

## §5.4 Effective mass approximation

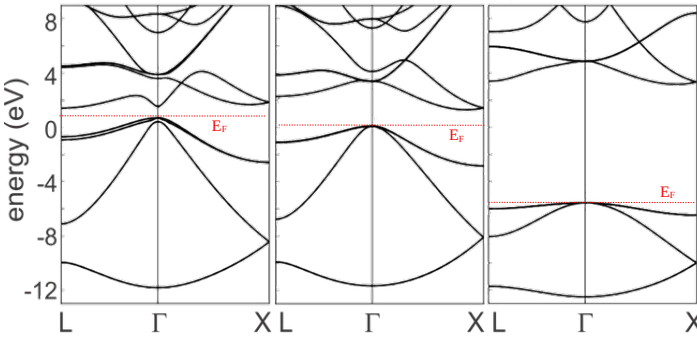


Figure 22

bands)  $E_n(k_x, k_y, k_z)$ . Here  $n$  – number of band. As example consider the calculated band structure for Ge crystal (Figure 22). Near the maximum and minimum of  $E_n(k_x, k_y, k_z)$ , this function can be expanded into the Taylor series:

The effective mass approximation is useful to simplify the description of the properties of electrons in semiconductors and dielectrics. The main idea is as follows. The general Schrödinger equation looks like this:

$$\left(-\frac{\hbar^2}{2m}\Delta + V\right)\varphi = E\varphi \quad (1)$$

Here  $V$  - exact periodic potential energy for electrons. The result of solution give the energy of electrons (set of

$$E_n(k_x, k_y, k_z) = E_n(k_{0x}, k_{0y}, k_{0z}) + \sum_{\alpha} \left. \frac{dE}{dk_{\alpha}} \right|_{k_0} (k_{\alpha} - k_{0\alpha}) + \sum_{\alpha, \beta} \left. \frac{d^2 E}{dk_{\alpha} dk_{\beta}} \right|_{k_0} (k_{\alpha} - k_{0\alpha})(k_{\beta} - k_{0\beta}) + \dots \quad (2)$$

But in extremum point first derivative is equal to zero so:

$$E_n(k_x, k_y, k_z) = E_n(k_{0x}, k_{0y}, k_{0z}) + \sum_{\alpha, \beta} \left. \frac{d^2 E}{dk_{\alpha} dk_{\beta}} \right|_{k_0} (k_{\alpha} - k_{0\alpha})(k_{\beta} - k_{0\beta}) + \dots \quad (3)$$

Introduce a new parameter  $m_{\alpha\beta}^* = \frac{\hbar^2}{2 \left( \left. \frac{d^2 E}{dk_{\alpha} dk_{\beta}} \right|_{k_0} \right)}$  in this case the (3) quadratic form looks like follows:

$$E_n(k_x, k_y, k_z) = E_n(k_{0x}, k_{0y}, k_{0z}) + \sum_{\alpha, \beta} \frac{\hbar^2}{2m_{\alpha\beta}^*} (k_{\alpha} - k_{0\alpha})(k_{\beta} - k_{0\beta}) \quad (4)$$

The sum can be diagonalized:

$$E_n(k_x, k_y, k_z) = E_0 + \sum_{\gamma} \frac{\hbar^2}{2m_{\gamma}^*} (k_{\gamma} - k_{0\gamma})^2 \quad (5)$$

Now this equation we can compare with corresponding equation for free electrons:  $E = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}$ . You can see that (5) and (5.1/16) are practically coincided. For cubic crystal in minimum of energy located in  $\Gamma$  point and on zero level of energy (5) looks like as follows:

$$E_n(k_x, k_y, k_z) = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m^*} \quad (6)$$

equations are exactly the same. There is only one difference in (6) instead of real mass we use a new parameter which have the name – effective mass of electron. It means that near of minimum or maximum of electron energy we can instead of equation (1) use much more simplest equation:

$$-\frac{\hbar^2}{2m^*}\Delta\varphi = E\varphi \quad (7)$$

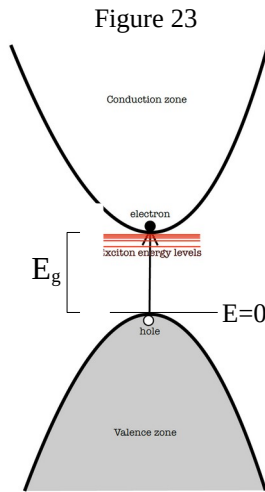
without any additional periodic potential. Near the extremum of energy electrons moving like free particles but instead of real masses we need to use in this case the mathematical parameter – effective mass. All effects concerned to real potential, created by other electrons and nuclei, are hidden in effective mass of electron. But this method is well working only near the extremum of electron energy (maximum or minimum).

Do not forget that the effective mass is a mathematical object, it is a second order tensor (second derivative with respect to wave vector projections), the values of which can be negative and depend on the direction of motion of the electron. For example in Ge there are two different effective masses: the transversal  $m_t=0.082m$  and longitudinal  $m_l=1.59m$  (here  $m$  is the mass of free electron).

The tensor of effective mass can be calculated directly for tight binding model by using equation (5.3/18). This tensor is diagonal and all diagonal elements are equal:

$$m_{\alpha\beta} = \frac{\hbar A}{2a^2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (8)$$

### §5.5 Excitons of large-radius



For semiconductors we have at least two zones, one of these completely filled by electrons (valence band) and the second is totally free (conductivity zone) (see Figure 23), so that the minimum excitation energy of an electron involves its transition from the filled valence band to the free conduction band. Such a transition results in the generation of charge carriers: of an electron in the conduction band and of a hole in the valence band.

But as show the experiment and theory the electron and hole can interact with each other and create a new quasiparticle. If the radius of such quasiparticle is comparable with lattice parameter then the electron-hole interaction can to a good approximation be regarded as Coulomb interaction of two point charges, where is the static dielectric constant of the crystal. As you guess the energy levels of this new object (exciton) is located internal the forbidden band and near the bottom of conductive zone.

So, we have two charged particles (one positive, and the other negative) interacting with a simple Coulomb potential. But we must take into account the polarizability of the crystal by dividing by the dielectric constant. The Schrodinger equation in this case is look like so:

$$\left[ -\frac{\hbar^2}{2m_e} \Delta_e - \frac{\hbar^2}{2m_p} \Delta_p - \frac{ke^2}{\varepsilon |r_n - r_p|} \right] \psi(r_n, r_p) = (E - E_g) \psi(r_n, r_p) \quad (9)$$

Here,  $m_n$  and  $m_p$  are the effective masses of electron and hole,  $k=1/4\pi\varepsilon_0$ ,  $\varepsilon$ -dielectric susceptibility of crystal,  $r_n, r_p$  – vector of position for electron and hole.

Introduce the position vectors of the center of gravity of the electron-hole system  $R$  and of the relative position of electron and hole  $r$ :

$$R = \frac{m_n r_n + m_p r_p}{m_n + m_p}, \quad r = r_n - r_p \quad (10)$$

Equation in the new coordinates is looks like so:

$$\left[ -\frac{\hbar^2}{2M} \Delta_R - \frac{\hbar^2}{2\mu} \Delta_r - \frac{ke^2}{\varepsilon |r|} \right] \psi(R, r) = (E - E_g) \psi(R, r), \quad (11)$$

here total mass  $M=m_e+m_p$  and reduced mass of exciton:

$$M = m_n + m_p, \mu = \frac{m_n m_p}{m_n + m_p} \quad (12)$$

Now we can separate the variables, it is mean that we can consider the motion of centre of gravity and rotational moving of exciton separately. The wave function of exciton can be presented so:

$$\psi(R, r) = \chi(R) \varphi(r) \quad (13)$$

And the Schrödinger equation can be rewritten in new coordinates:

$$-\frac{\hbar^2}{2M} \varphi(r) \Delta_R \chi(R) + \chi(R) \left[ -\frac{\hbar^2}{2\mu} \Delta_r - \frac{ke^2}{\varepsilon|r|} \right] \varphi(r) = (E - E_g) \varphi(R, r) \chi(R) \quad (14)$$

The new substitution describing the motion of center of gravity:

$$-\frac{\hbar^2}{2M} \Delta_R \chi(R) = W \chi(R) \quad (15)$$

gives a new Schrödinger equation describing the exciton motion relative to the center of gravity:

$$-\frac{\hbar^2}{2\mu} \Delta_r \varphi(r) - \frac{ke^2}{\varepsilon|r|} \varphi(r) = (E - E_g - W) \varphi(R, r) \quad (16)$$

The solution of first equation is well known and look like so:

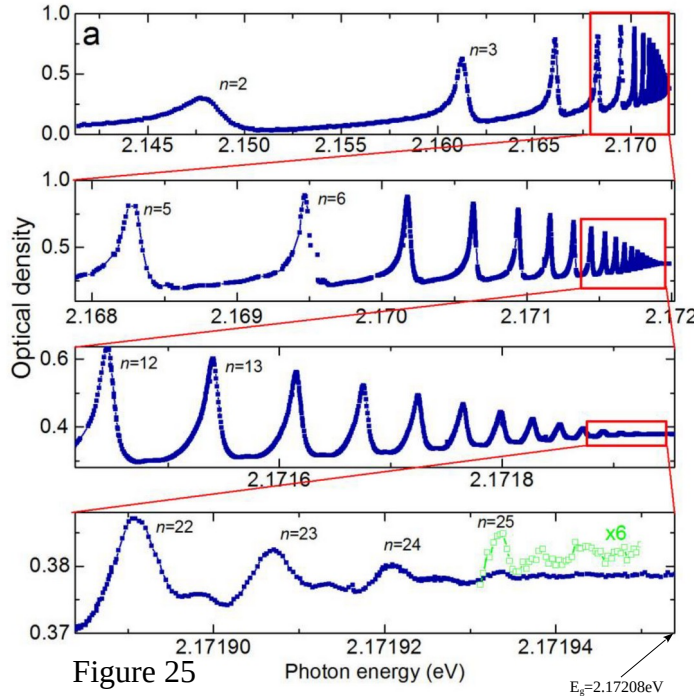


Figure 25

$$W = \frac{\hbar^2 K^2}{2M} \quad (17)$$

is the kinetic energy of the exciton moving as a whole. The second equation looks like a Schrodinger equation for hydrogen-like atom. The energy and wave function can be calculated directly:

$$E_n = E_g - \frac{\mu e^4}{8 \varepsilon_0^2 h^2 n^2} + W \quad (18)$$

It is mean that energy levels of exciton are located in the forbidden gap near the bottom of the conducting zone and it leads to the appearance of the set of lines near the edge of absorption (Figure 23). The Bohr radius for exciton can be calculated by the same way:  $a_B = \frac{4\pi \varepsilon_0 \varepsilon \hbar^2}{\mu e^2}$ . As you can see, large-radius excitons are formed in crystals with large

dielectric susceptibility. What about the exciton contribution to the absorption spectrum of dielectrics? Figure 25 shows the absorption spectrum for a copper oxide crystal ( $\text{Cu}_2\text{O}$ ) near the fundamental edge. The band gap at  $T=10\text{K}$  is equal 2.172 eV. A series of spectral lines associated with excitons can be seen in the forbidden zone.

It is important to note that exciton is neutral quasiparticles so cannot participate in electric current generation.

