

2. Semiconductor Physics

2.1 Basic Band Theory

2.1.1 Essentials of the Free Electron Gas

- This course requires that you must be familiar with some solid state physics including a working knowledge of thermodynamics and quantum theory.
- The **free electron gas** model is a paradigm for the behavior of electrons in a crystal, you should be *thoroughly familiar* with it.
- In case of doubt, refer to the Hyperscript "[MaWi II](#)" – which, however, is in *German*.
- In the following, the *essentials of the model* are repeated – briefly, without much text. If you have serious problems with the topic already here, you do indeed have a problem with this course!

The Energy Levels of an Electron in a Constant Potential

- The **free electron gas** model works with a **constant potential**. This is, of course, a doubtful approximation; essentially only justified because it works – up to a point.
 - Approximations:** Constant potential $U = U_0 = 0$ within a crystal with length L in all directions; only *one* electron is considered.
 - The true potential outside the crystal will turn out to be irrelevant due to *periodic* boundary conditions (see below).
- The major formulas and interpretations needed are:
- Time independent one-dimensional **Schrödinger equation** :

$$-\frac{\hbar^2}{2m_e} \left(\frac{\partial^2 \psi(x,y,z)}{\partial x^2} + \frac{\partial^2 \psi(x,y,z)}{\partial y^2} + \frac{\partial^2 \psi(x,y,z)}{\partial z^2} \right) + U(\mathbf{r}) \cdot \psi(x,y,z) = E \cdot \psi(x,y,z)$$

$= 0$

- $\hbar = h$ "bar" = $h/2\pi$ = Plancks constant/ 2π
 m_e = electron mass
 ψ = wave function
 E = **total energy** = kinetic energy + potential energy. Here it is identical to the *kinetic energy* because the *potential energy* is zero.
- Potential $U(\mathbf{x})$** as defined above; i.e. $U(\mathbf{x}) = U_0 = \text{const} = 0$ for $0 \leq x \leq L$. (Remember that L is the macroscopic size of the crystal.)
 - For the (potential) energy, there is always a free choice of zero point; here it is convenient to put the bottom of the potential well at zero potential energy. We will, however, change that later on.
- Boundary conditions:** Several choices are possible! Here, we use **periodic conditions** (also called **Born–von Karman** conditions), leading to a so-called supercell:

$$\psi(x + L) = \psi(x)$$

- Solution** (for 3-dimensional case)

$$\psi = \left(\frac{1}{L}\right)^{3/2} \cdot \exp(i \cdot \underline{k} \cdot \underline{r})$$

$$\begin{aligned} \underline{r} &= \text{position vector} \\ &= (x, y, z) \\ \underline{k} &= \text{wavevector} \\ &= (k_x, k_y, k_z) \\ k_x &= \pm n_x \cdot 2\pi/L \\ k_y &= \pm n_y \cdot 2\pi/L \\ k_z &= \pm n_z \cdot 2\pi/L \\ n_x, n_y, n_z &= \text{quantum numbers} \\ &= 0, 1, 2, 3, \dots \\ i &= (-1)^{1/2} \end{aligned}$$

● A somewhat [more general form](#) for crystals with unequal sides can be found in the link.

▸ There are infinitely many solutions, and every individual solution is selected or described by a set of the three quantum numbers n_x, n_y, n_z . The solution ψ describes a [plane wave](#) with amplitude $(1/L)^{3/2}$ [moving in the direction](#) of the **wave vector \underline{k}** .

▸ Next, we extract related quantities of interest in connection with moving particles or waves:

● The **wavelength** λ of the "electron wave" is given by

$$\lambda = \frac{2\pi}{|\underline{k}|} = \frac{2\pi}{k}$$

● The momentum \underline{p} of the electron is given by

$$\underline{p} = \hbar \cdot \underline{k}$$

● From this and with m = electron mass we obtain the [velocity](#) \underline{v} of the electron to be

$$\underline{v} = \frac{\underline{p}}{m_e} = \frac{\hbar \cdot \underline{k}}{m_e}$$

▸ The numbers n_x, n_y, n_z are **quantum numbers**; their values (together with the value of the [spin](#)) are characteristic for one particular solution of the Schrödinger equation of the system. A unique set of quantum numbers (always plus one of the two possibilities for the spin) describes a **state** of the electron

● Since these quantum numbers only appear in the wave vector \underline{k} , one often denotes a particular wave function by *indexing it with \underline{k} instead of n_x, n_y, n_z* because a given \underline{k} vector denotes a particular solution or **state** just as well as the set of the three quantum numbers.

$$\Psi_{n_x, n_y, n_z}(x, y, z) = \Psi_{\underline{k}}(x, y, z) = \Psi_{\underline{k}}(\underline{r})$$

● In other words, in a formal, more abstract sense we can regard the wave vector as a kind of vector quantum number designating a special solution of the Schrödinger equation for the given problem.

▸ Since in the present case the total energy E is identical to the kinetic energy $E_{\text{kin}} = \frac{1}{2}m_e v^2 = \frac{1}{2}p^2/m_e$, we have

$$E = \frac{\hbar^2 \cdot k^2}{2m_e}$$

We now have expressed the **total energy** as a function of the **wave vector**. Any relation of this kind is called a **dispersion function**. Spelt out we have

$$E = \frac{\hbar^2}{2m_e} \cdot \left(\frac{2\pi}{L} \right)^2 \cdot (n_x^2 + n_y^2 + n_z^2)$$

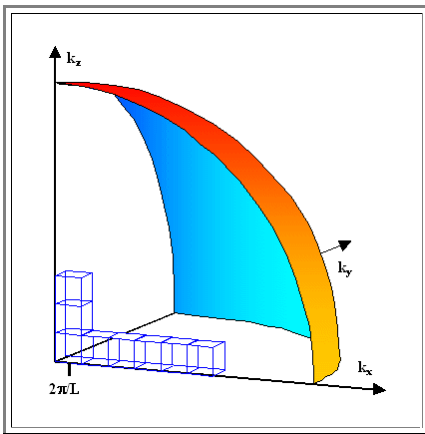
This is the first important result: There are only **discrete** energy levels for the electron in a box with constant potential that represents the crystal.

This result (as you simply must believe at this point) will **still be true** if we use the **correct potentials**, and if we consider **many** electrons. The formula, however, i.e. the relation between energy and wave vectors may become **much more complicated**.

The boundary conditions chosen and the length **L** of the box are somewhat arbitrary. We will see, however, that they do not matter for the relevant quantities to be derived from this model.

Density of States

Knowing the energy levels, we can count how many energy levels are contained in an interval ΔE at the energy **E**. This is best done in **k-space** or **phase space**.



- For the free electron gas, in phase space a surface of constant energy is a sphere, as schematically shown in the picture.
- Any "state", i.e. solution of the Schrodinger equation with a specific **k**, occupies the volume given by one of the little cubes in phase space, corresponding to the discrete states just discussed.
- The number of little cubes fitting inside the sphere at energy **E** thus is the number of **all** electronic states ψ up to **E**.
- Since every state (characterized by its set of quantum numbers **n_x**, **n_y**, **n_z**) can accommodate **2 electrons** (one with **spin** up, one with spin down), the total number of electrons that can occupy states up to **E** is twice the number of little cubes; let this number (that includes the spin degeneracy) be **N_s(E)**.

Looking just at the energy, it is clear that at higher energies there are more states available. Counting the number of little cubes just in an energy interval **E**, **E + ΔE** corresponds to taking the difference of the numbers of cubes contained in a sphere with "radius" **E + ΔE** and **E**.

We thus obtain the **density of states D(E)** as

$$D(E) = \frac{1}{V} \cdot \frac{N_s(E + \Delta E) - N_s(E)}{\Delta E} = \frac{1}{V} \cdot \frac{dN_s}{dE} = \frac{1}{L^3} \cdot \frac{dN_s}{dE}$$

Note that **D(E)** is a density both with respect to **E** and to **V = L³** (= volume of the crystal).

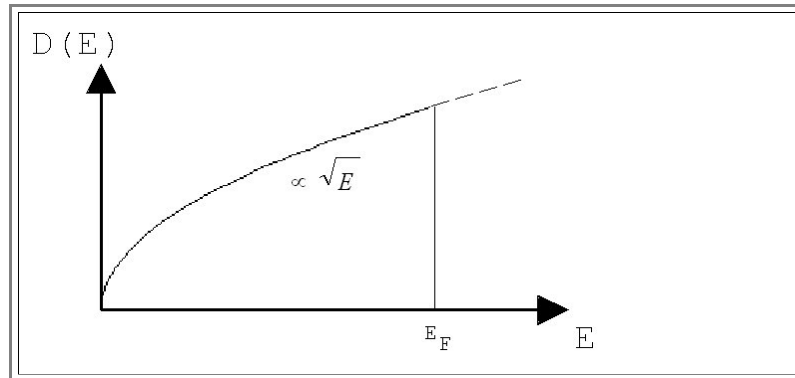
The final formula is

$$D(E) = \frac{1}{L^3} \cdot \frac{dN_s}{dE} = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \cdot E^{1/2}$$

The derivation of this formula and [more to densities of states](#) (including generating some numbers) can be found in the link.

Some important points are:

- $D(E)$ is proportional to $E^{1/2}$.
 - For different (but physically meaningful) boundary conditions we obtain the same D (see the exercise 2.1 below).
 - The artificial length L disappears because we are only considering specific quantities, i.e. volume densities.
 - D is kind of a *twofold* density: It is first the density of energy states in an *energy interval* and second the (trivial) density of that number in *space*.
- If we fill the available states with the available electrons at a *temperature of 0 K* (since we consider the free electrons of a material this number will be about 1 [or a few] per atom and thus is principally known) starting from $E = 0$, we find a special energy called **Fermi energy E_F** at the value where the last electron finds its place.



In order to get (re)acquainted with the formalism, we do two simple exercises:

Exercise 2.1-1

Solution of the free electron gas problem with fixed boundary conditions

Exercise 2.1-2

Density of states as a function of dimensionality

Carrier Statistics

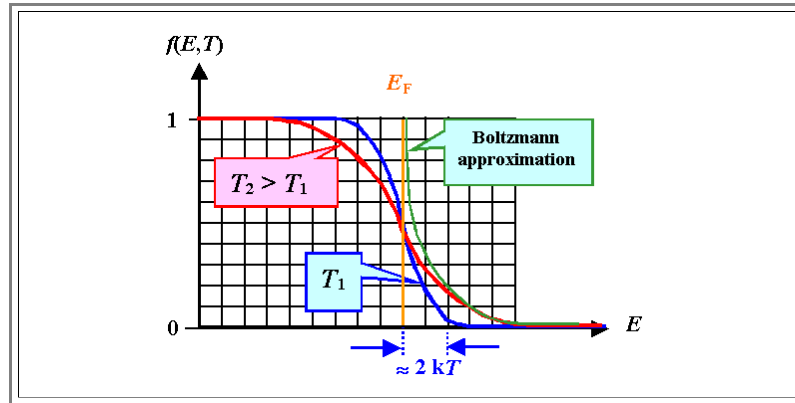
- We have the number of energy states for a given energy interval and want to know how many (charge) *carriers* we will find in the same energy interval *in thermal equilibrium*. Since we want to look at particles other than electrons too, but only at charged particles, we use the term "carrier" here.
- In other words, we want the distribution of carriers on the available energy levels satisfying three conditions:
- The **Pauli exclusion principle**: There may be at most **2** carries per energy state (one with spin "up", one with spin "down"), not more.
 - The **equilibrium condition**: Minimum of the appropriate thermodynamic potential, here always the *free Enthalpy G* (also called **Gibbs energy**).
 - The **conservation of particles** (or charge) condition; i.e. *constant number of carriers* regardless of the distribution.
- The mathematical procedure involves a variation principle of G . The result is the well-known **Fermi –Dirac** distribution $f(E, T)$:
- $f(E, T)$ = probability for occupation of (one!) state at E for the temperature T

$$f(E, T) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}$$

- If you are not very familiar with the distributions in general or the Fermi distribution in particular, read up on it in the (German) link.
- This is the "popular" version with the **Fermi energy E_F** as a parameter. In the "correct" version, we would have the chemical potential μ instead of E_F .

- Since the Fermi energy is a quantity defined independently of the equilibrium considerations above, equating E_F with μ is only correct at $T = 0 \text{ K}$. Most textbooks emphasize that small differences may occur at larger temperatures, but do not explain what those differences are. We, like everybody else, will ignore these fine points and use the term "*Fermi Energy*" without reservations.
- In all experience, many students (and faculty) of physics or materials science have problems with the concept of the "*chemical potential*". This is in part psychological (we want to do semiconductor physics and not chemistry), but mostly just due to little acquaintance with the subject. The [link](#) provides some explanations and examples which might help.

▶ The Fermi-Dirac distribution has some general properties which are best explained in a graphic representation.



- It contains a convenient definition of the Fermi energy: The energy where exactly half of the available levels are occupied (or would be occupied if there would be any!) is the Fermi energy:

$$f(E = E_F) = \frac{1}{2}$$

- The width of "soft zone" is $\approx 4 kT = 1 \text{ meV}$ at 3 K , and 103 meV at 300 K .
- For $E - E_F \gg kT$ the **Boltzmann** approximation can be used:

$$f_B(E, T) \approx \exp\left(-\frac{E - E_F}{kT}\right)$$

- In this case the exclusion principle is not important because there are always plenty of free states around – the electrons behave akin to classical particles.

▶ This leads to the final formula for the incremental number or **density of electrons**, dn , in the energy interval $E, E + \Delta E$ (and, of course, in thermodynamic equilibrium).

In words:	Formula
Density of electrons in the energy interval $E, E + \Delta E =$ density of states <i>times</i> probability for occupancy <i>times</i> energy interval	$dn = D(E) \cdot f(E, T) \cdot dE$

▶ This is an extremely important formula, which is easily generalized for almost everything. The number (or density) of something is given by the density of available places times the probability of occupation.

- This applies to the number of people found in a given church or stadium, the number of [photons inside a "black box"](#), the number of phonons in a crystal, and so on.
- The tricky part, of course, is to know the probabilities or the **distribution function** in each case. However, if we do not consider church goers or soccer fans, but only physical particles (including electrons and holes, but also "**quasi-particles**" like [phonons](#), excitons, ...), there are only *two* distribution functions (and the Boltzmann distribution as an approximation): The Fermi-Dirac distribution for Fermions, and the Bose-Einstein distribution for Bosons. Mother nature here made life real easy for physicists.

▶ Since all available electrons must be somewhere on the energy scale, we always have a normalization condition for the total electron density n :

$$n = \int_0^{\infty} D(E) \cdot f(E, T) \cdot dE$$

Questions

Quick Questions to 2.1.1