselves to the one electron approximation, i.e., all electron-electron interactions are neglected that can not be expressed in terms of a local potential for the single electron under consideration.

7.1 Bloch's Theorem

Consider the Schrödinger equation for a single electron subjected to a periodic potential:

$$H\Psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$
(7.1.1)

with

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}), \, \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3.$$
(7.1.2)

Bloch's theorem states (proof: see below) that the corresponding solutions can be written as the product of a plane wave and a lattice periodic function:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}},\tag{7.1.3}$$

with

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}). \tag{7.1.4}$$

The wavefunctions $\Psi_{\mathbf{k}}(\mathbf{r})$ are often called Bloch waves or Bloch functions.

Since the Bloch functions $\Psi_{\mathbf{k}}(\mathbf{r})$ are eigenfunctions of the Hamilton operator, they form a complete set of orthogonal functions. Hereafter, we assume that the normalization is chosen such that

$$\int \Psi_{\mathbf{k}'}^*(\mathbf{r})\Psi_{\mathbf{k}}(\mathbf{r})dV = \delta_{\mathbf{k}',\mathbf{k}}.$$
(7.1.5)

In the following two sections, we will present two different derivations of Bloch's theorem.

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Figure 7.1: A Bloch wave $\Psi_{\mathbf{k}}(\mathbf{r})$ (bottom) can be expressed as the product of a lattice periodic function $u(\mathbf{r})$ (top) and a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ (middle).

7.1.1 First Proof of Bloch's theorem

In the first step, we introduce the translation operator $\mathcal{T}_{\mathbf{R}}$ that shifts the argument of any function $f(\mathbf{r})$ by a lattice vector \mathbf{R} :

$$\mathcal{T}_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}). \tag{7.1.6}$$

Because the potential $V(\mathbf{r})$ exhibits the periodicity of the lattice, the Hamiltonian H and the translation operator $\mathcal{T}_{\mathbf{R}}$ commute:

$$[H, \mathcal{T}_{\mathbf{R}}] = 0. \tag{7.1.7}$$

Moreover, the translation operator $\mathcal{T}_{\mathbf{R}}$ commutes with any other translation operator. Hence, we can find a simultaneous eigenbasis of the Hamilton operator and the set of translation operators which shift the argument of a function by a lattice vector. For example, assume that $\Psi(\mathbf{r})$ is an eigenfunction of the Hamiltonian H. Applying $\mathcal{T}_{\mathbf{R}}$ to $\Psi(\mathbf{r})$ creates another eigenfunction of H with the same eigenvalue E:

$$H\left[\mathcal{T}_{\mathbf{R}}\Psi(\mathbf{r})\right] = \mathcal{T}_{\mathbf{R}}\left[H\Psi(\mathbf{r})\right] = \mathcal{T}_{\mathbf{R}}\left[E\Psi(\mathbf{r})\right] = E\left[\mathcal{T}_{\mathbf{R}}\Psi(\mathbf{r})\right].$$
(7.1.8)

Let $\Psi(\mathbf{r})$ be a common eigenfunction of the Hamilton operator

$$H\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{7.1.9}$$

and the set of translation operators

$$\mathcal{T}_{\mathbf{R}}\Psi(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{R}) = f(\mathbf{R})\Psi(\mathbf{r}).$$
(7.1.10)

The last equation holds for every lattice vector \mathbf{R} . Hence, for $\mathbf{R} = \mathbf{R}_1 + \mathbf{R}_2$, we find:

$$\Psi(\mathbf{r} + \mathbf{R}_1 + \mathbf{R}_2) = f(\mathbf{R}_1 + \mathbf{R}_2)\Psi(\mathbf{r}).$$
(7.1.11)

Since $\Psi(\mathbf{r})$ is an eigenfunction of both $\mathcal{T}_{\mathbf{R}_1}$ and $\mathcal{T}_{\mathbf{R}_2}$, we obtain:

$$\Psi(\mathbf{r} + \mathbf{R}_1 + \mathbf{R}_2) = f(\mathbf{R}_1)\Psi(\mathbf{r} + \mathbf{R}_2) = f(\mathbf{R}_1)f(\mathbf{R}_2)\Psi(\mathbf{r}).$$
(7.1.12)

A comparison of equation (7.1.11) and (7.1.12) yields:

$$f(\mathbf{R}_1 + \mathbf{R}_2) = f(\mathbf{R}_1)f(\mathbf{R}_2).$$
(7.1.13)

This condition can be fulfilled for any two lattice vectors \mathbf{R}_1 and \mathbf{R}_2 by setting

$$f(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}.\tag{7.1.14}$$

Hence, the common eigenfunctions of the Hamilton operator and the set of translation operators satisfy the condition:

$$\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\Psi_{\mathbf{k}}(\mathbf{r}). \tag{7.1.15}$$

By writing $\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$, we can easily verify that equation (7.1.15) is equivalent to the Bloch theorem (7.1.3).

7.1.2 Second Proof of Bloch's theorem

According to equation (3.2.25), the periodic potential $V(\mathbf{r})$ can be expanded in a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}.$$
(7.1.16)

Furthermore, we can write the wavefunction $\Psi(\mathbf{r})$ as a superposition of plane waves

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}},\tag{7.1.17}$$

where the wavevectors \mathbf{k} must be compatible with the applied boundary conditions. Substituting the expansions of $\Psi(\mathbf{r})$ and $V(\mathbf{r})$ in the one electron Schrödinger equation (7.1.1) yields:

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{k}',\mathbf{G}} C_{\mathbf{k}'} V_{\mathbf{G}} e^{i(\mathbf{k}'+\mathbf{G})\cdot\mathbf{r}} = E \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}.$$
(7.1.18)

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With $\mathbf{k} = \mathbf{k}' + \mathbf{G}$, the last equation can be rewritten as:

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} V_{\mathbf{G}} \right] = 0$$
(7.1.19)

Since this equation must hold for any position \mathbf{r} , we obtain:

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} V_{\mathbf{G}} = 0.$$
(7.1.20)

Note that this set of equations only couples those expansion coefficients $C_{\mathbf{k}}$, whose \mathbf{k} -values differ by some reciprocal lattice vector \mathbf{G} . Hence, each \mathbf{k} -value within the first Brillouin zone leads to a different solution of the Schrödinger equation.

For a given **k**-value, we can restrict the set of expansion coefficients of $\Psi_{\mathbf{k}}(\mathbf{r})$ to $C_{\mathbf{k}}, C_{\mathbf{k}-\mathbf{G}}, C_{\mathbf{k}-\mathbf{G}'}, \ldots$ and rewrite equation (7.1.17) as

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = \underbrace{\sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}}_{u_{\mathbf{k}}(\mathbf{r})} e^{i\mathbf{k}\cdot\mathbf{r}} = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}.$$
(7.1.21)

The function $u_{\mathbf{k}}(\mathbf{r})$ is by construction a lattice periodic function. Hence, we have shown again that the solutions $\Psi_{\mathbf{k}}(\mathbf{r})$ of the Schrödinger equation (7.1.1) obey Bloch's theorem.

With the help of equation (7.1.21), it is easy to verify that the Bloch wave $\Psi_{\mathbf{k}}(\mathbf{r})$ is a periodic function in reciprocal space:

$$\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \sum_{\mathbf{G}'} C_{\mathbf{k}+\mathbf{G}-\mathbf{G}'} e^{-\imath \mathbf{G}' \cdot \mathbf{r}} e^{\imath (\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$$
$$= \left(\sum_{\mathbf{G}''} C_{\mathbf{k}-\mathbf{G}''} e^{-\imath \mathbf{G}'' \cdot \mathbf{r}} \right) e^{\imath \mathbf{k} \cdot \mathbf{r}} = \Psi_{\mathbf{k}}(\mathbf{r}).$$
(7.1.22)

Substituting $\Psi_{\mathbf{k}}(\mathbf{r})$ and $\Psi_{\mathbf{k}+\mathbf{G}}$ in the Schrödinger equation yields

$$H\Psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\Psi_{\mathbf{k}}(\mathbf{r}) \tag{7.1.23}$$

and

$$H\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = E(\mathbf{k}+\mathbf{G})\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}), \qquad (7.1.24)$$

respectively. With $\Psi_{\mathbf{k}}(\mathbf{r}) = \Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$, the last equation can be rewritten as:

$$H\Psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k} + \mathbf{G})\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}).$$
(7.1.25)

A comparison of (7.1.23) and (7.1.25) finally yields:

$$E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G}). \tag{7.1.26}$$

Hence, the energy eigenvalue $E(\mathbf{k})$ of the Bloch wave $\Psi_{\mathbf{k}}(\mathbf{r})$ is a periodic function in reciprocal space.

7.1.3 Wannier functions

So far, we have considered Bloch waves $\Psi_{\mathbf{k}}(\mathbf{r})$ as functions in real space and \mathbf{k} was treated as an index that characterizes the respective Bloch wave. However, equation (7.1.22) suggests that we can also consider Bloch waves as functions $\Psi(\mathbf{k}, \mathbf{r})$ in reciprocal space. For this purpose, we expand $\Psi(\mathbf{k}, \mathbf{r})$ in a Fourier series:

$$\Psi(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} c_{\mathbf{R}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{R}}.$$
(7.1.27)

Here, the summation is taken over all lattice vectors \mathbf{R} and N is the number of unit cells in the crystal. Since \mathbf{k} can only assume discrete values, the expansion coefficients $c_{\mathbf{R}}(\mathbf{r})$ can be written as

$$c_{\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \Psi(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} = w(\mathbf{r}-\mathbf{R}).$$
(7.1.28)

Here, we have introduced in the last step the Wannier functions $w(\mathbf{r} - \mathbf{R})$. The Bloch waves can be written in terms of the Wannier functions as

$$\Psi(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}.$$
(7.1.29)

The Wannier functions tend to be localized around the lattice points. Moreover, they form a complete set of orthogonal functions (proof: exercise). The combination of these two properties make Wannier functions useful for the theoretical description of phenomena in which the spatial localization of electrons plays an important role (see e.g. section 7.3).

7.1.4 Crystal momentum

Consider a Bloch wave $\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$ with wave vector \mathbf{k} . In analogy to a free electron, one could be tempted to identify $\hbar\mathbf{k}$ as the momentum of the crystal electron. However, it is easy to show that $\Psi_{\mathbf{k}}(\mathbf{r})$ is not an eigenfunction of the momentum operator:

$$\hat{\mathbf{p}}\Psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar}{\imath} \nabla \left(u_{\mathbf{k}}(\mathbf{r}) e^{\imath \mathbf{k} \cdot \mathbf{r}} \right) = \hbar \mathbf{k} \Psi_{\mathbf{k}}(\mathbf{r}) + \frac{\hbar}{\imath} e^{\imath \mathbf{k} \cdot \mathbf{r}} \nabla u_{\mathbf{k}}(\mathbf{r}) \neq \text{const} \Psi_{\mathbf{k}}(\mathbf{r}).$$
(7.1.30)

Hence, $\hbar \mathbf{k}$ is not the "real" momentum of the crystal electron but has to be rather considered as a generalized momentum. For that reason, $\hbar \mathbf{k}$ is usually called crystal momentum. We will see in the next chapter that the crystal momentum plays an important role in the context of the semi-classical transport theory.

7.2 Quasi-free electrons

In this section we consider the effect of a weak periodic potential on the conduction electrons. We start with a discussion of the so-called empty lattice approximation. Here, we assume that all the Fourier coefficients $V_{\mathbf{G}}$ vanish but require nonetheless that the condition $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$ is fulfilled, i.e., we take the periodicity of the lattice into account. The dispersion relation of the conduction electrons in the empty lattice approximation reads:

$$E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G}) = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2.$$
(7.2.1)

The corresponding wavefunctions are plane waves:

$$\Psi_{\mathbf{k}} \sim e^{i\mathbf{k}\cdot\mathbf{r}}.\tag{7.2.2}$$



Figure 7.2: Dispersion relation of a conduction electron for a one dimensional empty lattice.

For simplicity reasons, we first consider the case of an one dimensional empty lattice with period a. According to condition (7.2.1), the parabolic energy curve of a conduction electron is repeated in reciprocal space with period $G = 2\pi/a$ [see Fig. 7.2]. Because of the periodicity of the problem, we can restrict the dispersion relation to the first Brillouin zone $(-\pi/a \le k \le \pi/a)$. Here, we find for every k value an infinite number of energy eigenvalues $E_n(k)$ with

$$E_n(k) = \frac{\hbar^2}{2m} \left(k + n \frac{2\pi}{a} \right)^2; n = 0, \pm 1, \pm 2, \dots$$
(7.2.3)

The set of energy levels $E_n(k)$ with the same value of n is called the n-th energy band.

In three dimensions, the dispersion relation of a conduction electron in the empty lattice approximation reads:

$$E_n(\mathbf{k}) = \frac{\hbar^2}{2m} \left(\mathbf{k} + \mathbf{G}\right)^2 = \frac{\hbar^2}{2m} \left[(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2 \right].$$
 (7.2.4)

Figure 7.3 exemplifies the dispersion relation of a conduction electron in an empty fcclattice. The large number of bands results from folding back of the dispersion relation to the first Brillouin zone along different directions.



Figure 7.3: Left: 1st Brillouin zone of the fcc lattice with high symmetry points. Right: Dispersion relation of a conduction electron for an empty fcc lattice. (Adopted from Wikipedia)

Next, we want to discuss qualitatively the effect of a small but finite periodic potential. For this purpose, we switch back to the one dimensional case. According to Fig. 7.2, the two dispersion curves E(k) and E(k-G) intersect at the boundary of the first Brillouin zone. To a first approximation, the states of the electron at the intersection point $k = \pi/a$ can be thus described by the superposition of a forward propagating wave and a counterpropagating Bragg-reflected wave $(e^{iG/2} \text{ and } e^{-iG/2})$. The relative phases of the plane waves have to be chosen such that the resulting standing waves are compatible with the symmetry of the lattice:

$$\Psi_{+} \sim \left(e^{iGx/2} + e^{-iGx/2}\right) \sim \cos\left(\pi \frac{x}{a}\right)$$
(7.2.5)

$$\Psi_{-} \sim \left(e^{iGx/2} - e^{-iGx/2}\right) \sim \sin\left(\pi\frac{x}{a}\right)$$
(7.2.6)

The probability density $|\Psi_+|^2$ has maxima at the positions of the positive cores ($R_m = ma; m = 0, \pm 1 \pm 2, \ldots$) and minima in between. The opposite is true for the probability density $|\Psi_-|^2$ [see Fig. 7.4 (a)]. Hence, an electron in the state Ψ_+ interacts stronger with the positive cores as compared to an electron in state Ψ_- . Consequently, the energies of the two states are different. In the dispersion relation, the two states are separated by a band gap, i.e., an energy interval for which no solutions of the Schrödinger equation exists [see Fig. 7.4 (b)].



Figure 7.4: (a) Probability density distributions of the electron states at the boundary of the first Brillouin zone. (b) Dispersion relation of a conduction electron for a one dimensional lattice with a weak potential.

After this qualitative discussion, we derive the magnitude of the band gap in a formal calculation. For this purpose, we start with equation (7.1.20):

$$\left(E - \frac{\hbar^2 |\mathbf{k} - \mathbf{G}|^2}{2m}\right) C_{\mathbf{k} - \mathbf{G}} = \sum_{\mathbf{G}''} C_{\mathbf{k} - \mathbf{G} - \mathbf{G}''} V_{\mathbf{G}''} = \sum_{\mathbf{G}'} C_{\mathbf{k} - \mathbf{G}'} V_{\mathbf{G}' - \mathbf{G}}$$
(7.2.7)

Solving for $C_{\mathbf{k}-\mathbf{G}}$, we obtain:

$$C_{\mathbf{k}-\mathbf{G}} = \frac{\sum_{\mathbf{G}'} C_{\mathbf{k}-\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}}}{E - \frac{\hbar^2 |\mathbf{k}-\mathbf{G}|^2}{2m}}.$$
(7.2.8)

In the following, we concentrate on the boundary of the first Brillouin zone. For weak potentials, we obtain an approximate solution for $C_{\mathbf{k}-\mathbf{G}}$, if we replace the true energy eigenvalue E by the energy of a free electron:

$$C_{\mathbf{k}-\mathbf{G}} \approx \frac{\sum_{\mathbf{G}'} C_{\mathbf{k}-\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}}}{\frac{\hbar^2}{2m} \left(|\mathbf{k}|^2 - |\mathbf{k}-\mathbf{G}|^2 \right)}.$$
(7.2.9)

We will only take the dominant expansion coefficients into account. Inspection of equation (7.2.9) shows that those expansion coefficients $C_{\mathbf{k}-\mathbf{G}}$ are particularly large, for which the condition

$$|\mathbf{k}|^2 \approx |\mathbf{k} - \mathbf{G}|^2 \tag{7.2.10}$$

is fulfilled. Hence, we can limit the expansion to the two coefficients $C_{\mathbf{k}}$ and $C_{\mathbf{k}-\mathbf{g}}$, where, **g** is a primitive translation vector of the reciprocal lattice.

With $V_0 = 0$, we obtain the following system of equations:

$$\left(E - \frac{\hbar^2}{2m}k^2\right)C_{\mathbf{k}} - V_{\mathbf{g}}C_{\mathbf{k}-\mathbf{g}} = 0$$
(7.2.11)

$$\left(E - \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{g}|^2\right) C_{\mathbf{k} - \mathbf{g}} - V_{-\mathbf{g}} C_{\mathbf{k}} = 0.$$
(7.2.12)

A non-trivial solution requires that the corresponding determinant vanishes:

$$\begin{vmatrix} \left(\frac{\hbar^2}{2m}k^2 - E\right) & V_{\mathbf{g}} \\ V_{-\mathbf{g}} & \left(\frac{\hbar^2}{2m}|\mathbf{k} - \mathbf{g}|^2 - E\right) \end{vmatrix} = 0.$$
(7.2.13)

With

$$E_{\mathbf{k}-\mathbf{g}}^{0} = \frac{\hbar^{2}}{2m} |\mathbf{k} - \mathbf{g}|^{2}$$
(7.2.14)

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we obtain after a short calculation two solutions with the energies

$$E^{\pm} = \frac{1}{2} \left(E^{0}_{\mathbf{k}-\mathbf{g}} + E^{0}_{\mathbf{k}} \right) \pm \sqrt{\frac{1}{4} \left(E^{0}_{\mathbf{k}-\mathbf{g}} - E^{0}_{\mathbf{k}} \right)^{2} + |V_{\mathbf{g}}|^{2}}$$
(7.2.15)

Here, we have used that the potential is real and hence $V_{-\mathbf{g}} = V_{\mathbf{g}}^*$. At the zone boundary, the band gap has a value

$$\Delta E = E^+ - E^- = 2|V_{\mathbf{g}}|. \tag{7.2.16}$$

7.3 Tight binding approximation

In this section, we turn our attention to the strongly bound core electrons and discuss the effect of atom-atom interaction on the core electronic states. Our starting point is the Schrödinger-equation for an isolated atom at the position \mathbf{R}_n :

$$H_A(\mathbf{r} - \mathbf{R}_n)\Phi_i(\mathbf{r} - \mathbf{R}_n) = E_i\Phi_i(\mathbf{r} - \mathbf{R}_n).$$
(7.3.1)

Here, H_A is the atomic Hamiltonian. Φ_i and E_i are the corresponding eigenfunction and energy eigenvalue, respectively, of the *i*th atomic state. In what follows, we assume that Φ_i and E_i are known.

The Hamiltonian for an electron in the crystal can be expressed as:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_l V_A(\mathbf{r} - \mathbf{R}_l).$$
(7.3.2)

Here, the total potential is given by the superposition of the potentials of all atoms in the crystal.

In what follows, we take the *n*-th atom at the position \mathbf{R}_n as our reference. Then, we rewrite the crystal Hamiltonian as the sum of the atomic Hamiltonian $H_A(\mathbf{r} - \mathbf{R}_n)$ and a perturbation potential $v(\mathbf{r} - \mathbf{R}_n)$:

$$H(\mathbf{r} - \mathbf{R}_n) = H_A(\mathbf{r} - \mathbf{R}_n) + v(\mathbf{r} - \mathbf{R}_n) = -\frac{\hbar^2}{2m}\nabla^2 + V_A(\mathbf{r} - \mathbf{R}_n) + v(\mathbf{r} - \mathbf{R}_n).$$
 (7.3.3)

where the perturbation potential is given by the sum of the potentials of all atoms apart from the reference atom:

$$v(\mathbf{r} - \mathbf{R}_n) = \sum_{m \neq n} V_A(\mathbf{r} - \mathbf{R}_m).$$
(7.3.4)

Electronic states in the crystal are Bloch waves $\Psi_{\mathbf{k}}(\mathbf{r})$ and obey the Schrödinger equation

$$H\Psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\Psi_{\mathbf{k}}(\mathbf{r}). \tag{7.3.5}$$



Figure 7.5: The potential $V(\mathbf{r})$ of the crystal can be expressed as the sum of the atomic potential $V_A(\mathbf{r})$ and the perturbation potential $v(\mathbf{r})$.

The energy eigenvalues are given by

$$E(\mathbf{k}) = \frac{\langle \Psi_{\mathbf{k}} | H | \Psi_{\mathbf{k}} \rangle}{\langle \Psi_{\mathbf{k}} | \Psi_{\mathbf{k}} \rangle}$$
(7.3.6)

where

$$\langle \Psi_{\mathbf{k}} | \Psi_{\mathbf{k}} \rangle = \int \Psi_{\mathbf{k}}^{*}(\mathbf{r}) \Psi_{\mathbf{k}}(\mathbf{r}) \, d\mathbf{r} \quad \text{and} \quad \langle \Psi_{\mathbf{k}} | H | \Psi_{\mathbf{k}} \rangle = \int \Psi_{\mathbf{k}}^{*}(\mathbf{r}) H \Psi_{\mathbf{k}}(\mathbf{r}) \, d\mathbf{r}.$$
(7.3.7)

The exact eigenfunctions $\Psi_{\mathbf{k}}(\mathbf{r})$ of the crystal Hamiltonian are not known. However, we expect that an approximate solution $\Phi_{\mathbf{k}}(\mathbf{r})$ can be constructed from an appropriate linear combination of atomic eigenfunctions:

$$\Psi_{\mathbf{k}}(\mathbf{r}) \simeq \Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{n} a_{n} \Phi_{i}(\mathbf{r} - \mathbf{R}_{n}).$$
(7.3.8)

To determine the expansion coefficients a_n , we require that $\Phi_{\mathbf{k}}(\mathbf{r})$ is a Bloch wave. One can easily show that the ansatz

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}_{n}} \Phi_{i}(\mathbf{r} - \mathbf{R}_{n})$$
(7.3.9)

has all the required properties. A comparison of the last equation with equation (7.1.29) shows, that in this ansatz the Wannier functions $w(\mathbf{r}-\mathbf{R}_n)$ are approximated by the atomic

7 Electronic band structure

orbitals $\Phi_i(\mathbf{r} - \mathbf{R}_n)$. Next, we substitute $\Phi_k(\mathbf{r})$ in equation (7.3.6). The denominator then reads:

$$\langle \Phi_{\mathbf{k}} | \Phi_{\mathbf{k}} \rangle = \sum_{n,m} e^{i \mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} \int \Phi_i^* (\mathbf{r} - \mathbf{R}_m) \Phi_i (\mathbf{r} - \mathbf{R}_n) \, d\mathbf{r}.$$
(7.3.10)

For strongly localized electrons, the electronic wavefunctions of different atoms do hardly overlap. Hence, we can neglect all terms in which $\mathbf{R}_n \neq \mathbf{R}_m$ and obtain:

$$\langle \Phi_{\mathbf{k}} | \Phi_{\mathbf{k}} \rangle \simeq \sum_{n} \int \Phi_{i}^{*}(\mathbf{r} - \mathbf{R}_{n}) \Phi_{i}(\mathbf{r} - \mathbf{R}_{n}) d\mathbf{r} = N_{c},$$
 (7.3.11)

where N_C is the number of atoms in the crystal. An approximate solution of the energy eigenvalue is given by

$$E(\mathbf{k}) \simeq \frac{1}{N_c} \sum_{n,m} e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} \int \Phi_i^*(\mathbf{r} - \mathbf{R}_m) \left[H_A(\mathbf{r} - \mathbf{R}_n) + v(\mathbf{r} - \mathbf{R}_n) \right] \Phi_i(\mathbf{r} - \mathbf{R}_n) \, d\mathbf{r}.$$
(7.3.12)

With

$$A_{i} = -\int \Phi_{i}^{*}(\mathbf{r} - \mathbf{R}_{n})v(\mathbf{r} - \mathbf{R}_{n})\Phi_{i}(\mathbf{r} - \mathbf{R}_{n})\,d\mathbf{r}$$
(7.3.13)

and

$$B_{i,m} = -\int \Phi_i^*(\mathbf{r} - \mathbf{R}_m) v(\mathbf{r} - \mathbf{R}_n) \Phi_i(\mathbf{r} - \mathbf{R}_n) \, d\mathbf{r}, \qquad (7.3.14)$$

we can rewrite equation (7.3.12) as

$$E(\mathbf{k}) \simeq E_i - A_i - \sum_m e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} B_{i,m}.$$
(7.3.15)

Here, we have tacitly assumed that the overlap of wavefunctions from different atoms plays no role for the calculation of the atomic energy eigenvalues E_i .

7.3.1 Band structure of a simple cubic crystal

The atom-atom interaction in a crystal has two effects on the energy eigenvalues. A_i describes the lowering of the atomic levels in a solid due to the potential of the neighboring atoms. The last term shows that the overlap of the wavefunctions causes a splitting up of the sharp atomic energy levels into an electronic band in a crystal. To further investigate the latter point, we consider in what follows a simple cubic crystal and atomic s-states. The atomic s-states posses spherical symmetry such that the coefficients $B_{i,m}$ only depend on the separation $|\mathbf{R}_n - \mathbf{R}_m|$. Furthermore, we assume that only nearest neighbors play a role in the evaluation of the last term of equation (7.3.15). With

$$\mathbf{R}_n - \mathbf{R}_m = (\pm a, 0, 0); (0, \pm a, 0); (0, 0, \pm a),$$
(7.3.16)

we obtain

$$E(\mathbf{k}) \simeq E_i - A_i - 2B_i \left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right].$$
(7.3.17)

The energy width of the electronic band is $12B_i$. It increases as the overlap between the relevant wavefunctions of neighboring atoms becomes larger. Consequently, bands which evolve from low lying and thus strongly localized atomic states are narrower than those band which originate from less tightly bound atomic states.



Figure 7.6: Formation of electronic bands in the tight-binding model.

7.3.2 Band structure of graphene

In this section, we consider the band structure of graphene as an example for the application of the tight-binding method to a crystal with a nontrivial basis. The corresponding crystal structure is depicted in Fig. 7.7. It consists of a two-dimensional triangular lattice with two carbon atoms per unit cell. Primitive translation vectors of the triangular lattice can be chosen as

$$\mathbf{a}_1 = \frac{a}{2} \left(\hat{\mathbf{e}}_x \sqrt{3} + \hat{\mathbf{e}}_y \right), \tag{7.3.18}$$

$$\mathbf{a}_2 = \frac{a}{2} \left(-\hat{\mathbf{e}}_x \sqrt{3} + \hat{\mathbf{e}}_y \right), \tag{7.3.19}$$

where a = 0.142 nm is the separation between two neighboring atoms. We select the center of the unit cell ($\mathbf{b}_1 = (0, 0)$) as the position of the first atom. The second atom is

displaced by

$$\mathbf{b}_2 = \frac{a}{2} \left(\frac{\hat{\mathbf{e}}_x}{\sqrt{3}} + \hat{\mathbf{e}}_y \right). \tag{7.3.20}$$

As in the case of a monoatomic basis, we construct an approximate solution $\Phi_{\mathbf{k}}(\mathbf{r})$ from a linear combination of atomic eigenfunctions that is compatible with Bloch's theorem:

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}_{n}} \left[c_{1}\Phi_{i,1}(\mathbf{r}-\mathbf{R}_{n}) + c_{2}\Phi_{i,2}(\mathbf{r}-\mathbf{b}_{2}-\mathbf{R}_{n}) \right].$$
(7.3.21)

Here, $\Phi_{i,1}(\mathbf{r})$ and $\Phi_{i,2}(\mathbf{r})$ are the atomic eigenfunction for the atomic energy eigenvalue E_i of the first and second atom, respectively, and c_1 and c_2 are constant coefficients. With this ansatz, the time-independent Schrödinger equation of the crystal reads

$$H\Phi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}_{n}} H \left[c_{1}\Phi_{i,1}(\mathbf{r}-\mathbf{R}_{n}) + c_{2}\Phi_{i,2}(\mathbf{r}-\mathbf{b}_{2}-\mathbf{R}_{n})\right]$$
$$= E(\mathbf{k})\sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}_{n}} \left[c_{1}\Phi_{i,1}(\mathbf{r}-\mathbf{R}_{n}) + c_{2}\Phi_{i,2}(\mathbf{r}-\mathbf{b}_{2}-\mathbf{R}_{n})\right]$$
(7.3.22)

Next, we calculate $\langle \Phi_{i,1} | H | \Phi_{\mathbf{k}} \rangle$:

$$\langle \Phi_{i,1} | H | \Phi_{\mathbf{k}} \rangle = c_1 \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}^*(\mathbf{r}) H \Phi_{i,1}(\mathbf{r} - \mathbf{R}) d\mathbf{r} + c_2 \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}^*(\mathbf{r}) H \Phi_{i,2}(\mathbf{r} - \mathbf{b}_2 - \mathbf{R}) d\mathbf{r} = c_1 E(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}(\mathbf{r}) \Phi_{i,1}(\mathbf{r} - \mathbf{R}) d\mathbf{r} + c_2 E(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}^*(\mathbf{r}) \Phi_{i,2}^*(\mathbf{r} - \mathbf{b}_2 - \mathbf{R}) d\mathbf{r}.$$
(7.3.23)

If only the overlap with the nearest neighbors gives rise to a significan contribution to the integrals, the last equation simplifies to

$$\langle \Phi_{i,1} | H | \Phi_{\mathbf{k}} \rangle = c_1 \int \Phi_{i,1}^*(\mathbf{r}) H \Phi_{i,1}(\mathbf{r}) \, d\mathbf{r} + c_1 \sum_{n.n} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}^*(\mathbf{r}) H \Phi_{i,1}(\mathbf{r} - \mathbf{R}) \, d\mathbf{r}$$

$$+ c_2 \sum_{n.n.} e^{i\mathbf{k}\cdot\mathbf{R}} \int \Phi_{i,1}^*(\mathbf{r}) H \Phi_{i,2}(\mathbf{r} - \mathbf{b}_2 - \mathbf{R}) \, d\mathbf{r}$$

$$= c_1 E(\mathbf{k}).$$

$$(7.3.24)$$

Here, the sums run over the lattice points closest to the origin. In the case of graphene, the nearest neighbors of the atom at the origin are located at \mathbf{b}_2 , at $\mathbf{b}_2 - \mathbf{a}_1$, and at



Figure 7.7: Left: Crystal structure of graphene. The nearest neighbors of the atom at the origin are marked by green dashed circles. Right: Band structure of graphene.

 $\mathbf{b}_2 - \mathbf{a}_1 - \mathbf{a}_2$ (see green dashed circles in Fig. 7.7). With this, we can rewrite equation (7.3.24) as

$$c_1 E_0 + c_2 U \left(1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot(\mathbf{a}_1 + \mathbf{a}_2)} \right) = c_1 E(\mathbf{k})$$
(7.3.25)

with

$$E_{0} = \int \Phi_{i,1}^{*}(\mathbf{r}) H \Phi_{i,1}(\mathbf{r}) d\mathbf{r}, \qquad (7.3.26)$$

$$U = \int \Phi_{i,1}^{*}(\mathbf{r}) H \Phi_{i,2}(\mathbf{r} - \mathbf{b}_{2}) d\mathbf{r}$$

$$= \int \Phi_{i,1}^{*}(\mathbf{r}) H \Phi_{i,2}(\mathbf{r} - \mathbf{b}_{2} + \mathbf{a}_{1}) d\mathbf{r}$$

$$= \int \Phi_{i,1}^{*}(\mathbf{r}) H \Phi_{i,2}(\mathbf{r} - \mathbf{b}_{2} + \mathbf{a}_{1} + \mathbf{a}_{2}) d\mathbf{r}. \qquad (7.3.27)$$

In an analogous calculation for $\langle \Phi_{i,2} | H | \Phi_{\mathbf{k}} \rangle$ we obtain

$$c_1 U \left(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot(\mathbf{a}_1 + \mathbf{a}_2)} \right) + c_2 E_0 = c_2 E(\mathbf{k}).$$
(7.3.28)

Equations (7.3.25) and (7.3.28) can be combined and written in matrix form as

$$\begin{pmatrix} E_0 & U\left(1+e^{-\imath\mathbf{k}\cdot\mathbf{a}_1}+e^{-\imath\mathbf{k}\cdot(\mathbf{a}_1+\mathbf{a}_2)}\right) \\ U\left(1+e^{\imath\mathbf{k}\cdot\mathbf{a}_1}+e^{\imath\mathbf{k}\cdot(\mathbf{a}_1+\mathbf{a}_2)}\right) & E_0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E(\mathbf{k}) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

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(7.3.29)

From this, we can easily calculate the energy eigenvalues

$$E(\mathbf{k}) = E_0 \pm U\sqrt{3 + 4\cos\left(\frac{k_x\sqrt{3}a}{2}\right)\cos\left(\frac{k_ya}{2}\right) + 2\cos\left(k_ya\right)}.$$
(7.3.30)

The corresponding band structure is depicted in Fig. 7.7. The overlap of the atomic orbitals results in the formation of two bands. For six points on the boundary of the first Brillouin zone the gap between the two bands closes and the energy dispersion in the vicinity of these k-points is approximately linear. The corresponding cone like structures are commonly denoted as Dirac cones and the touching points as Dirac points.

7.4 Metals, semiconductors, and insulators

We have seen in the previous section, that the sharp electronic states of isolated atoms evolve into electronic bands when the atoms are assembled in a crystal. In this process, no electronic states are lost or created. For example, the s- and p-states of an isolated atom can be each filled with 2 and 6 electrons, respectively. In a crystal with N_c atoms, the corresponding electronic bands can hold $2N_c$ and $6N_c$ electrons, respectively.

In the one-electron approximation at T = 0K, the electronic bands are filled with the available electrons from bottom to top according to the Pauli exclusion principle. The highest completely filled band is the so-called valence band. The lowest unoccupied or partially filled electronic band is the so-called conduction band.

- Materials with a partially filled conduction band are metals. For a metal, the Fermi level is located in the conduction band. The situation is particularly simple in the case of the monovalent metals, i.e., the alkali metals and the noble metals. For these elements, the conduction band evolves from an atomic s-state and is only half filled.
- In a semiconductor, the conduction band is empty and the valence band is completely filled. Hence, the Fermi level is in between these two bands. The so-called band gap between valence band and conduction band is smaller than 4 eV. Typical semiconductors are the group IV elements Si and Ge or the compound GaAs.
- Insulators exhibit by definition a band gap that is larger than 4 eV. Examples of insulators are diamond or NaCl.



Figure 7.8: Schematic band structures (Occupied states: blue. Empty states: white. CB: Conduction band. VB: Valence band. E_F : Fermi level. E_g : Band gap energy.)

7.5 Photoemission Spectroscopy

Photoemission spectroscopy is an important experimental method to investigate the band structure and the density of states of solid materials. It is based on the external photoeffect. The material under investigation is irradiated with UV or x-ray photons with photon energy $\hbar\omega$. Absorption of the photons results in the excitation of electrons from occupied states of the electronic band structure, i.e., states below the Fermi energy E_F to empty states of the quasi continuum of states above the vacuum level E_{vac} . Electrons which have been excited near the interface of the sample (typically within a few Å) can leave the the solid with a kinetic energy given by:

$$E_{kin} = \hbar\omega - \Phi - E_B,\tag{7.5.1}$$

where $\Phi = E_{vac} - E_F$ is the work function of the solid and E_B is the binding energy of the electrons relative to the Fermi level. These electrons are collected by an energy resolving detector. Since the photoexcitation probability of an electron depends only weakly on its binding energy, we can use the number of detected electrons with a certain kinetic energy to map the density of states at the corresponding binding energy (see Fig. 7.10).

7 Electronic band structure



Figure 7.9: Scheme of a photoemission spectroscopy setup. Image source: Wikipedia.



Figure 7.10: Principle of photoemission spectroscopy.

8 Electronic transport

8.1 Classical prelude

8.1.1 Drude model

We start our discussion of electronic transport in solids with the classical Drude model. This model was introduced to explain the conductivity of metals. It is based on the following assumptions:

- When metal atoms are brought together to form a solid, the weakly bound valence electrons become detached and are free to move in the solid. Each metal atom contributes Z electrons to these so-called conduction electrons. The nuclei and the tightly bound core electrons form the metallic ions.
- A conduction electron does not interact with other conduction electrons (independent electron approximation) or with the metallic ions (free electron approximation) between collisions.
- The mean time between successive collisions of a conduction electron is given by the relaxation time τ . Each collision results in an abrupt change of the velocity of the corresponding conduction electron.

In the absence of an external electric field, the conduction electrons perform an undirected thermal motion that results in a vanishing net current. By applying an external electric field $\boldsymbol{\varepsilon}$, the conduction electrons acquire an additional velocity component \mathbf{v} which is superimposed on the random thermal motion. This effect is described in the framework of the Drude model by the following classical equation of motion:

$$m\dot{\mathbf{v}} + \frac{1}{\tau}m\mathbf{v} = -e\boldsymbol{\mathcal{E}}(t). \tag{8.1.1}$$

Here, *m* is the electron mass and -e is the electron charge. In the following, we consider an AC field $\mathcal{E}(t) = \mathcal{E} e^{-i\omega t}$. Upon substitution of the ansatz

$$\mathbf{v}(t) = \tilde{\mathbf{v}}e^{-\imath\omega t}.\tag{8.1.2}$$

into equation (8.1.1) and solving for $\mathbf{v}(t)$, we obtain:

$$\mathbf{v}(t) = \frac{-e}{m} \frac{1}{\frac{1}{\tau} - \iota \omega} \,\mathcal{E}e^{-\iota \omega t}.$$
(8.1.3)

Next, we calculate the density of conduction electrons in the metal. Each mole of the metal contains $N_A = 6.022 \times 10^{23}$ atoms (Avogadro's number). The number of moles per cm^3 is given by ρ_m/A , where ρ_m is the mass density (in g/cm³) and A is the atomic mass (in atomic mass units¹) of a metal atom. The number of conduction electrons per cm³ is thus given by:

$$n = N_A \frac{Z\rho_m}{A}.$$
(8.1.4)

Example - Density of conduction electrons in gold,

- Number of valence electrons per gold atom: Z = 1.
- Mass density of gold: $\rho_m = 19.3 \,\mathrm{g/cm^3}$.
- Atomic mass of gold: A = 196, 97 u.
- Density of conduction electrons: $n = 5.9 \times 10^{22} / \text{cm}^3$.

The electric current density can be expressed as:

$$\mathbf{j} = -e\,n\,\mathbf{v}.\tag{8.1.5}$$

By inserting (8.1.3) in (8.1.5), we find:

$$\mathbf{j} = \frac{e^2 n}{m} \frac{1}{\frac{1}{\tau} - \imath \omega} \, \boldsymbol{\mathcal{E}} e^{-\imath \omega t}. \tag{8.1.6}$$

The factor of proportionality between the current density and the electric field is the AC-conductivity:

$$\sigma(\omega) = \frac{e^2 n}{m} \frac{1}{\frac{1}{\tau} - \iota \omega}.$$
(8.1.7)

The resistivity is defined as the inverse of the conductivity. For zero frequency, we obtain:

$$\rho_{\mathrm{D}C} = \frac{m}{\tau \, e^2 \, n}.\tag{8.1.8}$$

 $^{1}1u = g/mol$

We can use this equation to calculate the relaxation time τ :

$$\tau = \frac{m}{\rho_{\rm DC} \, e^2 \, n}.\tag{8.1.9}$$

Example - Relaxation time in gold

- Density of conduction electrons in gold: $n = 5.9 \times 10^{22} / \text{cm}^3$.
- DC-resistivity of gold: $\rho_{\rm DC} = 2.44 \times 10^{-8} \,\Omega\,{\rm m}$
- Electron mass: $m = 9.11 \times 10^{-31} \,\text{kg}$
- Electron charge: $q = 1.60 \times 10^{-19} \,\mathrm{C}$
- Relaxation time in gold: $\tau = 2.47 \times 10^{-14} \,\mathrm{s}$

It is instructive to consider the mean free path which is defined as the average distance that a conduction electron travels between two successive collisions:

$$\ell = \bar{v}\tau,\tag{8.1.10}$$

where \bar{v} is the average velocity of a conduction electron. The theorem of equipartion of energy provides a classical estimate of the average electron velocity:

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_BT.$$
(8.1.11)

Therefore, at room temperature, \bar{v} is in the order of 10^7 cm/s . Hence, the mean free path is in the order of a few Å which corresponds to typical interatomic distances. This agreement seems to suggest that the collisions are due to the electrons smashing into the metal ions. However, it turns out that this picture is wrong! The mean free path in carefully prepared samples at low temperatures can be in the order of centimeters! The flaws present in the classical treatment of electron conduction will be addressed below in the context of the Boltzmann transport theory.

8.1.2 Hall effect

In this section, we consider electronic transport under the combined influence of a static electric field and a static magnetic field. The corresponding classical equation of motion reads:

$$m\dot{\mathbf{v}}(t) + \frac{1}{\tau}m\mathbf{v}(t) = (-e)\left[\boldsymbol{\mathcal{E}} + \mathbf{v}(t) \times \boldsymbol{\mathcal{B}}\right].$$
(8.1.12)

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Under steady-state conditions ($\dot{\mathbf{v}} = 0$), the velocity is given by

$$\mathbf{v} = \frac{-e\tau}{m} \left[\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}} \right]. \tag{8.1.13}$$

In the following we consider the Hall bar geometry depicted in Fig. 8.1. We assume that the magnetic field is oriented along the z-axis. The Cartesian components of the velocity vector then read:

$$v_x = -\omega_c \tau \left(\frac{\mathcal{E}_x}{\mathcal{B}_z} + v_y\right) \tag{8.1.14}$$

$$v_y = -\omega_c \tau \left(\frac{\mathcal{E}_y}{\mathcal{B}_z} - v_x\right) \tag{8.1.15}$$

$$v_z = -\omega_c \tau \left(\frac{\mathcal{E}_z}{\mathcal{B}_z}\right) \tag{8.1.16}$$

with the cyclotron frequency

$$\omega_c = \frac{e\mathcal{B}_z}{m}.\tag{8.1.18}$$

The corresponding current density can be written as

$$\begin{pmatrix} j_x \\ j_y \\ j_z \end{pmatrix} = -\frac{\sigma_0}{1 + \omega_c^2 \tau^2} \begin{pmatrix} 1 & -\omega_c \tau & 0 \\ \omega_c \tau & 1 & 0 \\ 0 & 0 & 1 + \omega_c^2 \tau^2 \end{pmatrix} \begin{pmatrix} \mathcal{E}_x \\ \mathcal{E}_y \\ \mathcal{E}_z \end{pmatrix}$$
(8.1.19)

where

$$\sigma_0 = \frac{ne^2\tau}{m} \tag{8.1.20}$$

is the DC conductivity.

If the external electric field is applied along the x-axis, the moving electrons would be deflected under the influence of the magnetic field in negative y-direction. In steady state, this effect is however exactly compensated by an electric field \mathcal{E}_y that results from the surplus charges at the sides of the Hall bar (see Fig. 8.1). This is the so-called Hall effect and the field \mathcal{E}_y is the Hall field. The condition $j_y = 0$ implies:

$$\omega_c \tau \mathcal{E}_x + \mathcal{E}_y = 0. \tag{8.1.21}$$

Together with equation (8.1.19), we find

$$\mathcal{E}_y = -\frac{e\tau \mathcal{B}_z}{m} \mathcal{E}_x = -\frac{e\tau \mathcal{B}_z}{m} \frac{j_x}{\sigma_0} = R_H \mathcal{B}_z j_x.$$
(8.1.22)

Here, we have introduced in the last step the Hall coefficient

$$R_H = \frac{-1}{ne}.\tag{8.1.23}$$

The Hall effect can used to determine the charge carrier concentration in a solid (known magnetic field) or to measure the magnetic field strength (Hall sensor with known charge carrier concentration).



Figure 8.1: Scheme of a Hall bar.

8.2 Semiclassical equation of motion and the effective mass

According to section 7.1, the solutions of the one-electron Schrödinger equation of a crystal are Bloch waves:

$$\Psi_{\mathbf{k},n}(\mathbf{r},t) = u_{\mathbf{k},n}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\omega_n(\mathbf{k})t}.$$
(8.2.1)

Here, **k** is the wave vector of the Bloch wave and *n* is the index of the corresponding band. The frequency $\omega_n(\mathbf{k})$ is proportional to the energy eigenvalue $E_n(\mathbf{k})$:

$$E_n(\mathbf{k}) = \hbar\omega_n(\mathbf{k}). \tag{8.2.2}$$

A single Bloch wave $\Psi_{\mathbf{k},n}(\mathbf{r},t)$ describes an electronic state in which the electron is completely delocalized over the whole crystal. Obviously, this description is unsuitable for

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the discussion of transport phenomena in solids. To describe a localized electron, we construct a wave packet composed of Bloch waves:

$$\Psi(\mathbf{r},t) = \sum_{\mathbf{k}} g(\mathbf{k}) \Psi_{\mathbf{k},n}(\mathbf{r},t).$$
(8.2.3)

Here, $g(\mathbf{k})$ characterizes the weight of a Bloch wave $\Psi_{\mathbf{k},n}(\mathbf{r},t)$ in the wave packet. The real-space localization diameter δx and the wavevector spread δk of the wave packet fulfill the following inequality, which expresses a general property of the Fourier transform:

$$\delta x \,\hbar \delta k \ge \hbar. \tag{8.2.4}$$

In what follows, we assume that δk is much smaller than the diameter of the Brillouin zone. Equation (8.2.4) implies, that the real-space diameter of the wave packet is then larger than the lattice constant a. Hence, an electron is "spread" over several unit cells.



Figure 8.2: Electron wavepacket.

The expectation value of the velocity of the electron is given by the group velocity of the wave packet:

$$\dot{\mathbf{r}} = \mathbf{v}_n = \nabla_{\mathbf{k}}\omega_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}E_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}}.$$
(8.2.5)

Next, we consider the effect of an external electromagnetic field on the electron. At this, we assume that the wavelength λ of the field is much larger than δx (see Fig. 8.2). In that case, the temporal evolution of the wave vector is governed by the following semiclassical equation of motion:

$$\hbar \mathbf{k} = \mathbf{F} = -e \left[\boldsymbol{\mathcal{E}} \left(\mathbf{r}, t \right) + \mathbf{v}_n \times \boldsymbol{\mathcal{B}} \left(\mathbf{r}, t \right) \right].$$
(8.2.6)

In analogy to classical mechanics, we expect that the electron is accelerated in the external field. The time derivative of the expectation value of the electron velocity is given by:

$$\dot{v}_{n,j} = \frac{\partial}{\partial t} \left[\frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial k_j} \right] = \frac{1}{\hbar} \sum_l \frac{\partial}{\partial k_l} \left[\frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial k_j} \right] \hbar \dot{k}_l$$
$$= \frac{1}{\hbar^2} \sum_l \frac{\partial^2 E_n(\mathbf{k})}{\partial k_j \partial k_l} F_l = \sum_l \left(\frac{1}{m^*} \right)_{jl} F_l.$$
(8.2.7)

Here, we have introduced in the last step the effective mass tensor element m_{jl}^* through the relation:

$$\left(\frac{1}{m^*}\right)_{jl} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_j \partial k_l}.$$
(8.2.8)

We can rewrite equation (8.2.7) in vectorial form:

$$\dot{\mathbf{v}} = \left[\frac{1}{m^*}\right] \mathbf{F} = -e \left[\frac{1}{m^*}\right] \left[\boldsymbol{\mathcal{E}}\left(\mathbf{r},t\right) + \mathbf{v}_n \times \boldsymbol{\mathcal{B}}\left(\mathbf{r},t\right)\right].$$
(8.2.9)

This equation has the same form as Newton's equation of motion in classical mechanics if one formally replaces the scalar mass m by the effective mass m^* . However, the effective mass m^* is a second order tensor whose elements are functions of the wavevector \mathbf{k} . Note, that the elements of the effective mass tensor can have both positive and negative values. All these aspects result from the fact, that only the external fields are explicitly included in equation (8.2.9). The effect of the crystal potential $V(\mathbf{r})$ on the electron is implicitly taken into account by the effective mass m^* .



Figure 8.3: Effective mass m^* for the case of a 1D tight-binding model.

8.3 Bloch oscillations

The wavevector dependence of the effective mass can lead to counterintuitive effects. Consider a DC electric field with field strength \mathcal{E} that is applied to a perfect crystal. An electron experiences in the presence of this field a constant force $F = -e\mathcal{E}$. As a result, the magnitude of the wavevector changes with a constant rate:

$$|\dot{k}| = \frac{e\mathcal{E}}{\hbar} = \text{const.}$$
(8.3.1)

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The motion of the electron in reciprocal space is schematically depicted in Fig. 8.4. Whenever the wavevector reaches the boundary of the first Brillouin zone, we can add an appropriate reciprocal lattice vector such that the electron enters the first Brillouin zone at the other side. Since the effective mass changes its sign as \mathbf{k} varies (see Fig. 8.3), the electron is periodically accelerated and decelerated. This results in an oscillatory motion (Bloch oscillation) of the electron with period:

$$T_B = \frac{2\pi/a}{e\mathcal{E}/\hbar} = \frac{h}{ae\mathcal{E}}.$$
(8.3.2)

Hence, we have the surprising result that an ideal crystal exhibits a vanishing DC conductivity in the absence of scattering events!

So far we have neglected scattering events which disturb the motion of the electron. For typical parameters ($\mathcal{E} = 1 \text{ kV}/m$ and a = 2Å), the period of the Bloch oscillation is $T_B \approx 20 \text{ ns}$. This value is much larger than the characteristic relaxation time derived in section 8.1.1 ($\tau \approx 20 \text{ fs}$). Hence, electrons in metals will complete only a small part of an oscillation period before they undergo a scattering event. For that reasons, real metallic crystals exhibit a finite DC conductivity. Note however, that Bloch oscillation have been observed experimentally in artificial periodic semiconductor heterostructures.



Figure 8.4: Motion of an electron in reciprocal space due to an applied DC electric field.

8.4 Currents in bands: Electrons and holes

The current density caused by the electrons of a single band is given by:

$$\mathbf{j} = \frac{-e}{V_c} \sum_{\text{occupied}} \mathbf{v}(\mathbf{k})$$
$$= \frac{-e}{4\pi^3} \int \mathbf{v}(\mathbf{k}) f(E,T) d^3k.$$
(8.4.1)
For simplicity, we consider the case of low temperatures $(k_B T \ll E_F)$ such that the Fermifunction can be approximated by a step-function. In this limit, we can rewrite equation (8.4.1) as:

$$\mathbf{j} = \frac{-e}{4\pi^3} \int_{\text{occupied}} \mathbf{v}(\mathbf{k}) \, d^3k = \frac{-e}{4\pi^3\hbar} \int_{\text{occupied}} \nabla_{\mathbf{k}} E(\mathbf{k}) \, d^3k. \tag{8.4.2}$$

For crystals with inversion symmetry, the energy eigenvalues for the wavevectors \mathbf{k} and $-\mathbf{k}$ are identical:

$$E(\mathbf{k}) = E(-\mathbf{k}). \tag{8.4.3}$$

In contrast, the corresponding electron velocities have opposite signs:

$$\mathbf{v}(-\mathbf{k}) = \frac{1}{\hbar} \nabla_{-\mathbf{k}} E(-\mathbf{k}) = -\frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) = -\mathbf{v}(\mathbf{k}).$$
(8.4.4)

The situation is a little bit more complicated in the case of a crystal without inversion symmetry. In that case, we have to take the spin of the electron explicitly into account. For reasons of time reversal of the Schrödinger equation, one has:

$$\mathbf{k} \to -\mathbf{k} \text{ and } |\uparrow\rangle \to |\downarrow\rangle; |\downarrow\rangle \to |\uparrow\rangle.$$
 (8.4.5)

Hence, we obtain:

$$E(\mathbf{k},\uparrow) = E(-\mathbf{k},\downarrow); E(\mathbf{k},\downarrow) = E(-\mathbf{k},\uparrow).$$
(8.4.6)

Applying the gradient in reciprocal space yields:

$$\mathbf{v}(\mathbf{k},\uparrow) = -\mathbf{v}(-\mathbf{k},\downarrow); \mathbf{v}(\mathbf{k},\downarrow) = -\mathbf{v}(-\mathbf{k},\uparrow).$$
(8.4.7)

In both cases, one can easily see that a fully occupied band results in a vanishing current density. For each electron with wavevector \mathbf{k} there always is a corresponding electron with wavevector $-\mathbf{k}$ in the first Brillouin zone (1st BZ) which exactly compensates the contribution of the former electron to the current density.

From this observation, we can draw the important conclusion that a finite current density requires a partially filled electronic band in which the electrons are distributed unsymmetrically with respect to $\mathbf{k} = 0$. Next, we rewrite equation (8.4.2) as:

$$\mathbf{j} = \frac{-e}{4\pi^3} \int_{\text{occupied}} \mathbf{v}(\mathbf{k}) d^3 k = \frac{-e}{4\pi^3 \hbar} \left[\int_{1^{\text{st}} BZ} \nabla_{\mathbf{k}} E(\mathbf{k}) d^3 k - \int_{\text{empty}} \nabla_{\mathbf{k}} E(\mathbf{k}) d^3 k \right]$$
$$= \frac{+e}{4\pi^3 \hbar} \int_{\text{empty}} \nabla_{\mathbf{k}} E(\mathbf{k}) d^3 k.$$
(8.4.8)

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We can formally interpret this equation in two different ways. In the first interpretation, we take the view that the current density is caused by the negatively charged electrons in the occupied states of the band. Alternatively we can also say that the current density results from the motion of positively charged particles which we assign to the empty states in the band. These positively charged particles are usually called holes. A hole can be created, e.g., by transfer of an electron from the fully occupied valence band to the empty conduction band after optical absorption of a photon (see Fig. 8.5).

The following relationships between electron properties and hole properties can easily be proven as an exercise 2 :

• Quasi-Momentum:

$$\mathbf{k}_h = -\mathbf{k}_n. \tag{8.4.9}$$

• Spin:

$$|s\rangle_h = -|s\rangle_n. \tag{8.4.10}$$

• Energy:

$$E_h(\mathbf{k}_h) = -E_n(\mathbf{k}_n). \tag{8.4.11}$$

• Velocity:

$$\mathbf{v}_h(\mathbf{k}_h) = \mathbf{v}_n(\mathbf{k}_n). \tag{8.4.12}$$

• Effective mass:

$$m_h^* = -m_n^*. (8.4.13)$$

A combination of the above results yields the following equations of motion for electrons and holes, respectively:

$$\hbar \mathbf{k}_{n} = -e \left(\boldsymbol{\mathcal{E}} \left(\mathbf{r}, t \right) + \mathbf{v}_{n} \times \boldsymbol{\mathcal{B}} \left(\mathbf{r}, t \right) \right), \qquad (8.4.14)$$

$$\hbar \mathbf{k}_{h} = +e \left(\boldsymbol{\mathcal{E}} \left(\mathbf{r}, t \right) + \mathbf{v}_{h} \times \boldsymbol{\mathcal{B}} \left(\mathbf{r}, t \right) \right).$$
(8.4.15)

(8.4.16)

²Here, we use the indices n and p to distinguish between properties of electrons and holes, respectively.



Figure 8.5: Optical absorption of a photon creates a hole in the otherwise occupied valence band (state A) and an electron in the otherwise empty conduction band (state B).

8.5 Motion of electrons in a static magnetic field

Next, we discuss how a static magnetic field affects the motion of the crystal electrons. On this occasion, we assume that no additional electric field is applied to the crystal. In this case, the the semi-classical equation of motion reads:

$$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F} = (-e) \left[\mathbf{v} \times \boldsymbol{\mathcal{B}} \right] = \frac{e}{\hbar} \left[\boldsymbol{\mathcal{B}} \times \nabla_{\mathbf{k}} E(\mathbf{k}) \right], \qquad (8.5.1)$$

with

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}). \tag{8.5.2}$$

In the following, we consider the electron trajectories in k-space. Because of the properties of the vector product, we find from equation (8.5.1) that the component of the wave vector parallel to the magnetic field is conserved:

$$\frac{dk_{\parallel}}{dt} = 0. \tag{8.5.3}$$

Furthermore, we can easily show that the energy of the electrons does not change with time:

$$\frac{dE}{dt} = \frac{dE}{d\mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} = \mathbf{F} \cdot \mathbf{v} = (-e) \left[\mathbf{v} \times \boldsymbol{\mathcal{B}} \right] \cdot \mathbf{v} = 0.$$
(8.5.4)

Hence, the electron trajectories in k-space are the intersections of the surface of constant energy E(k) = const with the plane defined by $k_{\parallel} = \text{const}$ (perpendicular to \mathcal{B}).

Depending on the shape of the surface of constant energy E(k) = const, one can distinguish between several different cases. Fig. 8.6 (a) depicts an open trajectory in the

periodic zone scheme while Fig. 8.6 (b) and (c) correspond to closed trajectories. The circumferential direction is determined by the relative orientation of the magnetic field \mathcal{B} and the gradient of energy in k-space $\nabla_{\mathbf{k}} E(\mathbf{k})$.

Next, we calculate the period of revolution of the electrons on a closed trajectory. For this purpose we consider an element $d\mathbf{k}$ of the trajectory. With the help of equation (8.5.1), we find that

$$d\mathbf{k} = \frac{e}{\hbar^2} \left[\boldsymbol{\mathcal{B}} \times \nabla_{\mathbf{k}} E(\mathbf{k}) \right] dt = \frac{e}{\hbar^2} \boldsymbol{\mathcal{B}} \left(\frac{dE(\mathbf{k})}{d\mathbf{k}} \right)_{\perp} dt.$$
(8.5.5)

Here, $\left(\frac{dE(\mathbf{k})}{d\mathbf{k}}\right)_{\perp}$ is the component of $\nabla_{\mathbf{k}}E(\mathbf{k})$ that is oriented perpendicular to **B**. Integration over one cycle of the motion yields the period of revolution

$$T = \int_0^T dt = \frac{\hbar^2}{e\mathcal{B}} \oint \frac{1}{(dE/d\mathbf{k})_\perp} dk$$
(8.5.6)

To evaluate this integral, we consider the area dS_E enclosed by the curves with constant energy E and E + dE. Inspection of Fig. 8.7 shows that

$$dS_E(\mathbf{k}) = \oint \delta k_{\perp}(\mathbf{k}) \, dk = \oint \frac{1}{(dE/d\mathbf{k})_{\perp}} \, dE \, dk.$$
(8.5.7)

The derivative of the last equation with respect to energy yields

$$\frac{dS_E(\mathbf{k})}{dE} = \oint \frac{1}{(dE/d\mathbf{k})_\perp} dk.$$
(8.5.8)

Hence, the period of revolution of the electrons can be written as.

$$T(E, \mathbf{k}) = \frac{\hbar^2}{eB} \frac{dS_E(\mathbf{k})}{dE}.$$
(8.5.9)



Figure 8.6: Electron motion in k-space under the influence of a static magnetic field. (a) Open trajectory. (b) Closed trajectory (electron like). (c) Closed trajectory (hole like)

The corresponding angular frequency is the so-called cyclotron frequency. It reads

$$\omega_c = \frac{2\pi}{T} = \frac{e\mathcal{B}}{m_c},\tag{8.5.10}$$

with the cyclotron mass

$$m_c = \frac{\hbar^2}{2\pi} \frac{dS_E(\mathbf{k})}{dE}.$$
(8.5.11)



Figure 8.7: Motion of an electron on a closed loop in k-space in the presence of a static magnetic field.

Example: Free electrons in a magnetic field For free electrons, the trajectory in k-space is a circle and $S_E(k) = \pi k^2$. With $\frac{dS_E(k)}{dE} = \frac{2\pi m}{\hbar^2}$ we find that $\omega_c = \frac{eB}{m}$.

The cyclotron frequency can be measured by the resonant absorption of an incident microwave electric field. A prerequisite for these experiments is that the electrons can perform several periods before being scattered. For that reason, cyclotron resonance experiments require strong magnetic fields and the cooling of the sample to low temperatures. The microwave has to be polarized perpendicular to the magnetic field. Resonant absorption of energy from the microwave occurs if its frequency coincides with the cyclotron frequency. A discussion of this method is given by G. Dresselhaus et al. in Phys. Rev. **9**8, 368 (1955).

8.6 Boltzmann transport theory

In thermal equilibrium, the distribution of the electrons over the available electronic states is governed by the Fermi-Dirac distribution function:

$$f_0[E(\mathbf{k})] = \frac{1}{e^{[E(\mathbf{k}) - \mu]/k_B T} + 1}.$$
(8.6.1)

By applying either an external electric field \mathcal{E} , an external magnetic field \mathcal{B} , a temperature gradient $\nabla_{\mathbf{r}} T$, or a gradient of the chemical potential $\nabla_{\mathbf{r}} \mu$ to the sample, the state of equilibrium is disturbed. Consequently, the electron distribution function $f(\mathbf{r}, \mathbf{k}, t)$ deviates from the equilibrium distribution function f_0 . This is a prerequisite for transport of carriers.

8.6.1 Linearized Boltzmann equation

To derive the electron distribution function $f(\mathbf{r}, \mathbf{k}, t)$, we neglect in the first instance scattering of the electrons. In that case, the phase space coordinates of an electron change during the time dt from $(\mathbf{r} - \mathbf{v}dt, \mathbf{k} + \frac{e}{\hbar} (\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}}) dt)$ to (\mathbf{r}, \mathbf{k}) . As a result, the electron distribution function has to satisfy the condition

$$f(\mathbf{r}, \mathbf{k}, t) = f\left(\mathbf{r} - \mathbf{v}dt, \mathbf{k} + \frac{e}{\hbar} \left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}}\right) dt, t - dt\right).$$
(8.6.2)

In the next step, we account for scattering processes by adding a correction term:

$$f(\mathbf{r}, \mathbf{k}, t) = f\left(\mathbf{r} - \mathbf{v}dt, \mathbf{k} + \frac{e}{\hbar}\left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}}\right) dt, t - dt\right) + \left(\frac{\partial f}{\partial t}\right)_{s} dt.$$
(8.6.3)

Expansion of $f\left(\mathbf{r} - \mathbf{v}dt, \mathbf{k} + \frac{e}{\hbar}\left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}}\right) dt, t - dt\right)$ up to linear order in dt leads to the so-called Boltzmann equation:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f - \frac{e}{\hbar} \left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}} \right) \cdot \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t} \right)_{s}.$$
(8.6.4)

In the following, we restrict ourselves to the stationary state $(\partial f/\partial t = 0)$ and assume that the corresponding distribution function $f(\mathbf{r}, \mathbf{k})$ does not significantly differ at each position \mathbf{r} from the value of the equilibrium distribution function $f_0(E(\mathbf{k}), T(\mathbf{r}), \mu(\mathbf{r}))$. For further analysis, it is convenient to define

$$g(\mathbf{r}, \mathbf{k}) = f(\mathbf{r}, \mathbf{k}) - f_0(E(\mathbf{k}), T(\mathbf{r}), \mu(\mathbf{r})).$$
(8.6.5)

Upon substitution of $g(\mathbf{r}, \mathbf{k})$ in the Boltzmann equation (8.6.4), we obtain

$$\begin{pmatrix} \frac{\partial f}{\partial t} \end{pmatrix}_{s} = \mathbf{v} \cdot \left(\frac{\partial f_{0}}{\partial T} \nabla_{\mathbf{r}} T + \frac{\partial f_{0}}{\partial \mu} \nabla_{\mathbf{r}} \mu \right) + \mathbf{v} \cdot \nabla_{\mathbf{r}} g - \frac{e}{\hbar} \left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}} \right) \cdot \nabla_{\mathbf{k}} f_{0} - \frac{e}{\hbar} \left(\boldsymbol{\mathcal{E}} + \mathbf{v} \times \boldsymbol{\mathcal{B}} \right) \cdot \nabla_{\mathbf{k}} g.$$

$$(8.6.6)$$

The term $\frac{e}{\hbar} \boldsymbol{\mathcal{E}} \cdot \nabla_{\mathbf{k}} g$ leads to deviations from Ohm's law $[\mathcal{O}(\boldsymbol{\mathcal{E}}^2)]$ and is hence neglected in the following. With $\nabla_{\mathbf{k}} f_0 = \frac{\partial f_0}{\partial E} \nabla_{\mathbf{k}} E = \frac{\partial f_0}{\partial E} \hbar \mathbf{v}, \ \frac{\partial f_0}{\partial T} = \left(-\frac{\partial f_0}{\partial E}\right) \frac{E-\mu}{T}$, and $\frac{\partial f_0}{\partial \mu} = \left(-\frac{\partial f_0}{\partial E}\right)$, we

obtain the linearized Boltzmann equation

$$\begin{pmatrix} \frac{\partial f}{\partial t} \end{pmatrix}_{s} = \left(\frac{\partial f_{0}}{\partial E} \right) \mathbf{v} \cdot \left[-e \left(\boldsymbol{\mathcal{E}} + \frac{\nabla_{\mathbf{r}} \mu}{e} \right) - \frac{E - \mu}{T} \nabla_{\mathbf{r}} T \right] + \mathbf{v} \cdot \nabla_{\mathbf{r}} g - \frac{e}{\hbar} \left(\mathbf{v} \times \boldsymbol{\mathcal{B}} \right) \cdot \nabla_{\mathbf{k}} g.$$

$$(8.6.7)$$

For the scattering term, we introduce a relaxation time ansatz:

$$\left(\frac{\partial f}{\partial t}\right)_{s} = -\frac{f\left(\mathbf{r}, \mathbf{k}\right) - f_{0}\left(E(\mathbf{k}), T(\mathbf{r}), \mu(\mathbf{r})\right)}{\tau(\mathbf{k})} = -\frac{g(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})}.$$
(8.6.8)

Here, $\tau(\mathbf{k})$ characterizes the time it takes for the electronic distribution function to return to the equilibrium value once the external perturbation is switched off.

As an instructive example, we consider the case of a homogeneous medium to which we apply an external electric field \mathcal{E} . We assume that there is no external magnetic field and that both the temperature as well as the chemical potential are constant. With these assumptions ($\nabla_{\mathbf{r}}g = \nabla_{\mathbf{r}}T = \nabla_{\mathbf{r}}\mu = \mathcal{B} = 0$), equation (8.6.7) simplifies to:

$$g(\mathbf{k}) = \left(\frac{\partial f_0}{\partial E}\right) e \,\tau(\mathbf{k}) \,\mathbf{v} \cdot \boldsymbol{\mathcal{E}}$$
(8.6.9)

Solving for $f(\mathbf{k})$, we find:

$$f(\mathbf{k}) = f_0(\mathbf{k}) + \frac{e}{\hbar} \tau(\mathbf{k}) \boldsymbol{\mathcal{E}} \cdot \nabla_{\mathbf{k}} f_0.$$
(8.6.10)

This equation can be regarded as an expansion of $f(\mathbf{k})$ about the point \mathbf{k} :

$$f(\mathbf{k}) \simeq f_0 \left(\mathbf{k} + \frac{e}{\hbar} \tau(\mathbf{k}) \boldsymbol{\mathcal{E}} \right).$$
 (8.6.11)

Under the influence of the external electric field, the electron distribution function becomes a Fermi distribution shifted by $\delta \mathbf{k} = -\frac{e}{\hbar} \tau(\mathbf{k}) \boldsymbol{\mathcal{E}}$ from the origin (see Fig. 8.8).

8.6.2 Transport equations

In this section we consider transport phenomena which result from deviations of the electronic distribution function from its equilibrium value. On this occasion, we restrict ourselves to homogeneous media and assume that no external magnetic field is applied $(\nabla_{\mathbf{r}} g = \mathcal{B} = 0)$. In this case, the linearized Boltzmann equation can be written as:

$$g(\mathbf{k}) = \left(-\frac{\partial f_0}{\partial E}\right) \tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \cdot \mathbf{\mathcal{A}},\tag{8.6.12}$$

with

$$\boldsymbol{\mathcal{A}} = -e\left(\boldsymbol{\mathcal{E}} + \frac{\nabla_{\mathbf{r}}\mu}{e}\right) - \frac{E-\mu}{T}\nabla_{\mathbf{r}}T = -e\boldsymbol{\mathcal{E}}' - \frac{E-\mu}{T}\nabla_{\mathbf{r}}T.$$
(8.6.13)



Figure 8.8: Effect of an electric field on the electron distribution function.

Current density

According to equation (8.4.1), the current density is given by:

$$\mathbf{j}_{q} = \frac{-e}{4\pi^{3}} \int \mathbf{v}(\mathbf{k}) f(\mathbf{k}) d^{3}k$$

$$= \frac{-e}{4\pi^{3}} \int \mathbf{v}(\mathbf{k}) g(\mathbf{k}) d^{3}k$$

$$= \frac{-e}{4\pi^{3}} \int \int \left[-\frac{\partial f_{0}}{\partial E} \right] \tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \left[\mathbf{v}(\mathbf{k}) \cdot \boldsymbol{\mathcal{A}} \right] \frac{dS_{E}}{\hbar |\mathbf{v}(\mathbf{k})|} dE.$$
(8.6.14)

Here, we have replaced in the last step $\int d^3k$ by $\int \int \frac{dS_E}{\hbar |\mathbf{v}(\mathbf{k})|} dE$. Substitution of equation (8.6.13) into equation (8.6.14) yields:

$$\mathbf{j}_{q} = \left(\frac{e^{2}}{4\pi^{3}\hbar} \int \int \left[-\frac{\partial f_{0}}{\partial E}\right] \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dE dS_{E}\right) \cdot \boldsymbol{\mathcal{E}}' + \left(\frac{-e}{4\pi^{3}\hbar} \int \int \left[-\frac{\partial f_{0}}{\partial E}\right] [E(\mathbf{k}) - \mu] \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dE dS_{E}\right) \cdot \frac{-\nabla_{\mathbf{r}} T}{T} \\ = \hat{\mathbf{L}}^{11} \boldsymbol{\mathcal{E}}' + \hat{\mathbf{L}}^{12} \frac{-\nabla_{\mathbf{r}} T}{T}, \qquad (8.6.15)$$

In the last step, we have introduced for later reference the transport coefficients $\hat{\mathbf{L}}^{11}$ and $\hat{\mathbf{L}}^{21}$, respectively. In general, these transport coefficients are second-order tensors.

For $k_BT \ll E_F$, the Fermi distribution f_0 can be approximated by a step function and we obtain:

$$\frac{\partial f_0(\mathbf{k})}{\partial E} \approx -\delta(E - E_F). \tag{8.6.16}$$

Hence, equation (8.6.15) simplifies to a surface integral over the Fermi surface

$$\mathbf{j}_{q} = \left(\frac{e^{2}}{4\pi^{3}\hbar} \int_{E_{F}} \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dS_{E}\right) \cdot \boldsymbol{\mathcal{E}'} + \left(\frac{-e}{4\pi^{3}\hbar} \int_{E_{F}} \left[E(\mathbf{k}) - \mu\right] \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dS_{E}\right) \cdot \frac{-\nabla_{\mathbf{r}} T}{T}.$$
(8.6.17)

In what follows, we restrict our analysis to homogeneous media with constant temperature $(\nabla_{\mathbf{r}}T = 0)$ and consider that the electric field is applied in the $\hat{\mathbf{e}}_x$ -direction $[\mathcal{E}' = (\mathcal{E}'_x, 0, 0)]$. The $\hat{\mathbf{e}}_x$ -component of the current density is then given by:

$$j_{q,x} = \left(\frac{e^2}{4\pi^3\hbar} \int_{E_F} \frac{\tau(\mathbf{k}) v_x^2(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dS_E\right) \mathcal{E}'_x.$$
(8.6.18)

In general, $v_x(\mathbf{k})$ and $\tau(\mathbf{k})$ vary over the Fermi surface. However, for reasons of mathematical simplicity, we assume that these quantities are only weakly dependent on \mathbf{k} such that we can take an average value $v(E_F)\tau(E_F)/3$ outside the integral. Furthermore, we assume that the conduction band is parabolic such that

$$v(E_F) = \frac{\hbar k_F}{m^*},\tag{8.6.19}$$

where m^* is the effective mass of the electrons in the conduction band. The integral over the Fermi surface yields:

$$\int_{E_F} dS_E = 4\pi k_F^2. \tag{8.6.20}$$

For $k_BT \ll E_F$, the Fermi wavevector is connected with the density of electrons via

$$k_F^3 = 3\pi^2 n. \tag{8.6.21}$$

This finally allows us to write the current density as

$$j_{q,x} = \sigma \mathcal{E}'_x,\tag{8.6.22}$$

with

$$\sigma = \frac{e^2 \tau(E_F)}{m^*} n. \tag{8.6.23}$$

Note that this result formally agrees with the result of the Drude model. However, there is an important difference: In the Drude model, all conduction electrons are equally important for the electric current density. Here however, only the electrons at the Fermi level are relevant.

Thermal current density

Next, we consider the thermal current density. The heat transported by an electron is given by the difference between its inner energy $E(\mathbf{k})$ and the chemical potential μ . Hence, the thermal current density can be written as

$$\mathbf{j}_{t} = \frac{1}{4\pi^{3}\hbar} \int [E(\mathbf{k}) - \mu] \mathbf{v}(\mathbf{k}) g(\mathbf{k}) d^{3}k$$

$$= \left(\frac{-e}{4\pi^{3}\hbar} \int \int \left[-\frac{\partial f_{0}}{\partial E}\right] [E(\mathbf{k}) - \mu] \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dEdS_{E}\right) \cdot \boldsymbol{\mathcal{E}}' + \left(\frac{1}{4\pi^{3}\hbar} \int \int \left[-\frac{\partial f_{0}}{\partial E}\right] [E(\mathbf{k}) - \mu]^{2} \frac{\tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} dEdS_{E}\right) \cdot \frac{-\nabla_{\mathbf{r}} T}{T}$$

$$= \hat{\mathbf{L}}^{21} \boldsymbol{\mathcal{E}}' + \hat{\mathbf{L}}^{22} \frac{-\nabla_{\mathbf{r}} T}{T}, \qquad (8.6.24)$$

where $\hat{\mathbf{L}}^{21}$ and $\hat{\mathbf{L}}^{22}$ are the corresponding transport coefficients. The last equation shows that the thermal current density is driven either by an external electric field or by a gradient of the temperature.

8.6.3 Thermoelectric effects

In the following, we want to take a closer look at effects that allow for a direct conversion of a temperature difference into an electric voltage and vice versa. Historically, such thermoelectric effects are described by the following set of equations:

$$\boldsymbol{\mathcal{E}}' = \hat{\boldsymbol{\rho}} \mathbf{j}_q + \hat{\boldsymbol{\mathcal{S}}} \nabla_{\mathbf{r}} T, \qquad (8.6.25)$$

$$\mathbf{j}_t = \hat{\mathbf{\Pi}} \mathbf{j}_q - \hat{\boldsymbol{\kappa}} \nabla_{\mathbf{r}} T. \tag{8.6.26}$$

Here, $\hat{\rho}$ is the electric resistivity, \hat{S} is the so-called Seebeck coefficient, $\hat{\Pi}$ is the so-called Peltier coefficient, and $\hat{\kappa}$ is the thermal conductivity. In general, all these quantities are second-order tensors.

The transport equations derived within the the framework of the Boltzmann transport theory read (see equations (8.6.15) and (8.6.24)):

$$\mathbf{j}_q = \hat{\mathbf{L}}^{11} \boldsymbol{\mathcal{E}}' + \hat{\mathbf{L}}^{12} \frac{-\nabla_{\mathbf{r}} T}{T}, \qquad (8.6.27)$$

$$\mathbf{j}_t = \hat{\mathbf{L}}^{21} \boldsymbol{\mathcal{E}}' + \hat{\mathbf{L}}^{22} \frac{-\nabla_{\mathbf{r}} T}{T}.$$
(8.6.28)

One can easily show that the following relations between the different coefficients hold:

$$\hat{\boldsymbol{\rho}} = \left(\hat{\mathbf{L}}^{11}\right)^{-1}, \qquad (8.6.29)$$

$$\hat{\boldsymbol{S}} = \frac{1}{T} \left(\hat{\mathbf{L}}^{11} \right)^{-1} \hat{\mathbf{L}}^{12}.$$
(8.6.30)

$$\hat{\Pi} = \hat{\mathbf{L}}^{21} \left(\hat{\mathbf{L}}^{11} \right)^{-1}, \qquad (8.6.31)$$

$$\hat{\boldsymbol{\kappa}} = \frac{1}{T} \left[\mathbf{L}^{21} \left(\hat{\mathbf{L}}^{11} \right)^{-1} \hat{\mathbf{L}}^{12} + \hat{\mathbf{L}}^{22} \right].$$
(8.6.32)

Seebeck effect

Consider the thermocouple circuit depicted in Fig. 8.9. A wire made from metal A is connected to two wires made from metal B. The temperature at the contact points 1 and 2 is T_1 and T_2 , respectively. The free ends of the two wires both have the same temperature T_0 and are connected to a voltage meter.



Figure 8.9: Thermocouple circuit to demonstrate the Seebeck effect.

The reading of the voltage meter is given by the integral of the electric field along the circuit:

$$U = \int_0^1 \mathcal{E}_B ds + \int_1^2 \mathcal{E}_A ds + \int_2^0 \mathcal{E}_B ds = \int_2^1 \mathcal{E}_B ds + \int_1^2 \mathcal{E}_A ds.$$
(8.6.33)

Since the voltmeter has a very large resistance, there is no current flowing in the circuit $(j_q = 0)$. In this case, the electric fields can be written as

$$\mathcal{E}_A = \mathcal{S}_A \frac{\partial T}{\partial s}$$
 and $\mathcal{E}_B = \mathcal{S}_B \frac{\partial T}{\partial s}$. (8.6.34)

Here, \mathcal{S}_A and \mathcal{S}_B are the Seebeck coefficients of metal A and metal B, respectively.

Substitution of \mathcal{E}_A and \mathcal{E}_B in equation (8.6.33) yields

$$U = \int_{2}^{1} \mathcal{S}_{B} \frac{\partial T}{\partial s} ds + \int_{1}^{2} \mathcal{S}_{A} \frac{\partial T}{\partial s} ds = \int_{T_{1}}^{T_{2}} (\mathcal{S}_{A} - \mathcal{S}_{B}) dT.$$
(8.6.35)

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Hence, the voltage U is a function of the temperature difference of the two contact points and the difference of the Seebeck coefficients of the two metals.

This so-called Seebeck effect can be used for temperature measurements. In that case, one of the contacts of the thermocouple is kept at a fixed, known temperature. The voltage U then depends only on the temperature of the other contact.

Peltier effect

Next, we discuss the so-called Peltier effect. For this purpose we consider the circuit depicted in Fig. 8.10. Unlike to the previous section, we assume that the temperature is initially constant throughout the circuit. A battery drives an electric current through the wires. According to equation (8.6.26), the electric current density j_q is accompanied by a thermal current density $j_{t,A} = \prod_A j_q$ in the wire made from metal A and a thermal current density $j_{t,B} = \prod_B j_q$ in the wires made from metal B. Hence, the thermal current density is discontinuous at the contacts. This jump results in the liberation of heat at one contact point and absorption of heat at the other one. In other words, one contact becomes hot while the other one cools down.



Figure 8.10: Circuit to demonstrate the Peltier effect.

In practice, Peltier elements are usually not made from metals but doped semiconductors (see next chapter). They can be used for example to cool CCD chips in scientific grade cameras.

Wiedemann-Franz law

The thermal conductivity $\hat{\kappa}$ can be written in terms of the transport coefficients as

$$\hat{\boldsymbol{\kappa}} = \frac{1}{T} \left[\mathbf{L}^{21} \left(\hat{\mathbf{L}}^{11} \right)^{-1} \hat{\mathbf{L}}^{12} + \hat{\mathbf{L}}^{22} \right].$$
(8.6.36)

8.7 Scattering of electrons



Figure 8.11: Peltier element (image source: Wipipedia).

In typical metals, the second term is much larger than the first one. Hence, we can approximate the thermal conductivity of metals by

$$\hat{\boldsymbol{\kappa}} = \frac{\hat{\mathbf{L}}^{22}}{T}.$$
(8.6.37)

The transport coefficient $\hat{\mathbf{L}}^{22}$ is defined by an integral of the form $\int K(E) (-\partial f_0/\partial E) dE$. With the Sommerfeld expansion

$$\int K(E) \left(-\frac{\partial f_0}{\partial E}\right) dE = K(\mu) + (k_B T)^2 \frac{\pi^2}{6} \left(\frac{\partial^2 K(E)}{\partial E^2}\right)_{E=\mu} + \mathcal{O}\left(\frac{k_B T}{\mu}\right)^4, \quad (8.6.38)$$

we find that

$$\hat{\mathbf{L}}^{22} \approx \frac{\pi^2}{3} \frac{(k_B T)^2}{e^2} \hat{\boldsymbol{\sigma}}.$$
 (8.6.39)

Here, $\hat{\boldsymbol{\sigma}}$ is the electric conductivity of the metal. Substitution of equation (8.6.39) into (8.6.37) leads to the so-called Wiedemann-Franz law:

$$\hat{\boldsymbol{\kappa}} = \frac{\pi^2}{3} \frac{k_B^2 T}{e^2} \hat{\boldsymbol{\sigma}}.$$
(8.6.40)

8.7 Scattering of electrons

In this section we qualitatively discuss the different electron scattering processes, i.e., scattering from static defects in the lattice, electron-phonon scattering, and electronelectron scattering. We assume that the different scattering processes are independent from each other. Since the scattering probability of a process is inversely proportional to the corresponding relaxation time, we obtain for the total relaxation time τ :

$$\frac{1}{\tau} = \frac{1}{\tau_{def}} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{ee}}.$$
(8.7.1)

Here, τ_{def} , τ_{ph} , and τ_{ee} are the average times between scattering from defects, from phonons, and from other electrons, respectively.

• The scattering of an electron from a static defect is an elastic process. Hence, the wavevector of the electron changes its direction (from \mathbf{k} to \mathbf{k}') but not its magnitude $(|\mathbf{k}| = |\mathbf{k}'|)$. In an elastic scattering process, the momentum is conserved:

$$\hbar \mathbf{k} = \hbar \mathbf{k}' + \hbar \mathbf{K}. \tag{8.7.2}$$

Here, $\hbar \mathbf{K}$ is the momentum that is transferred to the whole crystal during the scattering process. Electron scattering from a static defect results in a temperature independent relaxation time τ_{def} .

• The scattering of an electron from a phonon is an inelastic process. Quasimomentum conservation requires, that

$$\hbar \mathbf{k} = \hbar \mathbf{k}' \pm \hbar \mathbf{q} + \hbar \mathbf{G}. \tag{8.7.3}$$

Here, **q** is the wavevector of the phonon and **G** is a reciprocal lattice vector. Scattering events with $\mathbf{G} = 0$ are normal processes while $\mathbf{G} \neq 0$ corresponds to an umklapp process (compare with section 5.4.2). For temperatures $T > \Theta_D$, the scattering probability is proportional to the number of phonons. Hence, the relaxation time τ_{ph} scales as 1/T.

• Electron-electron scattering is an effect which goes beyond the one-electron approximation. Because of the high density of electrons, one might assume that electronelectron scattering is a very efficient process in metals. However, we will see below that because of the Pauli exclusion principle, the probability of electron-electron scattering is very small.

Let us consider a metal with N electrons inside the Fermi sphere plus a single electron in state $|1\rangle$ with quasi momentum \mathbf{k}_1 and energy $E_1(\mathbf{k}_1) = E_F + \delta E$, where $\delta E \ll E_F$. Next, we assume that this electron scatters with another electron in state $|2\rangle$ with quasi momentum \mathbf{k}_2 and energy $E_2(\mathbf{k}_2)$. Since only states with $E(\mathbf{k}_2) \leq E_F$ are occupied, we find that $E_2(\mathbf{k}_2) \leq E_F$. In contrast, the states $|3\rangle$ and $|4\rangle$ in which the two electrons scatter must be unoccupied so that $E_3(\mathbf{k}_3) > E_F$ and $E_4(\mathbf{k}_4) > E_F$. Furthermore, energy conservation and quasi moment conservation dictate that

$$E_1(\mathbf{k}_1) + E_2(\mathbf{k}_2) = E_3(\mathbf{k}_3) + E_4(\mathbf{k}_4)$$
(8.7.4)

8.7 Scattering of electrons



Figure 8.12: Electron-electron scattering process.

and

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4 + \mathbf{G},\tag{8.7.5}$$

respectively.

Since $E_3 + E_4 > 2E_F$, we can conclude that the energy of state $|2\rangle$ must be in the interval $]E_F - \delta E, E_F]$, i.e., state $|2\rangle$ lies in a shell with width δE below the Fermi level. The fraction of electrons $\delta N/N$, whose energy falls in this interval, is given by

$$\frac{\delta N}{N} = \frac{4\pi k_F^2 \delta k}{\frac{4}{3}\pi k_F^3} \propto \frac{\delta_k}{k_F}.$$
(8.7.6)

With $\delta k = \frac{2m}{\hbar^2} \frac{\delta E}{k_F}$, we find that only the fraction $\frac{\delta N}{N} = \frac{\delta E}{E_F}$ of all occupied electron states comes into question as scattering partner of electron |1>. Furthermore, energy conservation requires that the energies of states |3> and |4> must fall in the interval $|E_F, E_F + \delta E|$. An analog argument shows that only the fraction $\frac{\delta N}{N} = \frac{\delta E}{E_F}$ of all states with energy smaller than or equal to $E_F + \delta E$ fulfills this condition. All in all, we can conclude that the scattering rate of electron-electron scattering reads

$$\frac{1}{\tau_{ee}} = \frac{1}{\tau_{ee}^0} \left(\frac{\delta E}{E_F}\right)^2,\tag{8.7.7}$$

where $\frac{1}{\tau_{ee}^0}$ is the scattering rate that would be effective without validity of the Pauli principle. Since δE is in the order of $k_B T$, we can conclude that the Pauli principle extremely reduces the probability of electron-electron scattering.

The resistivity is given by:

$$\rho = \frac{1}{\sigma} = \frac{m^*}{e^2 n\tau}.\tag{8.7.8}$$

With equation (8.7.1), we get:

$$\rho = \rho_{def} + \rho_{ph} = \frac{m^*}{e^2 n \tau_{def}} + \frac{m^*}{e^2 n \tau_{ph}(T)}.$$
(8.7.9)

This formula is known as the Matthiesen's rule. For low temperatures, one expects a constant resistivity due to scattering from static impurities.



Figure 8.13: Relative resistivity $(\rho(T)/\rho(290K)))$ of sodium for three different samples. Adopted from: D. K. C. MacDonald and K. Mendelssohn, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, **202**, 103 (1950).

8.8 Electron transport in a quantum wire

In the following, we consider electric transport along a quantum wire (x-axis), which connects two electron reservoirs with chemical potentials μ_1 and μ_2 , respectively. At this, we assume that the free mean path of the electrons is much longer than the length of the quantum wire such that the transport within the quantum wire is ballistic. Hence, all electrons which enter the quantum wire from the left or the right are transmitted with unity probability. The drop in the chemical potential $\Delta \mu = \mu_1 - \mu_2$ happens at the contacts of the quantum wire with the reservoirs. In this situation, the right-moving and the left-moving electrons have different chemical potentials. Furthermore, we assume that the confinement in y- and z direction is such that only the states $E(k_x, n_y = 1, n_z = 1)$ in the lowest subband contribute to the transport (see section 6.8).



Figure 8.14: Top: Scheme of a quantum wire attached to two electron reservoirs with chemical potentials μ_1 and μ_2 , respectively. Bottom: Chemical potential as a function of the coordinate x.

The current in the wire is given by

$$I_q = -e\frac{2}{L}\sum_{occupied} \frac{\hbar \left(\mathbf{k}_r - \mathbf{k}_l\right)}{m},\tag{8.8.1}$$

where \mathbf{k}_r and \mathbf{k}_l are the wave vectors of the electrons moving to the right and to the left, respectively. Next we replace the sum by an integral and write

$$I_q = -\frac{2e}{2\pi} \int_0^\infty \frac{\hbar \mathbf{k}}{m} \left[f_r(\mathbf{k}) - f_l(\mathbf{k}) \right] dk.$$
(8.8.2)

Here, the factor 2 takes the spin degree of freedom into account. $f_r(\mathbf{k})$ and $f_l(\mathbf{k})$ are the occupation functions of the right- and left-moving electrons, respectively. Using $dk = dE/\hbar v_k$ and $v_k = \hbar k/m$, the current through the wire can be expressed as

$$I_q = -\frac{2e}{2\pi\hbar} \int_0^\infty \left[f(E - \mu_1) - f(E - \mu_2) \right] dE.$$
(8.8.3)

With $\int_0^\infty [f(E - \mu_1) - f(E - \mu_2)] dE = \mu_1 - \mu_2 = (-e)U$, we finally obtain

$$I_q = 2\frac{e^2}{h}U.$$
 (8.8.4)

This results shows that the ballistic transport through a quantum wire leads to a finite resistance of

$$R = \frac{1}{2} \frac{h}{e^2}.$$
(8.8.5)

The quantity $R_Q = 2R = \frac{h}{e^2} = 25812.807557\Omega$ is called the resistance quantum.

Despite of its simplicity, this model can be used to describe for example the electronic transport through a single carbon nanotube [S. Frank et al., Carbon Nanotube Quantum Resistors, Science **2**80, 5370 (1998)].

9 Semiconductors

Semiconductor materials are of great technological importance. A distinct feature is that the conductivity of semiconductor materials can be altered in a wide range by introducing impurities in a controlled way. This forms the basis for semiconductor junctions such as diodes, transistors and integrated circuits.

9.1 Band structure of direct and indirect semiconductors

The characteristic feature of a semiconductor is the energy gap E_G that separates the valence band (VB) from the conduction band (CB). The size of the band gap is in the range of $E_G = 0.1 \dots 4 \text{ eV}$. Materials with a larger band gap are by definition insulators. Depending on the respective positions of the maximum of the valence band and the minimum of the conduction band in the Brillouin zone, semiconductors can be divided in two groups:

- Direct semiconductor (e.g. GaAs): Minimum of the CB and maximum of the VB are at the same position in the Brillouin zone.
- Indirect semiconductor (e.g. Si): Minimum of the CB and maximum of the VB lie at different positions in the Brillouin zone.

In the vicinity of the extrema of the CB and VB, respectively, the band structure E(k) can be expressed in the parabolic approximation (only terms up to oder k^2 are kept). The surfaces of constant energy are ellipsoids. Within the parabolic approximation the dispersion of the conduction band can be written as:

$$E_{\rm CB}(\mathbf{k}) = E_{\rm c} + \hbar^2 \left[\frac{k_x^2 + k_y^2}{2m_t^*} + \frac{k_z^2}{2m_l^*} \right].$$
(9.1.1)

Here, m_t^* and m_l^* are the so-called transverse and longitudinal effective mass, respectively. E_c is the energy of the conduction band minimum. For Si, the ratios of the effective masses and the free electron mass m are given by $\frac{m_t^*}{m} = 0.19$ and $\frac{m_l}{m} = 0.98$, respectively.

The bandstructure in the vicinity of the VB maximum is usually more complicated than suggested by Fig. 9.1. Two bands with different curvatures meet at the VB maximum.

9 Semiconductors



Figure 9.1: Scheme of the bandstructure of (a) GaAs and (b) Si. Adopted from Wikipedia.

These bands are called the heavy hole band and the light hole band. The corresponding effective masses are given by m_{hh}^* and m_{lh}^* , respectively (see Fig. 9.2). A third band, the so-called split-off band, with effective mass m_{soh}^* is lowered by the split-off energy Δ from the other two bands due to spin-orbit interaction. The values for Si and GaAs are presented in table 9.1.

	m_{hh}^{*}/m	m_{lh}^{*}/m	m_{soh}^*/m	$\Delta(eV)$
Si	0.49	0.16	0.23	0.044
GaAs	0.45	0.082	0.17	0.34

Table 9.1: Effective masses and split-off energy of Si and GaAs. Source: Hunklinger, Festkörperphysik.

9.2 Charge carrier density in intrinsic semiconductors

In what follows, we assume that the dispersion relations in the vicinity of the CB minium and the VB maximum, respectively, are given by:

$$E_{CB}(k) = E_c + \frac{\hbar^2 k^2}{2m_c}$$
(9.2.1)

$$E_{VB}(k) = E_v - \frac{\hbar^2 k^2}{2m_v}.$$
(9.2.2)



Figure 9.2: Scheme of the bandstructure in the vicinity of the VB maximum.

Here, E_c is the energy of an electron at the CB minimum, E_v is the energy of an electron at the VB maximum, m_c is the effective mass of an electron near the CB minimum, and m_v is the effective mass of an electron near the VB maximum.

The densities of states of the conduction band and the valence band are given by

$$D_c = \frac{(2m_c)^{3/2}}{2\pi^2\hbar^3} \sqrt{E - E_c} \quad \text{with} \quad E \ge E_c, \tag{9.2.3}$$

$$D_v = \frac{(2m_v)^{3/2}}{2\pi^2\hbar^3}\sqrt{E_v - E} \quad \text{with} \quad E \le E_v.$$
(9.2.4)

The density of states within the energy gap is zero.

In thermal equilibrium, the occupation of the electronic states is governed by the Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp\left[\left(E - E_F\right)/k_B T\right] + 1}.$$
(9.2.5)

For undoped semiconductors, the Fermi energy E_F lies within the energy gap (see below). For $E - E_F \gg 2k_BT$, the Fermi-Dirac distribution can be approximated by the Boltzmann distribution:

$$f(E) = \frac{1}{\exp\left[(E - E_F)/k_B T\right] + 1} \approx \exp\left(-\frac{E - E_F}{k_B T}\right) \ll 1.$$
 (9.2.6)

The density of electrons in the conduction band follows from

$$n = \int_{E_c}^{\infty} f(E) D_c(E) dE.$$
(9.2.7)

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With equations (9.2.3) and (9.2.6), the electron density n can be written as

$$n = \frac{(2m_c)^{3/2}}{2\pi^2\hbar^3} e^{\frac{E_F}{k_B T}} \int_{E_c}^{\infty} \sqrt{E - E_c} e^{-\frac{E}{k_B T}} dE.$$
(9.2.8)

Substituting $X = (E - E_c)/k_B T$, we obtain:

$$n = \frac{(2m_c)^{3/2}}{2\pi^2\hbar^3} (k_B T)^{3/2} e^{-\frac{E_c - E_F}{k_B T}} \underbrace{\int_0^\infty \sqrt{X} e^{-X} dX}_{\frac{\sqrt{\pi}}{2}}, \qquad (9.2.9)$$

$$= 2\left(\frac{m_c k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-\frac{E_c - E_F}{k_B T}}.$$
(9.2.10)

The corresponding density of holes in the valence band is given by:

$$p = \int_{-\infty}^{E_v} D_v(E) \left[1 - f(E)\right] dE.$$
(9.2.11)

After a short calculation, we find:

$$p = 2\left(\frac{m_v k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\frac{E_v - E_F}{k_B T}}.$$
(9.2.12)

Next, we define the so-called effective densities of states for the electrons and holes, respectively:

$$N_c = 2\left(\frac{m_c k_B T}{2\pi\hbar^2}\right)^{3/2}, (9.2.13)$$

$$N_v = 2\left(\frac{m_v k_B T}{2\pi\hbar^2}\right)^{3/2}.$$
(9.2.14)

The product of the electron and hole concentrations is given by the so-called law of mass action:

$$np = n_i^2 = N_c N_v e^{-\left(\frac{E_g}{k_B T}\right)} = 4 \left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_c m_v)^{3/2} e^{-\left(\frac{E_g}{k_B T}\right)}.$$
(9.2.15)

For an intrinsic semiconductor, charge neutrality demands that

$$n = p. \tag{9.2.16}$$

The intrinsic charge carrier concentration can be thus calculated as:

$$n_i = p_i = \sqrt{N_c N_v} e^{-\left(\frac{E_g}{2k_B T}\right)} = 2 \left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_c m_v)^{3/4} e^{-\left(\frac{E_g}{2k_B T}\right)}.$$
(9.2.17)

For Si at room temperature (300 K), the intrinsic carrier concentration is $n_i = 1.5 \times 10^{10} \text{cm}^{-3}$.

The Fermi-level $E_F(T)$ takes the value for a given temperature T such that the charge neutrality condition is fulfilled. With

$$n = p = N_c e^{-\frac{E_c - E_F}{k_B T}} = N_v e^{\frac{E_v - E_F}{k_B T}},$$
(9.2.18)

we obtain

$$E_F(T) = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln\left(\frac{N_v}{N_c}\right) = \frac{E_c + E_v}{2} + \frac{3k_B T}{4} \ln\left(\frac{m_v}{m_c}\right).$$
(9.2.19)

9.3 Optical absorption in semiconductors

Optical absorption spectroscopy provide access to many essential electronic properties of semiconductors. In particular, it can be utilized to determine the size of the electronic band gap E_G . Below, we discuss electronic transistions in a semiconductor between the valence and the conduction band caused by light absorption. In doing so, we assume that the temperature is low enough such that valence band is essentially completly filled and the conduction band is empty.



Figure 9.3: Near-band gap transitions in (a) a direct semiconductor, (b) in an indirect semiconductor with phonon absorption, and (c) in an indirect semiconductor with phonon emission.

9.3.1 Direct semiconductors

We first consider interband transitions in the case of direct semiconductor. In the fundamental transition process, a photon with energy $\hbar\omega$ of the incident light field is absorbed

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and an electron is excited from a state with energy E_{VB} in the valence band to a state with energy E_{CB} in the conduction band (see Fig. 9.3 (a)). We can consider this process as the creation of an electron-hole pair, where the hole corresponds to the now empty electronic state in the valence band and the electron occupies a state in the conduction band. Conservation of energy demands that

$$E_{\rm CB} - E_{\rm VB} = \hbar\omega. \tag{9.3.1}$$

Obviously, light can only be absorbed if $\hbar \omega \geq E_G$. For smaller photon energies, the semiconductor is transparent.

A second condition follows from the conservation of momentum:

$$\hbar \mathbf{k}_{\rm CB} - \hbar \mathbf{k}_{\rm VB} = \hbar \mathbf{k}_{\gamma}.\tag{9.3.2}$$

Here, $\hbar \mathbf{k}_{\rm VB}$ and $\hbar \mathbf{k}_{\rm CB}$ are the crystal momentum of the electron before and after the transition, respectively, and $\hbar \mathbf{k}_{\gamma}$ is the photon momentum. For optical frequencies, the photon wave vector is much smaller than the size of the Brillouin zone. Hence, we can neglect the photon momentum and the crystal momentum of the electron essentially does not change during a direct interband transition:

$$\hbar \mathbf{k}_{\rm CB} = \hbar \mathbf{k}_{\rm VB}.\tag{9.3.3}$$

In the E-k diagram, interband transitions are therefore represented by vertical arrows.

Herafter, we assume that the bands have parabolic shapes in the vicinity of the conduction band minium and the valence band maximum. In this case, we can rewrite equation (9.3.1) as:

$$\hbar\omega = E_{\rm CB}(\mathbf{k}) - E_{\rm VB}(\mathbf{k}) = E_c + \frac{\hbar^2 |\mathbf{k}|^2}{2m_c} - E_v + \frac{\hbar^2 |\mathbf{k}|^2}{2m_v} = E_G + \frac{\hbar^2 |\mathbf{k}|^2}{2\mu}, \qquad (9.3.4)$$

where the reduced electon-hole mass μ is defined by

$$\frac{1}{\mu} = \frac{1}{m_c} + \frac{1}{m_v}.$$
(9.3.5)

The excitation rate $W_{\mathbf{k}}$ for a certain **k**-point follows from Fermi's golden rule:

$$W_{\mathbf{k}} = \frac{2\pi}{\hbar} |\langle c|H_d|v\rangle|^2 \delta(E_{\rm CB}(\mathbf{k}) - E_{\rm VB}(\mathbf{k}) - \hbar\omega).$$
(9.3.6)

Here, $\langle c|H_d|v\rangle$ is the matrix element of the perturbation Hamiltonian for the electromagnetic interaction between the two states. The total excitation rate can be calculated by integration over all **k**-points:

$$W = \frac{2\pi}{\hbar} \int |\langle c|H_d|v\rangle|^2 \frac{2}{8\pi^3} \delta(E_{\rm CB}(\mathbf{k}) - E_{\rm VB}(\mathbf{k}) - \hbar\omega) d^3k.$$
(9.3.7)

In the following we assume that the matrix element is independent of \mathbf{k} . This allows us to write the excitation rate per unit volume as

$$W = \frac{2\pi}{\hbar} |\langle c|H_d|v\rangle|^2 \mathcal{D}_j(\hbar\omega), \qquad (9.3.8)$$

where we have introduced the joint density of states

$$\mathcal{D}_{j}(\hbar\omega) = \frac{2}{8\pi^{3}} \int \delta(E_{\rm CB}(\mathbf{k}) - E_{v}VB(\mathbf{k}) - \hbar\omega)d^{3}k.$$
(9.3.9)

With

$$d^{3}k = dSdk_{\perp} = dS\left[\frac{d(E_{\rm CB} - E_{\rm VB})}{\nabla_{\mathbf{k}}(E_{\rm CB} - E_{\rm VB})}\right]$$
(9.3.10)

we obtain after integration over $d(E_{\rm CB} - E_{\rm VB})$:

$$\mathcal{D}_j(\hbar\omega) = \frac{2}{8\pi^3} \int_S \frac{1}{|\nabla_{\mathbf{k}}(E_{\rm CB} - E_{\rm VB})|_{E_{\rm CB} - E_{\rm VB} = \hbar\omega}} dS.$$
(9.3.11)

After a short calculation we obtain:

$$\mathcal{D}_{j}(\hbar\omega) = \begin{cases} 0 & \text{for } \hbar\omega < E_{g} \\ \frac{(2\mu)^{3/2}}{2\pi^{2}\hbar^{3}}\sqrt{\hbar\omega - E_{g}} & \text{for } \hbar\omega \ge E_{g} \end{cases}$$
(9.3.12)

The absorption coefficient $\alpha(\hbar\omega)$ characterizes the attuantion of the light intensity $I(\hbar\omega)$ inside of a material along the propagation path. It is defined as

$$\alpha(\hbar\omega) = -\frac{1}{I}\frac{dI}{dz}.$$
(9.3.13)

For a direct semiconductor, we expect that

$$\alpha(\hbar\omega) \propto \mathcal{D}_j(\hbar\omega) \propto \sqrt{\hbar\omega - E_g}.$$
(9.3.14)

9.3.2 Indirect semiconductors

In the case of an indirect semiconductor, the minimum of the conduction band and the maximum of the maximum of the valence band lie at different positions in the Brillouin zone. Hence, one can not fulfill simultaneously momentum and energy conversion in interband transitions that invole only a photon and an electron. For this reason, near-band gap transitions in indirect semiconductors additionally require either the absorption

or emission of a phonon with energy $\hbar\Omega$ and momentum $\hbar \mathbf{q}$ (see Fig. 9.3 (b) and (c)). Conservation of energy and momentum demand that:

$$E_{\rm CB} = E_{\rm VB} + \hbar\omega \pm \hbar\Omega \tag{9.3.15}$$

$$\hbar \mathbf{k}_{\rm CB} = \hbar \mathbf{k}_{\rm VB} \pm \hbar \mathbf{q}. \tag{9.3.16}$$

Here, the + and - sign correspond to the absorption and emission of a phonon, respectively.

The involvement of phonons in the transition process makes the absorption of light in indirect semiconductors inefficient. Hence light with a photon energy close to the band gap can typically penetrate deeper into a indirect semiconductor than in a direct semiconductor with comparable band gap before being absorbed.

9.4 Excitons

In the previous section we discussed that light absorption is only possible for photon energies $\hbar \omega \geq E_g$. However, in low-temperature absorption experiments with direct semiconductors one often finds features in the absorption spectrum below E_g . The reason of this apparent contradiction is that we have neglected so far the Coulomb interaction between the electron and the hole. In a first approximation, we can treat a bound electronhole pair, a so-called exciton, as a hydrogen like atom with binding energy

$$E_n = -\frac{\mu}{m_0} \frac{1}{\epsilon_r^2} \frac{R_H}{n^2},$$
(9.4.1)

where m_0 is the free electron mass, ϵ_r is the dielectric permittivity of the semiconductor and R_H is the Rydberg constant. The first factor accounts for the effective masses of the electron and the hole in the semiconductor. The second factor treats the semiconductor as a homogeneous dielectric material. Both factors greatly reduce the binding energy of excitons compared to hydrogen. Experimentally one finds that typical exciton binding energies in direct bulk semiconductors are in the order of a few meV to a few tenth of meV.

Excitons can be observed in many solid state systemes. Depending on the size of the dielectric constant ϵ_r , one distinguishes two types of excitons:

• Wannier-Mott type excitons are found in materials with large ϵ_r , e.g., semiconductors. Strong screening leads to small binding energies and large Bohr-radii. Wannier-Mott excitons are hence delocalized and can move freely through the crystal. • Frenkel excitons occure in materials with small ϵ_r , e.g., molecular crystals. They have an extend comparable to the unit-cell size and are tightly bound.



Figure 9.4: Wannier-Mott and Frenkel excitons.

Excitons can be also found in two-dimensional transition metal dichalcogenide (TMD) semiconductors, e.g., MoS_2 , MoS_2 , and WS_2 . In these monolayers the dielectric screening is strongly reduced such that excitons can be observed in optical experiments, e.g., reflection measurements, even at room temperature (see Fig. 9.5).



Figure 9.5: A-Exciton resonance of WS_2 at room temperature.

9.5 Doping of semiconductors

The free carrier concentration in semiconductors can be in increased by doping, i.e, by the addition of electrically active impurities to the semiconductor. In this connection, one distinguishes between two types of impurities:

- Impurities which increase the number of electrons in the conduction band are called donors.
- Impurities which increase the number of holes in the valence band are called acceptors.

Commonly used doping techniques are diffusion doping and ion implantation. Diffusing doping results in a montonically decreasing dopant concentration away from the surface while ion implantation results in a non-monotonic profile (see Fig. 9.6).







Figure 9.6: Doping methods.

In what follows, we will discuss doping using the example of a Si crystal. Here, each Si atom is covalently bound to four neighboring Si atoms. A donor is created by replacing a Si atom by a valence-five atom such as P. Four of the five valence electrons of the P atom are required to bind the P atom in the crystal. The fifth electron, however, "finds no partner" and is only weakly bound to the positively charged donor core. Because of its small binding energy, the fifth electron can be easily promoted to the conduction band.

To estimate the binding energy E_d of the fifth electron, we again use a simple hydrogenatom model in which we replace the free electron mass m by the effective mass m^* and include the screening effect of the surrounding Si via the dielectric constant ϵ_r :

$$E_d = -\frac{1}{2} \frac{m^* e^4}{\left(4\pi\epsilon_r\epsilon_0\right)^2 \hbar^2} \frac{1}{\nu^2} = E_{H,\nu} \frac{m^*}{m\epsilon_r^2}.$$
(9.5.1)



Figure 9.7: Scheme of two commonly used doping techniques.

Here, ν is the principal quantum number and $E_{H,\nu}$ is the corresponding energy level of the hydrogen atom.

The ionization energy of the $\nu = 1$ level of a hydrogen atom is 13.6 eV. For the P atom in silicon, we find with $m^* = 0.3m$ and $\epsilon_r = 11.7$, that the ionization energy is in the order of 30 meV. The modified Bohr radius of the electron in the Si crystal is given by

$$r = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m^*e^2} = a_0\epsilon_r\frac{m}{m^*},\tag{9.5.2}$$

where, a_0 is the Bohr radius of the hydrogen atom. For the values mentioned above, we find $r \approx 2 \text{ nm}$. This value is considerably larger than the interatomic separation between two Si atoms in the crystal (0.23 nm). This is an a posteriori justification of the use of the dielectric constant to describe screening.

Replacing a Si atom by a valence-three atom such as B creates an acceptor. Here, one bond with a neighboring Si atom is unsatisfied. This unsatisfied bond can easily accept an electron from the valence band. Formally, this process can be interpreted as the promotion of a hole from the acceptor level to the valence band. The binding energy E_a of the hole can be estimated in a calculation analogous to the case of a donor. Here, however, the effective mass is that of a hole in the valence band.

9.6 Carrier densities in doped semiconductors

In the following, we want to calculate the densities of electrons and holes as well as the value of the Fermi level for a doped semiconductor. Our starting point is the law of mass action. When we derived the law of mass action, we did not specify whether the electrons in the conduction band originate from the valence band or from a donor level. Similarly,



Figure 9.8: Energy levels of donors and acceptors.

we made no assumptions about the origin of the holes in the valence band. Hence, the law of mass action is also valid for doped semiconductors:

$$np = N_c N_v e^{-\left(\frac{E_g}{k_B T}\right)}.$$
(9.6.1)

The total donor concentration N_D is given by the sum of the concentrations of the neutral donors N_D^0 and the ionized donors N_D^+ :

$$N_D = N_D^0 + N_D^+. (9.6.2)$$

Likewise, we can write the total acceptor concentration as

$$N_A = N_A^0 + N_A^-. (9.6.3)$$

Here, N_A^0 is the concentration of the neutral acceptors and N_A^- is the concentration of the ionized acceptors. The charge neutrality condition in the presence of acceptors and donors reads:

$$n + N_A^- = p + N_D^+. (9.6.4)$$

The electron-occupation probability of the donor level can be calculated with the help of the Fermi-Dirac distribution:

$$N_D^0 = \frac{N_D}{\exp\left[\left(E_D - E_F\right)/k_B T\right] + 1}.$$
(9.6.5)

At this point, we neglect a slight complication that arises from the fact that the donor level can be usually only occupied by a single electron. Similarly, the hole-occupation probability of the acceptor level is given by

$$N_A^0 = \frac{N_A}{\exp\left[\left(E_F - E_A\right)/k_B T\right] + 1}.$$
(9.6.6)

In what follows, we consider a n-type semiconductor $(N_A = 0)$. In that case, electrons in the conduction band originate either from the valence band or from donors:

$$n = N_D^+ + p = N_c e^{-\frac{E_c - E_F}{k_B T}}.$$
(9.6.7)

As a further simplification, we assume that the effect of doping dominates over the intrinsic carrier concentration:

$$n \approx N_D^+ = N_D - N_D^0$$

= $N_D \left(1 - \frac{1}{\exp\left[(E_D - E_F) / k_B T \right] + 1} \right).$ (9.6.8)

The value of the Fermi level E_F follows from equation (9.6.7):

$$e^{\frac{E_F}{k_B T}} = \frac{n}{N_c} e^{\frac{E_c}{k_B T}}.$$
(9.6.9)

Substituting equation (9.6.9) in (9.6.8), we obtain:

$$n \approx \frac{N_D}{1 + e^{\frac{E_d}{k_B T}} n/N_C} \tag{9.6.10}$$

with

$$E_d = E_c - E_D. (9.6.11)$$

This is a quadratic equation for n

$$n+n^2 \frac{e^{\frac{E_d}{k_B T}}}{N_c} \approx N_D, \tag{9.6.12}$$

which has the following physically meaningful solution:

$$n \approx 2N_D \left(1 + \sqrt{1 + 4\frac{N_D}{N_c} e^{\frac{E_d}{k_B T}}} \right)^{-1}.$$
(9.6.13)

The corresponding hole concentration p follows from the law of mass action:

$$p = \frac{n_i p_i}{n}.\tag{9.6.14}$$

The temperature behavior of the electron densisty and the Fermi-level shows the following behaviour:

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• Freeze-out regime (low temperatures with $4\frac{N_D}{N_c}e^{\frac{E_d}{k_BT}} \gg 1$):

$$n \approx \sqrt{N_D N_C} e^{-\frac{E_d}{2k_B T}},\tag{9.6.15}$$

$$E_F(T) \approx E_C - \frac{E_d}{2} - \frac{k_B T}{2} \ln\left(\frac{N_c(T)}{N_D}\right).$$
 (9.6.16)

• Saturation regime (intermediate temperatures with $4\frac{N_D}{N_c} e^{\frac{E_d}{k_B T}} \ll 1$):

$$n \approx N_D = const.$$
 (9.6.17)

$$E_F(T) \approx E_C - k_B T \ln\left(\frac{N_c(T)}{N_D}\right).$$
(9.6.18)

• Intrinsic regime (high temperatures):

$$n \approx n_i \gg N_D. \tag{9.6.19}$$



Figure 9.9: Qualitative temperature dependence of the carrier concentration n and the Fermi energy E_F of a n-type semiconductor.

9.7 Mobility of semiconductors

In thermal equilibrium, the average kinetic energy of a conduction electron in a semiconductor can be estimated with the help of the theorem for equipartition of energy:

$$\frac{1}{2}m^*v_{th}^2 = \frac{3}{2}k_BT.$$
(9.7.1)

The thermal velocity v_{th} for Si at room temperature is in the order of 10^7 cm/s . Because of its random nature, the thermal motion leads to a vanishing average displacement of the electrons.

If we apply a small electric DC-field \mathcal{E} , the electrons will acquire an additional velocity component, the so called drift-velocity \mathbf{v}_d , which is superimposed on the thermal velocity. This drift velocity is responsible for the net current density.

To calculate the drift velocity, we use the classical equation of motion:

$$m^* \dot{\mathbf{v}} + \frac{m^*}{\tau} \mathbf{v} = -e\boldsymbol{\mathcal{E}}.$$
(9.7.2)

In steady state ($\dot{\mathbf{v}} = 0$), the average electron velocity is the drift velocity:

$$\mathbf{v}_d = \frac{-e\boldsymbol{\mathcal{E}}\boldsymbol{\tau}}{m^*}.\tag{9.7.3}$$

The electron mobility b is defined by:

$$b = \frac{e\tau}{m^*}.$$

Using this definition, we can write the drift velocity as

$$\mathbf{v}_d = -b\boldsymbol{\mathcal{E}}.\tag{9.7.5}$$

So far, we have only considered electrons. The total current density results from the motion of both electrons and holes. It is given by:

$$\mathbf{j} = -en\mathbf{v}_{d,e} + ep\mathbf{v}_{d,h} = e\left(nb_e + pb_h\right)\boldsymbol{\mathcal{E}}.$$
(9.7.6)

In what follows, we consider the temperature dependence of the electron mobility. The hole mobility follows a similar trend and will not be explicitly discussed. The scattering rate $1/\tau$ is proportional to the average electron velocity $\langle v \rangle$ and the scattering cross section Σ of the corresponding scattering process:

$$\frac{1}{\tau} \propto \langle v \rangle \Sigma. \tag{9.7.7}$$

Since the drift velocity is usually much smaller than the thermal velocity for small field strength, we find

$$\langle v \rangle \propto \sqrt{T}.$$
 (9.7.8)

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First, we will consider scattering of electrons from acoustic phonons. For this purpose, we assume that the scattering cross section is proportional to the average vibrational amplitude $\langle s^2 \rangle$ of a phonon. For temperatures above the Debye temperatue, one finds

$$M\omega^2 \langle s^2 \rangle = k_B T. \tag{9.7.9}$$

Hence, we expect that the relaxation time due to scattering from acoustic phonons varies as

$$\frac{1}{\tau_{\rm ph}} \propto \langle v \rangle \Sigma_{\rm ph} \propto T^{3/2}.$$
(9.7.10)

For the mobility, we thus obtain the estimate

$$b_{\rm ph} \propto T^{-3/2}$$
. (9.7.11)

Another important source of scattering in semiconductors is scattering from charged defects (ionized donors or acceptors). Here, we assume that this process can be described analogous to Rutherford scattering. The corresponding scattering cross section is proportional to the inverse fourth power of the velocity:

$$\Sigma_{\mathrm{def}} \propto \langle v \rangle^{-4}.$$
 (9.7.12)

The inverse scattering time varies as

$$\frac{1}{\tau_{def}} \propto T^{-3/2}$$
 (9.7.13)

and the mobility is proportional to

$$b_{\rm def} \propto T^{3/2}.$$
 (9.7.14)



Figure 9.10: Qualitative temperature dependence of the electron mobility of a semiconductor.

9.8 Continuity equation

In the previous section we considered the transport of carriers in homogeneous semiconductor samples under the influence on an external electric field. Next, we additionally allow for a gradient of the electron density and also include local generation and recombination processes. The latter are characterized by the generation rate $G_n(x)$ and recombination rate $R_n(x)$, respectively. Inspection of Fig. 9.11 shows that the electron number in the volume V = Adx changes with the rate

$$\frac{\partial n}{\partial t}Adx = \left[\frac{j_n(x)}{-e} - \frac{j_n(x+dx)}{-e}\right]A + (G_n(x) - R_n(x))Adx.$$
(9.8.1)

With

$$j_n(x+dx) = j_n(x) + \frac{\partial j_n}{\partial x}dx$$
(9.8.2)

we can rewrite equation (9.8.1) as

$$\frac{\partial n}{\partial t} = \frac{1}{e} \frac{\partial j_n}{\partial x} + \left(G_n(x) - R_n(x)\right). \tag{9.8.3}$$

Following a similar derivation for the holes, we can express the rate at which the concentration of holes changes as

$$\frac{\partial p}{\partial t} = -\frac{1}{e} \frac{\partial j_p}{\partial x} + \left(G_p(x) - R_p(x)\right).$$
(9.8.4)



Figure 9.11: Charge transport and generation and recombination processes in a slab of semiconductor.

The current densities comprise two components: (i) the drift currents j_n^{drift} and j_p^{drift} caused by the electric field and (ii) the diffusion currents j_n^{diff} and j_p^{diff} resulting from

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the charge carrier concentration gradients:

$$j_n = j_n^{diff} + j_n^{drift} = e\left(D_n \frac{\partial n}{\partial x} + nb_n \mathcal{E}\right)$$
(9.8.5)

$$j_p = j_p^{diff} + j_p^{drift} = e\left(-D_p\frac{\partial p}{\partial x} + pb_p\mathcal{E}\right).$$
(9.8.6)

Here, D_n and D_p are the diffusion constants of the electrons and holes, respectively.

In the following, we consider the minority carriers, i.e., electrons in a p-type semiconductor and holes in a n-type semiconductor. Using a relaxation time ansatz, the relaxation rates of the electrons and holes can be written as

$$R_n(x) = \frac{n_p - n_{p0}}{\tau_n} \tag{9.8.7}$$

$$R_p(x) = \frac{p_n - p_{n0}}{\tau_p}, \tag{9.8.8}$$

where n_{p0} and p_{n0} are the corresponding electron and hole densities at thermal equilibrium and τ_n and τ_p are the relaxation times. The continuity equations for the minority carriers then read:

$$\frac{\partial n_p}{\partial t} = D_n \frac{\partial^2 n_p}{\partial x^2} + b_n \mathcal{E} \frac{\partial n_p}{\partial x} + n_p b_n \frac{\partial \mathcal{E}}{\partial x} + G_n - \frac{n_p - n_{p0}}{\tau_n}$$
(9.8.9)

$$\frac{\partial p_n}{\partial t} = D_p \frac{\partial^2 p_n}{\partial x^2} - b_p \mathcal{E} \frac{\partial p_n}{\partial x} - p_n b_p \frac{\partial \mathcal{E}}{\partial x} + G_p - \frac{p_n - p_{n0}}{\tau_p}.$$
(9.8.10)

9.8.1 Excess carrier injection at the surface

As a first example, we consider a n-type semiconductor which is illuminated on one side. If the photon energy is larger than the electronic band gap, photons can be absorbed and create additional electron-hole pairs. While the density of majority carriers is hardly changed, the concentration of holes is increased at the interface. This results in a hole concentration gradient in the interior of the semiconductor. Under steady state conditions, the continuity equation reads

$$\frac{\partial p_n}{\partial t} = 0 = D_p \frac{\partial^2 p_n}{\partial x^2} - \frac{p_n - p_{n0}}{\tau_p}.$$
(9.8.11)

With the boundary conditions $p_n(x=0) = const$ and $p_n(x \to \infty) = p_{n0}$, we obtain

$$p_n(x) = p_{n0} + [p_n(0) - p_{n0}] e^{-x/L_p}$$
(9.8.12)

with the diffusion length $L_p = \sqrt{D_p \tau_p}$.


Figure 9.12: Concentration of holes in a n-type semiconductor which is illuminated on one side.

9.8.2 Photo conductor

Consider an intrinsic semiconductor that is uniformly illuminated with light. The total charge carrier density of electrons n (holes p) is given by the sum of the charge carrier density of electrons n_0 (holes p_0) in the absence of optical illumination and the density of photogenerated excess electrons Δn (holes Δp):

$$n = n_0 + \Delta n, \tag{9.8.13}$$

$$p = p_0 + \Delta p. \tag{9.8.14}$$

Since the excess electrons and holes are created pairwise, the condition $\Delta n = \Delta p$ holds.



Figure 9.13: Photoconductive detector.

The generation rate G of electron-hole pairs in the crystal with volume V = wA (see Fig.9.13) is given by

$$G = \eta \Phi / w A, \tag{9.8.15}$$

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where η is the fraction of the incident photons that generate an electron hole-pair and Φ is the number of incident photons per second. The recombination rate of excess charge carriers is given by

$$R = \frac{\Delta n}{\tau_R},\tag{9.8.16}$$

where τ_R is the excess-carrier recombination lifetime. Under steady-state conditions, the two rates balance each other (G = R) and we obtain:

$$\Delta n = \frac{\eta \Phi \tau_R}{wA}.\tag{9.8.17}$$

The photogenerated free charge carriers change the conductivity of the semiconductor by

$$\Delta \sigma = q(\Delta n b_e + \Delta p b_h). \tag{9.8.18}$$

Inserting Δn in the last equation yields

$$\Delta \sigma = q \Delta n (b_e + b_h) = \frac{q \eta \tau_R (b_e + b_h)}{w A} \Phi.$$
(9.8.19)

The total current I_t can be written as the sum of the current I_0 in the absence of optical illumination and the photo current I_p . The latter is given by

$$I_p = \frac{q\eta\tau_R(v_{d,e} + v_{d,h})}{w}\Phi.$$
 (9.8.20)

The electron transit time across the sample can be calculated as

$$\tau_{t,e} = w/v_{d,e}.$$
(9.8.21)

For many semiconductors, the condition $v_{d,e} \gg v_{d,h}$ holds. The photo current can thus be written as

$$I_p \approx q\eta \frac{\tau_R}{\tau_{t,e}} \Phi. \tag{9.8.22}$$

9.8.3 The Haynes-Shockley experiment

The Haynes-Schockley experiment¹ is one of the classical experiments in semiconductor physics. It can be used to determine the mobility, the lifetime, and the diffusion coefficient of the minority carriers in a semiconductor. A scheme of the Haynes-Schockley experiment is shown in Fig. 9.14.

¹J. R. Haynes and W. Shockley, Investigation of Hole Injection in Transistor Action, Phys. Rev. **75**, 691 (1949)



Figure 9.14: Scheme of the Haynes-Schockley experiment.

Electron-hole pairs are locally generated in a n-type semiconductor at the time time t = 0and the position x = 0 by illumination with a short focused light pulse. As before, we assume that the electron concentration(majority carriers) is not noticeably altered by this. However, the hole concentration (minority carriers) is locally increased and assumes the value $p_n(x = 0, t = 0)$. After the light pulse, the generation rate G_p is zero. If the electric field is constant across the sample, the continuity equation can be written as

$$\frac{\partial p_n}{\partial t} = D_p \frac{\partial^2 p_n}{\partial x^2} - b_p \mathcal{E} \frac{\partial p_n}{\partial x} - \frac{p_n - p_{n0}}{\tau_p}.$$
(9.8.23)

The hole concentration varies as

$$p_n(x,t) = \frac{N}{\sqrt{4\pi D_p t}} \exp\left(-\frac{(x-b_p \mathcal{E}t)^2}{4\pi D_p t} - \frac{t}{\tau_p}\right) + p_{n0}.$$
(9.8.24)

By measuring the current at the contact (x = L) as a function of time after the arrival of the light pulse one can determine the drift velocity and hence the mobility of the holes.



Figure 9.15: Hole concentration after illumination of a n-type semiconductor with a short light pulse. The holes move under the influence of the electric field \mathcal{E} with the drift velocity v_d .

9.9 The p-n junction

9.9.1 Unbiased p-n junction

In what follows, we consider a p-n junction, i.e., a semiconductor crystal which is doped on one half with acceptors (p-type semiconductor) and on the other half with donors (n-type semiconductor). In a gedankenexperiment, we start with the two separate halves. The properties of separated halves, e.g., the values of the corresponding Fermi-levels, have been discussed in the previous sections.



Figure 9.16: Unbiased p-n junction.

If we combine the two halves and apply no voltage, the large carrier concentration gradients cause carrier diffusion. The electrons from the n-side diffuse into the p-side and recombine there with holes. Likewise, holes from the p-side diffuse into the n-side and recombine with electrons. As a result, a double layer of uncompensated negative acceptors and positive donors forms near the junction. This space-charge zone creates an electric field that counteracts the diffusion. The corresponding potential difference is called built-in potential or diffusion voltage V_D .

In thermal equilibrium, the Fermi level takes a constant value within the whole crystal. The bending of the bands near the junction can be described by a macropotential V(x). This macropotential is related to the space charge density $\rho(x)$ via the Poisson equation:

$$\frac{\partial^2 V(x)}{\partial x^2} = -\frac{\rho(x)}{\epsilon \epsilon_0}.$$
(9.9.1)

Far away from the junction, the concentration of majority carriers (electrons in the nregion, holes in the p-region) is given by:

$$n_n = N_c \, e^{-\frac{E_c^n - E_F}{k_B T}},\tag{9.9.2}$$

$$p_p = N_v \, e^{-\frac{E_F - E_v^p}{k_B T}}.$$
(9.9.3)

The concentration of the corresponding minority carriers (holes in the n-region, electrons in the p-region) can be calculated from

$$n_i^2 = n_n p_n = N_v N_c e^{-\frac{E_c^n - E_v^n}{k_B T}}.$$
(9.9.4)

The diffusion voltage is related to the carrier concentrations:

$$eV_D = -(E_v^n - E_v^p) = k_B T \ln\left(\frac{p_p n_n}{n_i^2}\right) = k_B T \ln\left(\frac{N_A N_D}{n_i^2}\right).$$
 (9.9.5)

Here, we assumed in the last step that we are in the saturation regime.

In thermal equilibrium, the net current flow of carriers (electrons and holes) across the junction vanishes. For each type of carrier, the drift current caused by V_D is exactly compensated by the diffusion current due to the carrier concentration gradient:

$$j_n = j_n^{diff} + j_n^{drift} = e\left(D_n \frac{\partial n}{\partial x} + nb_n \mathcal{E}\right) = 0, \qquad (9.9.6)$$

$$j_p = j_p^{diff} + j_p^{drift} = e\left(-D_p\frac{\partial p}{\partial x} + pb_p\mathcal{E}\right) = 0.$$
(9.9.7)

Here, D_n and D_p are the diffusion constants for electrons and holes, respectively. With the help of equation (9.9.6), we find

$$D_n \frac{\partial n}{\partial x} = n b_n \frac{\partial V}{\partial x},\tag{9.9.8}$$

where

$$\mathcal{E} = -\frac{\partial V}{\partial x} \tag{9.9.9}$$

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has been used.

In the space-charge region, the electron concentration is position dependent with

$$n(x) = N_c \exp\left(-\frac{E_c^p - eV(x) - E_F}{k_B T}\right).$$
(9.9.10)

The gradient of the electron concentration can be calculated as

$$\frac{\partial n}{\partial x} = n \frac{e}{k_B T} \frac{\partial V}{\partial x}.$$
(9.9.11)

A comparison with equation (9.9.8) yields the so-called Einstein relation:

$$D_n = \frac{k_B T}{e} b_n. \tag{9.9.12}$$

The analogous relationship for the holes reads:

$$D_p = \frac{k_B T}{e} b_p. \tag{9.9.13}$$

In what follows, we use the so-called Schottky model of the space charge zone:

$$\rho(x) = \begin{cases}
0 & \text{for} \quad x < -d_p \\
-eN_A & \text{for} \quad -d_p < x < 0 \\
eN_D & \text{for} \quad 0 < x < d_n \\
0 & \text{for} \quad x > d_n
\end{cases}$$
(9.9.14)

With a piecewise constant space-charge density, the Poisson equation can be easily integrated. We find for the n-region $(0 < x < d_n)$ of the space-charge zone:

$$\mathcal{E} = -\frac{eN_D}{\epsilon\epsilon_0}(d_n - x) \tag{9.9.15}$$

and

$$V(x) = V_n(\infty) - \frac{eN_D}{2\epsilon\epsilon_0}(d_n - x)^2.$$
(9.9.16)

For the p-region $(d_p < x < 0)$, we get

$$\mathcal{E} = -\frac{eN_A}{\epsilon\epsilon_0}(x+d_p) \tag{9.9.17}$$

and

$$V(x) = V_p(-\infty) + \frac{eN_A}{2\epsilon\epsilon_0}(x+d_p)^2.$$
(9.9.18)

Charge neutrality requires, that

$$N_D d_n = N_A d_p \tag{9.9.19}$$

and the continuity of V(x) at x = 0 demands:

$$\frac{e}{2\epsilon\epsilon_0}\left(N_D d_n^2 + N_A d_p^2\right) = V_n(\infty) - V_p(-\infty) = V_D.$$
(9.9.20)

With the help of the last two equations, we can calculate the spatial extend of the spacecharge zone:

$$d_n = \sqrt{\frac{2\epsilon\epsilon_0 V_D}{e} \frac{N_A/N_D}{N_A + N_D}},\tag{9.9.21}$$

$$d_p = \sqrt{\frac{2\epsilon\epsilon_0 V_D}{e} \frac{N_D/N_A}{N_A + N_D}}.$$
(9.9.22)

9.9.2 Biased p-n junction

In this section, we consider the effect of an external voltage U on the p-n junction. Because of the depletion of free carriers, the space-charge zone has a considerable larger resistance than the rest of the semiconductor crystal. Hence, we can assume that the potential drop across the space-charge zone is equal to the externally applied voltage. Outside of the space-charge zone, $E_c(x)$, $E_v(x)$, and V(x) are constant within the respective regions. The total potential drop across the space-charge region is thus given by:

$$V_n(\infty) - V_p(-\infty) = V_D - U.$$
 (9.9.23)

Here, we define that the potential U is positive when the potential of the p side is increased with respect to the n side.

As an effect of the applied voltage, the extent of the space-charge zone becomes:

$$d_n(U) = d_n(U=0)\sqrt{1 - \frac{U}{V_D}}$$
(9.9.24)

$$d_p(U) = d_p(U=0)\sqrt{1 - \frac{U}{V_D}}$$
(9.9.25)

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Figure 9.17: Biased p-n junction.

In thermal equilibrium and without applied voltage, the drift currents of electrons and holes are compensated by the corresponding diffusion currents. The electron drift current (hole drift current) results from electrons (holes) which have been thermally generated within the p-side (n-side) of the space-charge zone and which move under the influence of V_D to the n-side (p-side). For that reason, the drift currents are often called generation currents (I_n^{gen} and I_p^{gen} , respectively). They are largely independent of the externally applied voltage. However, they can be increased if we increase the generation rates of the minority carriers by illumination of the p-n junction.

The situation is different for the diffusion currents which stem from the majority carriers. Since the majority carriers have to move against the potential, only the fraction $\exp -e(V_d - U)/k_BT$ (Boltzmann-factor) of the majority carriers can overcome the barrier and reach the other side. There the electrons and holes each are minority carriers which recombine with the corresponding majority carriers (holes and electrons, respectively). The diffusion current is thus often called the recombination current (I_n^{rec} and I_p^{rec} , respectively).

Combining these effects, we obtain for the electron currents:

$$|I_n^{rec}(U=0)| = |I_n^{gen}| = const,$$
(9.9.26)

$$I_n^{rec}(U) \propto e^{-e\frac{V_d - U}{k_B T}}.$$
 (9.9.27)

Together, we thus have

$$I_n^{rec}(U) = |I_n^{gen}| \, e^{\frac{eU}{k_B T}}.$$
(9.9.28)

The total electron current is given by

$$I_n = I_n^{rec} + I_n^{gen} = |I_n^{gen}| \left(e^{\frac{eU}{k_B T}} - 1 \right).$$
(9.9.29)

For the hole current, we find after the analogous analysis a corresponding expression. The total current through the p-n junction is thus given by:

$$I(U) = (|I_n^{gen}| + |I_p^{gen}|) \left(e^{\frac{eU}{k_B T}} - 1 \right) = I_s \left(e^{\frac{eU}{k_B T}} - 1 \right).$$
(9.9.30)

Here, we have introduced in the last step the so-called saturation current $I_s = |I_n^{gen}| + |I_p^{gen}|$.



Figure 9.18: Schematic representation of the current voltage characteristic of a p-n junction.

9.10 Metal-semiconductor contacts

Metal-semiconductor contacts are an integral part of every electronic semiconductor device. A profound understanding of the properties of these contacts is thus important from a technological point of view.



Figure 9.19: (a) Energy band diagram of an isolated n-type semiconductor adjacent to an isolated metal $(e\Phi_M > e\Phi_H)$. (b) Energy band diagram of the Schottky-contact in thermal equilibrium $(e\Phi_M > e\Phi_H)$.

Fig. 9.19 (a) depicts the energy band diagrams of an isolated n-type semiconductor adjacent to an isolated metal. As a common reference energy we choose the vacuum energy E_{vac} that corresponds to an electron that has been just released from either the metal or the semiconductor. The work functions $e\Phi_M$ and $e\Phi_S$ are the energies required to bring an electron from the Fermi level of the metal and the semiconductor, respectively, to the vacuum level. Note that the work function $e\Phi_S$ of the semiconductor depends on the doping concentration. The electron affinity $e\chi$ is the energy that is required to promote an electron from the conduction-band minimum to the vacuum level.

If the metal and the semiconductor are brought in close contact, electrons flow across the contact until the Fermi levels E_F take the same value in both materials. Furthermore, the vacuum level E_{vac} must be continuous.

9.10.1 Schottky-contact

We first discuss the so-called Schottky-contact with $\Phi_M > \Phi_S$ (see Fig. 9.19 (b)). When the two materials are brought into contact, electrons flow from the semiconductor to the metal in order to reduce the total energy of the combined system. As a result, the semiconductor is depleted of electrons near the contact and a positive space charge zone made up from the spatially fixed ionized donors is formed. The additional electrons in the metal give rise to a negative space charge zone. Because of the large electron concentration in the metal, the spatial extent of this negative space charge zone is however very small. The bending of the bands near the contact can be described by a macropotential V(x). The potential barrier for the electrons passing from the metal to semiconductor has the height $\Phi_b = \Phi_M - \chi$. Electrons passing from the semiconductor to the metal must overcome the so-called built-in potential barrier $\Phi_i = (\Phi_M - \Phi_S)$. The potential difference between the bottom of the conduction band and the Fermi-level is V_n . In what follows, we assume that the space charge zone is given by

$$\rho(x) = \begin{cases}
eN_D & \text{for} & -d_n < x < 0 \\
-eN_D d_n \delta(x) & \text{for} & x = 0 \\
0 & \text{elsewhere.}
\end{cases}$$
(9.10.1)

In this case, the Poisson equation can be easily integrated. After a short calculation (Proof: Exercise) we find for the region $-d_n < x < 0$:

$$V(x) = \Phi_i - \frac{eN_D}{2\epsilon\epsilon_0}(x+d_n)^2.$$
 (9.10.2)

With V(0) = 0, the width of the space charge zone in the semiconductor can be calculated as:

$$d_n = \sqrt{\frac{2\epsilon\epsilon_0}{eN_D}\Phi_i}.$$
(9.10.3)

In thermal equilibrium, the density of electrons in the semiconductor in the vicinity of the boundary is given by

$$n_S = N_D e^{-\frac{e\Phi_i}{k_B T}} = N_D e^{-\frac{e(\Phi_b - V_n)}{k_B T}} = N_c e^{-\frac{e\Phi_b}{k_B T}}.$$
(9.10.4)

The electron current from the semiconductor to the metal, $j_{S\to M}$, is proportional to n_S . This current is exactly canceled by the flow of electrons from the metal to the semiconductor:

$$|j_{M\to S}| = |j_{S\to M}| \propto n_S.$$
 (9.10.5)

Next, we consider the effect of an external voltage U. We define that the voltage U is positive if the potential of the metal is increased with respect to the semiconductor. Since the resistance of the metal and the bulk of the semiconductor is much smaller than that of the depletion region, almost all of the voltage drops across the depletion region. When a positive voltage U is applied to the contact, the potential difference across the depletion region is decreased. As a result the, the electron density in the semiconductor in the vicinity of the boundary increases to

$$n_S = N_D e^{-\frac{e(\Phi_i - U)}{k_B T}} = N_c e^{-\frac{e(\Phi_b - U)}{k_B T}}.$$
(9.10.6)

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The electron current from the semiconductor to the metal rises by the same factor. In contrast to this, the electron current from the metal to the semiconductor is not altered since the potential barrier Φ_B is (to a first approximation) not affected by the external voltage. The total current across the Schottky-contact is hence given by:

$$j(U) = j_{S \to M} + j_{M \to S} \tag{9.10.7}$$

$$= CN_{c}e^{-\frac{e(\Phi_{b}-U)}{k_{B}T}} - CN_{c}e^{-\frac{e\Phi_{b}}{k_{B}T}}$$
(9.10.8)

$$= C N_c e^{-\frac{e\Phi_b}{k_B T}} \left(e^{\frac{eU}{k_B T}} - 1 \right).$$
(9.10.9)

Here, C is a proportionality factor. Following similar arguments, we find that the current across the Schottky-contact for a negative voltage -U is given by

$$j(-U) = CN_c e^{-\frac{e\Phi_b}{k_B T}} \left(e^{\frac{-eU}{k_B T}} - 1 \right).$$
(9.10.10)

This result shows that a Schottky-contact has rectifying characteristics similar to that of a pn-junction. In contrast to the latter, the current across the Schottky-contact is however governed by the majority carriers.

9.10.2 Ohmic contact

Next, we consider a so-called Ohmic contact with $\Phi_M < \Phi_S$ (see Fig. 9.20). When the two materials are brought into contact, electrons flow from the the metal to the semiconductor. As a result, electrons accumulate in the semiconductor near the contact. If an external voltage is applied to the Ohmic-contact, electrons can easily flow in both directions.

9.11 Semiconductor devices

9.11.1 Photodiode

Illumination of a p-n junction results in extra minority carriers in the space-charge zone which add to the generation current. This photo current I_p is proportional to the incident photon rate Φ :

$$I_p = q\eta\Phi,\tag{9.11.1}$$

where η is the probability that an incident photon generates an electron-hole pair that contributes to the photo current.



Figure 9.20: (a) Energy band diagram of an isolated n-type semiconductor adjacent to an isolated metal $(e\Phi_M < e\Phi_H)$. (b) Energy band diagram of the Ohmic-contact in thermal equilibrium $(e\Phi_M < e\Phi_H)$.

The current-voltage characteristic of a photodiode is given by:

$$I(U) = I_s \left(e^{\frac{eU}{k_B T}} - 1 \right) - I_p.$$
(9.11.2)

Photodiodes can be used in different modes of operation:

- In the photoconductive mode a reverse bias is applied to the photodiode (third quadrant of the current-voltage relation). The current through the diode is a linear function of the photon flux Φ . The reverse bias increases the width of the depletion layer which leads to a larger photosensitive volume. At the same time, the capacitance of the p-n junction is decreased such that the response time is reduced.
- In the short-circuit mode (U = 0), the current through the photodiode is the photo current I_p .
- In the photovoltaic mode no bias is applied to the p-n junction. The photogenerated carriers give rise to a terminal voltage U_p (fourth quadrant of the current-voltage relation), which is a nonlinear function of the photon flux Φ . Solar cells are used in this mode.

The spectral responsivity of a photodiode depends on the semiconductor material it is made of. The following table summarizes the useable wavelength range for some typical semiconductors:



Figure 9.21: Enhanced generation current due to illumination of a reverse biased pn-junction.

Semiconductor	Wavelength range (nm)
Gallium phosphide	150 - 550
Silicon	190 - 1100
Germanium	400 - 1700
Indium gallium arsenide	800 - 2600

An avalanche diode is a diode operated at a large reverse bias that is designed to go through avalanche breakdown after generation of an electron hole-pair by an incident photon. The avalanche breakdown is due to minority carriers accelerated enough to create ionization in the crystal lattice, producing more carriers which in turn create more ionization. Avalanche diodes can be used to detect single photons.

9.11.2 Light emitting diode

A light emitting diode (LED) is semiconductor lighting device that is based on the radiative recombination of electrons and holes in the space-charge region of a p-n junction.

The internal energy flux density per energy interval $d\hbar\omega$ and solid angle $d\Omega$ of a LED is given by:

$$j_{em,d\Omega}^{\text{LED}}(\hbar\omega) \approx a(\hbar\omega) \frac{(\hbar\omega)^3}{4\pi^3 \hbar^3 c^2} \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right]^{-1} \exp\left[\frac{eU}{k_B T}\right].$$
(9.11.3)



Figure 9.22: Current-voltage characteristic of a photodiode.



Figure 9.23: Scheme of the avalanche process.

Here, $a(\hbar\omega)$ is the optical absorption of the semiconductor material and U is the applied voltage. Compared to a gray body, the radiation of a LED is amplified by the factor $\exp[eU/k_BT]$. Near the band gap, the absorption of a direct semiconductor is given by:

$$a(\hbar\omega) \propto \sqrt{\hbar\omega - E_g}.$$
 (9.11.4)

The emitted spectrum of the LED has the form:

$$j_{em}^{\text{LED}}(\hbar\omega) \propto \sqrt{\hbar\omega - E_g} \left(\hbar\omega\right)^3 e^{-\frac{\hbar\omega}{k_B T}}$$
(9.11.5)

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Figure 9.24: Radiative recombination in the space-charge zone of a p-n junction.

9.11.3 Laser diode

A homojunction laser²diode consists of a highly doped p-n junction. Applying a forward electrical bias causes the injection of holes and electrons from opposite sides of the p-n junction into the depletion region. Here, the electrons and holes recombine and generate photons. The corresponding emission frequency is determined by the size of the electronic band gap. Often, the semiconductor crystal is cleaved in such a way that two parallel facets of the crystal can be used as the mirrors of a simple Fabry-Perot cavity. Homojunction laser diodes are very inefficient as they require large current densities because of the large volume of the active region. Hence, they can be only operated in pulsed mode.

In a double-heterojunction laser diode, a thin layer of a low band gap material (e.g. GaAs) is sandwiched between two high band gap layers (e.g. AlGaAs). This results in a better confinement of the carriers in the active region. Furthermore, the refractive index profile of the double-heterojunction causes a confinement of the optical field to the active region. Both effects reduce the required current density such that continuous wave operation of double-heterojunction laser diodes at room temperature is possible.

9.11.4 Bipolar junction transistor

A bipolar junction transistor is formed by three differently doped semiconductor regions, the emitter region, the base region, and the collector region. Each of the three regions

²Laser: Light amplification by stimulated emission of radiation.



Figure 9.25: Qualitative emission spectrum of a LED.



Figure 9.26: Scheme of a homojunction laser diode .

is connected to a separate terminal. The base region is very thin and physically located between the emitter region and the collector region. In a so-called NPN transistor, the emitter and collector region are n-doped semiconductors while the base region is a pdoped semiconductor. Accordingly, a PNP transistor consists of a n-doped base region sandwiched between the p-doped emitter region and collector region. In a typical bipolar junction transistor, the emitter region is heavily doped.

In the following we consider a NPN transistor and assume that the base-emitter junction is forward biased whereas the base-collector junction is reverse biased (active mode). The corresponding band diagram is shown in Fig. 9.28.

The emitter current I_E in the forward-biased base-emitter junction is given by:

$$I_e = I_{s,e} \left(e^{\frac{eU_e}{k_B T}} - 1 \right) \approx I_{s,e} e^{\frac{eU_e}{k_B T}}.$$
(9.11.6)

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Figure 9.27: Scheme of a heterojunction laser diode.

Here, $I_{s,e}$ is the corresponding saturation current and $U_e = U_{EB} + \tilde{U}_E$ is the applied voltage.

Due to the small thickness of the base region, only a small fraction of the injected electrons recombines with holes. The large fraction $\alpha \approx 1$ of the injected electrons diffuses through the base-region and reaches the base-collector junction. The collector current can be thus written as

$$I_c = I_{s,c} + \alpha I_e \approx \alpha I_e, \tag{9.11.7}$$

where $I_{s,c}$ is the saturation current of the base-collector junction. The corresponding voltage measured across a load resistor reads

$$U_L = R_L I_c = \alpha R_L I_e. \tag{9.11.8}$$

Small variations in \tilde{U}_E can lead to a large change in U_L :

$$\frac{dU_L}{d\tilde{U}_E} = \frac{e\alpha R_L I_e}{k_B T}.$$
(9.11.9)

For typical parameters ($I_e = 10 \text{ mA}$, $k_B T/e \approx 0,025 \text{ V}$, $R_L = 1 \text{ k}\Omega$), we find a value of the voltage gain of 400.



Figure 9.28: Scheme of a bipolar npn transistor.

10 Magnetism in condensed matter

In this chapter we discuss the fundamentals of magnetism in condensed matter systems. We start with the dia- and paramagnetic response of insulators. Here, it is sufficient to take only the magnetic properties of isolated atoms into account. That followed, we consider paramagnetism of the free electron gas. The main part of this chapter is devoted to magnetic order phenomena, for which we have to go beyond the single electron approximation. In this context, we discuss aspects of ferromagnetism, spin waves, and the formation of magnetic domains.

10.1 Magnetization and magnetic susceptibility

The magnetization \mathcal{M} of a material is defined as the density of the magnetic dipole moment **m**:

$$\mathcal{M} = \mathbf{m}\frac{N}{V}.\tag{10.1.1}$$

In many materials, the magnetization \mathcal{M} is proportional to the local¹ magnetic field strength \mathcal{H} . In this case, we can write

$$\mathcal{M} = \hat{\chi} \mathcal{H}, \tag{10.1.2}$$

where $\hat{\chi}$ is the magnetic susceptibility. Note that $\hat{\chi}$ usually is a tensor. However, for sake of mathematical simplicity we often consider a scalar magnetic susceptibility. Materials with a negative susceptibility are called diamagnetic and the induced magnetization opposes the applied magnetic field. In contrast, paramagnetic materials have a positive susceptibility and the induced magnetization is parallel to the applied field. In matter, the magnetic induction \mathcal{B} is related to the magnetic field \mathcal{H} by

$$\mathcal{B} = \mu_0 \left(\mathcal{H} + \mathcal{M} \right). \tag{10.1.3}$$

with the vacuum permeability

$$\mu_0 = 4\pi \cdot 10^{-7} \,\mathrm{Vs/Am}.\tag{10.1.4}$$

¹Typically, the magnetic field inside a solid differs from the externally applied magnetic field. The reason for this is the magnetic field produced by all magnetic moments in the sample.

A convenient starting point for the theoretical description of the magnetic properties of many condensed matter systems is the free energy:

$$F = U - TS. \tag{10.1.5}$$

Its differential is given by:

$$dF = dU - SdT - TdS = -SdT - pdV - V\mathcal{M} \cdot d\mathcal{B}.$$
(10.1.6)

If we consider a process with dT = 0 and dV = 0, the magnetization can be calculated by taking the derivative of the free energy with respect to the magnetic field:

$$\mathcal{M}_{i} = -\frac{1}{V} \left(\frac{\partial F}{\partial \mathcal{B}_{i}} \right)_{V,T}.$$
(10.1.7)

The elements of the magnetic susceptibility tensor can be calculated as

$$\chi_{ij} = \mu_0 \left(\frac{\partial \mathcal{M}_i}{\partial \mathcal{B}_j} \right)_{V,T} = -\frac{\mu_0}{V} \left(\frac{\partial^2 F}{\partial \mathcal{B}_i \partial \mathcal{B}_j} \right)_{V,T}.$$
(10.1.8)

10.2 Dia- and paramagnetism of insulators

In this section, we discuss the magnetic response of insulators. We make the assumption that the interaction between the magnetic moments of the different atoms can be ignored. It is therefore sufficient to consider the effect of an external magnetic field on the individual atoms. In the absence of an external magnetic field, the Hamiltonian of a single atom is given by:

$$H_0 = \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m} + V_i \right), \tag{10.2.1}$$

where the sum is taken over all Z electrons of the atom. Next, we add an external magnetic field \mathcal{B} given by

$$\boldsymbol{\mathcal{B}} = \nabla \times \boldsymbol{\mathcal{A}}.\tag{10.2.2}$$

Here, \mathcal{A} is the magnetic vector potential. We chose the gauge such that

$$\mathcal{A}(\mathbf{r}) = \frac{1}{2}\mathbf{r} \times \mathcal{B}.$$
 (10.2.3)

In the presence of the external magnetic field, the Hamiltonian of the atom reads:

$$H = \sum_{i=1}^{Z} \left(\frac{\left[\mathbf{p}_{i} + e \mathbf{\mathcal{A}}(\mathbf{r}_{i}) \right]^{2}}{2m} + V_{i} \right) + g_{0} \mu_{b} \mathbf{\mathcal{B}} \cdot \mathbf{S}.$$
(10.2.4)

The second term is the potential energy of the spin magnetic moment in the magnetic field. After a few lines of math, we obtain:

$$H = H_0 + \mu_B \left(\mathbf{L} + g_0 \mathbf{S} \right) \cdot \mathbf{\mathcal{B}} + \frac{e^2}{8m} \sum_{i=1}^{Z} (\mathbf{\mathcal{B}} \times \mathbf{r}_i)^2.$$
(10.2.5)

Here, μ_B is the Bohr magneton, **L** is the total orbital angular momentum of the electrons and **S** is the corresponding total spin angular momentum.

The shift of the energy levels due to the presence of the magnetic field can be calculated by perturbation theory. Retaining terms up to second order in the magnetic field, we obtain:

$$\Delta E_n = \mu_B \langle n | (\mathbf{L} + g_0 \mathbf{S}) \cdot \boldsymbol{\mathcal{B}} | n \rangle + \mu_B^2 \sum_{m \neq n} \frac{|\langle n | (\mathbf{L} + g_0 \mathbf{S}) \cdot \boldsymbol{\mathcal{B}} | m \rangle|^2}{E_n - E_m} + \frac{e^2}{8m} \sum_{i=1}^Z \langle n | (\boldsymbol{\mathcal{B}} \times \mathbf{r}_i)^2 | n \rangle.$$
(10.2.6)

10.2.1 Larmor diamagnetism

In the first instance, we consider atoms with completely filled shells ($\mathbf{L} = \mathbf{S} = 0$), i.e., the total magnetic dipole moment of the electrons is zero. Furthermore, we assume that the external magnetic field $\boldsymbol{\mathcal{B}}$ is oriented along $\hat{\mathbf{e}}_z$. The latter condition allows us to write

$$(\boldsymbol{\mathcal{B}} \times \mathbf{r}_i)^2 = \boldsymbol{\mathcal{B}}^2 \left(x_i^2 + y_i^2 \right).$$
(10.2.7)

The first-order shift of the ground state energy due to the diamagnetic term can be calculated as

$$\Delta E_0 = \frac{e^2 \mathcal{B}^2}{8m} \sum_{i=1}^{Z} \langle 0 | \left(x_i^2 + y_i^2 \right) | 0 \rangle.$$
(10.2.8)

Because of the completely filled shells, the atoms possess spherical symmetry and we find

$$\langle 0|x_i^2|0\rangle = \langle 0|y_i^2|0\rangle = \frac{1}{3}\langle 0|r_i^2|0\rangle, \qquad (10.2.9)$$

where r_i is the distance of the *i*-th electron from the nucleus. This allows us to rewrite equation (10.2.8) as

$$\Delta E_0 = \frac{e^2 \mathcal{B}^2}{12m} \sum_{i=1}^{Z} \langle 0 | r_i^2 | 0 \rangle.$$
(10.2.10)

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The corresponding diamagnetic susceptibility is given by

$$\chi_{dia} = -\frac{\mu_0}{V} \left(\frac{\partial^2 F}{\partial \mathcal{B}^2}\right)_{V,T} = -\mu_0 \frac{e^2}{6m} \frac{N}{V} \sum_{i=1}^Z \langle 0|r_i^2|0\rangle.$$
(10.2.11)

The electrons in the outer shell of the atome give the largest contribution to the sum. We can thus approximate the sum by

$$\sum_{i=1}^{Z} \langle 0|r_i^2|0\rangle \approx Z_a r_a^2, \tag{10.2.12}$$

where Z_a is the number of electrons in the outer shell and r_a is the radius of the atom. With this approximation, the diamagnetic susceptibility reads

$$\chi_{dia} \approx -\mu_0 \frac{e^2}{6m} \frac{N}{V} Z_a r_a^2. \tag{10.2.13}$$

Diamagnetism is a weak effect and the diamagnetic susceptibility typically is in the order of $\chi_{dia} = -10^{-4} \dots 10^{-6}$.

10.2.2 Paramagnetism of insulators

For atoms where the spin-orbit coupling is weak, the total orbital angular momentum \mathbf{L} and the total spin angular momentum \mathbf{S} couple to form the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (\text{Russel} - \text{Saunders coupling}). \tag{10.2.14}$$

In the following, we consider the case $\mathbf{J} \neq 0$, i.e., the atoms possess a magnetic moment. Furthermore, we assume that the external magnetic field is oriented in the $\hat{\mathbf{e}}_z$ -direction. The dominant contribution to the shift of the energy levels is then given by

$$\Delta E_n = g_J \mu_b m_j \mathcal{B}. \tag{10.2.15}$$

Here, g_J is the so-called Landé g-factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$
(10.2.16)

and m_J is the magnetic quantum number that can take all integer values $-J \leq m_j \leq J$. The average value of the magnetic quantum number can be calculated as

$$\langle m_J \rangle = \frac{\sum\limits_{m_J=-J}^{J} m_j e^{-\frac{g_J \mu_B m_J \mathcal{B}}{k_B T}}}{\sum\limits_{m_J=-J}^{J} e^{-\frac{g_J \mu_B m_J \mathcal{B}}{k_B T}}} = -\frac{1}{Z} \frac{\partial Z}{\partial x}, \qquad (10.2.17)$$

where $Z = \sum_{m_J} e^{-m_J x}$ is the partition function and $x = g_J \mu_B \mathcal{B}/k_B T$. The corresponding magnetization is given by

$$\mathcal{M} = -\frac{N}{V} g_J \mu_B \langle m_J \rangle = \frac{N}{V} \frac{g_J \mu_B}{Z} \frac{\partial Z}{\partial \mathcal{B}} \frac{\partial \mathcal{B}}{\partial x} = \frac{N}{V} k_B T \frac{\partial \ln(Z)}{\partial \mathcal{B}}.$$
 (10.2.18)

The evaluation of the partition function yields:

$$Z = \frac{\sinh\left[\left(2J+1\right)\frac{x}{2}\right]}{\sinh\left[\frac{x}{2}\right]}.$$
(10.2.19)

Upon substitution of Z into equation (10.2.18), we obtain

$$\mathcal{M} = \frac{N}{V} g_J \mu_B J B_J(xJ). \tag{10.2.20}$$

Here, we have introduced the so-called Brillouin function

$$B_J(xJ) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}xJ\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}xJ\right).$$
(10.2.21)



Figure 10.1: Brillouin function.

For $xJ \gg 1$, i.e., for very low temperatures, the Brillouin function becomes $B_J(xJ) = 1$ and the magnetization reaches its maximum value. At room temperature, the condition $xJ \ll 1$ is fulfilled. In this case, we can approximate the Brillouin function by

$$B_J(xJ) \approx \frac{J+1}{3J} xJ. \tag{10.2.22}$$

With this approximation, the magnetization is given by

$$\mathcal{M} = \frac{N}{V} \frac{g_J^2 \mu_B^2 J(J+1)}{3k_B T} \mathcal{B}$$
(10.2.23)

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The corresponding susceptibility can be written as

$$\chi_{para} = \frac{C}{T},\tag{10.2.24}$$

where the so-called Curie constant is given by

$$C = \frac{N}{V} \frac{\mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B}.$$
(10.2.25)

Equation (10.2.24) is known as the Curie law. Typical values of the paramagnetic susceptibility at room temperature are in the order of $\chi_{para} = 10^{-3}$.

10.3 Pauli paramagnetism

Next, we consider the magnetic response of the free electron gas. At this point we neglect correlation effects. These will be later included in the Stoner model of ferromagnetism (see below). The magnetic moment due to the electron spin is given by

$$\mu_s = -g_0 \mu_B m_s = \mp \mu_B, \tag{10.3.1}$$

with $m_s = \pm 1/2$. The magnetization of the electron gas can be expressed as

$$\mathcal{M} = (n_+ - n_-)\mu_B. \tag{10.3.2}$$

Here, n_+ is the density of electrons with μ_s parallel to the external magnetic field and n_- is the corresponding density of electrons with anti-parallel orientation of μ_s . The density of electrons with spin up can be calculated as

$$n_{+} = \frac{1}{2V} \int_{0}^{\infty} \mathcal{D}(E + \mu_{B} B_{ext}) f(E) \, dE.$$
(10.3.3)

Likewise, we obtain for the electrons with spin down:

$$n_{-} = \frac{1}{2V} \int_{0}^{\infty} \mathcal{D}(E - \mu_{B} B_{ext}) f(E) \, dE.$$
(10.3.4)

Substitution of n_+ and n_- into equation (10.3.2) yields:

$$\mathcal{M} = (n_{+} - n_{-})\mu_{B} = \frac{\mu_{B}}{V} \frac{1}{2} \int_{0}^{\infty} \frac{d\mathcal{D}}{dE} 2\mu_{B}B_{ext}f(E) dE$$

$$= \frac{\mu_{B}^{2}B_{ext}}{V} \int_{0}^{\infty} \frac{d\mathcal{D}}{dE}f(E) dE$$

$$= \frac{\mu_{B}^{2}B_{ext}}{V} \left[\mathcal{D}(E)f(E)|_{0}^{\infty} - \int_{0}^{\infty} \mathcal{D}(E)\frac{df}{dE} dE \right]$$

$$= -\frac{\mu_{B}^{2}B_{ext}}{V} \int_{0}^{\infty} \mathcal{D}(E)\frac{df}{dE} dE.$$
(10.3.5)

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Figure 10.2: Pauli paramagnetism.

For low temperatures, we can approximate the derivative of the Fermi-function by

$$-\frac{df}{dE} \approx \delta(E - E_F). \tag{10.3.6}$$

With the density of states at the Fermi-level

$$\mathcal{D}(E_F) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2} = \frac{3}{2} \frac{nV}{k_B T_F},$$
(10.3.7)

we can write the magnetization of the free electron gas as

$$\mathcal{M} = \frac{3n\mu_B^2 B_{ext}}{2k_B T_F}.$$
(10.3.8)

The so-called Pauli spin paramagnetic susceptibility is given by

$$\chi_P = \mu_0 \left(\frac{\partial M}{\partial B_{ext}}\right)_{T,V} = \frac{3n\mu_0\mu_B^2}{2k_B T_F}.$$
(10.3.9)

In contrast to the paramagnetic response of insulators, χ_P does not depend on temperature.

10.4 Magnetic interactions

So far, we have only considered the effect of an external magnetic field on isolated magnetic moments. This approach is however insufficient if we want to discuss magnetic order phenomena. A prominent example for such a magnetic order phenomenon is ferromagnetism. Here, the magnetic interactions result in a parallel orientation of the microscopic magnetic moments and create through this a macroscopic magnetization of the ferromagnetic substance even in the absence of an external magnetic field. In materials that show antiferromagnetism, the magnetic moments of the atoms or molecules align in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions. This is, like ferromagnetism, a manifestation of a magnetic order phenomenon. If the sublattices are populated with different types of atoms or ions, it can happen that the macroscopic magnetization does not vanish even though neighboring spins point in opposite directions. This kind of magnetic order is called ferrimagnetism.



Figure 10.3: Schematic representation of different magnetic order phenomena.

10.4.1 Magnetic dipolar interaction

At first, one might expect that the magnetic dipolar interaction plays an important role in magnetic order phenomena. Two magnetic dipoles \mathbf{m}_1 and \mathbf{m}_2 separated by a distance r have an energy equal to

$$E = \frac{\mu_0}{4\pi r^3} \left[\mathbf{m}_1 \cdot \mathbf{m}_2 - \frac{3}{r^2} \left(\mathbf{m}_1 \cdot \mathbf{r} \right) \left(\mathbf{m}_2 \cdot \mathbf{r} \right) \right].$$
(10.4.1)

For two magnetic dipoles each with a moment $m \approx \mu_B$ separated by $r \approx 1 \text{\AA}$, the interaction energy is in the order of 10^{-23} J which is equivalent to roughly 1 K in temperature. However, magnetic order phenomena can be observed in some materials even at room temperature. This back-of-the envelope calculation hence shows that the magnetic dipolar interaction is to weak to play an important role in magnetic order phenomena.

10.4.2 Exchange interaction of localized electrons

In the following, we consider a system consisting of two electrons that occupy the atomic one-electron states Ψ_a and Ψ_b . Using the Heitler-London-Ansatz, we can write the joint

two-electron spatial wave functions as:

$$\Psi_S(1,2) = \frac{1}{\sqrt{2}} \left[\Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) + \Psi_a(\mathbf{r}_2) \Psi_b(\mathbf{r}_1) \right], \qquad (10.4.2)$$

$$\Psi_T(1,2) = \frac{1}{\sqrt{2}} \left[\Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) - \Psi_a(\mathbf{r}_2) \Psi_b(\mathbf{r}_1) \right].$$
(10.4.3)

The Pauli exclusion principle requires that the total wavefunction is anti-symmetric under exchange of the two electrons. Hence, the symmetric spatial wave function $\Psi_S(1,2)$ corresponds to an anti-symmetric spin wave function with total spin S = 0 (singlet state). Accordingly, the anti-symmetric spatial wave function $\Psi_T(1,2)$ requires that the corresponding spin wave function is antisymmetric with total spin S = 1 (triplet state).

Let H be the Hamiltonian of the system. The energies of the two states are given by

$$E_S = \int \int \Psi_S^* H \,\Psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2, \tag{10.4.4}$$

$$E_T = \int \int \Psi_T^* H \Psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2. \tag{10.4.5}$$

The difference between the two energies is given by

$$A = E_S - E_T = 2 \int \int \Psi_a^*(\mathbf{r}_1) \Psi_b^*(\mathbf{r}_2) H \Psi_a(\mathbf{r}_2) \Psi_b(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2.$$
(10.4.6)

Here, we have introduced the exchange constant A. For A > 0, a parallel orientation of the electron spins is favored. This is the primary cause of ferromagnetism in materials in which the electrons are localized. In contrast, if A < 0, an antiparallel orientation of the electron spins is favored, potentially causing antiferromagnetism.

The Pauli exclusion principle causes a strict interdependence of the symmetry properties of the spatial part and the spin part of the total wave function. We will use this fact to introduce an effective Hamiltonian that has the same eigenvalues as the Hamiltonian considered above.

Let s_1 and s_2 be the operators for the spins of the two electrons. The operator for the total spin is given by

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \tag{10.4.7}$$

so that

$$\mathbf{S}^{2} = (\mathbf{s}_{1} + \mathbf{s}_{2})^{2} = \mathbf{s}_{1}^{2} + \mathbf{s}_{2}^{2} + 2\mathbf{s}_{1} \cdot \mathbf{s}_{2}.$$
 (10.4.8)

The last equation can be rewritten as

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{1}{2} \left[\mathbf{S}^2 - \mathbf{s}_1^2 - \mathbf{s}_2^2 \right].$$
(10.4.9)

The eigenvalues of the operator $\mathbf{s}_1 \cdot \mathbf{s}_2$ are given by

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \begin{cases} \frac{1}{4} & \text{if } S = 1 \quad \text{(triplet)} \\ -\frac{3}{4} & \text{if } S = 0 \quad \text{(singlet)} \end{cases}$$
(10.4.10)

Here we have used that the eigenvalues of the operator \mathbf{S}^2 for the singlet state and the triplet state are given by S(S+1) = 0(0+1) = 0 and S(S+1) = 1(1+1) = 2, respectively, and that the eigenvalue of both \mathbf{s}_1^2 and \mathbf{s}_2^2 are 3/4.

Next, we consider the effective Hamiltonian given by

$$H = \frac{1}{4} \left(E_S + 3E_T \right) - \left(E_S - E_T \right) \mathbf{s}_1 \cdot \mathbf{s}_2.$$
(10.4.11)

One can easily show that its eigenvalues for the singlet state and the triplet state are E_S and E_T , respectively. If one considers the interaction with several neighbors and neglect the constant first term, we obtain the Hamiltonian of the so-called Heisenberg model:

$$H = -\sum_{j \neq i, i > j} A_{ij} \mathbf{s}_i \cdot \mathbf{s}_j.$$
(10.4.12)

10.4.3 Exchange interaction of conduction electrons

Next, we discuss the exchange interaction of conduction electrons. For this purpose, we consider two conduction electrons i and j and assume that their spins are oriented parallel. The Pauli exclusion requires that the corresponding two-electron spatial wave function is anti-symmetric:

$$\Psi_{ij} = \frac{1}{\sqrt{2}V} \left(e^{i\mathbf{k}_i \cdot \mathbf{r}_i} e^{i\mathbf{k}_j \cdot \mathbf{r}_j} - e^{i\mathbf{k}_i \cdot \mathbf{r}_j} e^{i\mathbf{k}_j \cdot \mathbf{r}_i} \right) = \frac{1}{\sqrt{2}V} e^{i\mathbf{k}_i \cdot \mathbf{r}_i} e^{i\mathbf{k}_j \cdot \mathbf{r}_j} \left(1 - e^{-i(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right).$$
(10.4.13)

The probability of finding electron i in the volume d^3r_i and the electron j in the volume d^3r_j is given by:

$$|\Psi_{ij}|^2 d^3 r_i d^3 r_j = \frac{1}{V^2} \left[1 - \cos\left\{ (\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j) \right\} \right] d^3 r_i d^3 r_j.$$
(10.4.14)

This equation shows that the probability of finding two conduction electrons with the same spin orientation at the same place is zero regardless of the wave vectors \mathbf{k}_i and \mathbf{k}_j .

It is instructive to discuss this effect in a little bit more detail. For this purpose, we will average the probability of finding two spin- \uparrow -electron in the volume d^3r over all possible k-values:

$$P(\mathbf{r}) d^3 r = n_{\uparrow} d^3 r \overline{[1 - \cos\{(\mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{r}\}]}, \qquad (10.4.15)$$

where, $n_{\uparrow} = n/2$. Next, we write the effective density of spin- \uparrow -electrons as

$$\rho(\mathbf{r}) = \frac{en}{2} \overline{\left[1 - \cos\left\{\left(\mathbf{k}_{i} - \mathbf{k}_{j}\right) \cdot \mathbf{r}\right\}\right]} \\
= \frac{en}{2} \left[1 - \frac{1}{\left(\frac{4\pi}{3}k_{F}^{3}\right)^{2}} \int d^{3}k_{i} \int d^{3}k_{j} \frac{1}{2} \left(e^{i(\mathbf{k}_{i} - \mathbf{k}_{j}) \cdot \mathbf{r}} + e^{-i(\mathbf{k}_{i} - \mathbf{k}_{j}) \cdot \mathbf{r}}\right)\right] \\
= \frac{en}{2} \left[1 - 9 \frac{\left[\sin(k_{F}r) - k_{F}r\cos(k_{F}r)\right]^{2}}{(k_{F}r)^{6}}\right].$$
(10.4.16)

The total density of electrons seen by the spin- \uparrow -electron is given by:

$$\rho_t(r) = en \left[1 - \frac{9}{2} \frac{\left[\sin(k_F r) - k_F r \cos(k_F r) \right]^2}{(k_F r)^6} \right]$$
(10.4.17)

Hence, if we consider a certain electron with e.g. spin \uparrow , we find that the other spin- \uparrow -electrons are less effective to locally screen the Coulomb potential of the ion cores. As a result, the energy of the spin- \uparrow -electron is reduced. The energy reduction is maximized if an as large as possible portion of the conduction electrons has the same spin-orientation.



Figure 10.4: Normalized total electron density seen by a conduction electron.

10.5 Ferromagnetism

10.5.1 Mean field theory for localized magnetic moments

In the following, we use a mean field theory to explain ferromagnetism resulting from the interaction of localized magnetic moments. Our starting point is the Heisenberg-Hamiltonian defined in equation (10.4.12). The exchange energy of the *i*-th atom with its z neighbors is given by:

$$E = -A \sum_{j=1}^{z} \mathbf{S}_j \cdot \mathbf{S}_i.$$
(10.5.1)

Here, the exchange constant A is taken to be possitive and identical for all pairs.

We assume that \mathbf{S}_j can be approximated by the temporal average value $\langle \mathbf{S}_j \rangle$. In this case, we can write E as

$$E = -zA\langle \mathbf{S}_i \rangle \cdot \mathbf{S}_i \tag{10.5.2}$$

and the magnetization of the sample is given by

$$\mathcal{M} = -n_0 g_J \mu_B \langle \mathbf{S}_j \rangle, \tag{10.5.3}$$

where n_0 is the relevant density of atoms. Substituting equation (10.5.3) into (10.5.2) yields:

$$E = -\left(-g_J \mu_B \mathbf{S}_i\right) \cdot \frac{zA}{n_0 g_J^2 \mu_B^2} \mathcal{M}.$$
(10.5.4)

The second factor can be formally interpreted as a magnetic field:

$$\boldsymbol{\mathcal{B}}_{mf} = \frac{zA}{n_0 g_J^2 \mu_B^2} \boldsymbol{\mathcal{M}}.$$
 (10.5.5)

It is usually referred to as the exchange field or the molecular field. It can be also expressed as

$$\mathcal{B}_{mf} = \mu_0 \lambda \mathcal{M} \tag{10.5.6}$$

with the molecular field constant

$$\lambda = \frac{1}{\mu_0} \frac{zA}{n_0 g_J^2 \mu_B^2}.$$
(10.5.7)

If we apply an external magnetic field \mathcal{B}_{ext} to the sample, the total magnetic field \mathcal{B}_t acting on the *i*-th atom is given by

$$\mathcal{B}_{eff} = \mathcal{B}_{ext} + \mathcal{B}_{mf}.$$
(10.5.8)

Within the mean-field theory of ferromagnetism, the only effect of the exchange interaction is to replace \mathcal{B}_{ext} by \mathcal{B}_{eff} . Consequently, we can apply the formalism developed in section (10.2.2) to calculate the magnetization of the system:

$$\mathcal{M} = \frac{N}{V} g_J \mu_B J B_J(\alpha). \tag{10.5.9}$$

with

$$\alpha = \frac{g_J \mu_B J \mathcal{B}_{eff}}{k_B T} = \frac{g_J \mu_B J \left(\mathcal{B}_{ext} + \mu_0 \lambda \mathcal{M}\right)}{k_B T}$$
(10.5.10)

Since the argument of the Brillouin function, α , also depends on \mathcal{M} , we can not directly solve equation (10.5.9). However, the correct solution can be easily found by a graphical method. For this purpose, we first write equation (10.5.10) as

$$\mathcal{M} = \frac{k_B T}{\mu_0 \lambda g_J \mu_B J} \alpha - \frac{\mathcal{B}_{ext}}{\mu_0 \lambda}.$$
(10.5.11)

Next, we plot equation (10.5.9) and equation (10.5.11) in one figure. The correct solution is the intersection of the two curves (see Fig. 10.5).



Figure 10.5: Graphical solution to the magnetization of a ferromagnet. Left hand side: $\mathcal{B}_{ext} \neq 0$. Right hand side: $B_{ext} = 0$.

By setting $\mathcal{B}_{ext} = 0$, we can determine the spontaneous magnetization \mathcal{M} of the system as the function of temperature T. The right hand side of Fig. 10.5 shows that a non-vanishing spontaneous magnetization requires that the slope of the linear function (10.5.11) is smaller than the slope of the function defined in (10.5.9) for small values of α . Using the Taylor expansion (10.2.22) of the Brillouin function, we find that the system is in the ferromagnetic state if

$$\frac{k_B T}{\mu_0 \lambda g_J \mu_B J} < n_0 g_J \mu_B \frac{J+1}{3}.$$
(10.5.12)

This requires that the temperature is smaller than the Curie temperature T_C defined by

$$T_C = n_0 \frac{\mu_0 g_J^2 J (J+1) \mu_B^2}{3k_B} \lambda.$$
 (10.5.13)

Materials with a large exchange constant A, i.e., large molecular field constant λ , posses a large Curie temperature T_C .

For $T > T_C$, the system is in the paramagnetic state. For small values of α , equation (10.5.9) can be written as

$$\mathcal{M} = \frac{1}{\mu_0} \frac{N}{V} \frac{\mu_0 g_J^2 \mu_B^2 J(J+1)}{3k_B T} \left(\mathcal{B}_{ext} + \mu_0 \lambda \mathcal{M} \right) = \frac{1}{\mu_0} \frac{C}{T} \left(\mathcal{B}_{ext} + \mu_0 \lambda \mathcal{M} \right).$$
(10.5.14)

This equation can be rearranged as

$$\mathcal{M} = \frac{1}{\mu_0} \frac{C}{T - T_C} \mathcal{B}_{ext}.$$
(10.5.15)

Here, we have used that $T_C = \lambda C$. The corresponding susceptibility is given by the so-called Currie-Weiss law:

$$\chi = \frac{C}{T - T_C}.$$
(10.5.16)

Material	Curie temperature T_C (K)
Fe	1044
Co	1360
Ni	629
Gd	289
EuO	69.4
MnAs	630

Table 10.1: Curie temperature of some ferromagnetic materials. Source: Gross, Marx; Festkörperphysik.

10.5.2 Band ferromagnetism

Hereinafter, we discuss the Stoner model that allows to explain the occurrence of ferromagnetism in some metals (Fe, Co, Ni). Our starting point is an electron gas with Fermi energy E_F . Now assume that we redistribute δN spin down electrons near the Fermi level into empty spin up states. By doing so, we increase the kinetic energy of each of these electrons by the amount δE (see Fig. 10.6).



Figure 10.6: Redistribution of spin down electrons into empty spin up states in a band ferromagnet.

The number of redistributed electrons can be expressed as

$$\delta N = \frac{1}{2} D(E_F) \delta E, \qquad (10.5.17)$$

where $D(E_F)$ is the density of states at the Fermi level. The total kinetic energy of the electron system hence rises by

$$\Delta E_{kin} = \frac{\delta N}{V} \delta E = \frac{1}{2V} D(E_F) \left(\delta E\right)^2.$$
(10.5.18)

As discussed in section (10.4.3), electrons with parallel spin are less effective to locally screen the Coulomb potential of the ion cores. The redistribution of the electrons hence reduces the potential energy of the electron system. With the modified densities of the spin down and spin up electrons

$$n_{\uparrow,\downarrow} = \frac{N}{2V} \pm \frac{\delta N}{V} = \frac{n}{2} \pm \delta n, \qquad (10.5.19)$$

we can express the magnetization of the electron system after the redistribution as

$$\mathcal{M} = -\frac{1}{2}g\mu_B \left(n_{\uparrow} - n_{\downarrow}\right) = -\mu_B \frac{D(E_F)}{V} \delta E.$$
(10.5.20)

As in the previous section, we can formally introduce an exchange field

$$\mathcal{B}_{mf} = \mu_0 \lambda \mathcal{M},\tag{10.5.21}$$

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where λ is the corresponding molecular field constant. The reduction of the potential energy can then be calculated as

$$\Delta E_{\text{pot}} = -\int_0^{\mathcal{B}_{mf}} \mathcal{M}' d\mathcal{B}' = -\mu_0 \lambda \int_0^{\mathcal{M}} \mathcal{M}' d\mathcal{M}' = -\frac{1}{2} \mu_0 \lambda \mathcal{M}^2.$$
(10.5.22)

With the Stoner parameter

$$U = \frac{2\lambda\mu_0\mu_B^2}{V},\tag{10.5.23}$$

we can express ΔE_{pot} as:

$$\Delta E_{\text{pot}} = -\frac{1}{4V} U \left(D(E_F) \delta E \right)^2. \tag{10.5.24}$$

The total energy change is given by

$$\Delta E = \Delta E_{kin} + \Delta E_{pot} = \frac{1}{2V} D(E_F) \left(\delta E\right)^2 \left[1 - \frac{1}{2} U D(E_F)\right].$$
 (10.5.25)

If the redistribution of the electrons is favorable from an energetic point of view, i.e., $\Delta E < 0$, the system will spontaneously pass into the ferromagnetic state. Obviously, this requires that the so-called Stoner criterion

$$\frac{1}{2}UD(E_F) > 1 \tag{10.5.26}$$

is fulfilled. According to the Stoner model, band ferromagnetism is expected for those metals which posses a large density of states at the Fermi level and a large Stoner-parameter. Numerical calculations² show that only the ferromagnetic metals Fe, Co, and Ni meet this requirement.

10.6 Spin waves

In the ground state of the Heisenberg-Hamiltonian at zero temperature, all the spins are oriented parallel to each other. In the following, we want to discuss excitations of the system. For this purpose we consider a simple model a 1D chain of spins. The exchange energy of the *l*-th spin reads:

$$E = -A\mathbf{S}_{l} \cdot (\mathbf{S}_{l-1} + \mathbf{S}_{l+1}).$$
(10.6.1)

With

$$\mathbf{m}_l = -g_0 \mu_B \mathbf{S}_l \tag{10.6.2}$$

²J. F. Janak, Phys. Rev. B **16**, 255 (1977).
10.6 Spin waves

and

$$\boldsymbol{\mathcal{B}}_{mf} = -\frac{2A}{g_0\mu_B} \left(\mathbf{S}_{l-1} + \mathbf{S}_{l+1} \right), \tag{10.6.3}$$

the exchange energy can be written as

$$E = -\mathbf{m}_l \cdot \boldsymbol{\mathcal{B}}_{mf}.\tag{10.6.4}$$

In the presence of an external magnetic field \mathcal{B}_{ext} , the total magnetic field \mathcal{B}_t acting on the spins is given by

$$\boldsymbol{\mathcal{B}}_{t} = \boldsymbol{\mathcal{B}}_{ext} - \frac{2A}{g_{0}\mu_{B}} \left(\mathbf{S}_{l-1} + \mathbf{S}_{l+1} \right).$$
(10.6.5)

The dynamics of the spin can be described in a semiclassical model by

$$\hbar \frac{d\mathbf{S}_{l}}{dt} = \mathbf{m}_{l} \times \boldsymbol{\mathcal{B}}_{t} = -g_{0}\mu_{b} \left(\mathbf{S}_{l} \times \boldsymbol{\mathcal{B}}_{ext}\right) + 2A \left[\mathbf{S}_{l} \times \left(\mathbf{S}_{l-1} + \mathbf{S}_{l+1}\right)\right].$$
(10.6.6)

In the following, we assume that the external magnetic field is parallel to the z-axis

$$\boldsymbol{\mathcal{B}}_{ext} = \boldsymbol{\mathcal{B}} \, \hat{\mathbf{e}}_z. \tag{10.6.7}$$

For low temperatures, the spins are then predominately oriented in the $\hat{\mathbf{e}}_z$ direction, such that

$$|S_{l,z}| \gg |S_{l,x}|, |S_{l,x}|. \tag{10.6.8}$$

Neglecting terms quadratic in $S_{l,x}$ and $S_{l,y}$, we obtain with $S_{l,z} = -S$:

$$\frac{dS_{l,x}}{dt} = -\frac{g_0\mu_B\mathcal{B}}{\hbar}S_{l,y} - \frac{2AS}{\hbar}\left(2S_{l,y} - S_{l-1,y} - S_{l+1,y}\right), \qquad (10.6.9)$$

$$\frac{dS_{l,y}}{dt} = \frac{g_0 \mu_B \mathcal{B}}{\hbar} S_{l,x} + \frac{2AS}{\hbar} \left(2S_{l,x} - S_{l-1,x} - S_{l+1,x} \right), \qquad (10.6.10)$$

$$\frac{dS_{l,z}}{dt} = 0. (10.6.11)$$

We now look for plane-wave solutions of the form

$$S_{l,x} = S_x e^{i(kla-\omega t)},$$
 (10.6.13)

$$S_{l,y} = S_y e^{i(kla-\omega t)},$$
 (10.6.14)



Figure 10.7: A Spin wave on a line of spins. Image adopted from Wikipedia.

where k is the wave vector and a is the separation between the spins.

Substituting this ansatz for $S_{l,x}$ and $S_{l,y}$ into equations (10.6.9) and (10.6.10), we obtain after a view lines of math:

$$S_y = iS_x, \tag{10.6.15}$$

$$\omega = \frac{g_0 \mu_B \mathcal{B}}{\hbar} + \frac{4AS}{\hbar} \left[1 - \cos(ka)\right]. \tag{10.6.16}$$



Figure 10.8: Dispersion relation of a magnon.

The quasi-particle associated with such a spin wave is referred to as a magnon. The dispersion relation of magnons is usally determined by inelastic neutron scattering experiments.

10.7 Magnetic domains

The discussion above suggests that a ferromagnetic sample shows a non-vanishing magnetization for $T < T_C$. However, iron and other ferromagnets are often found in an "unmagnetized" state. The reason for that is that the material is divided in so-called magnetic domains (see Fig. 10.9). Within each domain, the *m*icroscopic magnetic moments are aligned parallel resulting in a *m*esoscopic magnetization. However, the magnetization directions of different domains need not be parallel such that the *m*acroscopic magnetization of the complete sample vanishes.

The interface between two domains is usually referred to as a domain wall.



Magnetic field energy decreases





Figure 10.10: Hysteresis curve of a ferromagnet.

11.1 Some elementary properties of superconductors

11.1.1 Zero electric resistance

On the basis of our discussion in section 8.7, we should expect that all metals exhibit a finite constant resistance at very low temperatures caused by electron scattering from impurities. Surprisingly, for a number of metals and ceramic materials the electric resistance drops abruptly to zero below a material specific critical temperature T_c . This effect is called superconductivity and was first observed for mercury (see Fig. 11.1). Materials which show superconductivity are called superconductors.



Figure 11.1: First observation of superconductivity by Heike Kamerlingh Onnes in 1911. The resistance of Hg vanishes for temperatures below 4.19 K. Image: Wikipedia.

11.1.2 Meisser-Ochsenfeld effect

The interior of a superconductor is free of electric or magnetic fields. The resistance-free flow of carriers immediately counteracts any potential difference across the superconductor. Moreover, a persistent current at the surface of the superconductor expels weak magnetic fields from the interior as soon as the temperature is decreased below T_C . This is the so-called Meisser-Ochsenfeld effect.



Figure 11.2: A permanent magnet levitating above a high-temperature superconductor. The persistent current at the surface of the superconductor expels the magnetic field of the magnet and effectively forms an electromagnet. Image: Wikipedia.

We note that a superconductor is not simply a perfect conductor since in the latter case the magnetic field distribution would depend on the order of cool-down and application of the magnetic field (see Fig. 11.3). A superconductor rather behaves like a perfect diamagnet.



Figure 11.3: Difference between a perfect conductor and a superconductor.

11.1.3 Critical field

The superconducting state is destroyed if a strong magnetic field is applied. In type I superconductors, the superconductor directly returns to the normal conducting state. The magnetic field strength at which this transition happens is called critical field $B_C(T)$. The critical field decreases with temperature and vanishes for $T = T_C$. It follows the empirical rule:

$$B_C(T) = B_C(0) \left(1 - \left(\frac{T}{T_C}\right)^2 \right).$$
(11.1.1)

Type II superconductors show a more complicated behavior. Above a critical filed strength $B_{C1}(T)$, the superconductor gradually looses its superconducting properties and it can no longer completely expel the magnetic field from its interior. At a higher critical field strength $B_{C2}(T)$, the superconducting state is completely destroyed and it becomes normal conducting.



Figure 11.4: Phase diagram of a type I superconductor (left) and a type II superconductor (right).

11.1.4 Isotope effect

The critical temperature T_c of a superconducting sample depends on its isotope composition and hence on the average mass number M. For a number of materials, e.g. Tin, the following relation holds:

$$M^{1/2}T_c = \text{const} \tag{11.1.2}$$

This so-called isotope effect is an indication that superconductivity is related to properties of the lattice.



Figure 11.5: Isotope effect. Data taken from: E. Maxwell, Superconductivity of the Isotopes of Tin, Phys. Rev. 86,235 (1952).

11.2 London equations

In the following, we discuss a phenomenological model that allows us to describe the Meissner-Ochsenfeld effect. Our starting point is the classical Drude transport theory of electrons. According to section 8.1.1, the DC resistivity $\rho_{\rm DC}$ of a conductor is proportional to the scattering rate τ^{-1} . Consequently, a perfect conductor with $\rho_{\rm DC} = 0$ exhibits a vanishing scattering rate, i.e, $\tau \to \infty$ and the corresponding classical equation of motion reads

$$m_s \frac{\partial \mathbf{v}}{\partial t} = -q_s \boldsymbol{\mathcal{E}}.$$
(11.2.1)

Here, m_s and q_s are the mass and charge, respectively, of the electrons contributing to the supercurrent. The corresponding current density can be written as

$$\mathbf{j} = -n_s q_s \mathbf{v},\tag{11.2.2}$$

where n_s is the density of superconducting electrons. By combining the last two equations, we obtain the first London equation

$$\frac{\partial \left(\Lambda \mathbf{j}\right)}{\partial t} = \boldsymbol{\mathcal{E}},\tag{11.2.3}$$

with the London coefficient

$$\Lambda = \frac{m_s}{n_s q_s^2}.\tag{11.2.4}$$

Inserting the first London equation into the Maxwell equation $\nabla \times \mathbf{E} = -\partial \mathbf{B}/\partial t$ yields

$$\frac{\partial}{\partial t} \left(\nabla \times (\Lambda \mathbf{j}) + \mathbf{B} \right) = 0. \tag{11.2.5}$$

On integration we obtain the second London equation

$$\nabla \times (\Lambda \mathbf{j}) + \mathbf{B} = 0. \tag{11.2.6}$$

At this point we have set the integration constant to zero in order to account for the Meisser-Ochsenfeld effect. Using $\nabla \times \mathbf{B} = \mu_0 \mathbf{j}$, we can rewrite the second London equation as

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B},\tag{11.2.7}$$

with

$$\lambda = \sqrt{\frac{\Lambda}{\mu_0}} = \sqrt{\frac{m_s}{\mu_0 n_s q_s^2}}.$$
(11.2.8)

We can use equation (11.2.7) to calculate the magnetic field distribution inside of a superconductor. We assume that the magnetic field outside of the superconductor is constant and parallel to the surface, $\mathbf{B}_{ext} = (0, 0, B_z)$. The magnetic field inside of the superconductor falls off exponentially

$$\mathbf{B}_s(x) = \mathbf{B}_{ext} e^{-\frac{x}{\lambda}},\tag{11.2.9}$$

where λ characterizes its penetration depth into the superconductor. The suppression of the magnetic field is caused by a supercurrent near the inteface. Using the second London equation, we find that

$$J_{s,y}(x) = J_{s,y}(0)e^{-\frac{x}{\lambda}},$$
(11.2.10)

with

$$J_{s,y}(0) = \frac{H_{ext}}{\lambda}.$$
(11.2.11)

11.3 Macroscopic quantum model of superconductivity

Next, we want to discuss a macroscopic quantum model of superconductivity. The basic assumption of this model is that the electrons in the superconducting state are characterized by a common macroscopic wave function of the form:

$$\Psi(\mathbf{r},t) = \Psi_0(\mathbf{r},t)e^{i\theta(\mathbf{r},t)}.$$
(11.3.1)

 $^{^1\}mathrm{Note}$ that we use microscopic Maxwell equations in this section.

The normalization is chosen such that

$$\int \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)dV = \int n_s(\mathbf{r},t)dV = N_s.$$
(11.3.2)

Here, $n_s(\mathbf{r}, t)$ is the local density of superconducting electrons and N_s is the total number of superconducting electrons. The evolution of $\Psi(\mathbf{r}, t)$ in the presence of an electromagnetic field is governed by the Schrödinger equation:

$$\frac{1}{2m_s} \left(\frac{\hbar}{\imath} \nabla - q_s \mathbf{A}(\mathbf{r}, t)\right)^2 \Psi(\mathbf{r}, t) + \left(q\phi(\mathbf{r}, t) + \mu(\mathbf{r}, t)\right) \Psi(\mathbf{r}, t) = \imath \hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}, \quad (11.3.3)$$

where $\mathbf{A}(\mathbf{r}, t)$ is the vector potential, $\phi(\mathbf{r}, t)$ is the scalar electrostatic potential, and $\mu(\mathbf{r}, t)$ is the chemical potential. We note that the microscopic electric and magnetic field can be written as :

$$\boldsymbol{\mathcal{E}}(\mathbf{r},t) = -\frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} - \nabla \left(\phi(\mathbf{r},t) + \frac{\mu(\mathbf{r},t)}{q} \right), \qquad (11.3.4)$$

 $\boldsymbol{\mathcal{B}}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t). \tag{11.3.5}$

Using elementary quantum mechanics, we obtain the following continuity equation:

$$\frac{\partial n_s}{\partial t} + \nabla \cdot \mathbf{J}_p = 0 \tag{11.3.6}$$

with the probability flux density

$$\mathbf{J}_{p} = \frac{1}{m_{s}} \Re \left\{ \Psi^{*}(\mathbf{r}, t) \left(\frac{\hbar}{\imath} \nabla - q_{s} \mathbf{A}(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t) \right\}.$$
(11.3.7)

The corresponding supercurrent density is then given by

$$\mathbf{J}_s = q_s \mathbf{J}_p = \frac{q_s \hbar}{2m_s \imath} \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^* \right) - \frac{q_s^2}{m_s} |\Psi|^2 \mathbf{A}.$$
 (11.3.8)

With $\Psi(\mathbf{r},t) = \sqrt{n_s(\mathbf{r},t)}e^{i\theta(\mathbf{r},t)}$, the supercurrent density can be rewritten as

$$\mathbf{J}_{s} = q_{s} n_{s}(\mathbf{r}, t) \left(\frac{\hbar}{m_{s}} \nabla \theta(\mathbf{r}, t) - \frac{q_{s}}{m_{s}} \mathbf{A}(\mathbf{r}, t) \right).$$
(11.3.9)

Next, we calculate he time derivative of the phase θ :

$$-\hbar \frac{\partial \theta}{\partial t} = \frac{\imath\hbar}{2n_s} \left[\Psi^* \frac{\partial \Psi}{\partial t} - \Psi \frac{\partial \Psi^*}{\partial t} \right]. \tag{11.3.10}$$

Using the Schrödinger equation (11.3.3) and assuming slowly varying potentials², we obtain after some algebra the expression:

$$-\hbar \frac{\partial \theta}{\partial t} = \frac{1}{2n_s} \Lambda \mathbf{J}_s^2 + q_s \phi + \mu, \qquad (11.3.11)$$

with the London coefficient

$$\Lambda = \frac{m_s}{n_s q_s^2}.\tag{11.3.12}$$

Next, we show that the London equations can be recovered in the framework of the macroscopic quantum model. For this purpose, it is useful to rewrite equation (11.3.9) as:

$$\Lambda \mathbf{J}_s = -\left(\mathbf{A}(\mathbf{r},t) - \frac{\hbar}{q_s} \nabla \theta(\mathbf{r},t)\right).$$
(11.3.13)

Next, we take its time derivative

$$\frac{\partial}{\partial t} \left(\Lambda \mathbf{J}_s \right) = -\left[\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} - \frac{\hbar}{q_s} \nabla \left(\frac{\partial \theta(\mathbf{r}, t)}{\partial t} \right) \right].$$
(11.3.14)

With equations (11.3.11) and (11.3.4), we obtain

$$\frac{\partial}{\partial t} \left(\Lambda \mathbf{J}_s \right) = \boldsymbol{\mathcal{E}} - \frac{1}{q_s n_s} \nabla \left(\frac{1}{2} \Lambda \mathbf{J}_s^2 \right).$$
(11.3.15)

Usually, the second term can be neglected, so that we obtain the first London equation

$$\frac{\partial}{\partial t} \left(\Lambda \mathbf{J}_s \right) = \boldsymbol{\mathcal{E}}. \tag{11.3.16}$$

The second London equation can be retrieved by taking the curl of equation (11.3.13):

$$\nabla \times (\Lambda \mathbf{J}_s) + \nabla \times \mathbf{A} = \nabla \times (\Lambda \mathbf{J}_s) + \mathbf{\mathcal{B}} = 0.$$
(11.3.17)

Thus, we can put the London equations on a quantum fundament if we assume that the superconducting state can be characterized by a macroscopic wavefunction $\Psi(\mathbf{r}, t)$.

11.4 Microscopic theory of superconductivity

In this section we discuss a microscopic theory of superconductivity. The basic idea is that even a weak attractive interaction between electrons can result in electron pairing and an

²In the case of slowly varying potentials we can neglect terms of the order ∇^2 .

overall reduction of the energy. A possible mechanism for an effective attractive electronelectron interaction is the exchange of virtual phonons. This can be understood as follows (see Fig. 11.6). An electron moving through the crystal interacts with the positively charged ions leading to a retarded distortion of the lattice. The resulting local increase of the positive charge density then attracts other electrons. Since the first electron has already left this region of the crystal before the positive charge is build up, the lattice mediated attractive interaction between electrons can overcome their repulsive Coulomb interaction.



Figure 11.6: Schematic representation of the lattice mediated attractive interaction between two electrons.

11.4.1 Cooper pairs

We start with a gas of free electrons at T=0 K, in which all states up to the Fermi energy $E_F = \hbar^2 k_F^2/2m$ are occupied. Next we add two electrons and assume that the continuous exchange of virtual phonons mediates an effective attractive interaction between them. During a phonon exchange, one electron emits a phonon with wave vector \mathbf{q} which is shortly thereafter absorbed by the second electron. As a result, the wave vectors of the two electrons change from \mathbf{k}_1 and \mathbf{k}_2 to

$$\mathbf{k}_1' = \mathbf{k}_1 - \mathbf{q} \tag{11.4.1}$$

$$\mathbf{k}_2' = \mathbf{k}_2 + \mathbf{q}. \tag{11.4.2}$$

For reasons of momentum conservation, the sum of the electron wave vectors does not change during the phonon exchange:

$$\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2' = \text{const.}$$
 (11.4.3)

Since all electron states with an energy below E_F are occupied and the maximum phonon energy is $\hbar\omega_D$, all accessible states for the two electrons lie in the energy range between



Figure 11.7: Interaction between two electrons via the exchange of a virtual phonon.

 E_F and $E_F + \hbar \omega_D$. In k-space, this corresponds to a shell with radius k_F and thickness

$$\Delta k \approx \frac{m\omega_D}{\hbar k_F}.\tag{11.4.4}$$

Momentum conservation further restricts the number of accessible states. As depicted in Fig. 11.8, the states compatible with condition (11.4.3) are in the overlap region of two shells with radius k_F and thickness Δk , whose centers are shifted by **K**. Obviously, the number of accessible states is maximal and hence phonon exchange is most likely if the two shells overlap completely, i.e., for so-called Cooper³ pairs with $\mathbf{K} = 0$.



Figure 11.8: Momentum conservation during the interaction between two electrons.

In the following, we consider an ansatz for the wavefunction of a Cooper pair that consist of a superposition of pair states with K = 0:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=k_F}^{k_F + \Delta k} a_k e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} = \sum_{k=k_F}^{k_F + \Delta k} a_k e^{i\mathbf{k} \cdot \mathbf{r}}$$
(11.4.5)

³Leon N. Cooper, Bound electron pairs in a degenerate Fermi gas, Physical Review **104**, 1189 (1956).

with the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{11.4.6}$$

This pair wavefunction is a solution of the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left(\nabla_1^2 + \nabla_2^2\right) \Psi(\mathbf{r}_1, \mathbf{r}_2) + V(\mathbf{r})\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2).$$
(11.4.7)

Here we assume that the effective interaction potential V(r) depends only on **r**. Next, we insert the ansatz (11.4.5) into the Schrödinger equation, multiply with $e^{-i\mathbf{k}'\cdot\mathbf{r}}$ and integrate over the crystal volume V_c . This results in

$$\left(E - \frac{\hbar^2}{m}k^2\right)a_k = \frac{1}{V_c}\sum_{k'=k_F}^{k_F + \Delta k} a_{k'}V_{k,k'}$$
(11.4.8)

with

$$V_{k,k'} = \int V(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV.$$
(11.4.9)

As a further simplification, we assume that the interaction potential (11.4.9) has the form

$$V_{k,k'} = \begin{cases} -V_0 & \text{for} \quad k_F < k, k' < k_F + \Delta k \\ 0 & \text{else} \end{cases}$$
(11.4.10)

With this, we can rewrite equation (11.4.8) as

$$a_k = -\frac{V_0}{V_c} \frac{1}{E - \frac{\hbar^2}{m} k^2} \sum_{k'=k_F}^{k_F + \Delta k} a_{k'}.$$
(11.4.11)

Upon summation over all allowed k-values, we obtain

$$1 = \frac{V_0}{V_c} \sum_{k=k_F}^{k_F + \Delta k} \frac{1}{\frac{\hbar^2}{m} k^2 - E}.$$
(11.4.12)

Next, we replace the sum by an integral:

$$1 = V_0 \frac{D(E_F)}{2} \int_{E_F}^{E_F + \hbar\omega_D} \frac{dE'}{2E' - E}.$$
(11.4.13)

Here, we have used the abbreviation $E' = \frac{\hbar^2}{2m}k^2$. After the integration, we find

$$E = 2E_F - \frac{2\hbar\omega_D e^{-4/[D(E_F)V_0]}}{1 - e^{-4/[D(E_F)V_0]}}.$$
(11.4.14)

In the case of weak interactions $(D(E_F)V_0 \ll 1)$, we obtain the approximate solution

$$E \approx 2E_F - 2\hbar\omega_D \, e^{-4/[D(E_F)V_0]}.\tag{11.4.15}$$

This result indicates that it is energetically favorable for the electrons to form pairs.

The total wave function of the pair state must be antisymmetric. Since the spatial part of the wave function is symmetric (see equation 11.4.5), we can conclude that the spin part is antisymmetric, i.e., the total spin of the pair vanishes, S = 0. In order to reflect this point, we use the notation $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$ to address a pair state.

11.4.2 BCS theory

BCS ground state

In the previous section we made the assumption that only a single electron pair interacts via the exchange of virtual phonons. We now abandon this restriction and allow that all electrons near the Fermi level can in principle form Cooper pairs. In the framework of the BCS-theory⁴, we assume that the many-body wavefunction of the interacting electron system at T = 0 K can be written as a product of pair states:

$$|\phi_{\text{BCS}}\rangle = \prod_{k} \left(u_k |0\rangle_k + v_k |1\rangle_k \right). \tag{11.4.16}$$

Here, $|1\rangle_k$ corresponds to the occupied pair state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ while $|0\rangle_k$ denotes that this pair state is empty. Normalization requires that

$$v_k^2 + u_k^2 = 1. (11.4.17)$$

The energy of the interacting electron system can be written as

$$W_{\rm BCS} = 2\sum_{k} v_k^2 \eta_k - \frac{V_0}{V_c} \sum_{k,k'} v_k u_{k'} u_k v_{k'}$$
(11.4.18)

with

$$\eta_k = \left(\hbar^2 k^2 / 2m - E_F\right). \tag{11.4.19}$$

The first term in equation (11.4.18) corresponds to the kinetic energy measured relative to the Fermi level E_F . The second term characterizes the reduction of the energy due to the attractive electron-electron interaction. Here, $v_k u_{k'}$ is the probability amplitude of the initial state⁵ and $u_k v_{k'}$ is that of the final state⁶.

For the further analysis, it is convenient to express v_k and u_k as

$$v_k = \cos(\theta_k) \tag{11.4.20}$$

$$u_k = \sin(\theta_k). \tag{11.4.21}$$

This allows us to rewrite the energy of the interacting electron system as

$$W_{\rm BCS} = 2\sum_{k}\cos^2(\theta_k)\eta_k - \frac{V_0}{V_c}\sum_{k,k'}\cos(\theta_k)\sin(\theta_k)\cos(\theta_{k'})\sin(\theta_{k'}).$$
(11.4.22)

 $^{{}^4}Bardeen-Cooper-Schrieffer\ theory\ named\ after\ John\ Bardeen,\ Leon\ Cooper,\ and\ John\ Robert\ Schrieffer.$

⁵In the initial state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ is occupied and $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$ is empty.

⁶In the final state $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ is empty and $(\mathbf{k}^{\prime}\uparrow,-\mathbf{k}^{\prime}\downarrow)$ is occupied

In order to find the ground state, we minimize W_{BCS} with respect to θ_k :

$$\frac{\partial W_{\text{BCS}}}{\partial \theta_k} = -2\eta_k \sin(2\theta_k) - \frac{V_0}{V_c} \sum_{k'} \cos(2\theta_k) \sin(2\theta_{k'}) = 0$$
(11.4.23)

This can be rewritten as

$$\eta_k \tan(2\theta_k) = -\frac{1}{2} \frac{V_0}{V_c} \sum_{k'} \sin(2\theta_{k'})$$
(11.4.24)

Next, we define the so-called gap parameter

$$\Delta = \frac{V_0}{V_c} \sum_{k'} \sin(\theta_{k'}) \cos(\theta_{k'}) = \frac{V_0}{V_c} \sum_{k'} u_{k'} v_{k'}$$
(11.4.25)

and

$$E_k = \sqrt{\eta_k^2 + \Delta^2}.\tag{11.4.26}$$

Using simple trigonometric relations, we find

$$\sin(2\theta_k) = 2\sin(\theta_k)\cos(\theta_k) = 2u_k v_k = \frac{\Delta}{E_k},$$
(11.4.27)

$$\cos(2\theta_k) = \cos^2(\theta_k) - \sin^2(\theta_k) = v_k^2 - u_k^2 = -\frac{\eta_k}{E_k}.$$
(11.4.28)

With $v_k^2 + u_k^2 = 1$, we can calculate the probability that the pair state $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$ is occupied:

$$v_k^2 = \frac{1}{2} \left(1 - \frac{\eta_k}{E_k} \right) = \frac{1}{2} \left(1 - \frac{\eta_k}{\sqrt{\eta_k^2 + \Delta^2}} \right)$$
(11.4.29)

By substituting equation (11.4.29) and (11.4.25) into (11.4.18), we find the energy of the BCS ground state to be

$$W_{\rm BCS}^{0} = \sum_{k} \eta_{k} \left(1 - \frac{\eta_{k}}{E_{k}} \right) - \frac{V_{c} \Delta^{2}}{V_{0}}.$$
(11.4.30)

Condensation energy

The condensation energy W_c is the energy reduction of the electron system in the BCS state relative to the normal conducting state. The latter can be expressed as

$$W_n = \sum_{k < k_F} 2\eta_k.$$
(11.4.31)



Figure 11.9: Occupation probability of the Cooper pair states.

To calculate W_n , we rewrite equation (11.4.30) as

$$W_{BCS}^{0} = 2 \sum_{k < k_{F}} \left(1 - u_{k}^{2} \right) \eta_{k} + 2 \sum_{k > k_{F}} v_{k}^{2} \eta_{k} - \frac{V_{c} \Delta^{2}}{V_{0}}$$
$$= W_{n} - 2 \sum_{k < k_{F}} u_{k}^{2} \eta_{k} + 2 \sum_{k > k_{F}} v_{k}^{2} \eta_{k} - \frac{V_{c} \Delta^{2}}{V_{0}}.$$

Replacing the sums by integrals and using Taylor expansions for v_k^2 and u_k^2 at $\eta = 0$, we find after a few lines of algebra:

$$W_c = W_{\rm BCS}^0 - W_n = -\frac{1}{2}\mathcal{D}(E_F)\Delta^2 V_c.$$
 (11.4.32)

Excitations of the BCS ground state

By breaking up a single Cooper pair, we create the first excited state of the BCS model. During this process, a single electron is scattered from a state with wavevector $\mathbf{k_1}$ to a state with wavevector $\mathbf{k_2}$. As a result, the two pair states $(\mathbf{k_1}\uparrow, -\mathbf{k_1}\downarrow)$ and $(\mathbf{k_2}\uparrow, -\mathbf{k_2}\downarrow)$ are no longer available for the BCS-state. The excitation energy can thus be calculated

$$W_{BCS}^{1} - W_{BCS}^{0} = \eta_{k_{1}} + \eta_{k_{2}} - 2v_{k_{1}}^{2}\eta_{k_{1}} - 2v_{k_{2}}^{2}\eta_{k_{2}} + \frac{2V_{0}}{V_{c}}\sum_{k'}v_{k_{1}}u_{k'}u_{k_{1}}v_{k'} + \frac{2V_{0}}{V_{c}}\sum_{k'}v_{k_{2}}u_{k'}u_{k_{2}}v_{k'}$$

$$= (1 - 2v_{k_{1}}^{2})\eta_{k_{1}} + (1 - 2v_{k_{2}}^{2})\eta_{k_{2}} + 2\Delta v_{k_{1}}u_{k_{1}} + 2\Delta v_{k_{2}}u_{k_{2}}$$

$$= \frac{\eta_{k_{1}}^{2}}{\sqrt{\eta_{k_{1}}^{2} + \Delta^{2}}} + \frac{\eta_{k_{2}}^{2}}{\sqrt{\eta_{k_{2}}^{2} + \Delta^{2}}} + \frac{\Delta^{2}}{\sqrt{\eta_{k_{2}}^{2} + \Delta^{2}}}$$

$$= \sqrt{\eta_{k_{1}}^{2} + \Delta^{2}} + \sqrt{\eta_{k_{2}}^{2} + \Delta^{2}} = E_{k_{1}} + E_{k_{2}}.$$
(11.4.33)

Since η_{k_1} and η_{k_2} can be arbitrarily small, we find that the minimum excitation energy to break up a Cooper pair is

$$\Delta E_{min} = 2\Delta. \tag{11.4.34}$$

This discussion shows that we can interpret $E_k = 2\sqrt{\eta_k^2 + \Delta^2}$ as the dispersion relation of a quasiparticle that arises from the excitation of the BCS ground state. These quasiparticles are sometimes called Bogolons, named after the Russian physicist Nikolai Nikolajewitsch Bogoljubow.

Obviously, there are no quasiparticle states with $E_k < \Delta$ in a superconductor while in a normal conductor corresponding one-electron states exist. To determine the quasiparticle density of states we note that the number of states is conserved during the transition from a normal conducting state to the superconducting state. We thus require that

$$\mathcal{D}_s(E_k)dE_k = \mathcal{D}_n(\eta_k)d\eta_k,\tag{11.4.35}$$

where $\mathcal{D}_s(E_k)$ is the quasiparticle density of states in a superconductor and $\mathcal{D}_n(\eta_k)$ is the electron density of states of the normal conductor. Since we are only interested in a small energy interval around the Fermi level, we can assume that the density of states for a normal conductor is constant $\mathcal{D}_n(\eta_k) = \mathcal{D}_n(E_F)$ and we find:

$$\frac{\mathcal{D}_s(E_k)}{\mathcal{D}_n(E_F)} = \frac{d\eta_k}{dE_k} = \begin{cases} \frac{E_k}{\sqrt{E_k^2 - \Delta^2}} & \text{for } E_k > \Delta\\ 0 & \text{for } E_k < \Delta \end{cases}$$
(11.4.36)

The existence of the energy gap in the excitation spectrum of the BCS-model allows us to give an intuitive explanation for the persistence of currents in a superconductor. As discussed in section 8.4, a current requires a non-equilibrium electron distribution. In a normal conductor, the scattering of the individual electrons quickly restores the equilibrium electron distribution if we switch off the field responsible for the current (see Fig. 11.11 (a)). The situation is different for a superconductor. The existence of the energy gap protects the Cooper pairs from breaking up during a scattering event at

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Figure 11.10: Density of states of quasiparticles in a superconductor.

sufficiently low temperatures. Figuratively speaking, electrons can only scatter in pairs from an occupied pair state $((\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ to an empty state $((\mathbf{k}'\uparrow,-\mathbf{k}'\downarrow)$. This does however not change the centroid of the electron distribution, i.e., the current persists even if we switch of the applied field.



Figure 11.11: Left: Scattering of single electrons restores the equilibrium electron distribution. Right: Scattering of Cooper pairs preserves a nonequilibrium electron distribution.

Size of a Cooper pair

In the following we want to give an estimate for the spatial extend of a Cooper-pair. We start by noting that the energy uncertainty for a Cooper-pair is in the order of $\delta E = 2\Delta$.

The corresponding uncertainty of momentum can be estimated from

$$\delta E = 2\Delta = \delta \left(\frac{p^2}{2m}\right) \approx \frac{p_F}{m} \delta p. \tag{11.4.37}$$

Using Heisenberg's uncertainty relation, we find that the approximate size of the Cooperpair is given by

$$\delta x = \frac{\hbar}{\delta p} \approx \frac{\hbar p_F}{m2\Delta}.$$
(11.4.38)

For typical parameters, this corresponds to a size of approximately 10 nm to 100 nm. From the ratio $E_F/\Delta \approx 10^4$ and the typical electron density, we can estimate that the volume occupied by a given Cooper pair also contains approximately 10⁶ other Cooper pairs. Hence, we have a strong spatial overlap of the Cooper pairs, which results in the formation of a macroscopic wavefunction.

Gap parameter

By combining equation (11.4.25) and (11.4.27), we find that the gap parameter Δ has to fulfill the condition

$$\Delta = \frac{V_0}{V_c} \sum_k u_k v_k = \frac{1}{2} \frac{V_0}{V_c} \sum_k \frac{\Delta}{E_k} = \frac{1}{2} \frac{V_0}{V_c} \sum_k \frac{\Delta}{\sqrt{\eta_k^2 + \Delta^2}}.$$
(11.4.39)

Next, we replace the sum by an integral $(V_c^{-1}\sum_k\to\int d^3k/4\pi^3)$ and obtain

$$1 = \frac{V_0}{2} \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{\mathcal{Z}(E_F + \eta)}{\sqrt{\eta^2 + \Delta^2}} d\eta$$
(11.4.40)

with the pair density of states

$$\mathcal{Z}(E_F + \eta) = \frac{1}{2}\mathcal{D}(E_F + \eta). \tag{11.4.41}$$

In the energy interval $[E_F - \hbar\omega_D, E_F + \hbar\omega_D]$ the pair density of states can be considered to be constant so that we can rewrite equation (11.4.40) as

$$\frac{1}{V_0 \mathcal{Z}(E_F)} = \int_0^{\hbar\omega_D} \frac{d\eta}{\sqrt{\eta^2 + \Delta^2}}$$
(11.4.42)

$$= \operatorname{arcsinh}\left(\frac{\hbar\omega_D}{\Delta}\right). \tag{11.4.43}$$

For weak interactions $(V_0 \mathcal{Z}(E_F) \ll 1)$, we finally obtain

$$\Delta = \frac{\hbar\omega_D}{\sinh\left(\frac{1}{V_0\mathcal{Z}(E_F)}\right)} \approx 2\hbar\omega_D e^{-1/[V_0\mathcal{Z}(E_F)]}.$$
(11.4.44)

Critical temperature

So far, we considered superconductivity at T = 0 T. At finite temperature, some of the Cooper pairs break up. The occupation of the corresponding quasiparticle states with energy $E_k = \sqrt{\eta_k^2 + \Delta^2(T)}$ is governed by the Fermi-distribution function $f(E_k + E_F, T)$. Since these occupied state are no longer available for the Cooper pairs, we have to modify equation (11.4.42):

$$\frac{1}{V_0 \mathcal{Z}(E_F)} = \int_0^{\hbar\omega_D} \frac{d\eta}{\sqrt{\eta^2 + \Delta^2(T)}} \left[1 - 2f\left(\sqrt{\eta_k^2 + \Delta^2(T)} + E_F, T\right) \right].$$
 (11.4.45)

For $T \to T_c$, the gap parameter $\Delta(T)$ has to approach zero. By setting $\Delta(T_c) = 0$ in equation (11.4.45), we can determine the critical temperature T_c . After numerical integration, we obtain:

$$k_B T_c = 1.14 \,\hbar\omega_D e^{-1/[V_0 \mathcal{Z}(E_F)]}.$$
(11.4.46)

Since $\omega_D \propto M^{-1/2}$, we find that $T_c M^{1/2} = const$, i.e., the BCS theory correctly describes the isotope effect.

Current carrying wavefunction

The flow of a supercurrent \mathbf{j}_s requires that the electron distribution of the superconductor is shifted in k-space away from the origin. Let us denote this shift by \mathbf{Q} . As a consequence, also the pair states are modified $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow) \rightarrow (\mathbf{k} + \mathbf{Q} \uparrow, -\mathbf{k} + \mathbf{Q} \downarrow)$. Obviously, each pair state has a total momentum $\hbar \mathbf{K} = 2\hbar \mathbf{Q}$.

The wave function of the Cooper-pair in the current-carrying case is given by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k a_k e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} = \sum_k a_k e^{i\frac{\mathbf{K}}{2} \cdot (\mathbf{r}_1 + \mathbf{r}_2)} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}.$$
(11.4.47)

With the coordinate of the centroid

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \tag{11.4.48}$$

and the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,\tag{11.4.49}$$

this can be rewritten as

$$\Psi(\mathbf{K}, \mathbf{r}_1, \mathbf{r}_2) = e^{i\mathbf{K}\cdot\mathbf{R}} \sum_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i\mathbf{K}\cdot\mathbf{R}} \Psi(\mathbf{K} = 0, \mathbf{r}_1, \mathbf{r}_2).$$
(11.4.50)

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We can conclude that the current flow only modifies the phase of the Cooper pair wavefunction. The probability density is not affected:

$$\Psi(\mathbf{K}, \mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{K} = 0, \mathbf{r}_1, \mathbf{r}_2)|^2.$$
(11.4.51)

Following a similar line of arguments, we can write the BCS-wavefunction in the currentcarrying case as

$$\phi_{\text{BCS}}(\mathbf{K}) = e^{i\varphi(\mathbf{R}_1, \mathbf{R}_2, \dots)} \phi_{\text{BCS}}(\mathbf{K} = 0)$$
(11.4.52)

with

$$\varphi(\mathbf{R}_1, \mathbf{R}_2, \ldots) = \mathbf{K} \cdot \mathbf{R}_1 + \mathbf{K} \cdot \mathbf{R}_2 + \ldots$$
(11.4.53)

Here, $\mathbf{R}_1, \mathbf{R}_2, \ldots$ are coordinates of the centroids of the different pair states.

In the presence of a magnetic field, the supercurrent density can be shown to take the form (compare with section 11.3):

$$\mathbf{j}_{s} = \frac{-2e}{4m} \left[4e\mathbf{A} |\phi_{\mathrm{BCS}}(0)|^{2} + 2\hbar |\phi_{\mathrm{BCS}}(0)|^{2} \sum_{\nu} \nabla_{\mathbf{R}_{\nu}} \varphi(\dots, \mathbf{R}_{\nu}, \dots) \right].$$
(11.4.54)

With $\nabla \times \nabla \varphi = 0$ and $\nabla \times A = \mathbf{B}$, we obtain

$$\nabla \times \mathbf{j}_s = -\frac{2e^2}{m} |\phi_{\mathrm{BCS}}(0)|^2 \mathbf{B}.$$
(11.4.55)

This is precisely the second London equation with

$$|\phi_{\rm BCS}(0)|^2 = \frac{n_s}{2}.\tag{11.4.56}$$

Hence, we can also explain the Meisener-Ochsenfeld effect in the framework of the BCS theory.

11.5 Josephson effects

In this section, we consider two superconducting layers that are separated by an insulating barrier. For large barrier thicknesses, the two superconductors are decoupled and the dynamics of the macroscopic wavefunctions is governed by

$$i\hbar \frac{\partial \psi_1}{\partial t} = E_1 \psi_1, \qquad (11.5.1)$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = E_2 \psi_2. \tag{11.5.2}$$

Here, E_1 and E_2 are the energies of the superconducting states.

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In a so-called Josephson junction, the insulating barrier is very thin (typically 1 to 2 nm) and the tunneling of Cooper pairs from one superconductor to the other is possible. This process can be considered as a weak perturbation that we can take into account by adding coupling terms to the two equations:

$$i\hbar \frac{\partial \psi_1}{\partial t} = E_1 \psi_1 + T \psi_2, \qquad (11.5.3)$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = E_2 \psi_2 + T \psi_1. \tag{11.5.4}$$

Here, T characterizes the contribution to the energy due to the tunneling of Cooper pairs.



Figure 11.12: Scheme of a Josephson junction.

For the following analysis, we write the macroscopic wavefunctions as

$$\psi_1 = \sqrt{n_{c,1}} e^{i\phi_1}, \tag{11.5.5}$$

$$\psi_2 = \sqrt{n_{c,2}} e^{i\phi_2}, \tag{11.5.6}$$

where $n_{c,1}$ and $n_{c,2}$ are the densities of Cooper pairs in superconductor 1 and superconductor 2, respectively. Upon substitution of ψ_1 and ψ_2 into equation (11.5.3) and (11.5.4), we obtain:

$$\frac{i\hbar}{2}\dot{n}_{c,1} - \hbar n_{c,1}\dot{\phi}_1 = E_1 n_{c,1} + T\sqrt{n_{c,1}}\sqrt{n_{c,2}}e^{i(\phi_2 - \phi_1)}, \qquad (11.5.7)$$

$$\frac{i\hbar}{2}\dot{n}_{c,2} - \hbar n_{c,2}\dot{\phi}_2 = E_2 n_{c,2} + T\sqrt{n_{c,1}}\sqrt{n_{c,2}}e^{-i(\phi_2 - \phi_1)}.$$
(11.5.8)

Separating real and imaginary parts yields:

$$\dot{n}_{c,1} = \frac{2T}{\hbar} \sqrt{n_{c,1}} \sqrt{n_{c,2}} \sin(\phi_2 - \phi_1), \qquad (11.5.9)$$

$$\dot{n}_{c,2} = -\frac{2T}{\hbar}\sqrt{n_{c,1}}\sqrt{n_{c,2}}\sin(\phi_2 - \phi_1), \qquad (11.5.10)$$

$$\dot{\phi}_1 = -\frac{T}{\hbar} \sqrt{\frac{n_{c,2}}{n_{c,1}}} \cos(\phi_2 - \phi_1) - \frac{E_1}{\hbar},$$
(11.5.11)

$$\dot{\phi}_2 = -\frac{T}{\hbar} \sqrt{\frac{n_{c,1}}{n_{c,2}}} \cos(\phi_2 - \phi_1) - \frac{E_2}{\hbar}.$$
(11.5.12)

(11.5.13)

In the following we assume that the junction is made from two identical superconductors $(n_{c,1} = n_{c,2} = n_c)$. In this case, the first two lines of the previous set of equations simplify to

$$\dot{n}_{c,1} = \frac{2T}{\hbar} n_c \sin(\phi_2 - \phi_1) = -\dot{n}_{c,2}.$$
(11.5.14)

With this, we can calculate the supercurrent resulting from Cooper pair tunneling:

$$I_s = 2e\dot{n}_{c,1} = I_{\max}\sin(\phi_2 - \phi_1), \tag{11.5.15}$$

with

$$I_{\max} = \frac{4Ten_c}{\hbar}.$$
(11.5.16)

Equation (11.5.19) is often called the first Josephson equation. It predicts that the supercurrent is controlled by the phase difference $\Delta \phi = \phi_2 - \phi_1$ and can take values in the range $\pm I_{\text{max}}$.

If there is a voltage U across the Josephson junction, the energy levels of the two halves are shifted by $\Delta E = E_1 - E_2 = 2eU$ with respect to each other. The resulting temporal evolution of the phase difference then follows the second Josephson equation:

$$\hbar\left(\dot{\phi}_2 - \dot{\phi}_1\right) = 2eU. \tag{11.5.17}$$

Let us first consider the case that the Voltage across the junction vanishes (U = 0). According to equation (11.5.17), the phase difference $\Delta \phi_0 = \phi_2 - \phi_1$ is then a constant that may, depending on the history of the device, take any value between 0 and 2π . For $\Delta \phi_0 \neq 0$, equation (11.5.19) predicts a constant supercurrent $I_s = I_{\text{max}} \sin(\Delta \phi)$ even in the absence of an external field⁷. This is the so-called DC Josephson effect.

 $^{^7\}mathrm{In}$ order to avoid charging , we have to connect the Josephson junction with an appropriate load resistor to a current source

For a finite constant voltage U across the junction, the phase difference grows with time

$$\Delta\phi(t) = \frac{2eU}{\hbar}t + \Delta\phi_0 \tag{11.5.18}$$

and we obtain an alternating current

$$I_s(t) = I_{\max} \sin(\omega t + \Delta \phi_0) \tag{11.5.19}$$

with oscillation frequency

$$\omega = \frac{2eU}{\hbar}.\tag{11.5.20}$$

This is the so-called AC Josephson effect. Since the ratio ω/U depends only on natural constants, we can use the AC Josephson effect for very precise voltage measurements.