

5. Zone Theory of Solids

To study the elementary particle system (in particular to find its energy levels), it is necessary to solve the corresponding Schrödinger equation. That differential equation contains the number of variables equal to that of freedom degrees of the system under investigation.

5.1. The Schrödinger Equation for a Crystal

A crystal can be characterized by coordinates of electrons $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_i$, and coordinates of atomic nuclei $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_\alpha$.

The stationary Schrödinger equation of entire system has the form:

$$\hat{H}\psi = E\psi, \quad (5.1)$$

\hat{H} – The energy operator (Hamiltonian) of the system, E – the total energy, ψ – the wave function (the proper function of \hat{H} -operator).

The operator \hat{H} includes:

The kinetic energy of electrons

$$\hat{T}_e = \sum_i \hat{T}_i = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right), \quad (5.2)$$

m – the electron mass, \hbar – the Plank constant, ∇_i^2 – the Laplas operator of a i -electron.

The kinetic energy of nuclei

$$\hat{T}_Z = \sum_\alpha \hat{T}_\alpha = \sum_\alpha \left(-\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \right), \quad (5.3)$$

M_α – the nucleus mass.

The energy of pair interaction between electrons

$$\hat{U}_e = \frac{1}{2} \sum_{i, j \neq i} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} = \frac{1}{2} \sum_i \hat{U}_{ij}, \quad (5.4)$$

The energy of pair interaction between nuclei

$$\hat{U}_Z = \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |R_\alpha - R_\beta|} = \frac{1}{2} \sum_{\alpha \neq \beta} \hat{U}_{\alpha\beta}, \quad (5.5)$$

The energy of pair interaction between electrons and nuclei

$$\hat{U}_{eZ} = -\sum_{i, \alpha} \frac{Z_\alpha e^2}{4\pi\epsilon_0 |r_i - R_\alpha|} = \sum_{i, \alpha} \hat{U}_{i\alpha}, \quad (5.6)$$

The energy of particles in an external field

$$\hat{V} = \hat{V}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots; \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots) \quad (5.7)$$

Thus:

$$\begin{aligned} \hat{H} &= \hat{T}_e + \hat{T}_Z + \hat{U}_e + \hat{U}_Z + \hat{U}_{eZ} + \hat{V} \\ \hat{H}\psi &= E\psi \end{aligned} \quad (5.8)$$

In 1 cm^3 of crystal there are about 10^{22} atoms. Hence the number of degrees of freedom (hence, the number of equations) is huge (of the order of $10^{22} - 10^{24}$). That system of equations can not be solved exactly. Certain approximation should be made.

We assume that there is no external field, i.e.:

$$\hat{V} = \hat{V}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots; \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots) = 0 \quad (5.9)$$

5.2. Adiabatic Approximation

The adiabatic approximation (Born, Oppenheimer) takes into account the different motion of the light electrons and heavy nuclei. In accordance with zero approximation, it is assumed that the nuclei are at rest: $\mathbf{R}_\alpha = \mathbf{R}_\alpha^0$. Thus, the kinetic energy of nuclei is zero. The interaction energy of nuclei \hat{U}_Z is small and can be neglected. Thus, the Hamilton operator of electrons \hat{H}_e :

$$\hat{H}_e = \hat{T}_e + \hat{U}_e + \hat{U}_{eZ} \quad (5.10)$$

The wave function of electrons ψ_e follows the normalization condition:

$$\int \psi_e^*(\mathbf{r}_1, \dots; \mathbf{R}_1^0, \dots) \psi_e(\mathbf{r}_1, \dots; \mathbf{R}_1^0, \dots) d\tau_e = 1 \quad (5.11)$$

The Schrödinger equation:

$$\hat{H}_e \psi_e = E_e \psi_e, \quad (5.12)$$

or

$$\left[\sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) + \frac{1}{8\pi\epsilon_0} \sum_{i,j \neq i} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{i,\alpha} \frac{Z_\alpha e^2}{|r_i - R_\alpha^0|} \right] \psi_e = E_e \psi_e, \quad (5.13)$$

The energy of crystal E_e represents the energy of electrons moving in the field of nuclei at rest.

$$E_e = \int \psi_e^* \hat{H}_e \psi_e d\tau_e = E_e(\mathbf{R}_1^0, \mathbf{R}_2^0, \dots) \quad (5.14)$$

Let us designate the wave function of nuclei by $\Phi_Z(\mathbf{R}_1, \dots)$.

The Hamilton operator of nuclei:

$$\hat{H}_Z = \sum_\alpha \left(-\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \right) + \hat{U}_Z + \hat{E}_\alpha(\dots, \mathbf{R}_\alpha, \dots) \quad (5.15)$$

The Hamilton operator of entire crystal can be written as follows:

$$\hat{H} = \hat{H}_e + \hat{H}_Z - \hat{E}_e, \quad (5.16)$$

The wave function is a product of wave functions of nuclei and electrons:

$$\psi(\dots \mathbf{r}_i, \dots; \dots \mathbf{R}_\alpha, \dots) = \psi_e(\dots \mathbf{r}_i, \dots; \dots \mathbf{R}_\alpha, \dots) \Phi_Z(\dots \mathbf{R}_\alpha, \dots). \quad (5.17)$$

Obviously:

$$\begin{aligned} \hat{H}_e \psi_e &= E_e \psi_e \\ \hat{H}_Z \Phi_Z &= E \Phi_Z \end{aligned} \quad (5.18)$$

I.e. the total energy of crystal coincides with the energy of nuclei with great accuracy.

In spite of essential simplification, the equation (5.13) can not be solved.

The electrons of the inner atomic shells of solids do not affect a great number of electric, magnetic, and optic phenomena. Thus we can restrict our approximation only by valence electrons. We remind our readers that the valence electrons build up the bonds of a crystalline lattice, the inner electrons together with nuclei build up the lattice skeleton. That assumption is called the *valence approximation*.

5.2. A Single Electron Approximation

Let us try to reduce the many-electron equation (5.13) to a single electron problem. Introducing the *self-congruent field* can do it. That field is the field produced by all electrons and nuclei at a point where the given (with number i) electron is located. Designate the self-congruent field by $\Omega_i = \Omega_i(\mathbf{r}_i)$. The field not only acts on an electron, but itself is affected by the electron. It explains the definition. Thus, the energy of the pair interaction of electrons can be replaced by the sum of $\Omega_i(\mathbf{r}_i)$:

$$\frac{1}{2} \sum_{i,j \neq i} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} \rightarrow \sum_i \Omega_i(\mathbf{r}_i). \quad (5.19)$$

Assume that the field is found. Then the Hamilton operator \hat{H}_e can be written as follows:

$$\sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) + \sum_i \Omega_i(\mathbf{r}_i) - \sum_i \left(\sum_{\alpha} U_{i,\alpha} \right) = \sum_i \hat{H}_i \quad (5.20)$$

\hat{H}_i - the Hamilton operator of a single electron:

$$\hat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 + \Omega_i(\mathbf{r}_i) + U_i(\mathbf{r}_i). \quad (5.21)$$

$\Omega_i(\mathbf{r}_i)$ is the potential energy of a single electron in the field of other electrons and $U_i(\mathbf{r}_i)$ is the potential energy of a single electron in the field of nuclei. There are no the pair interaction energy in the Hamilton operator, so the wave function of entire system is the product of separate functions and the system energy is the sum of electron energies:

$$\Psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots) = \prod_i \psi_i(\mathbf{r}_i); \quad (5.22)$$

$$E_e = \sum_i E_i, \quad (5.23)$$

We remind:

$$\hat{H}_i \psi_i = E_i \psi_i. \quad (5.24)$$

Thus, introducing the self-congruent field we managed to reduce the many-particle task to the problem of a single electron.

The procedure of finding functions $\Omega_i(\mathbf{r}_i)$ leads to the Hartree equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}_i) + \left[\frac{1}{2} \sum_{i \neq j} \int |\psi_j(\mathbf{r}_j)|^2 \frac{e^2 d\tau_j}{4\pi\epsilon_0 r_{ij}} \right] \psi_i(\mathbf{r}_i) + U_i(\mathbf{r}_i, \mathbf{R}_1, \mathbf{R}_2, \dots) \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i). \quad (5.25)$$

That equation does not take into account the Pauli exclusion principle. In accordance with that principle, the wave function should be anti-symmetric, relative the spin and space coordinates of a pair of particles. Equation (5.22) does not hold that principle. The Hartree-Fock equation follows the exclusion principle. The Slater determinant expresses the electron wave functions:

$$\Psi_e(q_1, q_2, \dots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(q_1) & \psi_1(q_2) & \dots \\ \psi_2(q_1) & \psi_2(q_2) & \dots \\ \dots & \dots & \dots \end{vmatrix}, \quad (5.26)$$

N - the number of electrons, q_i – arguments x_i, y_i, z_i и s_{z_i} . The wave function Ψ_e flows condition:

$$\Psi_e(\dots q_i \dots q_k \dots) = \Psi_e(\dots q_k \dots q_i \dots), \quad (5.27)$$

$$\int \Psi_e^* \Psi_e dq_e = 1$$

Introducing

$$V(\mathbf{r}) = \Omega(\mathbf{r}) + U(\mathbf{r}), \quad (5.28)$$

We get:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (5.25)$$

The analytical expression of function $V(\mathbf{r})$ is not known, but a great number of characteristics of the system can be understood without it. It is needed only to know the periodicity properties of the function $V(\mathbf{r})$.

5.3. The periodic Field of a Crystalline Lattice

It is natural to assume that the crystalline field is periodic:

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{n}) \quad (5.26)$$

I.e. the potential energy is invariant relative the translation *vector* \mathbf{n} .

$$\mathbf{n} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, \quad (5.27)$$

\mathbf{a} , \mathbf{b} , and \mathbf{c} are the identity periods of a lattice along the directions determined by integers n_1, n_2 , and n_3 .

F.Bloch assumed that the wave functions of equation (5.25) has the form:

$$\psi_k(\mathbf{r}) = U_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}); \quad (5.28)$$

The translation symmetry leads to conclusion that the wave functions of neighbor cells are proportional one another.

$$\psi(\mathbf{r} + \mathbf{n}) = C \psi(\mathbf{r}), \quad (5.29)$$

C is a constant. The normalization condition leads to:

$$|C|^2 = 1. \quad (5.30)$$

The condition (5.30) holds if

$$C = e^{i\mathbf{k}\mathbf{n}}. \quad (5.31)$$

\mathbf{k} – the wave vector with a module $k = 2\pi/\lambda$.

Taking into account (5.31) we get:

$$\psi(\mathbf{r} + \mathbf{n}) = e^{i\mathbf{k}\mathbf{n}} \psi(\mathbf{r}), \quad (5.32)$$

$$\psi(\mathbf{r}) = e^{-i\mathbf{k}\mathbf{n}} \psi(\mathbf{r} + \mathbf{n}) = U_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{n}}, \quad (5.33)$$

$$U_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}(\mathbf{r}+\mathbf{n})} \psi(\mathbf{r} + \mathbf{n}) \quad (5.34)$$

Thus, the potential energy is periodic (with the period of the lattice).

Equation (5.28) represents the *Bloch theorem*: The wave function of an electron moving in a periodic field is a modulated plane wave. In other words it is a product of the exponent $U_k(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}$ and periodic function $U_k(\mathbf{r})$. The function (5.32) and (5.33) are called sometime the *Bloch functions**

Often the vector \mathbf{k} is called the *quasi-wave vector*. The dimension of its components is reversible to that one of the length. Usually the vector \mathbf{k} is written as follows:

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar}, \quad (5.35)$$

Vector \mathbf{p} is called the *quasi-momentum*.

The definition ‘quasi-wave vector’ and ‘quasi-momentum’ stresses the analogue between the situation described and the problem of a free electron.

It is very easy to understand the likelihood and difference between the momentum and quasi-momentum. The first one characterizes the motion of a free electron when the system is isotropic. The second one characterizes the motion of an electron in the periodic force field when the system is invariant relative the translation by the period of a lattice.

The quasi-momentum operator \hat{P} is commutative with the energy operator:

$$\hat{P}\hat{H} - \hat{H}\hat{P} = 0, \quad (5.36)$$

Thus, we can postulate that the electron energy depends on quasi-momentum:

$$E = E(\mathbf{p}). \quad (5.37)$$

In accordance with the commutation condition, the quasi-momentum operator can not be taken in form of $-i\hbar\nabla$ (it would be commutative with the Hamilton operator). It should contain an addend, which depend on the field potential:

$$\hat{P} = -i\hbar\nabla + \hat{\gamma}(\mathbf{r}), \quad (5.38)$$

$\hat{\gamma}(\mathbf{r})$ Provides the commutation between \hat{P} and \hat{H} .

In order to find operator \hat{P} , the wave function ψ_k should be represented as the Bloch wave. Then after rather simple transformations we get:

$$\hat{P} = -i\hbar\nabla + i\hbar(\nabla \ln U_k(\mathbf{r})). \quad (5.39)$$

When $\hat{\gamma}(\mathbf{r}) \rightarrow 0$, the quasi-momentum transforms into conventional quantity.

5.3. The Brillouin Zones

Let us again discuss the translation condition for the electron wave function in a crystal.

$$\psi(\mathbf{r} + \mathbf{n}) = e^{i\mathbf{k}\mathbf{n}}\psi(\mathbf{r}). \quad (5.40)$$

For a vector $\mathbf{k} + 2\pi\mathbf{G}$, ($\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ - vector of the inverse lattice), the condition (5.40) is not violated. Indeed:

$$e^{i(\mathbf{k} + 2\pi\mathbf{G})\mathbf{n}} = e^{i\mathbf{k}\mathbf{n}} e^{i2\pi(\mathbf{n}\mathbf{G})} = e^{i\mathbf{k}\mathbf{n}}. \quad (5.41)$$

We have taken into account that

$$(\mathbf{n}\mathbf{G}) = Q, \quad e^{i2\pi Q} = 1. \quad (5.42)$$

$(\mathbf{n}\mathbf{G}) = n_1h + n_2k + n_3l = Q$ – целое число

Hence, the vector \mathbf{k} and $\mathbf{k} + 2\pi\mathbf{G}$ (or \mathbf{p} and $\mathbf{p} + 2\pi\hbar\mathbf{G}$) are physically equivalent. Both of them determine the same transformation of a wave function. The energy of an electron in those states is identical. We remind our readers that the energy is a periodic function of momentum (or quasi-momentum)

$$\begin{aligned} E(\mathbf{k} + 2\pi\mathbf{G}) &= E(\mathbf{k}) \\ E(\mathbf{p} + 2\pi\hbar\mathbf{G}) &= E(\mathbf{p}) \end{aligned} \quad (5.43)$$

If t in \mathbf{p} (or \mathbf{k}) space, we construct the reciprocal lattice with basis $2\pi\hbar\mathbf{a}^*$, $2\pi\hbar\mathbf{b}^*$, $2\pi\hbar\mathbf{c}^*$ (or $2\pi\mathbf{a}^*$, $2\pi\mathbf{b}^*$, $2\pi\mathbf{c}^*$), then entire crystal would be divided into the equivalent regions called the Brillouin zones.

A polyhedron of minimal volume built about the origin of coordinates of \mathbf{p} (or \mathbf{k}) space, which contains all non-equivalent states, is called the first Brillouin zone.

In order to determine the type of the first Brillouin zone, it is necessary to build the reciprocal lattice and the Vigner-Zeitz cell. If to all selected points to add vectors $2\pi\hbar\mathbf{G}$ (or $2\pi\mathbf{G}$), we will get all points of \mathbf{p} (or \mathbf{k}) space.

It follows that any point of \mathbf{p} (or \mathbf{k}) space can be transformed into the first Brillouin zone with the aid of a certain vector of reciprocal lattice.

For example, for a cubic cell of parameter a , the reciprocal lattice is also cubic with parameter $a^* = \frac{1}{a}$. The Wigner-Zeitz cell (the first Brillouin zone) is a cube of the

volume $\frac{8\pi^3}{a^3}$. The points of a cube constructed upon three reciprocally perpendicular

vectors $\frac{2\pi}{a}$ are not equivalent. These points can not be reproduced with the aid of a

certain vector \mathbf{G} . All external points can be easily produced from the inner ones. In order to build the first Brillouin zone, it is necessary to transmit all points by the vector $(-)\pi\mathbf{a}^*$. The center of the cube would transmit into the origin of the coordinate frame $\mathbf{k} = 0$.

Thus:

$$\begin{aligned} -\frac{\pi}{a} &\leq k_x \leq \frac{\pi}{a} \\ -\frac{\pi}{a} &\leq k_y \leq \frac{\pi}{a} \\ -\frac{\pi}{a} &\leq k_z \leq \frac{\pi}{a} \end{aligned} \quad (5.44)$$

When the lattice is cubic:

$$-\frac{\pi}{a_i} \leq k_i \leq \frac{\pi}{a_i} \quad (5.45)$$

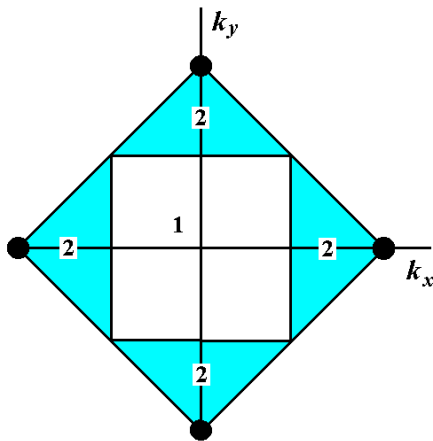


Fig.5.1. The Brillouin zones of a simple cubic lattice.

The Brillouin zones of a simple cubic lattice are shown in Fig.5.1.

The real crystal is finite. Thus, the allowed magnitudes of an electron wave vector are discrete.

For a cubic crystal with a lattice parameter a , we can write:

$$L_x = N_x a; \quad L_y = N_y a; \quad L_z = N_z a, \quad (5.46)$$

The quantities N_x , N_y , and N_z are the number of atoms located along the edges L_x , L_y , and L_z . Assume that the wave function follows the Born-Karmann condition:

$$\psi(x, y, z) = \psi(x + L_x, y + L_y, z + L_z). \quad (5.47)$$

Applying condition (5.47) on function (5.47) and taking into account the periodicity of the Bloch function, we get:

$$\begin{aligned} \psi_{\mathbf{k}}(x+L_x, y+L_y, z+L_z) &= \\ + e^{i[k_x(x+L_x)+k_y(y+L_y)+k_z(z+L_z)]} \times U_{\mathbf{k}}(x+L_x, y+L_y, z+L_z), & \quad (5.48) \\ = U_{\mathbf{k}}(x, y, z) e^{i[k_x L_x + k_y L_y + k_z L_z]} e^{i\mathbf{k}\mathbf{r}} &= \psi_{\mathbf{k}}(x, y, z) \end{aligned}$$

The length L is great, and we can assume that in the edges L_x , L_y , and L_z there are the integer numbers of the lattice periods. Thus, to satisfy condition (5.28), it is necessary:

$$e^{i[k_x L_x + k_y L_y + k_z L_z]} = 1 \text{ или} \\ e^{ik_x L_x} = e^{ik_y L_y} = e^{ik_z L_z} = 1, \quad (5.49)$$

Hence,

$$k_x L_x = 2\pi n_1; \quad k_y L_y = 2\pi n_2; \quad k_z L_z = 2\pi n_3, \quad (5.50)$$

n_1, n_2, n_3 – integers (0, $\pm 1, \pm 2, \dots$). The allowed components of a wave vector are:

$$k_x = \frac{2\pi}{L_x} n_1; \quad k_y = \frac{2\pi}{L_y} n_2; \quad k_z = \frac{2\pi}{L_z} n_3, \quad (5.51)$$

Using (5.46) we can write:

$$k_i = \frac{2\pi}{a} \frac{n_i}{N_i} = 2\pi a^* \frac{n_i}{N_i}. \quad (5.52)$$

Taking into account the equivalence of states \mathbf{k} and $\mathbf{k} + 2\pi\mathbf{G}$, we make restriction on the possible number of n_i

$$k_i = 2\pi a^*; \quad n_i = N_i. \quad (5.53)$$

The entire quantity of the wave vectors in the Brillouin zone is:

$$N = N_x N_y N_z = \frac{L_x L_y L_z}{a^3} \quad (5.54)$$

Thus, the number of allowed wave vectors coincides with the number of elementary cells in a crystal. The greater the size of a crystal, the less is the influence of discrete structure of the wave vector. Indeed, if $a^3 = 64 \cdot 10^{-25} \text{ cm}^3$, then in a crystal of the volume 1 cm^3 , $N \approx 10^{22}$. Taking into account that the energy of the state \mathbf{k} and $\mathbf{k} + 2\pi\mathbf{G}$ is identical, we assume that the periodicity condition is true:

$$\begin{aligned} \Psi_{n, \mathbf{k} + 2\pi\mathbf{G}}(\mathbf{r}) &= \Psi_{n, \mathbf{k}}(\mathbf{r}), \\ E_{n, \mathbf{k} + 2\pi\mathbf{G}} &= E_{n, \mathbf{k}} \end{aligned} \quad (5.55)$$

The set of all electron energy levels $E_{n, \mathbf{k}}$ (for fixed n) is called the energy zone. называют энергетической зоной. For every set, there is the upper and down limits. All levels are located inside the interval between those limits. When the width of the zone is about 1eV, the average distance between the levels is $\sim 10^{-22} \text{ eV}$, i.e. much less than kT . So we can not take into account the energy discreteness inside the zone.

5.4. The Crowing-Penny

The energy spectrum of electrons is to be found from the Schrödinger equation (5.56). The potential of a lattice $V(\mathbf{r})$ is a periodic function of crystalline structure.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = E \psi_{\mathbf{k}}(\mathbf{r}) . \quad (5.56)$$

The proper functions $\psi_{\mathbf{k}}(\mathbf{r})$ and energies $E_{\mathbf{k}}(\mathbf{r})$ essentially depend on the form of a potential $V(\mathbf{r})$. A number of approximations is used.

- 1) Only atomic constants are used as parameters in self-congruent calculations (for example, the method of orthogonal plane waves).
- 2) In order to coordinate the theory and experiment, the experimental data are used (the interpolation schemes, the method of pseudo-potential).
- 3) The methods based on selection of a special type potential are used (the Grin functions, added plane waves, the linear combination of atomic orbital).

The main part of those calculations is made numerically.

In one-dimensional model of Crowing and Penny, the simple rectangular barriers are used (Fig.5.2). The width of the barrier is b , the distance between barriers is a . Thus, the lattice period is $c = a + b$.

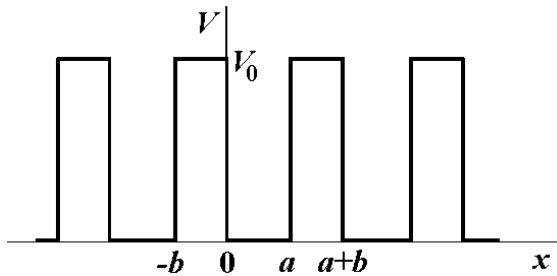


Fig.5.2. The electron potential energy as function of inter-atomic distance in Kroning-Penni model.

The potential energy can be written as follows:

$$\begin{aligned} V(x) &= 0; & nc < z < nc + a; \\ V(x) &= V_0; & nc + a < z < (n+1)c. \end{aligned} \quad (5.57) \quad n \text{ is}$$

an integer ($0, \pm 1, \pm 2, \dots$). The one-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi . \quad (5.58)$$

The Bloch function is chosen as the solution of that equation:

$$\psi(x) = U(x) e^{ikx} \quad (5.59)$$

$U(x)$ – a periodic (period c) function:

$$U(x) = U(x+c) = U(x+2c) = \dots \quad (5.60)$$

Introducing (5.59) into (5.58), we get for $0 \leq x \leq a$ (and for each well):

$$\frac{d^2 U}{dx^2} + 2ik \frac{dU}{dx} + (\alpha^2 - k^2) U = 0 . \quad (5.61)$$

We get for $a \leq x \leq a+b$ (and for each potential barrier):

$$\frac{d^2 U}{dx^2} + 2ik \frac{dU}{dx} - (\beta^2 + k^2) U = 0 . \quad (5.62)$$

$\alpha = \frac{1}{\hbar} \sqrt{2mE}$, $\beta = \frac{1}{\hbar} \sqrt{2m(V_0 - E)}$. Solution of equation (5.61) and (5.62) are:

$$U_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}, \quad 0 \leq x \leq a; \quad (5.63)$$

$$U_2 = Ce^{(\beta-ik)x} + De^{-(\beta-ik)x}, \quad a \leq x \leq a+b. \quad (5.64)$$

We can exclude four unknown quantities A , B , C , and D using the continuity of the function $\psi(x)$ and its derivative:

$$\begin{aligned} U_1 &= U_2 \\ \frac{dU_1}{dx} &= \frac{dU_2}{dx} \quad \text{if} \quad x = \begin{cases} n(a+b) \\ a+n(a+b) \end{cases}. \end{aligned} \quad (5.65)$$

Thus, we get the system of four linear equations relative A , B , C , and D . To have a solution, its determinant should be zero. It leads to:

$$\cos k(a+b) - \frac{\beta^2 - \alpha^2}{2\alpha\beta} \text{sh}(\beta b) \sin(\alpha a) - \text{ch}(\beta b) \cos(\alpha a) = 0 \quad (5.66)$$

In order to solve equation (5.66) suppose that the barriers are high and thin. Let $b \rightarrow 0$, $V_0 \rightarrow \infty$, but the product $b \cdot V_0$ is finite. It means that quantity $\beta^2 b$ is finite, but $\beta b \rightarrow 0$. When $b \rightarrow 0$ $\text{ch} \beta b \rightarrow 1$, $\text{sh} \beta b \rightarrow \beta b$. Thus, instead of equation (5.66), we get:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \beta b \sin(\alpha a) + \cos(\alpha a) = \cos ka \quad \text{или} \quad (5.67)$$

$$\frac{\beta^2 ab}{2} \cdot \frac{\sin \alpha a}{\alpha a} + \cos(\alpha a) = \cos ka \quad (5.68)$$

Introduce a designation:

$$\lim_{\substack{b \rightarrow 0 \\ \beta \rightarrow \infty}} \frac{\beta^2 ab}{2} = P \quad (5.69)$$

The parameter P characterizes the transparency of a barrier, in other words the degree of bonding of electron inside the potential well. Obviously:

$$P \frac{\sin \alpha a}{\alpha a} + \cos(\alpha a) = \cos ka \quad (5.70)$$

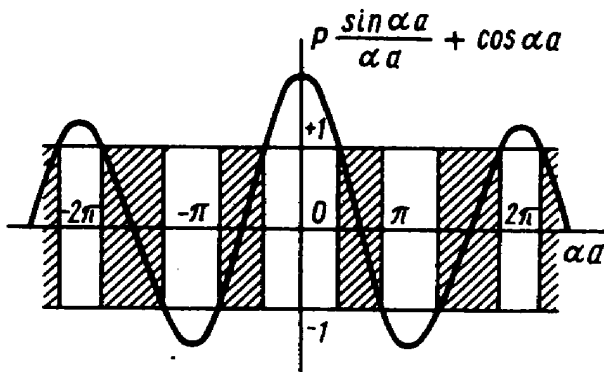


Fig.5.3. The left side function of the equation (5.72).

It should be noted that the function $\cos \alpha a$ is an even function: replacing k by $(-)k$ does not change equation (5.68). Hence, the electron energy is also an even function of the wave vector:

$$E(-k) = E(k) \quad (5.71)$$

The left part of function (5.70) is shown in Fig.5.3. The right part of equation (5.70) is limited by the interval from $(+)1$ up to $(-)1$. The allowed quantities of αa are dashed. The width of the intervals

depends on the parameter P . The less the parameter, the wider are the intervals. Besides,

their width depends on the quantity αa . At any P , the intervals widens when parameter αa increases. Thus, the electron energy can not be arbitrary. The allowed and forbidden zones alternate.

When $P \rightarrow 0$, $V_0 \rightarrow 0$ (*the weak bond approximation*). It follows from (5.70) that $\alpha a = ka = \kappa a$, i.e. $a = k$. Taking into account that $\alpha = \frac{1}{\hbar} \sqrt{2mE}$ we get:

$$E = \frac{\hbar^2 \alpha^2}{2m} = \frac{\hbar^2 k^2}{2m} . \quad (5.72)$$

The relation (5.72) is known to describe the free electron.

When $P \rightarrow \infty$, $V_0 \rightarrow \infty$ (*the strong bond approximation*). When $P \rightarrow \infty$, it follows from equation (5.70) that

$$\frac{\sin \alpha a}{\alpha a} = 0, \quad \text{m.e.} \quad \alpha a = \pi j, \quad (5.73)$$

$j = \pm 1, \pm 2, \dots$,

$$E = \frac{\hbar^2 \pi^2}{2ma^2} j^2 . \quad (5.74)$$

Equation (5.74) is known as standart result for a particle in one-dimensional box with the width a . The dispersion law in the strong bond approximation for an electron in the perodic field of a lattice is found as follows:

$$E = \frac{\hbar^2 \pi^2 j^2}{2ma^2} \left[1 - \frac{2}{P} + (-1)^j \frac{2 \cos ka}{P} \right] \quad \text{или} \quad (5.75)$$

$$E = E_{0j} - C_j + (-1)^j A_j \cos ka \quad (5.76)$$

$$E_{0j} = \frac{\hbar^2 \pi^2 j^2}{2ma^2}, \quad C_j = \frac{\hbar^2 \pi^2 j^2}{ma^2 P} .$$

The first addend in (5.75) is the energy of an electron in the well of infinite depth. The second and the third addends describe the influence of the periodic field. In the periodic

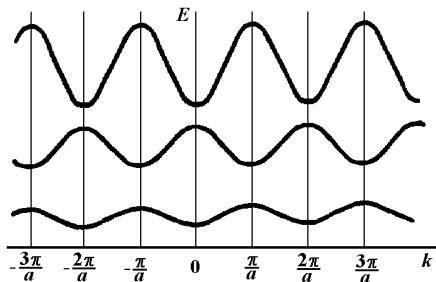


Fig.5.4. Dependence of electron energy on wave number in one-dimensional lattice.

lattice field, the levels are low than those ones for the isolated electron by the quantity C_j . The third addend in (5.75) associated with zones. That addend oscillates. The function $E(k)$ is shown in Fig.5.4. The interval from $-\frac{\pi}{a}$ up to

$\frac{\pi}{a}$ is the first Brillouin zone. Two segments from $-\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and from $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ represent the second Brillouinzone, and so on. All possible energies of any zone can be got by varying the vave number of the first zone.

The function $E(k)$ is usually given only for the first zone. All other quantity of energy can be reduced in that zone (*the method of reduced zone*, Fig.5.4). The scheme shown in Fig.5.5 is called the *periodic zone cheme*. The metod of *expanded zone cheme* is also used (Fig.5.7). Accordingb to that method, the different energy zones are located in different Brillouin zones. In Fig.5.7, the parabolic dependence $E(k)$ for a free electron is also shown. The origin of both graphs is the same.

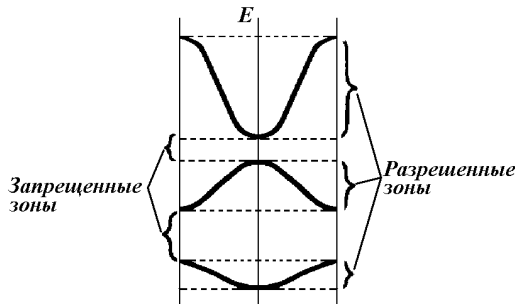


Fig.5.5. The method of reduced zones.

It follows from Fig.5.5 that in odd zones ($j = 1, 3, 5, \dots$) there is a minimum in the zone center and two equivalent maximums at the zone borders. In even zones there is a maximum in the zone center and two equivalent minimums at the zone borders.

At the borders of the Brillouin zone when the wave vector equals $\frac{n\pi}{a}$, the disrupters appear. The situation when the

function $E(k)$ disrupts is characterize by the condition:

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{a} \quad \text{или} \quad n\lambda = 2a \quad (5.77)$$

The condition (5.77) is the Wolf-Bragg condition for a wave falling normally upon a crystalline lattice. When that condition holds, the Bloch function represents the standing wave. Thus the electron undergoes the Bragg reflection. The falling and reflected waves can superpose forming the symmetric or non-symmetric combination:

$$\psi_1(x) = U(x) \left[e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x} \right] = 2U(x) \cos\left(\frac{\pi}{a}x\right) \quad (5.78)$$

$$\psi_2(x) = U(x) \left[e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x} \right] = 2U(x) \sin\left(\frac{\pi}{a}x\right) \quad (5.79)$$

Formulas (5.78) and (5.79) are written for $k = \pm \frac{\pi}{a}$. The wave function ψ_1 does not change when x is changed by $-x$, ψ_2 changes the sign. The function ψ_2 is imaginary. The different energy corresponds to function ψ_1 and ψ_2 . The less energy (the upper

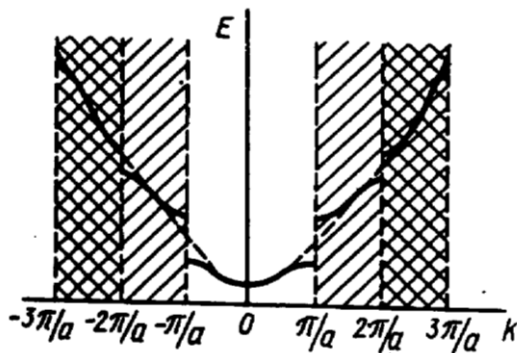


Fig.5.6. The zone dependence of electron energy on the wave number

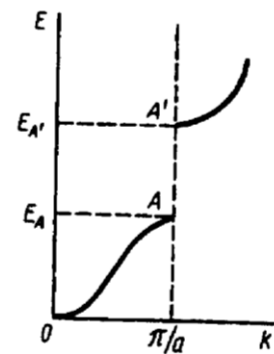


Fig.5.7. Disruption of electron energy

border of the first zone, point A in Fig.5.7) corresponds to the function ψ_1 . The down border of the second zone (point A') corresponds to function ψ_2 . When $k < \frac{\pi}{a}$ the electron energy is less than E_A , when $k > \frac{\pi}{a}$ the electron energy is greater than E_A . The interval from E_A up to $E_{A'}$ is forbidden.

We remind our readers that when the wave vector reaches the border of Brillouin zone ($k = \pm \frac{\pi}{a}$), the elastic waves reflect and standing waves are produced.

The zone structure of three-dimensional lattice is more complicated. The dependence $E(k)$ can be different for different orientations. The allowed zones can overlap. For example, the forbidden in certain direction zone can coincide with allowed one in other direction. It should be noted that there is no overlapping in one-dimensional model.

5.5. Metals, Dielectrics, Semiconductors

When a crystalline lattice is formed, the energy levels of an isolated atom split and the energy zone is produced. If the energy level was filled the energy zone is filled too. In any allowed zone there is a finite number of levels. In accordance with exclusion principle, only two electrons with the opposite spin can populate each level. The number of electrons in crystal is finite and only the lowest energy zones are filled. All the other zones are empty. The several types of filling the zones are possible.

1. When the last (valence) zone is filled partly, the electrons from the levels close the border would transit at the higher levels of the same zone under action of an external field. The electric current would be produced. Thus, the crystals with partially filled valence zone are metals. For example, the electron configuration of Sodium is $\text{Na} = [1s^2 2s^2 2p^6] 3s^1$. The inner zones (formed by $1s$, $2s$, and $2p$ levels) are completely filled. The valence zone is formed by $3s$ states. The number of states is $2N$, but there is only N electrons (one valence electron per atom). Thus, only half of the valence zone of crystalline Sodium is filled.

2. The valence zone is filled, but overlaps with the allowed neighbor empty zone. If the voltage is applied, the electric current is produced. Such crystal is a metal too, for instance $\text{Mg} = 1s^2 2s^2 2p^6 3s^2$. In crystalline Magnesium, the valence electrons fill $3s$ - zone. That zone overlaps with the following allowed zone formed by $3p$ -levels.

3. The valence zone is filled. Between the valence zone and the following free zone there is a wide forbidden zone (the $> 2 - 3$ eV). In a crystal of such zone structure, the electric current can not be produced because the electrons of the filled zone can not change its energy. Thus, the substance is a dielectric, for instance ionic crystal NaCl . The configuration of positive Sodium ion: $\text{Na}^+ = 1s^2 2s^2 2p^6$, and configuration of a negative Chlorine ion: $\text{Cl}^- = 1s^2 2s^2 2p^6 3s^2 3p^6$. The zones that consist of entirely filled atomic levels are entirely filled too. The last filled zone is $3p$ Cl^- , the following zone $3s$ Na^+ is free. The energy slit between zones is about 9eV.

If the width of forbidden zone is less than 2 – 3 eV, the crystal is called the semiconductor. In a semiconductor, the appreciate number of electrons are transmitted (due to heat energy) in the *conduction zone*. At very low temperature, any semiconductor becomes a good dielectric.

Thus, metals and dielectrics differ principally, dielectrics and semiconductors differ only quantitatively.

Fig.5.8 shows the zones of metals, semiconductors, and dielectrics. The widths of forbidden zones of certain dielectrics and semiconductors are tabulated in table 5.1.

The type of the filling of energy zone depends also on crystalline structure. For example the Carbon structured, as diamond is dielectric. The Carbon structured, as graphite is a metal.

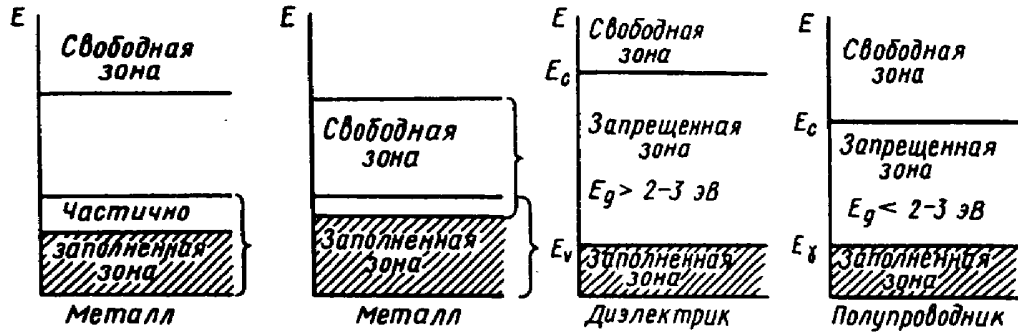


Fig.5.8. The electron zone occupation.. E_v – the border of valence zone; E_c – the border of conduction zone; E_g – the width of forbidden zone.

Table 5.1 The width of forbidden zone

Материал	E_g , эВ
С (алмаз)	5,2
BN	4,6
Al ₂ O ₃	7,0
Si	1,08
Ge	0,66
GaAs	1,43
InSb	0,17

5.6. Effective Mass. The Holes

The uniform electric field acts upon an electron (the velocity \mathbf{v}) with a force:

$$\frac{d\varepsilon}{dt} = -e\mathbf{E} \cdot \mathbf{v} \quad (5.80)$$

$$v_g = \frac{d\omega}{dk} = \frac{d}{dk} \left(\frac{\varepsilon_k}{\hbar} \right) = \frac{1}{\hbar} \nabla_k \varepsilon \quad (5.81)$$

Introducing (5.81) into (5.80) we get:

$$\hbar \left(\frac{d\mathbf{k}}{dt} \right) = -e\mathbf{E} \quad (5.82)$$

According to Eq.(5.82), the quantity $\hbar\mathbf{k}$ can be considered as the electron momentum. The acceleration of electron is:

$$\begin{aligned} \mathbf{a} &= \frac{d\mathbf{v}}{dt} = \frac{1}{\hbar} \nabla_k \left(\frac{d\varepsilon}{dt} \right) = \frac{1}{\hbar} \nabla_k (-e\mathbf{E} \cdot \mathbf{v}) = \\ &= \frac{1}{\hbar} \nabla_k \left[\frac{(-e\mathbf{E})}{\hbar} \nabla_k \varepsilon \right] = \frac{-1}{\hbar} \nabla_k \nabla_k \varepsilon (-e\mathbf{E}) \end{aligned} \quad (5.83)$$

$$a_i = \frac{-1}{\hbar} \sum_j \frac{\partial^2 \varepsilon}{\partial k_i \partial k_j} (eE) \quad (5.84)$$

Comparing equation (5.83) and (5.84) we arrive to the conclusion that the dimension of the quantity

$$m_{ij} = \hbar^2 \left(\frac{\partial^2 \varepsilon}{\partial k_i \partial k_j} \right)^{-1} \quad (5.85)$$

is mass. The quantity (5.85) represents the *effective mass tensor*. For certain solids of complex structure, the non-diagonal tensor components are great, and the direction of acceleration does coincide with that one of the applied field. If a solid is isotropic, all non-diagonal components are zero and three diagonal components are identical. The quantity (5.86) is called the *effective scalar mass*.

$$m^* = \hbar^2 \left(\frac{\partial^2 \varepsilon}{\partial k^2} \right)^{-1} \quad (5.86)$$

The effective mass does not depend on energy if the energy is a square power function of the wave vector.

If the electron energy is minimal at a point $k = k_1$, the diagonal components m_{ij} are (as a rule) positive at the point k_1 . And we can assume that for electrons located near the bottom of allowed zone:

$$\varepsilon = \varepsilon_1 + \frac{\hbar^2}{2m_1} (k - k_1)^2, \quad (5.87)$$

m_1 – the effective mass for given direction.

In the regions of the Brillouin zone where the electron energy is maximal, all three components $\left(\partial^2 \varepsilon / \partial k_j^2 \right)$ are negative. Thus:

$$\varepsilon = \varepsilon_2 - \frac{\hbar^2}{2m_2} (k - k_2)^2. \quad (5.88)$$

An electron belonging to such group of states responds to the field as if its mass is negative. Thus, the points of the geometric space near the zone ceiling behave as the positive particle, which is called the *hole*. The mass and electric charge of a hole is positive. When considering the zone filled almost up to the ceiling (for example, the valence zone of a semiconductor), it is more convenient to speak about the motion of holes but not electrons.

Thus, the conductivity of almost entirely populated zone is due to a small number of non-occupied states – positive holes with positive mass and charge.

5.6. Elementary Theory of Local States

In real solids there is a number of defects. It affects its energy spectrum. The very typical defects are implanted atoms (impurities). It is assumed that a defect violates the periodic potential of a lattice. Designating the violation by $W(\mathbf{r})$, which is located near the point r_0 , we can write:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + W(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = E \psi_{\mathbf{k}}(\mathbf{r}) . \quad (5.88)$$

The solution of equation (5,88) is represented by the Vanier functions:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_k e^{i\mathbf{k}\mathbf{r}_0} \Phi(\mathbf{r} - \mathbf{r}_0) \quad (5.89)$$

$\Phi(\mathbf{r} - \mathbf{r}_0)$ – is a Vanier function. The solution shows that when there is violation W , one energy level at the edge of allowed zone is split off. If $W < 0$ that level goes down, if $W > 0$ the level goes up. поднимается вверх.

Thus, if there is violation, the energy level $E_k(\mathbf{r})$ appears in the forbidden zone. When defects are generated (impurities, vacancies, dislocations, and others), the allowed states appear inside the forbidden zone (Fig.5.10).

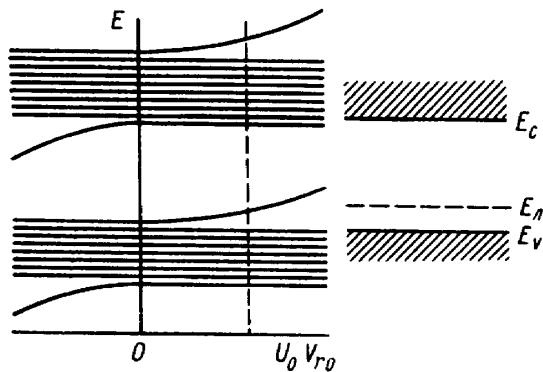


Fig.5.10. Generation of allowed states inside the forbidden zone under action of the local violation

To solve the equation (5.88) for certain energy of violation $W(\mathbf{r})$, a special method is used. The method is based on the fact that the free electron equation and equation for an electron in a crystal are identical if the last one is written as follows:

$$-\frac{\hbar^2}{2m^*} \nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) = E \psi_{\mathbf{k}}(\mathbf{r}) , \quad (5.90)$$

m^* - effective mass tensor. A plane wave is the solution of equation (5.90). That method is called the *effective mass method*.

The method can be applied if potential

$W(\mathbf{r})$ is changing more slowly than potential $V(\mathbf{r})$. It signifies that the region of localization of the violation is greater than the lattice period.

Acceptor and donor impurities affect the concentration of free charge carriers in a semiconductor. It is due to the fact that the activation (ionization) energy of impurities is essentially less than the ionization energy of the substance:

$$\Delta E_d = E_c - E_d \ll E_g ; \quad \Delta E_a = E_a - E_v \ll E_g , \quad (5.91).$$

E_a and E_d is the energy of an acceptor and donor level.

The donor levels are usually located at the bottom of conduction zone; the acceptor levels are located above the ceiling of valence zone. To describe those levels, the Hydrogen model is convenient.

The interaction between the impurity and substance atom leads to decreasing of the bond energy of the impurity atom electron. Its orbit becomes greater than that one of the other impurity atom electrons. For example, when antimony atoms (five valence electrons) are introduced in Silicon, four valence electrons of antimony atoms can take a part in covalent bond of silicon atoms. The bond of fifth electron (which does not take part in covalent bond) with the antimony ion is less. Obviously, the bond energy of the fifth electron with impurity ions is the ionization energy of the donor impurity ΔE_d .

The electron, which does not take part in covalent bond, can be considered as the free particle. Using the effective mass method we can write its motion equation as follows:

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\varepsilon_0 |\mathbf{r}|} \right] \psi_{\mathbf{k}}(\mathbf{r}) = E \psi_{\mathbf{k}}(\mathbf{r}), \quad (5.92)$$

The form of equation (5.92) is identical with that of the Hydrogen atom. Thus, we can write:

$$r = \frac{\varepsilon_0 \hbar^2}{m^* Z e^2} n^2, \quad (5.93)$$

$$E_d = E_c - \frac{1}{2} \frac{Z^2 e^4 m^*}{\hbar^2 \varepsilon^2 \varepsilon_0^2} \frac{1}{n^2} = E_c - \frac{1}{2} \frac{Z^2 e^4 m}{\hbar^2 \varepsilon^2 \varepsilon_0^2} \left(\frac{m^*}{m} \right) \frac{1}{n^2}. \quad (5.94)$$

It is assumed that the energy corresponding the bottom of conduction zone is zero. The ionization energy of the impurity atom ($n=1$) is:

$$\Delta E_d = \frac{13.52 \cdot Z^2}{\varepsilon^2} \left(\frac{m^*}{m} \right) (\text{эВ}). \quad (5.95)$$

For antimony in silicon, $\Delta E_d = 0,04\text{eV}$. In accordance with (5.95), the level of twice ionized donor impurity in forbidden zone is lower than the levels of once ionized or neutral impurity atom.

For acceptor impurity, formula (5.93) and (5.94) hold. For example, the ionization energy of acceptor impurity:

$$\Delta E_a = \frac{13.52 \cdot Z^2}{\varepsilon^2} \left(\frac{m_p^*}{m} \right) (\text{эВ}), \quad (5.96)$$

m_p^* - the hole effective mass.

The proper defects of the lattice as well as impurities produce the local states in forbidden zone.