
Condensed Matter Theory

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Sources

This script partly follows the excellent textbook “Theoretische Festkörperphysik” by Gerd Czycholl. Some parts are based on the script “Festkörpertheorie” by Claudius Gros, Universität Frankfurt. Also, the script “Theoretische Festkörperphysik I” by Erwin Müller-Hartmann has been used in parts. Further literature is cited in the text.

1. Non-interacting electrons in the crystal

The topic of this chapter and the following is the electronic structure of solids. We initially assume that the crystal lattice is rigid, *i.e.* the ions sit in fixed positions \vec{R}_n ; this corresponds to the decoupling of electron and lattice motion which is justified by the Born-Oppenheimer-approximation. We even assume that the temperature is so low that ions are not displaced from their equilibrium positions. We consider, at first, electrons which do not interact (*i.e.* whose Coulomb repulsion is neglected). Only in the next chapter we will supply the justification: an interacting electron system may often be mapped onto a non-interacting one, while the interaction is taken into account by parameters. Thus, the single-particle potential can be considered an effective potential.

We discuss the Hamiltonian

$$H = \sum_{i=1}^{N_e} \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^{N_e} \sum_{n=1}^N v(\vec{r}_i - \vec{R}_n) \quad (1.1)$$

with the number of electrons N_e , number of atoms N , electron momentum \vec{p}_i and the potential $v(\vec{r}_i - \vec{R}_n)$ which a single electron is subjected to and which is contributed by the unit cell n . If the crystal structure has a basis, *i.e.* more than one atom per unit cell, then the potential can be written as

$$v(\vec{r}_i - \vec{R}_n) = \sum_{\tau} \tilde{v}(\vec{r}_i - \vec{R}_n - \vec{R}_{\tau}). \quad (1.2)$$

A Hamiltonian (1.1) is called **single particle Hamiltonian**, because it is composed of single particle contributions. The exact single particle eigenfunctions can be written as an antisymmetric product of single particle wave functions (as Slater determinant). The antisymmetrization is necessary due to the Pauli principle and is here the only many-particle effect. A true many-particle Hamiltonian with electron-electron interaction terms $\bar{v}(\vec{r}_i - \vec{r}_j)$ can not be written as a sum of single particle contributions anymore, and the exact many-particle eigenstate cannot be represented as a single Slater determinant anymore.

1.1 Electrons in a periodic potential

We start with a single electron in a periodic potential, for which the Schrödinger equation

$$\mathbf{H}\psi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right)\psi(\vec{r}) = \varepsilon\psi(\vec{r}) \quad (1.3)$$

with translationally invariant $V(\vec{r})$

$$V(\vec{r}) = V(\vec{r} + \vec{\mathbf{R}}), \quad \vec{\mathbf{R}} \text{ lattice vector} \quad (1.4)$$

is valid. A conserved quantity which commutes with the Hamiltonian is connected to the symmetry of translational invariance: the operator $\mathbf{T}_{\vec{\mathbf{R}}}$ which brings about a translation by a lattice vector. It is defined by

$$\mathbf{T}_{\vec{\mathbf{R}}}\psi(\vec{r}) = \psi(\vec{r} + \vec{\mathbf{R}}) \quad (1.5)$$

for arbitrary $\psi(\vec{r})$. $\mathbf{T}_{\vec{\mathbf{R}}}$ commutes with \mathbf{H} : $[\mathbf{T}_{\vec{\mathbf{R}}}, \mathbf{H}] = 0$, because

$$\begin{aligned} \mathbf{T}_{\vec{\mathbf{R}}}\mathbf{H}\psi(\vec{r}) &= \mathbf{T}_{\vec{\mathbf{R}}}\left(\frac{\vec{\mathbf{p}}^2}{2m} + V(\vec{r})\right)\psi(\vec{r}) = \left(\frac{\vec{\mathbf{p}}^2}{2m} + V(\vec{r} + \vec{\mathbf{R}})\right)\psi(\vec{r} + \vec{\mathbf{R}}) \\ &= \left(\frac{\vec{\mathbf{p}}^2}{2m} + V(\vec{r})\right)\psi(\vec{r} + \vec{\mathbf{R}}) = \mathbf{H}\mathbf{T}_{\vec{\mathbf{R}}}\psi(\vec{r}) \end{aligned} \quad (1.6)$$

The translation operators also commute among themselves: $[\mathbf{T}_{\vec{\mathbf{R}}}, \mathbf{T}_{\vec{\mathbf{R}}'}] = 0$,

$$\mathbf{T}_{\vec{\mathbf{R}}}\mathbf{T}_{\vec{\mathbf{R}}'} = \mathbf{T}_{\vec{\mathbf{R}}'}\mathbf{T}_{\vec{\mathbf{R}}} = \mathbf{T}_{\vec{\mathbf{R}}+\vec{\mathbf{R}}'} \quad (1.7)$$

Thus, it must be possible to choose the eigenfunctions of \mathbf{H} as joint eigenfunctions of \mathbf{H} and all $\mathbf{T}_{\vec{\mathbf{R}}}$:

$$\mathbf{H}\psi(\vec{r}) = \varepsilon\psi(\vec{r}); \quad \mathbf{T}_{\vec{\mathbf{R}}}\psi(\vec{r}) = c(\vec{\mathbf{R}})\psi(\vec{r}) \quad (1.8)$$

with the joint eigenfunctions $\psi(\vec{r})$ and eigenvalues $c(\vec{\mathbf{R}})$ of $\mathbf{T}_{\vec{\mathbf{R}}}$. They obey:

$$c(\vec{\mathbf{R}})c(\vec{\mathbf{R}}') = c(\vec{\mathbf{R}} + \vec{\mathbf{R}}'); \quad c(\vec{\mathbf{R}})c(-\vec{\mathbf{R}}) = 1; \quad c(\vec{\mathbf{R}})^2 = c(2\vec{\mathbf{R}}). \quad (1.9)$$

From the normalization, we obtain

$$1 = \int d^3\mathbf{r} |\psi(\vec{r})|^2 = \int d^3\mathbf{r} |\psi(\vec{r} + \vec{\mathbf{R}})|^2 = \int d^3\mathbf{r} |c(\vec{\mathbf{R}})|^2 |\psi(\vec{r})|^2 = |c(\vec{\mathbf{R}})|^2. \quad (1.10)$$

This means

$$c(\vec{\mathbf{R}}) = e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}}, \quad (1.11)$$

and therefore the eigenfunctions of the lattice periodic Hamiltonian obey

$$\psi(\vec{\mathbf{r}} + \vec{\mathbf{R}}) = e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}} \psi(\vec{\mathbf{r}}) \quad (1.12)$$

The eigenfunctions can differ from unit cell to unit cell by a phase factor. However, the electron density is again periodic because

$$|\psi(\vec{\mathbf{r}})|^2 = |\psi(\vec{\mathbf{r}} + \vec{\mathbf{R}})|^2 \quad (1.13)$$

We take into account that we deal with a finite system by using periodic boundary conditions. Then we have for the eigenfunctions

$$\psi(\vec{\mathbf{r}}) = \psi(\vec{\mathbf{r}} + \mathbf{N}_i \vec{\mathbf{a}}_i) \quad (1.14)$$

with primitive unit vectors $\vec{\mathbf{a}}_i$, $i = 1, \dots, d$. The system consists of \mathbf{N}_i unit cells in the directions $i = 1, \dots, d$, in total $\mathbf{N} = \prod_i \mathbf{N}_i$. Thus, the crystal momentum values $\vec{\mathbf{k}}$ which can again be limited to the first Brillouin zone, are quantized and take on only \mathbf{N} discrete values:

$$\vec{\mathbf{k}} = \sum_{i=1}^d \frac{\mathbf{n}_i}{\mathbf{N}_i} \vec{\mathbf{b}}_i \quad \text{with } \mathbf{n}_i \in \left\{ -\frac{\mathbf{N}_i}{2}, \dots, \frac{\mathbf{N}_i}{2} - 1 \right\} \quad (1.15)$$

By the Taylor expansion

$$\begin{aligned} T_{\vec{\mathbf{R}}} f(\vec{\mathbf{r}}) &= f(\vec{\mathbf{r}} + \vec{\mathbf{R}}) = \sum_{n=0}^{\infty} \frac{1}{n!} (\vec{\mathbf{R}} \cdot \nabla)^n f(\vec{\mathbf{r}}) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i}{\hbar} \vec{\mathbf{R}} \cdot \vec{\mathbf{p}} \right)^n f(\vec{\mathbf{r}}) \\ &= e^{i \frac{\vec{\mathbf{R}} \cdot \vec{\mathbf{p}}}{\hbar}} f(\vec{\mathbf{r}}) \end{aligned} \quad (1.16)$$

we realize, that the translation operator is given explicitly by

$$T_{\vec{\mathbf{R}}} = e^{i \frac{\vec{\mathbf{R}} \cdot \vec{\mathbf{p}}}{\hbar}}. \quad (1.17)$$

For the construction of joint eigenfunctions $\psi_{\vec{\mathbf{k}}}(\vec{\mathbf{r}})$ of Hamiltonian and translation operator, where $e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}}$ are the eigenvalues of $T_{\vec{\mathbf{R}}}$, we define

$$\mathbf{u}_{\vec{\mathbf{k}}}(\vec{\mathbf{r}}) = e^{-i\vec{\mathbf{k}} \cdot \vec{\mathbf{r}}} \psi_{\vec{\mathbf{k}}}(\vec{\mathbf{r}}) \quad (1.18)$$

These functions are lattice periodic, because

$$\mathbf{u}_{\vec{k}}(\vec{r} + \vec{R}) = e^{-i\vec{k} \cdot (\vec{r} + \vec{R})} \psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{-i\vec{k} \cdot \vec{r}} e^{-i\vec{k} \cdot \vec{R}} e^{i\vec{k} \cdot \vec{R}} \psi_{\vec{k}}(\vec{r}) = \mathbf{u}_{\vec{k}}(\vec{r}) \quad (1.19)$$

Thus, we find for the normalized eigenfunctions of the single particle Hamiltonian with a lattice periodic potential

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k} \cdot \vec{r}} \mathbf{u}_{\vec{k}}(\vec{r}) \quad (1.20)$$

with lattice periodic Bloch factor $\mathbf{u}_{\vec{k}}(\vec{r})$. This is the **Bloch theorem**. The single-particle eigenfunctions of the lattice periodic Hamiltonian are given by a product of a plane wave and a lattice periodic Bloch factor. An example for a Bloch function in one dimension is shown in Figure 1.1.

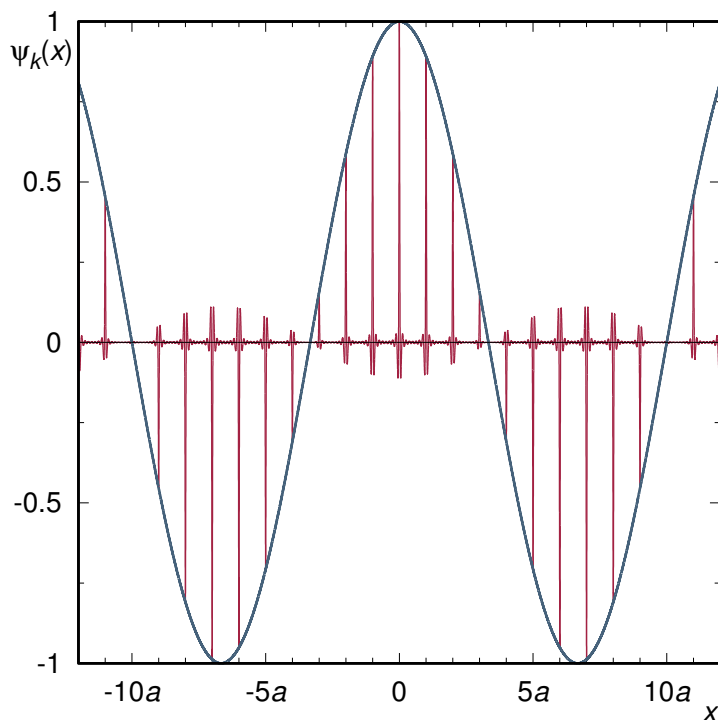


Figure 1.1: Bloch function $\psi_{\vec{k}}(x)$ for a one dimensional periodic potential with lattice constant a and for a wave number $k = 0.15\pi/a$.

From the Schrödinger equation, we can obtain a partial differential equation for the Bloch factors:

$$\begin{aligned} H\sqrt{\Omega}\psi_{\vec{k}}(\vec{r}) &= \left(-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) \right) e^{i\vec{k} \cdot \vec{r}} \mathbf{u}_{\vec{k}}(\vec{r}) = \epsilon e^{i\vec{k} \cdot \vec{r}} \mathbf{u}_{\vec{k}}(\vec{r}) \\ &= -\frac{\hbar^2}{2m} e^{i\vec{k} \cdot \vec{r}} (-k^2 + 2i\vec{k} \cdot \nabla + \nabla^2) \mathbf{u}_{\vec{k}}(\vec{r}) + V(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \mathbf{u}_{\vec{k}}(\vec{r}) \end{aligned} \quad (1.21)$$

For each \vec{k} from the first Brillouin zone, we have to solve a partial differential equation for $\mathbf{u}_{\vec{k}}(\vec{r})$:

$$\mathbf{h}(\vec{k})\mathbf{u}_{\vec{k}}(\vec{r}) \equiv \left[\frac{\hbar^2}{2m} \left(\frac{1}{i} \nabla + \vec{k} \right)^2 + V(\vec{r}) \right] \mathbf{u}_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k})\mathbf{u}_{\vec{k}}(\vec{r}) \quad (1.22)$$

The wave vector enters as a parameter. As $\mathbf{u}_{\vec{k}}(\vec{r})$ is periodic with respect to lattice translations, this is a boundary value problem in a single unit cell. As solutions, we expect for each fixed \vec{k} eigenvalues $\varepsilon_n(\vec{k})$ and eigenfunctions $\mathbf{u}_{n\vec{k}}(\vec{r})$. These can be orthonormalized in a unit cell (Ω_{puc} stands for the volume of the primitive unit cell):

$$\frac{1}{\Omega_{\text{puc}}} \int_{\Omega_{\text{puc}}} d^3r \mathbf{u}_{n\vec{k}}^*(\vec{r}) \mathbf{u}_{n'\vec{k}}(\vec{r}) = \delta_{nn'} \quad (1.23)$$

For the Bloch functions $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \mathbf{u}_{n\vec{k}}(\vec{r})$ we then have

$$\begin{aligned} & \int_{\Omega} d^3r \psi_{n\vec{k}}^*(\vec{r}) \psi_{n'\vec{k}'}(\vec{r}) \\ &= \frac{1}{\Omega} \sum_{\vec{R}} \int_{\Omega_{\text{puc}}(\vec{R})} d^3r e^{-i\vec{k}\cdot(\vec{R}+\vec{r})} \mathbf{u}_{n\vec{k}}^*(\vec{R}+\vec{r}) e^{i\vec{k}'\cdot(\vec{R}+\vec{r})} \mathbf{u}_{n'\vec{k}'}(\vec{R}+\vec{r}) \\ &= \frac{1}{N} \sum_{\vec{R}} e^{i(\vec{k}'-\vec{k})\cdot\vec{R}} \frac{1}{\Omega_{\text{puc}}} \int_{\Omega_{\text{puc}}} d^3r \mathbf{u}_{n\vec{k}}^*(\vec{r}) \mathbf{u}_{n'\vec{k}'}(\vec{r}) = \delta_{\vec{k}\vec{k}'} \delta_{nn'} \end{aligned} \quad (1.24)$$

Eigenfunctions $\psi_{n\vec{k}}(\vec{r})$ and energy eigenvalues $\varepsilon_n(\vec{k})$ for the electron in a periodic potential is thus characterized by two quantum numbers, the wave vector \vec{k} from the first Brillouin zone and the index n which numbers discrete eigenvalues of the boundary value problem for the Bloch functions $\mathbf{u}_{n\vec{k}}(\vec{r})$. This index is called **band index** n . There is an infinite number of bands as the effective Hamiltonian $\mathbf{h}(\vec{k})$ is self-adjoint; its eigenfunctions $\mathbf{u}_{n\vec{k}}(\vec{r})$ form a basis in the space of square integrable functions defined in the unit cell Ω_{puc} . Therefore, the completeness relation

$$\sum_n \mathbf{u}_{n\vec{k}}^*(\vec{r}) \mathbf{u}_{n\vec{k}}(\vec{r}') = \Omega_{\text{puc}} \delta(\vec{r} - \vec{r}') \quad (1.25)$$

must be fulfilled. For a finite system with periodic boundary conditions, the allowed \vec{k} values are discrete; however, as we are dealing with a macroscopic volume of a crystal, the \vec{k} values are dense in the first Brillouin zone, and

the dispersion relations $\varepsilon_{\mathbf{n}}(\vec{\mathbf{k}})$ are considered to be continuous functions of the variable $\vec{\mathbf{k}}$. At special points, lines or surfaces of the Brillouin zone, **band degeneracies** with $\varepsilon_{\mathbf{n}}(\vec{\mathbf{k}}) = \varepsilon_{\mathbf{n}'}(\vec{\mathbf{k}})$ for $\mathbf{n} \neq \mathbf{n}'$ can occur.

A different proof for the Bloch theorem uses the Fourier transformation of the Schrödinger equation which we will need later. As the potential is periodic, it can be expanded in a Fourier series, with Fourier coefficients determined by the reciprocal lattice vectors:

$$V(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}} \cdot \vec{\mathbf{r}}} \quad \text{with} \quad V_{\vec{\mathbf{G}}} = \frac{1}{\Omega_{\text{puc}}} \int_{\Omega_{\text{puc}}} d^3\mathbf{r} V(\vec{\mathbf{r}}) e^{-i\vec{\mathbf{G}} \cdot \vec{\mathbf{r}}} \quad (1.26)$$

The wave function we want to determine is also written as a Fourier series:

$$\psi(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{q}}} c_{\vec{\mathbf{q}}} e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \quad (1.27)$$

The wave function is not assumed to be lattice periodic; however, it has to obey the periodic boundary conditions: $\vec{\mathbf{q}} = \sum_{i=1}^3 \frac{n_i}{N_i} \vec{\mathbf{b}}_i$ with $n_i \in \mathbb{Z}$, where the $\vec{\mathbf{b}}_i$ span the reciprocal lattice, and the $\vec{\mathbf{q}}$ are not restricted to the first Brillouin zone. The system size is $N_i \vec{\mathbf{a}}_i$, $i = 1, \dots, 3$. Any function obeying periodic boundary conditions can be represented in this way. Now, we introduce the Fourier expansion for potential and wave function into the Schrödinger equation:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{\mathbf{r}}) \right) \psi(\vec{\mathbf{r}}) &= \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}} \cdot \vec{\mathbf{r}}} \right) \sum_{\vec{\mathbf{q}}} c_{\vec{\mathbf{q}}} e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \\ &= \sum_{\vec{\mathbf{q}}} \left(\frac{\hbar^2 \mathbf{q}^2}{2m} + \sum_{\vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} e^{i\vec{\mathbf{G}} \cdot \vec{\mathbf{r}}} \right) c_{\vec{\mathbf{q}}} e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = \sum_{\vec{\mathbf{q}}} \frac{\hbar^2 \mathbf{q}^2}{2m} c_{\vec{\mathbf{q}}} e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} + \sum_{\vec{\mathbf{q}}, \vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} e^{i(\vec{\mathbf{G}} + \vec{\mathbf{q}}) \cdot \vec{\mathbf{r}}} \\ &= \sum_{\vec{\mathbf{q}}} \left(\frac{\hbar^2 \mathbf{q}^2}{2m} c_{\vec{\mathbf{q}}} + \sum_{\vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} c_{\vec{\mathbf{q}} - \vec{\mathbf{G}}} \right) e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = \varepsilon \sum_{\vec{\mathbf{q}}} c_{\vec{\mathbf{q}}} e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \end{aligned} \quad (1.28)$$

and thus

$$\sum_{\vec{\mathbf{q}}} \left[\left(\frac{\hbar^2 \mathbf{q}^2}{2m} - \varepsilon \right) c_{\vec{\mathbf{q}}} + \sum_{\vec{\mathbf{G}}} V_{\vec{\mathbf{G}}} c_{\vec{\mathbf{q}} - \vec{\mathbf{G}}} \right] e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = 0 \quad (1.29)$$

As the functions $e^{i\vec{q}\cdot\vec{r}}$ form an orthonormal basis, we have

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_{\vec{q}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}-\vec{G}} = 0 \quad (1.30)$$

For each \vec{q} (from the entire \vec{k} space) there is now a unique vector \vec{k} from the first Brillouin zone and a unique reciprocal lattice vector \vec{G}_0 so that $\vec{q} = \vec{k} - \vec{G}_0$. Then we have

$$\left(\frac{\hbar^2}{2m}(\vec{k} - \vec{G}_0)^2 - \varepsilon\right) c_{\vec{k}-\vec{G}_0} + \sum_{\vec{G}} V_{\vec{G}-\vec{G}_0} c_{\vec{k}-\vec{G}} = 0 \quad (1.31)$$

This represents, for each \vec{k} from the first Brillouin zone, a homogeneous system of linear equations for the coefficients $c_{\vec{k}-\vec{G}}$. Only coefficients that differ by reciprocal lattice vectors are connected. Therefore, each \vec{k} from the first Brillouin zone has its own system of equations which is decoupled from the one belonging to \vec{k}' . Therefore, the possible solutions can be classified according to \vec{k} and the result is

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}} \quad (1.32)$$

Thus, the eigenfunctions of the Schrödinger equation can be represented as

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \quad (1.33)$$

with \vec{k} from the first Brillouin zone, and

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}} = u_{\vec{k}}(\vec{r} + \vec{R}) \quad \text{because of } e^{-i\vec{G}\cdot\vec{R}} = 1 \quad (1.34)$$

We again obtain the Bloch theorem.

1.2 Nearly free electrons

In this approximation, the starting point are free electrons for which the periodic potential is a small perturbation which can be treated in quantum mechanical, time independent perturbation theory. We start with the

Fourier transformed Schrödinger equation

$$\left(\frac{\hbar^2}{2m} (\vec{k} - \vec{G}_0)^2 - \varepsilon \right) c_{\vec{k}-\vec{G}_0} + \sum_{\vec{G}} V_{\vec{G}-\vec{G}_0} c_{\vec{k}-\vec{G}} = 0 \quad (1.35)$$

with \vec{k} from the first Brillouin zone and reciprocal lattice vectors \vec{G}, \vec{G}_0 . In zero-th order in the potential, it can be neglected completely ($V \approx 0$).

In this case, all Fourier coefficients $V_{\vec{G}}$ are identically zero; therefore, (1.35) implies

$$\left(\frac{\hbar^2}{2m} (\vec{k} - \vec{G}_0)^2 - \varepsilon \right) c_{\vec{k}-\vec{G}_0} = 0 \quad (1.36)$$

Consequently

$$\varepsilon = \varepsilon_{\vec{G}_0}^{(0)}(\vec{k}) \equiv \varepsilon_{\vec{k}-\vec{G}_0}^{(0)} = \frac{\hbar^2}{2m} (\vec{k} - \vec{G}_0)^2 \quad (1.37)$$

The lattice is taken into account as we introduced a reciprocal lattice and Brillouin zone. However, only the periodic non-zero potential will have a noticeable effect. For free electrons we have as usual the dispersion

$$\varepsilon^{(0)}(\vec{q}) = \frac{\hbar^2 q^2}{2m} \quad (1.38)$$

and plane waves as eigenfunctions

$$\psi_{\vec{q}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{q}\cdot\vec{r}} \quad (1.39)$$

with the volume Ω of the system and discrete \vec{q} , which runs over all values that are compatible with the periodic boundary conditions and which are thus not confined to the first Brillouin zone. We can however always represent it by \vec{k} from the first Brillouin zone and with reciprocal lattice vector \vec{G}_0 , as soon as we assume a lattice structure:

$$\vec{q} = \vec{k} - \vec{G}_0, \quad \varepsilon_{\vec{G}_0}^{(0)}(\vec{k}) = \frac{\hbar^2}{2m} (\vec{k} - \vec{G}_0)^2, \quad \psi_{\vec{G}_0}(\vec{k}) = \frac{1}{\sqrt{\Omega}} e^{-i\vec{G}_0\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} \quad (1.40)$$

Eigenenergies and -functions are characterized by two quantum numbers, \vec{k} from the first Brillouin zone and \vec{G}_0 . The eigenfunctions are a product of plane waves $e^{i\vec{k}\cdot\vec{r}}$ and the lattice periodic function $e^{-i\vec{G}_0\cdot\vec{r}}$, which is the

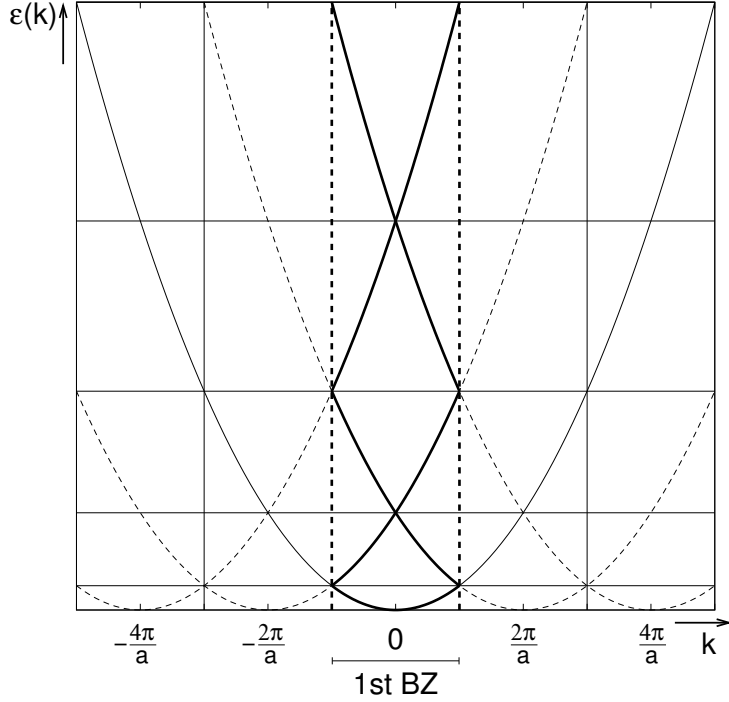


Figure 1.2: Free electron bands in one dimension; extended and reduced zone scheme.

Bloch factor in case of free electrons. The \vec{G}_0 play the role of the band index \mathbf{n} .

Figure 1.2 shows the band structure of free electrons for a one dimensional system without periodic potential; however, periodicity is taken into account by Brillouin zone boundaries. Due to translational invariance, the dispersion is periodic with period $\frac{2\pi}{a}$, *i.e.* the free electron parabola can start at each reciprocal lattice vector $\vec{G}_0 = \frac{2n\pi}{a}$, $\mathbf{n} \in \mathbb{Z}$. This leads to the so-called **extended zone scheme**, where each copy of the first Brillouin zone contains the same information. This means that it is enough to restrict to the first Brillouin zone which is called **reduced zone scheme**. Here, each \vec{k} from the first Brillouin zone is associated with an infinite number of energy eigenvalues which differ by a reciprocal lattice vector \vec{G}_0 .

We now proceed to the case of a (small) finite periodic potential. As a first step, we can choose the zero of the potential such that the mean value of the potential, the 0-th Fourier component, vanishes:

$$V_{\vec{G}_0} \equiv V_0 = \frac{1}{\Omega_{\text{puc}}} \int_{\Omega_{\text{puc}}} d^3\mathbf{r} V(\vec{r}) = 0 \quad (1.41)$$

Then, the Fourier transformed Schrödinger equation (1.35) implies

$$(\varepsilon_{\vec{k}-\vec{G}_0}^{(0)} - \varepsilon) c_{\vec{k}-\vec{G}_0} = - \sum_{\vec{G} \neq \vec{G}_0} V_{\vec{G}-\vec{G}_0} c_{\vec{k}-\vec{G}} \quad (1.42)$$

Here, ε is the desired new eigenenergy in the presence of a potential; it should, however, not be too far different from $\varepsilon_{\vec{k}-\vec{G}_0}^{(0)}$ because we assumed the potential to be weak. We now consider the band corresponding to \vec{G}_1 . We can assume that the Fourier coefficients $c_{\vec{k}-\vec{G}}^{\rightarrow}$ for $\vec{G} \neq \vec{G}_1$ are small as they disappear for negligible potential.

In this case, only $c_{\vec{k}-\vec{G}_0}^{\rightarrow} = \frac{1}{\sqrt{\Omega}} \neq 0$ (see equation (1.40)). We can now convince ourselves that the right hand side of (1.42) is second order in V . For this purpose, we again consider equation (1.35), this time writing it for a different \vec{G} , *i.e.* we look for the $c_{\vec{k}-\vec{G}}^{\rightarrow}$ which belong to the same eigenenergy in the band \vec{G}_0 :

$$(\varepsilon - \varepsilon_{\vec{k}-\vec{G}_0}^{(0)})c_{\vec{k}-\vec{G}}^{\rightarrow} = \sum_{\substack{\vec{G}' \neq \vec{G} \\ \vec{G}' \neq \vec{G}_0}} V_{\vec{G}-\vec{G}'}^{\rightarrow} c_{\vec{k}-\vec{G}'}^{\rightarrow} = V_{\vec{G}_0-\vec{G}}^{\rightarrow} c_{\vec{k}-\vec{G}_0}^{\rightarrow} + \sum_{\substack{\vec{G}' \neq \vec{G}_0, \vec{G} \\ \vec{G}' \neq \vec{G}}} V_{\vec{G}-\vec{G}'}^{\rightarrow} c_{\vec{k}-\vec{G}'}^{\rightarrow} \quad (1.43)$$

We have taken the largest term out of the sum because $c_{\vec{k}-\vec{G}_0}^{\rightarrow}$ is of order $\mathcal{O}(1)$. This term is also linear in V , the other terms in the sum are at least of order $\mathcal{O}(V^2)$. This means that we can neglect them for small V , and we find

$$c_{\vec{k}-\vec{G}}^{\rightarrow} = \frac{V_{\vec{G}_0-\vec{G}}^{\rightarrow}}{\varepsilon - \varepsilon_{\vec{k}-\vec{G}_0}^{(0)}} c_{\vec{k}-\vec{G}_0}^{\rightarrow} \quad (1.44)$$

Introduction to equation (1.42) yields

$$(\varepsilon - \varepsilon_{\vec{k}-\vec{G}_0}^{(0)})c_{\vec{k}-\vec{G}_0}^{\rightarrow} = \sum_{\vec{G}} \frac{V_{\vec{G}-\vec{G}_0}^{\rightarrow} V_{\vec{G}_0-\vec{G}}^{\rightarrow}}{\varepsilon - \varepsilon_{\vec{k}-\vec{G}}^{(0)}} c_{\vec{k}-\vec{G}}^{\rightarrow} \quad (1.45)$$

and thus

$$\varepsilon = \varepsilon_{\vec{k}-\vec{G}_0}^{(0)} + \sum_{\vec{G} \neq \vec{G}_0} \frac{|V_{\vec{G}-\vec{G}_0}^{\rightarrow}|^2}{\varepsilon - \varepsilon_{\vec{k}-\vec{G}}^{(0)}} \quad (1.46)$$

This corresponds to the quantum mechanical Brillouin-Wigner perturbation series up to second order in the perturbation V (the energy ε we want to determine appears both on left and right hand sides, leading to a polynomial equation in ε). Now we have to distinguish two cases: If there is

no degeneracy, *i.e.* the investigated energy level $\varepsilon_{\vec{k}-\vec{G}_0}^{(0)}$ is not (not even approximately) degenerate with different energy levels $\varepsilon_{\vec{k}-\vec{G}}^{(0)}$, $\vec{G} \neq \vec{G}_0$, then we can replace, on the right hand side, the desired energy ε by its zeroth approximation $\varepsilon_{\vec{k}-\vec{G}_0}^{(0)}$; we continue to be exact up to order V^2 in the perturbation which is the periodic potential. This leads to

$$\varepsilon = \varepsilon_{\vec{k}-\vec{G}_0}^{(0)} + \sum_{\vec{G} \neq \vec{G}_0} \frac{|V_{\vec{G}-\vec{G}_0}|^2}{\varepsilon_{\vec{k}-\vec{G}_0}^{(0)} - \varepsilon_{\vec{k}-\vec{G}}^{(0)}}. \quad (1.47)$$

This corresponds to the Rayleigh-Schrödinger perturbation expansion up to second order. In those regions of the Brillouin zone in which no band degeneracies of the unperturbed free electron energies occur, the eigenenergies which are calculated in second order perturbation theory in the periodic potential are modified by terms of the order $\frac{V^2}{\Delta\varepsilon}$ compared to the energies of free electrons, where $\Delta\varepsilon$ is the energy separation of neighboring bands. Usually $|\Delta\varepsilon| = |\varepsilon_{\vec{k}-\vec{G}_0}^{(0)} - \varepsilon_{\vec{k}-\vec{G}}^{(0)}| \gg |V|$, and then the approximation for the eigenenergies is good. Above all, the band shift is second order in V . We will see in a moment that in the nearly degenerate case, a shift occurs which is linear in V and which is therefore the dominant shift. Now we discuss the second case of the case-by-case analysis: The \vec{k} points in the Brillouin zone at which there is a degeneracy: $\varepsilon_{\vec{k}-\vec{G}_0}^{(0)} = \varepsilon_{\vec{k}-\vec{G}_1}^{(0)}$ for different lattice vectors $\vec{G}_0 \neq \vec{G}_1$. In the vicinity of these \vec{k} points, the Rayleigh-Schrödinger perturbation theory is not possible anymore because vanishingly small denominators would lead to divergences. As a rule, degeneracy only occurs for two reciprocal lattice vectors, and for this term $\vec{G} = \vec{G}_1$ in (1.46) we cannot replace ε by $\varepsilon_{\vec{k}-\vec{G}_0}^{(0)}$; however, for the others we can:

$$\varepsilon(\vec{k}) = \varepsilon_{\vec{k}-\vec{G}_0}^{(0)} + \frac{|V_{\vec{G}_1-\vec{G}_0}|^2}{\varepsilon(\vec{k}) - \varepsilon_{\vec{k}-\vec{G}_1}^{(0)}} + \sum_{\vec{G} \neq \vec{G}_0, \vec{G}_1} \frac{|V_{\vec{G}-\vec{G}_0}|^2}{\varepsilon_{\vec{k}-\vec{G}_0}^{(0)} - \varepsilon_{\vec{k}-\vec{G}}^{(0)}} \quad (1.48)$$

The second term is now of order V , so that the third which is of order V^2

can be neglected. From the auxiliary calculation

$$\begin{aligned}
(\varepsilon - \varepsilon_0)(\varepsilon - \varepsilon_1) &= \mathbf{V}^2 \rightsquigarrow \varepsilon^2 - \varepsilon(\varepsilon_0 + \varepsilon_1) + \varepsilon_0\varepsilon_1 - \mathbf{V}^2 = 0 \\
\rightsquigarrow \varepsilon^\pm &= \frac{1}{2}((\varepsilon_0 + \varepsilon_1) \pm \sqrt{(\varepsilon_0 + \varepsilon_1)^2 + 4(\mathbf{V}^2 - \varepsilon_0\varepsilon_1)}) \\
&= \frac{1}{2}((\varepsilon_0 + \varepsilon_1) \pm \sqrt{(\varepsilon_0 - \varepsilon_1)^2 + 4\mathbf{V}^2})
\end{aligned} \tag{1.49}$$

we find

$$\varepsilon(\vec{\mathbf{k}}) = \frac{1}{2} \left[\varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_0}^{(0)} + \varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_1}^{(0)} \pm \sqrt{(\varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_0}^{(0)} - \varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_1}^{(0)})^2 + 4|\mathbf{V}_{\vec{\mathbf{G}}_0-\vec{\mathbf{G}}_1}^2|} \right] \tag{1.50}$$

Exactly at the point of the degeneracy $\vec{\mathbf{k}}$ with $\varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_0}^{(0)} = \varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_1}^{(0)}$ there are now the two new eigenenergies

$$\varepsilon^\pm(\vec{\mathbf{k}}) = \varepsilon_{\vec{\mathbf{k}}-\vec{\mathbf{G}}_0}^{(0)} \pm |\mathbf{V}_{\vec{\mathbf{G}}_0-\vec{\mathbf{G}}_1}| \tag{1.51}$$

The degeneracy is lifted by the presence of the periodic potential. The energy correction at the degenerate \mathbf{k} points is shown in Figure 1.3.

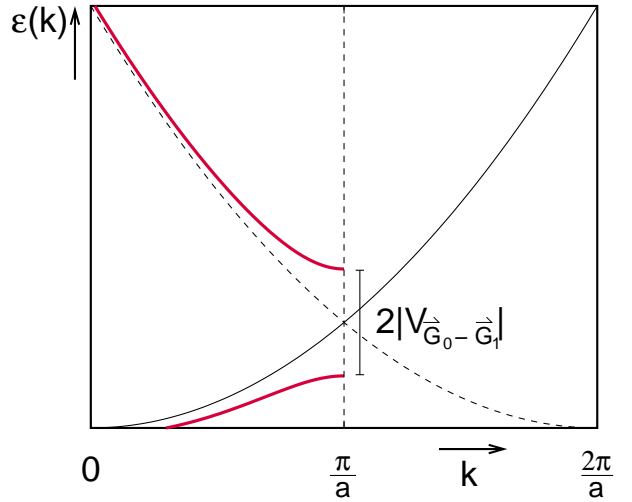


Figure 1.3: Corrections to the free electron bands at the edge of the first Brillouin zone in the presence of a small periodic potential.

Up to now, we have considered one-dimensional examples for band structures. As an example for a free electron dispersion in three dimensions, in Figure 1.4 the dispersion of a face centered cubic (fcc) lattice is shown. The dispersion which starts at the Γ point is folded back at the zone boundaries. Alternatively, the back-folded branches can be understood as parabolas which commence at Γ points of different Brillouin zones situated at reciprocal lattice vectors $\vec{\mathbf{G}}$. Some of these branches are degenerate. A weak periodic potential changes this picture by lifting some degeneracies and by

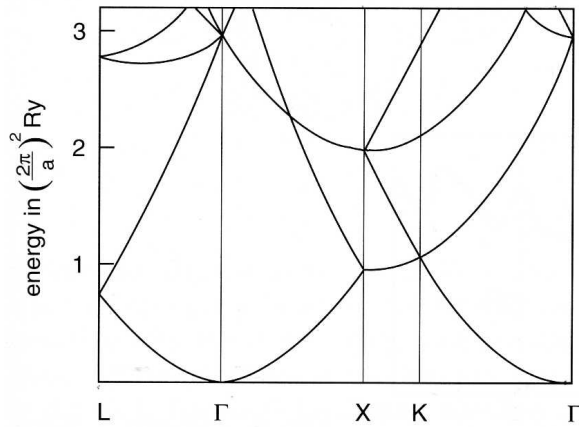


Figure 1.4: Free electron bands in a face centered cubic lattice.

Source: Rössler, Solid State Theory

introducing some band gaps. Aluminum is a good example for such a band structure which can be explained with the help of the nearly free electron approximation (see Figure 1.5). Due to the smallness of the energy corrections, the density of states (see Figure 1.6) deviates only a little bit from the square root behavior that we expect for free electrons.

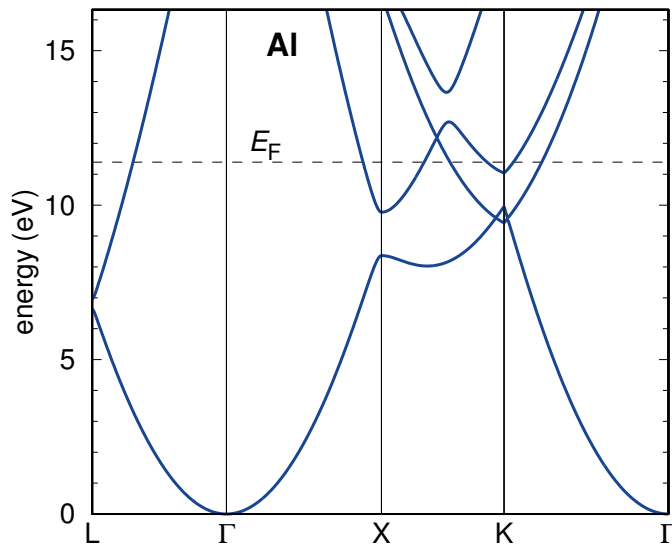


Figure 1.5: Band structure of face centered cubic Aluminum. Calculated with all electron density functional theory.

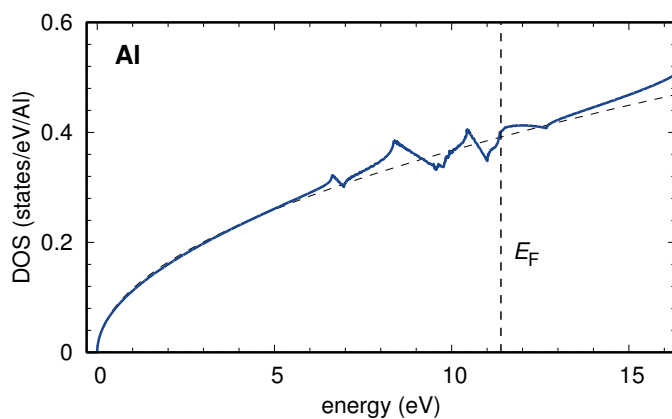


Figure 1.6: Density of states of face centered cubic Aluminum. Calculated with all electron density functional theory.

1.3 Tight binding model

The model of nearly free electrons provides a qualitative understanding for the formation of energy bands and band gaps as well as for the overall appearance of band structures for certain Bravais lattices, but it is not suitable for quantitative band structure calculations. Generally, the periodic potential which is the basis for the perturbation theory calculations is not weak. On the contrary, it is in reality strong, and this is the starting point of an alternative method which is based on the limiting case of strongly bound, localized electrons. We start with isolated atoms, assume that their eigenstates and eigenenergies are known and consider the modification of these states when the atoms are brought more closely together.

We assume the problem of an isolated atom at position \vec{R}

$$H_{\vec{R}}^{\text{atom}} \varphi_{\mathbf{n}}(\vec{r} - \vec{R}) = E_{\mathbf{n}} \varphi_{\mathbf{n}}(\vec{r} - \vec{R}) \quad \text{with} \quad H_{\vec{R}}^{\text{atom}} = \frac{\vec{p}^2}{2m} + v(\vec{r} - \vec{R}) \quad (1.52)$$

to have been solved already. $v(\vec{r} - \vec{R})$ is the potential – usually attractive – which an electron experiences from an atom at the position \vec{R} . The quantum number \mathbf{n} denotes a complete set of atomic quantum numbers, for example $\mathbf{n} = (\bar{n}, \mathbf{l}, \mathbf{m}, \sigma)$ with principal quantum number \bar{n} , angular momentum quantum numbers (\mathbf{l}, \mathbf{m}) and spin quantum number $\sigma = \pm \frac{1}{2}$. The spin degeneracy would only be lifted through spin-orbit interaction or through Coulomb interaction. We now have to find out how this atomic problem is modified when the atom is not isolated anymore but surrounded by like atoms in a crystal. The Hamiltonian is then

$$H = \frac{\vec{p}^2}{2m} + \sum_{\vec{R}} v(\vec{r} - \vec{R}) = H_{\vec{R}}^{\text{atom}} + \Delta V_{\vec{R}}(\vec{r}) \quad \text{with} \quad \Delta V_{\vec{R}}(\vec{r}) = \sum_{\vec{R}' \neq \vec{R}} v(\vec{r} - \vec{R}') \quad (1.53)$$

$\Delta V_{\vec{R}}(\vec{r})$ is the potential of all other atoms except for the one at position \vec{R} , and it will be considered as the perturbation here. The idea behind this approach is derived from an elementary theory of the chemical bond: When you bring two atoms together, pairs of atomic levels split into a binding and an antibinding state. In the same way, we expect three levels from three atoms and \mathbf{n} levels from \mathbf{N} atoms. If now \mathbf{N} is very large, as is the case in the solid, the \mathbf{N} states will become, for practical purposes, dense

and form a continuum of states in an energy interval, *i.e.* they form an energy band.

Now we need a suitable *ansatz* for the wave function of the full crystal Hamiltonian \mathbf{H} . Initially, the states will not be split if the atomic wave functions decay fast enough (*i.e.* are sufficiently localized) that they already vanish in the region in which $\Delta V_{\vec{R}}(\vec{r})$ is different from zero. Then, the $\varphi_n(\vec{r} - \vec{R})$ are also eigenstates of \mathbf{H} :

$$\mathbf{H}\varphi_n(\vec{r} - \vec{R}) = (\mathbf{H}_{\vec{R}}^{\text{atom}} + \Delta V_{\vec{R}}(\vec{r}))\varphi_n(\vec{r} - \vec{R}) = E_n\varphi_n(\vec{r} - \vec{R}) \quad (1.54)$$

They are not yet in the form of Bloch states; however, we can immediately construct a Bloch state:

$$\psi_{\vec{n}\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \varphi_n(\vec{r} - \vec{R}) \quad (1.55)$$

The $\psi_{\vec{n}\vec{k}}(\vec{r})$ defined in this way fulfills the condition for a Bloch function

$$\psi_{\vec{n}\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{\vec{n}\vec{k}}(\vec{r}) \quad (1.56)$$

because

$$\begin{aligned} \sqrt{N}\psi_{\vec{n}\vec{k}}(\vec{r} + \vec{R}) &= \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} \varphi_n(\vec{r} + \vec{R} - \vec{R}') = e^{i\vec{k}\cdot\vec{R}} \left[\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}' - \vec{R})} \varphi_n(\vec{r} - (\vec{R}' - \vec{R})) \right] \\ &= e^{i\vec{k}\cdot\vec{R}} \left[\sum_{\vec{\tilde{R}}} e^{i\vec{k}\cdot\vec{\tilde{R}}} \varphi_n(\vec{r} - \vec{\tilde{R}}) \right] = e^{i\vec{k}\cdot\vec{R}} \sqrt{N}\psi_{\vec{n}\vec{k}}(\vec{r}) \end{aligned} \quad (1.57)$$

where we used the fact that because of the periodic boundary conditions we can replace the sum over \vec{R}' by the sum over $\vec{R}' - \vec{R}$. Besides, we have

$$\mathbf{H}\psi_{\vec{n}\vec{k}}(\vec{r}) = E_n\psi_{\vec{n}\vec{k}}(\vec{r}).$$

The atomic levels remain eigenenergies in the crystal; they form dispersionless, \vec{k} independent bands. However, the assumption (very rapid decrease) applies only for core state, not for valence electrons; their wave functions form bonds by forming overlaps. Nevertheless, we can use equation (1.55) also in this case as *ansatz*, even though these Bloch functions will not be

exact eigenstates for the crystal. The $\psi_{n\vec{k}}(\vec{r})$ are not normalized; we have

$$\begin{aligned}\langle \psi_{n\vec{k}} | \psi_{n'\vec{k}} \rangle &= \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2} e^{i\vec{k}(\vec{R}_1 - \vec{R}_2)} \int d^3r \varphi_n^*(\vec{r} - \vec{R}_2) \varphi_{n'}(\vec{r} - \vec{R}_1) \\ &= \sum_{\vec{R}} e^{-i\vec{k}\vec{R}} \int d^3r \varphi_n^*(\vec{r} - \vec{R}) \varphi_{n'}(\vec{r}) = \delta_{nn'} + \sum_{\vec{R} \neq 0} e^{-i\vec{k}\vec{R}} \alpha_{nn'}(\vec{R})\end{aligned}\quad (1.58)$$

where in the spatial integration we have replaced $\vec{r} \rightarrow \vec{r} + \vec{R}_1$, and $\sum_{\vec{R}_1, \vec{R}_2} \rightarrow N \sum_{\vec{R}}$ because there is only a dependency on the difference vector $\vec{R} = \vec{R}_2 - \vec{R}_1$. Here, we have introduced

$$\alpha_{nn'}(\vec{R}) = \int d^3r \varphi_n^*(\vec{r} - \vec{R}) \varphi_{n'}(\vec{r}) \quad (1.59)$$

i.e. the overlap of the functions $\varphi_n, \varphi_{n'}$ which are localized at the sites 0 and \vec{R} . Due to the Ritz variational method, the best approximation for the energy eigenvalues within this *ansatz* is

$$\varepsilon_n(\vec{k}) = \frac{\langle \psi_{n\vec{k}} | H | \psi_{n\vec{k}} \rangle}{\langle \psi_{n\vec{k}} | \psi_{n\vec{k}} \rangle} \quad (1.60)$$

We still have to evaluate the matrix element in the numerator:

$$\begin{aligned}\langle \psi_{n\vec{k}} | H | \psi_{n\vec{k}} \rangle &= E_n \langle \psi_{n\vec{k}} | \psi_{n\vec{k}} \rangle \\ &+ \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2} e^{i\vec{k}(\vec{R}_1 - \vec{R}_2)} \int d^3r \varphi_n^*(\vec{r} - \vec{R}_2) \underbrace{\sum_{\vec{R}_3 \neq \vec{R}_1} v(\vec{r} - \vec{R}_3) \varphi_n(\vec{r} - \vec{R}_1)}_{=\Delta V_{\vec{R}_1}(\vec{r})}\end{aligned}\quad (1.61)$$

The integral runs over a product of three functions $\varphi_n^*(\vec{r} - \vec{R}_2)$, $v(\vec{r} - \vec{R}_3)$ and $\varphi_n(\vec{r} - \vec{R}_1)$, where each of the three factors represents a function localized around \vec{R}_i ; this means that only in the vicinity of the center \vec{R}_i it is significantly different from zero. In case that all three positions $\vec{R}_1, \vec{R}_2, \vec{R}_3$ are pairwise different, then in all areas of space at least two of the three factors are small; however, if two \vec{R}_i are equal and only different from the third, there is an integration region in which the integrand is not so small. The three cases are:

$$1) \vec{\mathbf{R}}_1 = \vec{\mathbf{R}}_2 \neq \vec{\mathbf{R}}_3$$

$$\beta : = \frac{1}{N} \sum_{\vec{\mathbf{R}}_1} \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}_1) \Delta V_{\vec{\mathbf{R}}_1}(\vec{\mathbf{r}}) \varphi_n(\vec{\mathbf{r}} - \vec{\mathbf{R}}_1) = \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}}) \Delta V_0(\vec{\mathbf{r}}) \varphi_n(\vec{\mathbf{r}}) \quad (1.62)$$

This corresponds to the expectation value of the potential of all other atoms in the atomic state of one atoms at a fixed lattice site which we can simply choose to be zero. Therefore, this represents a constant energy shift with respect to the atomic energy level.

$$2) \vec{\mathbf{R}}_2 = \vec{\mathbf{R}}_3 \neq \vec{\mathbf{R}}_1$$

Then

$$\begin{aligned} & \frac{1}{N} \sum_{\vec{\mathbf{R}}_1 \neq \vec{\mathbf{R}}_2} e^{i\vec{\mathbf{k}}(\vec{\mathbf{R}}_1 - \vec{\mathbf{R}}_2)} \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}_2) v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_2) \varphi_n(\vec{\mathbf{r}} - \vec{\mathbf{R}}_1) \\ & = \sum_{\vec{\mathbf{R}} \neq 0} e^{-i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}} \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}) v(\vec{\mathbf{r}} - \vec{\mathbf{R}}) \varphi_n(\vec{\mathbf{r}}) \equiv \sum_{\vec{\mathbf{R}} \neq 0} e^{-i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}} \lambda(\vec{\mathbf{R}}) \quad (1.63) \end{aligned}$$

$$3) \vec{\mathbf{R}}_1 \neq \vec{\mathbf{R}}_2 \neq \vec{\mathbf{R}}_3 \neq \vec{\mathbf{R}}_1$$

This is the case of three center integrals in which in all integration regions at least two of the three factors are small; we will neglect these contributions:

$$\int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}_2) v(\vec{\mathbf{r}} - \vec{\mathbf{R}}_3) \varphi_n(\vec{\mathbf{r}} - \vec{\mathbf{R}}_1) \approx 0 \quad (1.64)$$

Together, this already gives the band structure in the **tight binding approximation**:

$$\begin{aligned} \varepsilon_n(\vec{\mathbf{k}}) &= E_n + \frac{\beta + \sum_{\vec{\mathbf{R}} \neq 0} e^{-i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}} \lambda(\vec{\mathbf{R}})}{1 + \sum_{\vec{\mathbf{R}} \neq 0} e^{-i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}} \alpha(\vec{\mathbf{R}})} \\ \text{with } \beta &= \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}}) \sum_{\vec{\mathbf{R}} \neq 0} v(\vec{\mathbf{r}} - \vec{\mathbf{R}}) \varphi_n(\vec{\mathbf{r}}) \\ \lambda(\vec{\mathbf{R}}) &= \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}) v(\vec{\mathbf{r}} - \vec{\mathbf{R}}) \varphi_n(\vec{\mathbf{r}}) \\ \alpha(\vec{\mathbf{R}}) &= \int d^3\mathbf{r} \varphi_n^*(\vec{\mathbf{r}} - \vec{\mathbf{R}}) \varphi_n(\vec{\mathbf{r}}) \quad (1.65) \end{aligned}$$

Additionally, it is often assumed that the occurring \vec{R} sums can be restricted to nearest or next nearest neighbors; this is justified if the overlap decays quickly with increasing distance because of the localization of the atomic wave functions $\varphi_n(\vec{r} - \vec{R})$.

1.4 Wannier functions

In the tight binding method, the Bloch functions are constructed from localized atom wave functions $\varphi_n(\vec{r})$. The band structure $\varepsilon(\vec{k})$ is then obtained from matrix elements of the atomic potentials with respect to such localized states. Alternatively, an orthonormal basis of localized states can be chosen; these are the Wannier states. They are defined by

$$w_n(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in \text{1st BZ}} e^{-i\vec{k} \cdot \vec{R}} \psi_{n\vec{k}}(\vec{r}) \quad (1.66)$$

with Bloch functions $\psi_{n\vec{k}}(\vec{r})$. The orthonormality can be seen from

$$\begin{aligned} \int d^3r w_n^*(\vec{r} - \vec{R}_1) w_l(\vec{r} - \vec{R}_2) &= \frac{1}{N} \sum_{\vec{k}, \vec{k}'} e^{i(\vec{k} \cdot \vec{R}_1 - \vec{k}' \cdot \vec{R}_2)} \int d^3r \psi_{n\vec{k}}^*(\vec{r}) \psi_{l\vec{k}'}(\vec{r}) \\ &= \frac{1}{N} \sum_{\vec{k}, \vec{k}'} e^{i\vec{k} \cdot (\vec{R}_1 - \vec{R}_2)} \delta_{\vec{k}, \vec{k}'} \delta_{nl} = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}_1 - \vec{R}_2)} \delta_{nl} = \delta_{\vec{R}_1, \vec{R}_2} \delta_{nl} \end{aligned} \quad (1.67)$$

The \vec{k} sums are restricted to the first Brillouin zone. Conversely, we can also represent Bloch functions as linear combination of Wannier states:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{N} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} w_n(\vec{r} - \vec{R}) \quad (1.68)$$

If we use for the superposition of localized states in Equation (1.55) Wannier functions instead of atomic wave functions, the overlap matrix element $\alpha(\vec{r})$ disappears and we obtain the dispersion relations

$$\begin{aligned} \varepsilon_n(\vec{k}) &= \tilde{E}_n + \sum_{\vec{R} \neq 0} e^{-i\vec{k} \cdot \vec{R}} \tilde{\lambda}(\vec{R}) \\ \text{with } \tilde{E}_n &= \int d^3r w_n^*(\vec{r}) \left(\frac{\vec{p}^2}{2m} + \sum_{\vec{R}} v(\vec{r} - \vec{R}) \right) w_n(\vec{r}) \\ \text{and } \tilde{\lambda}(\vec{R}) &= \int d^3r w_n^*(\vec{r} - \vec{R}) v(\vec{r} - \vec{R}) w_n(\vec{r}) \end{aligned} \quad (1.69)$$

As before, three center contributions are neglected. Also for Wannier functions it is often assumed that the $\tilde{\lambda}(\vec{\mathbf{R}})$ are only nonzero for a few neighbors; the simplest version is

$$\tilde{\lambda}(\vec{\mathbf{R}}) = \begin{cases} \mathbf{t} & \text{for nearest neighbor vector} \\ 0 & \text{otherwise} \end{cases} \quad (1.70)$$

The parameter \mathbf{t} is called hopping matrix element because it quantifies the probability that an electron hops from one lattice site to the next and thereby becomes delocalized. For a one-dimensional linear chain, we find the dispersion

$$\varepsilon(\vec{\mathbf{k}}) = \varepsilon_0 - 2\mathbf{t} \cos(\mathbf{k}\mathbf{a}) \quad (1.71)$$

for a lattice constant \mathbf{a} . For a three-dimensional cubic system, we have

$$\varepsilon(\vec{\mathbf{k}}) = \varepsilon_0 - 2\mathbf{t}(\cos(\mathbf{k}_x\mathbf{a}) + \cos(\mathbf{k}_y\mathbf{a}) + \cos(\mathbf{k}_z\mathbf{a})) \quad (1.72)$$

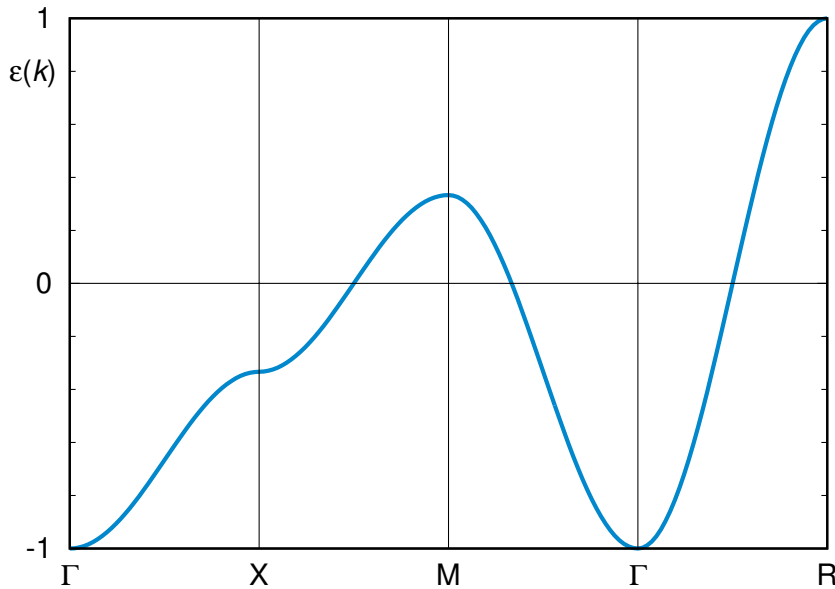


Figure 1.7: Tight binding dispersion for the simple cubic lattice (in three dimensions) along the high symmetry directions $\mathbf{X} = (1/2, 0, 0)$, $\mathbf{M} = (1/2, 1/2, 0)$, $\mathbf{R} = (1/2, 1/2, 1/2)$, all in units of $2\pi/\mathbf{a}$.

In Figure 1.7 the tight binding band structure is plotted for $6|\mathbf{t}| = 1$; the result is a band which is centered around ε_0 (ε_0 is the expectation value of the Hamiltonian \mathbf{H} in the Wannier state), with the band width $12|\mathbf{t}|$. The hopping matrix element \mathbf{t} can in general take on positive or negative values. Here, we have assumed s-like, spatially isotropic Wannier states, which leads to hoppings \mathbf{t} that are the same in all directions. It is possible to verify that the Wannier functions defined by Equation (1.66) represent spatially localized states; they can be considered a generalization

of wave packets for the case of a periodic potential. In one dimension, the volume Ω is simply the length $L = Na$ of the lattice; $\mathbf{k} \in [-\frac{\pi}{a}, \frac{\pi}{a}]$ (the first Brillouin zone of the one dimensional lattice). In order to explicitly calculate the Wannier functions, we need the Bloch functions. We know them for the case of negligible lattice potential $V(\vec{r}) = 0$. Then, following Equation (1.40) and specializing to one dimension, we have

$$\psi_{\vec{n}\vec{k}} = \frac{1}{\sqrt{L}} e^{i(k + \frac{2\pi n}{a})r} = e^{ikr} \mathbf{u}_n(r) \quad \text{with} \quad \mathbf{u}_n(r) = \frac{1}{\sqrt{L}} e^{i\frac{2\pi n}{a}r}, \quad n \in \mathbb{Z} \quad (1.73)$$

Because of $n = 0, \pm 1, \pm 2, \dots$, $k_{\text{eff}} = k + \frac{2\pi n}{a}$ takes on all values. The shape of the Wannier functions is then

$$\begin{aligned} w_n(r - R) &= \frac{1}{\sqrt{NL}} \sum_{\mathbf{k} \in \text{1.BZ}} e^{i(k + \frac{2\pi n}{a})(r-R)} = \frac{1}{\sqrt{NL}} \frac{L}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk e^{i(k + \frac{2\pi n}{a})(r-R)} \\ &= \frac{\sqrt{a}}{2\pi} \left[\frac{1}{i(r-R)} e^{i(k + \frac{2\pi n}{a})(r-R)} \right]_{-\frac{\pi}{a}}^{\frac{\pi}{a}} = \frac{\sqrt{a} \sin \frac{\pi}{a}(r-R)}{\pi (r-R)} e^{i\frac{2\pi n}{a}(r-R)} \end{aligned} \quad (1.74)$$

Thus, in contrast to the Bloch functions, the Wannier functions are localized. In this example, the Wannier functions go to zero algebraically; if there are gaps in the band structure, the decay becomes even exponential. However, it is also possible (and a common practice in model calculation in solid state theory) to forgo explicit knowledge of the shape of the Wannier functions and to use the matrix elements $\tilde{\lambda}(\vec{R})$ as effective parameters: They can be obtained as fit parameters for representing precise band calculations or for representing experimental data. If the hopping matrix elements are given as parameters, we work with a model Hamiltonian which, in matrix representation with respect to the Wannier basis, has the following form:

$$H = \sum_{\vec{n}\vec{R}} \tilde{E}_n |\vec{n}\vec{R}\rangle \langle \vec{n}\vec{R}| + \sum_{\vec{n}\vec{R} \vec{R}'} t_{\vec{R}\vec{R}'} |\vec{n}\vec{R}\rangle \langle \vec{n}\vec{R}'| \quad (1.75)$$

Here, in position representation $w_n(\vec{r} - \vec{R}) = \langle \vec{r} | \vec{n}\vec{R} \rangle$.

1.5 Velocity and effective mass

Group velocity

We now ask, for any (free) Bloch electron, what is the expectation value of the velocity

$$\vec{v} := \langle \psi_{\vec{n}\vec{k}} | \frac{\vec{p}}{m} | \psi_{\vec{n}\vec{k}} \rangle, \quad \psi_{\vec{n}\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \mathbf{u}_{\vec{n}\vec{k}}(\mathbf{r}). \quad (1.76)$$

$|\mathbf{u}_{\vec{n}\vec{k}}\rangle$ we abbreviate by $|\vec{n}\vec{k}\rangle$ and find

$$\begin{aligned} \vec{v} &= \langle \vec{n}\vec{k} | e^{-i\vec{k}\cdot\vec{r}} \frac{\hbar}{mi} \nabla e^{i\vec{k}\cdot\vec{r}} | \vec{n}\vec{k} \rangle = \langle \vec{n}\vec{k} | \vec{p} | \vec{n}\vec{k} \rangle + \langle \vec{n}\vec{k} | \frac{\hbar\vec{k}}{m} | \vec{n}\vec{k} \rangle \\ &= \langle \mathbf{u}_{\vec{n}\vec{k}} | \frac{\vec{p} + \hbar\vec{k}}{m} | \mathbf{u}_{\vec{n}\vec{k}} \rangle = \langle \vec{n}\vec{k} | \frac{\vec{p} + \hbar\vec{k}}{m} | \vec{n}\vec{k} \rangle. \end{aligned} \quad (1.77)$$

This quantity we want to express by $\varepsilon(\vec{k})$ (without explicit knowledge of $|\vec{k}\rangle$):

$$\varepsilon(\vec{k}) = \langle \vec{k} | H | \vec{k} \rangle, \quad H = \frac{(\vec{p} + \hbar\vec{k})^2}{2m} + V, \quad (1.78)$$

$$\begin{aligned} \frac{\partial \varepsilon(\vec{k})}{\partial \vec{k}} &= \left(\frac{\partial}{\partial \vec{k}} \langle \vec{k} | \right) H | \vec{k} \rangle + \langle \vec{k} | H \left(\frac{\partial}{\partial \vec{k}} | \vec{k} \rangle \right) + \langle \vec{k} | \frac{\partial H}{\partial \vec{k}} | \vec{k} \rangle \\ &= \hbar \langle \vec{k} | \frac{\vec{p} + \hbar\vec{k}}{m} | \vec{k} \rangle = \hbar \vec{v}, \end{aligned} \quad (1.79)$$

because $\langle \vec{k} | \vec{k} \rangle = 1$ implies $\frac{\partial}{\partial \vec{k}} \langle \vec{k} | \vec{k} \rangle = 0$ and

$$\left(\frac{\partial}{\partial \vec{k}} \langle \vec{k} | \right) H | \vec{k} \rangle + \langle \vec{k} | H \left(\frac{\partial}{\partial \vec{k}} | \vec{k} \rangle \right) = \varepsilon(\vec{k}) \frac{\partial}{\partial \vec{k}} \langle \vec{k} | \vec{k} \rangle = 0. \quad (1.80)$$

Therefore,

$$\vec{v}(\vec{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(\vec{k})}{\partial \vec{k}}$$

and we have:

- $\vec{v}(\vec{k})$ is continuous function of \vec{k} .
- $\vec{v}(\vec{k})$ is the expectation value of the velocity and corresponds to the group velocity of the Bloch electron.

Mass tensor

We define the effective mass tensor as the second derivatives of $\varepsilon(\vec{k})$

$$\boxed{\left(\frac{1}{\mathbf{m}_n^*}\right)_{ij}(\vec{k}) \equiv \frac{\partial}{\partial k_i} \frac{\partial}{\partial k_j} \frac{\varepsilon_n(\vec{k})}{\hbar^2}}$$

For calculating the effective mass at the Γ point (at $\vec{k} = 0$) we use the Schrödinger Equation (1.22) for the Bloch factors:

$$\left[\frac{(\vec{p} + \hbar\vec{k})^2}{2m} + V(\vec{r}) \right] \mathbf{u}_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k}) \mathbf{u}_{n\vec{k}}(\vec{r}) \quad (1.81)$$

We can rewrite this:

$$\left[\frac{\vec{p}^2}{2m} + V(\vec{r}) + \frac{\hbar\vec{k} \cdot \vec{p}}{m} \right] \mathbf{u}_{n\vec{k}}(\vec{r}) = \left(\varepsilon_n(\vec{k}) - \frac{(\hbar\vec{k})^2}{2m} \right) \mathbf{u}_{n\vec{k}}(\vec{r}) \quad (1.82)$$

Second order perturbation theory in $\vec{k} \cdot \vec{p}$ leads to

$$\begin{aligned} \varepsilon_n(\vec{k}) = \varepsilon_n(0) &+ \frac{(\hbar\vec{k})^2}{2m} + \frac{\hbar\vec{k}}{m} \cdot \langle n0 | \vec{p} | n0 \rangle \\ &+ \frac{\hbar^2}{m^2} \sum_{n'(\neq n)} \frac{\langle n0 | \vec{k} \cdot \vec{p} | n'0 \rangle \langle n'0 | \vec{k} \cdot \vec{p} | n0 \rangle}{\varepsilon_n(0) - \varepsilon_{n'}(0)}, \end{aligned} \quad (1.83)$$

because the $|n\vec{k}\rangle$ conserve lattice momentum and the \vec{k} are in the first Brillouin zone. To obtain this, quantum mechanical Rayleigh Schrödinger perturbation theory up to second order in the perturbation $\vec{k} \cdot \vec{p}$ was used again; this requires non-degeneracy of the bands at Γ . For the Bloch factors, we write $\mathbf{u}_{n\vec{k}}(\vec{r}) = \langle \mathbf{r} | n\vec{k} \rangle$.

Thus, we find for the effective mass tensor at Γ :

$$\left(\frac{1}{\mathbf{m}_n^*}\right)_{ij} = \frac{\delta_{ij}}{m} + \frac{2}{m^2} \sum_{n'(\neq n)} \frac{\langle n0 | p_i | n'0 \rangle \langle n'0 | p_j | n0 \rangle}{\varepsilon_n(0) - \varepsilon_{n'}(0)} \quad (1.84)$$

Usually, only a few n' are sufficient for calculating \mathbf{m}_n^* . In case of inversion symmetry, we have $\langle \vec{p} \rangle = 0$, so that in the expansion

$$\varepsilon_n(\vec{k}) = \varepsilon_n(0) + \left(\frac{\hbar^2}{2\mathbf{m}_n^*}\right)_{ij} k_i k_j + \mathcal{O}(k^4) \quad (1.85)$$

terms of odd order are missing.

In the vicinity of Γ , in every band we can expect for small \mathbf{k} a quadratic dependency on \mathbf{k} if the potential is inversion symmetric, as for free electrons. However, the effective mass \mathbf{m}^* can be considerably different from the free electron mass \mathbf{m} . If \mathbf{m}^* is diagonal and isotropic, we again have the free electron dispersion relations (with modified mass \mathbf{m}^*).

The $\vec{\mathbf{k}} \cdot \vec{\mathbf{p}}$ perturbation theory can also be performed for $\vec{\mathbf{k}}_0 \neq 0$. This leads to the generalization of Equation (1.83):

$$\begin{aligned} \varepsilon_n(\vec{\mathbf{k}}_0 + \vec{\mathbf{k}}) = \varepsilon_n(\vec{\mathbf{k}}_0) &+ \frac{\hbar}{\mathbf{m}} \vec{\mathbf{k}} \langle \psi_{n\vec{\mathbf{k}}} | \vec{\mathbf{p}} | \psi_{n\vec{\mathbf{k}}_0} \rangle + \frac{\hbar^2 \mathbf{k}^2}{2\mathbf{m}} \\ &+ \frac{\hbar^2}{\mathbf{m}^2} \sum_{n' \neq n} \frac{\langle \psi_{n\vec{\mathbf{k}}} | \vec{\mathbf{k}} \cdot \vec{\mathbf{p}} | \psi_{n'\vec{\mathbf{k}}_0} \rangle \langle \psi_{n'\vec{\mathbf{k}}_0} | \vec{\mathbf{k}} \cdot \vec{\mathbf{p}} | \psi_{n\vec{\mathbf{k}}_0} \rangle}{\varepsilon_n(\vec{\mathbf{k}}_0) - \varepsilon_{n'}(\vec{\mathbf{k}}_0)} \end{aligned} \quad (1.86)$$

Then we have as before

$$\nabla_{\mathbf{k}} \varepsilon_n(\vec{\mathbf{k}}) = \frac{\hbar^2}{\mathbf{m}} \langle \psi_{n\vec{\mathbf{k}}} | \vec{\mathbf{p}} | \psi_{n\vec{\mathbf{k}}} \rangle \quad (1.87)$$

the generalization of the relation $\langle \vec{\mathbf{k}} | \vec{\mathbf{p}} | \vec{\mathbf{k}} \rangle = \hbar \vec{\mathbf{k}}$ for free electrons to the lattice.

Remarks

- \mathbf{m}^* can become negative; this is often the case at the Brillouin zone boundary. We then refer to the carriers as holes.
- For cubic symmetry, we have

$$\left(\frac{1}{\mathbf{m}^*} \right)_{ij} = \frac{1}{\mathbf{m}^*} \delta_{ij}, \quad \curvearrowright \quad \varepsilon_n(\vec{\mathbf{k}}) = \varepsilon_n(0) + \frac{(\hbar \mathbf{k})^2}{2\mathbf{m}^*} + \mathcal{O}(\mathbf{k}^4).$$

- For alkali metals, we have bcc lattices and

metal	Li	Na	K	Rb	Cs
band	2s	3s	4s	5s	6s
\mathbf{m}^*/\mathbf{m}	1.33	0.96	0.86	0.78	0.73

In these metals, the effective masses \mathbf{m}^* are of the same order as the free electron mass \mathbf{m} .

- In some 4f and 5f compounds (rare earths) like for example CeRu₂Si₂, CeCu₆, UPt₃, CeAl₃ and others, m^*/m is anomalously large. Values of $m^*/m \sim 100 - 1000$ can occur. These are called heavy Fermions. The reason for this anomalous behavior is due to a failure of the Hartree-Fock approximation or other perturbative approaches; localized 4f or 5f moments interact strongly with the conduction electrons.

1.6 Electronic classification of solids

The electronic single particle states in the solid are characterized by the three quantum numbers $(\mathbf{l}, \vec{\mathbf{k}}, \sigma)$, with band index \mathbf{l} , wave vector $\vec{\mathbf{k}}$ and spin σ . Electrons are Fermions and obey the Pauli principle; each single particle state can only be occupied once. In the single particle picture, the eigenstate for N_e electrons can be described by specifying occupation numbers $\{n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma}\}$ with $n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma} \in \{0, 1\}$, and we have

$$H|n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma}\rangle = \sum_{i=1}^{N_e} \left(\frac{\vec{\mathbf{p}}_i^2}{2m} + \sum_{\vec{\mathbf{R}}} v(\vec{\mathbf{r}}_i - \vec{\mathbf{R}}) \right) |n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma}\rangle = \sum_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma} n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma} \varepsilon_{\mathbf{l}}(\vec{\mathbf{k}}) |n_{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma}\rangle \quad (1.88)$$

In the ground state, the single particle states that are lowest in energy are filled until all N_e electrons are accounted for. The energy which is situated between the highest occupied and the lowest unoccupied state is called **Fermi energy** E_F . It is determined by

$$\sum_{\substack{\vec{\mathbf{l}}\vec{\mathbf{k}}\sigma \\ |\varepsilon_{\mathbf{l}}(\vec{\mathbf{k}})| < E_F}} 1 = 2 \sum_{\substack{\vec{\mathbf{l}}\vec{\mathbf{k}} \\ |\varepsilon_{\mathbf{l}}(\vec{\mathbf{k}})| < E_F}} 1 = N_e \quad (1.89)$$

The ground state energy is given by

$$E_0 = 2 \sum_{\substack{\vec{\mathbf{l}}\vec{\mathbf{k}} \\ |\varepsilon_{\mathbf{l}}(\vec{\mathbf{k}})| < E_F}} \varepsilon_{\mathbf{l}}(\vec{\mathbf{k}}) \quad (1.90)$$

In each band \mathbf{l} there are exactly N different $\vec{\mathbf{k}}$ values and therefore $2N$ different single particle states (2 because of spin), if N is the number of unit cells. At $T = 0$, these states are filled from the bottom until all electrons are in place. There are two possibilities:

1. **Semiconductors/insulators:** The topmost band is completely filled, the one above it completely empty. The Fermi energy then is in the

band gap between highest filled and lowest empty band. The highest filled band is then called **valence band**. Excitations from the ground state are only possible if at least the energy of the band gap is available.

2. **Metals:** The Fermi energy is inside a band which is not yet fully filled. Such a band which is at $T = 0$ not fully filled (or even completely empty) is called **conduction band**. As the distance between highest occupied and lowest unoccupied level is negligibly small, excitations are possible with arbitrarily small energy cost.

Information from band structures

We consider unit cells with Z_e electrons, *i.e.* systems with $N_e = NZ_e$ electrons in total. If Z_e is odd and there is no band overlap, the $\frac{Z_e-1}{2}$ bands are filled completely and the band number $\frac{Z_e+1}{2}$ remains half filled. Following this simple consideration, we would always expect a metal if Z_e is odd; often, this is true. If however Z_e is even and there is no band overlap, the lower $\frac{Z_e}{2}$ are filled completely and we expect a semiconductor or insulator. This is less often true because the premise of not overlapping bands is often not fulfilled. In this discussion, we can however ignore the closed shells which correspond to noble gas configurations and consider only the outer, not fully filled shells. The number of these outer (or valence) electrons will be referred to as Z'_e .

- $Z'_e = 1$: This is the case of alkali metals (Li, K, Na, Rb, Cs) and noble metals (Cu, Ag, Au). We expect a half filled **s** band as conduction band and therefore good metals (see Figure 1.8).
- $Z'_e = 3$: Al, Ga, In, Tl: The Fermi energy should be inside the **p** bands, and we expect metals.
- $Z'_e = 2$: Earth alkali metals Be, Mg, Ca, Sr, Ba, Ra. In spite of even electron count, these are metals because **s** and **p** bands overlap.
- Transition metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn with electron configuration $3d^n 4s^2$ or $3d^{n+1} 4s^1$; the **3d** and **4s** bands overlap. The **4s** electrons are more delocalized and form a wide band; the **3d** electrons are localized and form narrow bands. Both types of bands hybridize and cross. The band structure of Cu in Figure 1.9 is a good example.

Figure 1.8: Band structure of bcc Na. The conduction band is marked by a more heavy line. The energy zero is chosen to be the Fermi level E_F .

Calculated with FPLO.

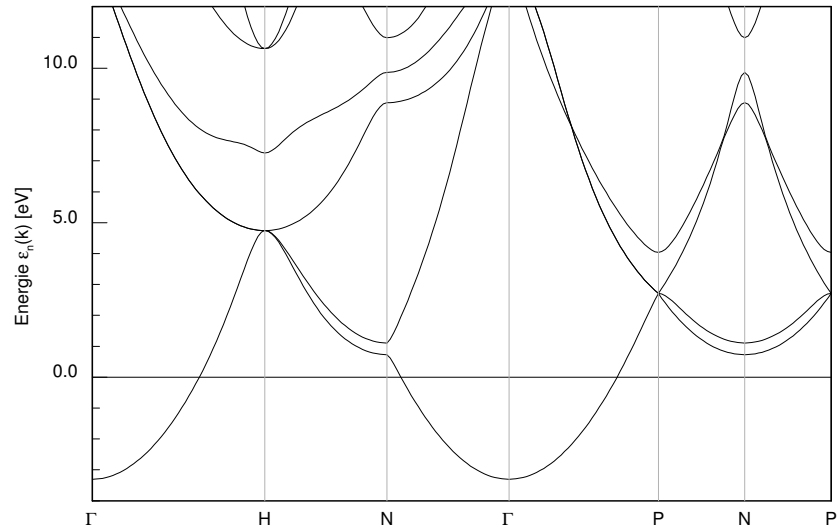
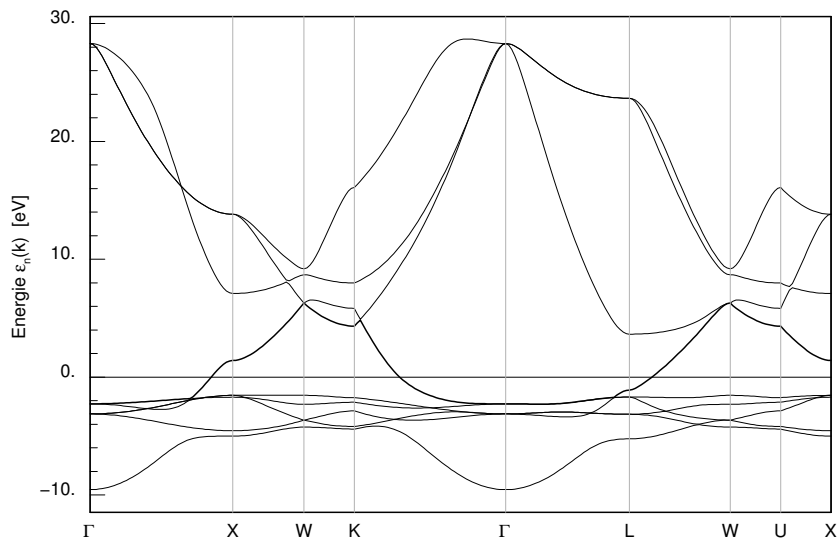
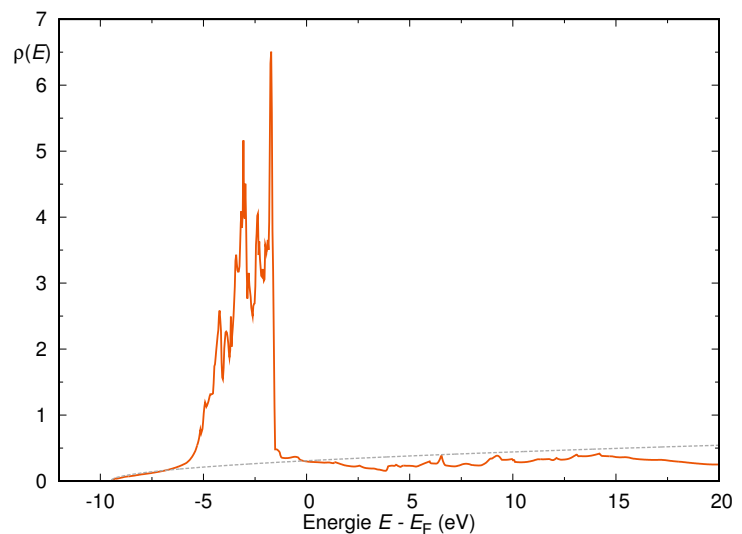


Figure 1.9: Band structure of fcc Cu. The five fully occupied 3d bands with little dispersion are inside the very wide 4s band. Calculated with FPLO.



- 4th main group: C, Si, Ge. These elements crystallize in diamond

Figure 1.10: Density of states of fcc Cu. The narrow 3d bands correspond to strong peaks below E_F . The remaining density of states due to 4s states shows an approximate \sqrt{E} behavior (dashed line).



structure with two atoms in the basis, *i.e.* $Z'_e = 8$ per unit cell. From atomic **s**- and **p** orbitals, per atom four sp^3 hybrid orbitals are formed, with a tetrahedral orientation. Thus, per unit cell we have 8 orbitals forming 8 spin degenerate bands; this leads to 4 (filled) valence bands and 4 (empty) conduction bands which are separated by a band gap (see Figure 1.11).

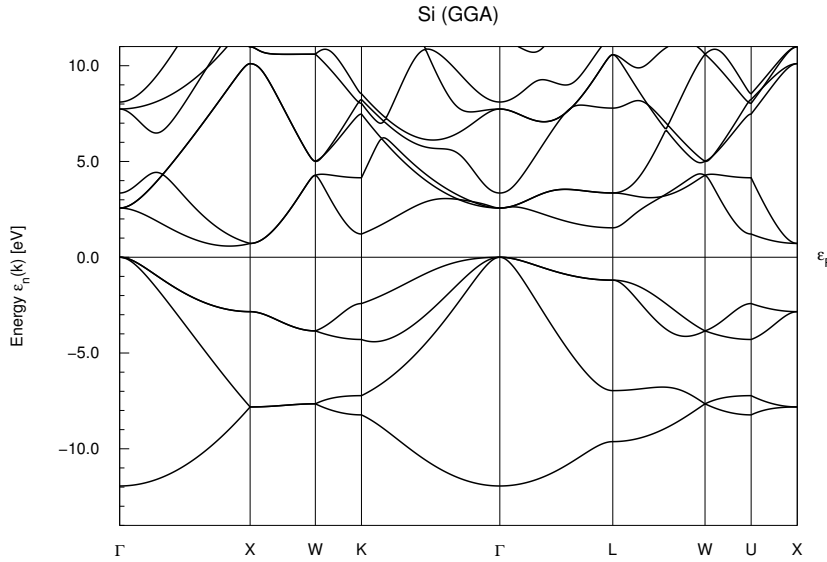


Figure 1.11:
Band structure of Si. The band gap is indirect.
Calculated with FPLO.

- III - V and II - VI semiconductors: In these systems like GaAs, InSb, ZnSe, ZnS the situation is similar to Si, only that we are dealing with two different atoms per elementary cell (Example in Figure 1.12).

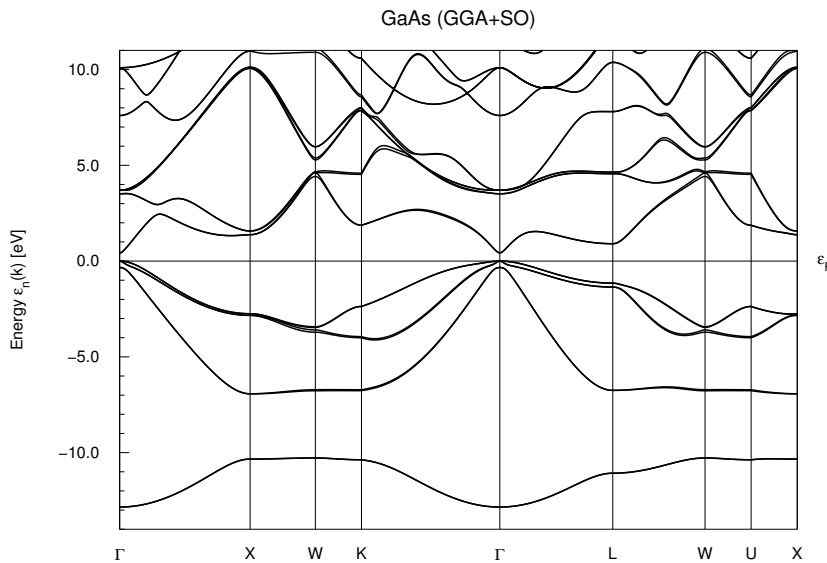


Figure 1.12:
Band structure of GaAs. The band gap is direct. Spin-orbit coupling is taken into account so that each band is singly degenerate.
Calculated with FPLO.

- 5th main group: Sb, As, Bi have 5 valence electrons, but they crystallize in structures with 2 atoms per unit cell, *i.e.* $Z'_e = 10$. Nevertheless, usually there is band overlap so that these elements are half metals rather than semiconductors.
- Ionic crystals from 1st and 7th main groups: NaCl, KBr, NaI crystallize in NaCl or CsCl structure with 2 atoms per unit cell, *i.e.* $Z'_e = 8$; as expected, they are insulators.

1.7 Electronic density of states and Fermi surface

As in the case of phonons, for many problems the full band structure $\varepsilon_n(\vec{k})$ contains more information than necessary. If it is sufficient to know in which energy regions there are states and how many, we use the **electronic density of states**:

$$\rho(E) = \frac{1}{N} \sum_{\vec{n}, \vec{k}, \sigma} \delta(E - \varepsilon_n(\vec{k})) \quad (1.91)$$

$\rho(E) \cdot \Delta E$ is the number of electronic single particle states with energy between E and $E + \Delta E$ per unit cell. The Fermi energy is fixed by

$$\int_{-\infty}^{E_F} dE \rho(E) = Z_e \quad (1.92)$$

with the total number of electron per unit cell Z_e . Again, the density of states can be expressed by a surface integral over a surface of constant energy $S(E)$ in \vec{k} space:

$$\rho(E) = \frac{V}{N} \frac{1}{4\pi^3 \hbar} \sum_n \int_{S(E)} \frac{ds}{|\vec{v}_{n\vec{k}}|} \quad (1.93)$$

with the group velocity of the n th band

$$\vec{v}_{n\vec{k}} = \frac{1}{\hbar} \nabla_{\vec{k}} \varepsilon_n(\vec{k}) \quad (1.94)$$

A further possibility is again

$$\rho(E) = -\frac{1}{\pi} \text{Im} G(E + i0^+) = -\frac{1}{\pi N} \text{Im} \sum_{\vec{n}, \vec{k}, \sigma} \frac{1}{E + i0^+ - \varepsilon_n(\vec{k})} \quad (1.95)$$

For free electrons, the density of states becomes especially simple; they have the dispersion relation $\varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m}$, also $\nabla_{\vec{k}} \varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}}{m}$, $\vec{v}_{\vec{k}} = \frac{\hbar \vec{k}}{m}$, $k = \frac{1}{\hbar} \sqrt{2mE}$. Then we have

$$\rho(E) = \frac{V}{N} \frac{1}{4\pi^3 \hbar} \int_{S(E)} \frac{ds}{\hbar k/m} = \frac{V}{N} \frac{4\pi k^2 m}{4\pi^3 \hbar^2 k} = \frac{Vm k}{N\pi^2 \hbar^2} = \frac{V}{N} \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \sqrt{E} \quad (1.96)$$

Similarly, we find that the density of states of free electrons in two dimensions is $\rho_{2D}(E) = \text{const}$ and in one dimension $\rho_{1D}(E) \propto \frac{1}{\sqrt{E}}$. The form of the density of states thus depends strongly on the dimension of the problem.

The density of states for free electrons can also be obtained from the definition $\rho(E) = \frac{1}{N} \sum_{n\vec{k}\sigma} \delta(E - \varepsilon_n(\vec{k}))$:

$$\begin{aligned} \rho(E) &= \frac{1}{N} \sum_{\vec{k}\sigma} \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) = \frac{V}{N(2\pi)^3} \int d^3k \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) \\ &= \frac{V}{8\pi^3 N} \underbrace{4\pi \int dk k^2 \delta\left(E - \frac{\hbar^2 k^2}{2m}\right)}_{:=I} = \frac{V}{\pi^2 N} \frac{m}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}} \sqrt{E} \quad (1.97) \end{aligned}$$

because $\delta(g(x)) = \sum_{i=1}^n \frac{\delta(x-x_i)}{|g'(x_i)|}$ with single zero points x_i of $g(x)$:

$$\begin{aligned} g(k) &= E - \frac{\hbar^2 k^2}{2m}; \quad g'(k) = -\frac{\hbar^2 k}{m}; \quad g(k) = 0 \leftrightarrow k_{1,2} = \pm \frac{1}{\hbar} \sqrt{2mE} \\ I &= \frac{m}{\hbar \sqrt{2mE}} \int dk k^2 \left[\delta\left(k - \frac{\sqrt{2mE}}{\hbar}\right) + \delta\left(k + \frac{\sqrt{2mE}}{\hbar}\right) \right] \\ &= \frac{m}{\hbar \sqrt{2mE}} \left\{ \frac{2mE}{\hbar^2} + \frac{2mE}{\hbar^2} \right\} = \frac{2m\sqrt{2mE}}{\hbar^3} \quad (1.98) \end{aligned}$$

A square root singularity at the band edge is typical for three dimensional densities of states; one also finds that the density of states for two dimensional systems has a jump at the band edge, and for one dimensional systems a $1/\sqrt{E}$ singularity occurs. These dimension dependent characteristics of densities of states can also be found in the simple cubic tight binding densities of states which are shown for one, two and three dimensions in Figures. 1.13-1.15.

Figure 1.13: 1D tight binding density of states.

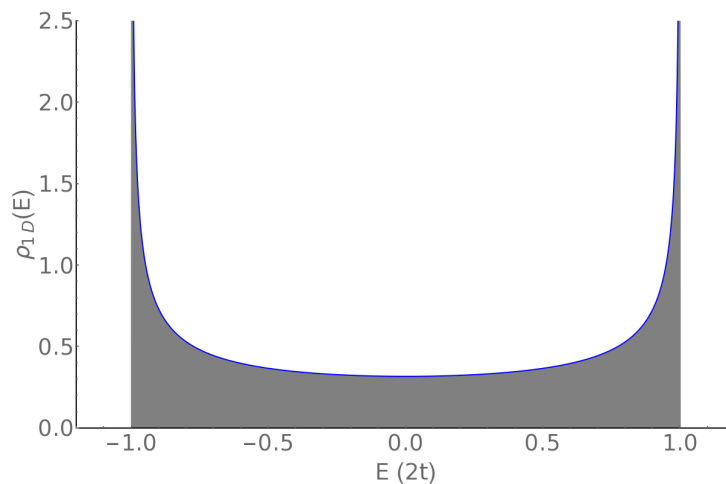
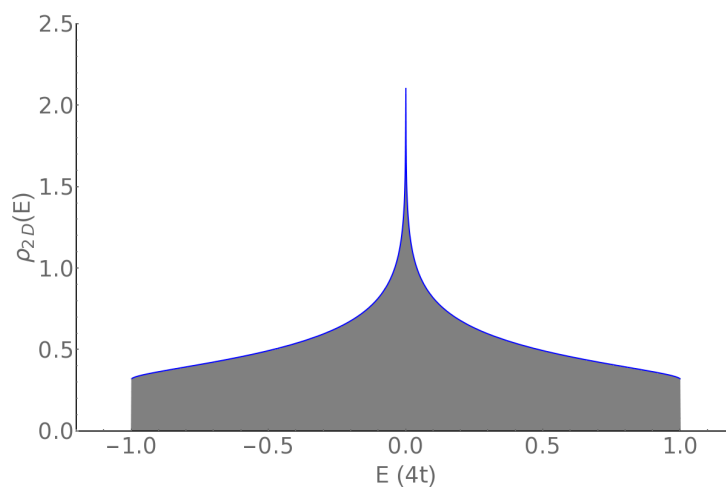
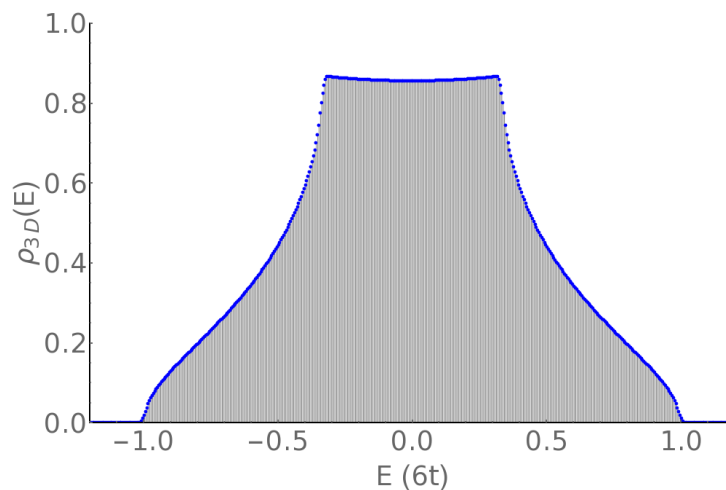


Figure 1.14: 2D tight binding density of states.



An especially important constant energy surface $S(E)$ defined by $\varepsilon_n(\vec{k}) = E$ in \vec{k} space is the **Fermi surface** $S(E_F)$, which in the ground states separates occupied from unoccupied states. For free electrons, the Fermi surface is the surface of a sphere; in general, the form is complicated and characteristic for materials and crystal structures.

Figure 1.15: 3D tight binding density of states.



Remarks about the Fermi surface

In Figure 1.16 constant energy surfaces $S(E)$ are shown for a two dimensional tight binding model on a square lattice. Depending on filling, these surfaces $S(E)$ can become the Fermi surfaces. Non-integer fillings arise in particular due to doping. At small filling, we have nearly a “Fermi sphere”, at half filling the Fermi surface becomes flat and square shaped, at more than half filling the Fermi surfaces intersect the boundaries of the Brillouin zone; then, the Fermi surface is not anymore simply connected within the first Brillouin zone. In the extended zone scheme in two dimensions however, again a connected Fermi surface is found which separates a closed region of occupied states from the region of unoccupied states in \underline{k} space. Here, the Fermi surface again becomes a “sphere”, but it encloses hole states rather than electron states.

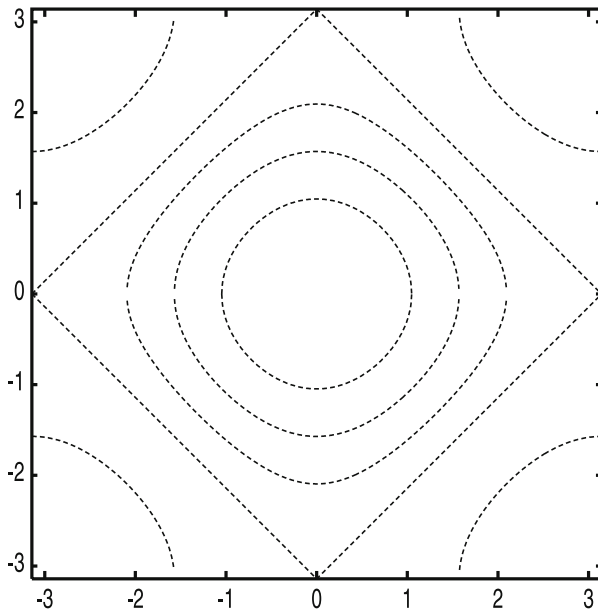


Figure 1.16: Constant energy surfaces $S(E)$ for the two dimensional tight binding model.

Source: Czycholl, Theoretische Festkörperphysik.