1.2 Free quantum mechanical particles and band structure

Particles within a regime of zero or constant potential energy are called "free particles". Momentum

$$\vec{p}(\vec{k}) = \hbar\vec{k} \quad \text{and energy} \quad E(\vec{k}) = \frac{\hbar^2 k^2}{2m_e} \tag{1.4}$$

are conserved properties where m_e is the mass of a free electron.

Within the periodic potential of a crystal electronic states can be described using the Bloch-Theorem leading to band energies $E_{band}(\vec{k})$. The position of the Fermi energy E_F (the standard name for the chemical potential in solid state physics, i.e. $E_F = \mu$) allows for the classification of solids:

- Metal: Fermi energy within band
- Semiconductor: Fermi energy within band gap ($E_g < 2$ eV)
- Insulator: Fermi energy within band gap (E_g large, typically > 3 eV)

For semiconductors a further distinction into

- Direct Semiconductor: Minimum of conduction band and maximum of valance band at same $\vec{k}$ vector (necessary for optoelectronic application)
- Indirect Semiconductor: Minimum of conduction band and maximum of valence band at different $\vec{k}$ vectors

is useful.

For nearly all analytical approaches the general band structure $E_{band}(\vec{k})$ is too complicated. Thus a very often used "trick" is needed, translating the band structure into quasi free electrons described by Eq. (1.4). The only parameter to adapt the "free electrons" to the real band structure is the mass m_e being now called "effective mass" $m_{e,eff}$ with the definition

$$\frac{\hbar^2}{m_{e,eff}(k)} = \frac{d^2E(k)}{dk^2} \quad . \tag{1.5}$$

i.e. the effective mass is (up to a scaling factor) just the inverse of the curvature of the band structure.

In case of a 3D band structure the inverse of the effective mass tensor is defined by the Hesse matrix

$$\hbar^2 m_e^{-1}(k)_{ij} = \frac{\partial^2 E(k)}{\partial k_i \partial k_j} \quad . \tag{1.6}$$

The main diagonal elements of the effective mass tensor (if necessary after unitary transformation) are often used for a 1D representation

$$m_{e,eff}(k) = (m_e(k)_{11} * m_e(k)_{22} * m_e(k)_{33})^{\frac{1}{3}} \quad . \tag{1.7}$$

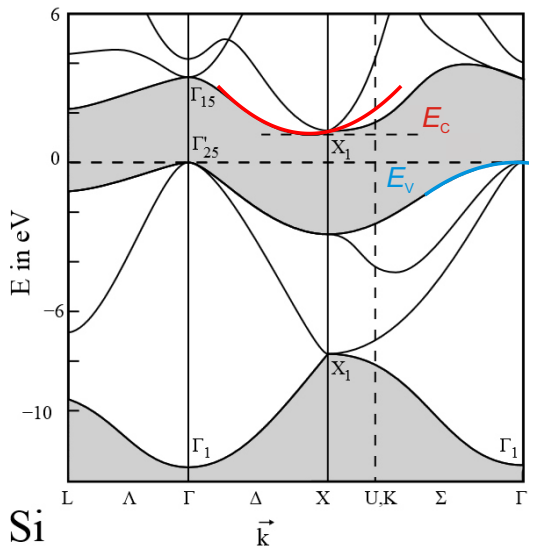


Figure 1.1: Silicon band structure including the relevant curvatures for defining effective masses

Fig. 1.1 shows the band structure of silicon including two parabolic functions which approximate the conduction band minimum (close to $k = X$) and valence band maximum at Γ. Since obviously minimum and maximum are at different k-values silicon (as well known) is an indirect band gap semiconductor. Using the effective electron mass concept the regime around the conduction band minimum can be described by

$$E(k) = E_C + \frac{\hbar^2(k - X)^2}{2m_{e,eff}(X)} \quad . \tag{1.8}$$

Obviously the curvature of the valence band is negative which is interpreted as an effective hole mass. The regime around the valence band maximum can thus be described by

$$E(k) = E_V - \frac{\hbar^2(k - \Gamma)^2}{2m_{h,eff}(\Gamma)} \quad . \tag{1.9}$$

In Eq. (1.9) we used a typical convention to take the negative sign of the curvature explicitly into account and the effective

hole mass is just the absolute value of the inverse curvature. The over all electron density n is calculated by

$$n = \int_{E_c}^{\infty} D_{cond\ band}(E) f(E,\mu,T) dE \quad , \tag{1.10}$$

and the over all hole density p by

$$p = \int_{-\infty}^{E_V} D_{val\ band}(E)\,(1 - f(E,\mu,T))\,dE \quad , \tag{1.11}$$

where $D_{cond\ band}(E)$ and $D_{val\ band}(E)$ are the densities of state for both bands. For non degenerated semiconductors $E_C \gg \mu$ and $E_V \ll \mu$. Thus in Eq. (1.10) we can approximate the Fermi-distribution by the Boltzmann distribution, i.e.

$$f(E,\mu,T) = \frac{1}{\exp\left(\frac{E-\mu}{kT}\right)+1} \approx \exp\left(-\frac{E-\mu}{kT}\right) \quad . \tag{1.12}$$

Correspondingly we find for the holes in the valence band

$$1 - f(E,\mu,T) = 1 - \frac{1}{\exp\left(\frac{E-\mu}{kT}\right)+1} = \frac{1}{\exp\left(\frac{\mu-E}{kT}\right)+1} \approx \exp\left(-\frac{\mu-E}{kT}\right) \quad . \tag{1.13}$$

Combining Eqs. (1.10 - 1.13) one can get

$$n(T) = n_i(T) = N_{C,eff} \exp\left(-\frac{E_C-\mu}{kT}\right) \quad , \tag{1.14}$$

$$p(T) = n_i(T) = N_{V,eff} \exp\left(-\frac{\mu-E_V}{kT}\right) \quad , \tag{1.15}$$

Here $N_{C,eff}$ and $N_{V,eff}$ are constants, depending on the effective masses $m_{eff}^{\frac{3}{2}}$.
Consequently we find the mass action law

$$n(T) * p(T) = n_i^2(T) = N_{V,eff} * N_{C,eff} \exp\left(-\frac{E_C-E_V}{kT}\right) \quad , \tag{1.16}$$

independent of the position of the chemical potential μ. Note that to get this result the Boltzmann approximation of the Fermi distribution of both conduction and valence band was necessary, i.e. the mass action law only holds for classical particles.
From charge neutrality we finally get

$$\mu = \frac{E_C+E_V}{2} + \frac{kT}{2} \ln\left(\frac{N_{V,eff}}{N_{C,eff}}\right) \quad . \tag{1.17}$$

Note: The results from Eq. (1.12) to Eq. (1.17) describe results when electrons and holes behave like purely classical particles. Thus they resemble results well known from classical chemistry.
Essentials:

- The ideal case is described by free particles. Non ideal properties are described by rephrasing parameters in the ideal equations (e.g. the effective mass).
- Particles can be interpreted as classical in extremely diluted systems, i.e. there exist many more quantum mechanical states than particles.

For the electron resp. hole mobility holds

$$\mu_e = \frac{q\tau}{m_{e,eff}} \quad , \quad \mu_h = \frac{q\tau}{m_{h,eff}} \tag{1.18}$$

where τ is the average time between two scattering events.
The Einstein relation allows to translate mobilities into diffusion coefficients

$$D_e = \mu_e \frac{kT}{q} \quad \text{respectively} \quad D_h = \mu_h \frac{kT}{q} \quad . \tag{1.19}$$

Finally the conductivity is defined by

$$\sigma = \sigma_e + \sigma_h = q\mu_e n + q\mu_h p \quad , \tag{1.20}$$

which completes the equations necessary to describe transport properties for electrons and holes (in semiconductors).

Essentials:

- Transport properties are a combination of quantum mechanics and classical physics.
- Quantum mechanics contributes the band structure, i.e. $E_g = E_C - E_V$, effective masses and scattering time τ.
- The remaining is classical physics.