1.Bonds in solids

In this section, the fundamental laws of the condensed matter physics are under consideration. The problems discussed are being studied very closely in the courses of general physics, theoretical physics, quantum mechanics and others.

1.1 Properties of Particles. The Wave–Particle Duality

The expression 'microparticicle' (or just particle) is used for designating the elementary particles and complex particles compounded of the small number of elementary particles. Every microparticle is a composition with the features of a particle and wave. That duality describes not only optic phenomena but is of the universal character (Luis de-Broglie, 1924). The motion of an electron (or other particle) is associated with the wave process with the wavelength and frequency:

$$\lambda = \frac{2\pi\hbar}{p} = \frac{2\pi\hbar}{mv} \ , \tag{1.1}$$
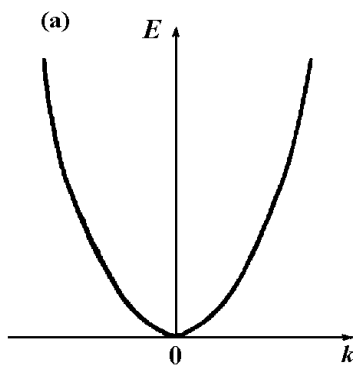
$$\omega = \frac{E}{\hbar} \tag{1.2}$$

λ– de-Broglie wavelength of a particle, m – its mass, v –velocity, $h = 6{,}6{\cdot}10^{-34}$ Jole·s – the Plank constant, $\hbar = h/(2\pi) = 1{,}05{\cdot}10^{-34}$ Jole·s.
We are going to investigate the behavior of electrons. In accordance with (1.1), the electron kinetic energy:

$$\frac{mv^2}{2} = \frac{h^2}{2m\lambda^2} \tag{1.3}$$

Having in mind that the wave number $k = 2\pi/\lambda$, we get:

$$E(k) = \frac{h^2 k^2}{8\pi^2 m} = \frac{\hbar^2 k^2}{2m} \ . \tag{1.4}$$

(a)

Fig.1.1

Equation (1.4) describes the dispersion law, i.e. the dependence of the kinetic energy of a free electron on the wave number (Fig.1.1). In accordance with equation (1.1),

$$p = \hbar k \ . \tag{1.5}$$

If the wave vector is normal to the wave front we can write Eq.(1.5) as follows:

$$\mathbf{p} = \hbar\mathbf{k} \tag{1.6}$$

Equation (1.1) – (1.6) describe the particle–wave duality. The wave propagates with the speed:

$$v = v\lambda = \frac{\omega}{k} \tag{1.7}$$

The frequency v and the angular frequency $\spadesuit$ are related by $\omega = 2\pi v$. In order to describe the properties of electrons, the harmonic wave is used:

$$\psi = \sin(kx - \omega t) \tag{1.8}$$

To illustrate the concepts of the wave – particle duality, let us consider the combination of two waves with a small difference of frequencies.

If ◆ is the frequency of the first wave, then $(\omega + \Delta\omega)$ is the frequency of the second wave and k and $(k + \Delta k)$ are their wave numbers. Using condition $\Delta\omega \ll \omega$ and $\Delta k \ll k$. We can write:

$$\psi_1 = \sin(kx - \omega t) \tag{1.9}$$

$$\psi_2 = \sin[(k + \Delta k)x - (\omega + \Delta\omega)t] \tag{1.10}$$

The wave ψ_1 and ψ_2 superpose and a new wave ψ is born:

$$\psi_1 + \psi_2 = \psi = 2\cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right) \cdot \sin\left[\left(k + \frac{\Delta k}{2}\right)x - \left(\omega + \frac{\Delta\omega}{2}\right)t\right] \tag{1.11}$$

Equation (1.11) describes a sine wave, the amplitude of which is modulated by a cosine function. That phenomenon is called *beating*.
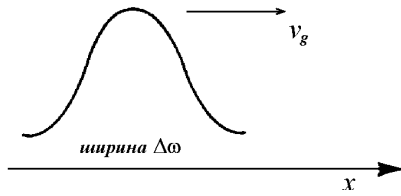

Fig.1.2 *The particle (the wave momentum) moves with the group velocity v_g. $\Delta\omega$ -the momentum width..*

Superposition of the great number of waves leads to a single wave packet (Fig.1.2). A wave (or a flux of particles having the same speed) propagates in a medium.

The phase velocity of the wave v is given by the second part of equation (1.11):

$$v = \frac{x}{t} = \frac{\omega + \omega/2}{k + k/2} = \frac{\omega'}{k'} \tag{1.12}$$

The expression (1.12) coincides with (1.7). The phase velocity depends on the wavelength.

Previously we defined a particle as a wave packet. The velocity of propagation of the wave packet (i.e. of the particle) is called the group velocity. In accordance with equation (1.11):

$$v = \frac{x}{t} = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk} \tag{1.13}$$

The more exactly the position ☞x of the particle is known, the greater is the frequency interval $\Delta\omega$ of the waves, which build up the wave packet. That principle is called *the Heisenberg uncertainty principle*. It states that the product of uncertainties of two canonically conjugate quantities can not be less than the Planck constant. In other words, the Heisenberg uncertainty principle defines the region of the space localization of a particle when the range of the canonically conjugate momentum is given, for example for the x-direction:

$$dx dp_x \geq h \tag{1.14}$$

1.2 Density of States

Equation (1.14) can be written for *all three dimesions* in the form:

$$dx dp_x \geq h; \quad dy dp_y \geq h; \quad dz dp_z \geq h.$$

Multiplying the right and left parts of these relations we get:

$$dxdydzdp_x dp_y dp_z \geq h^3. \quad (1.15)$$

Let us define a minimal (elementary) phase cell of the six-dimensional space of coordinates and moments for a particle to be localized inside this cell using the following condition.

$$dx^0 dy^0 dz^0 dp_x^0 dp_y^0 dp_z^0 = h^3. \quad (1.16)$$

Let dZ be the number of elementary cells inside an arbitrary volume $dxdydzdp_x dp_y dp_z$ of the six–dimensional coordinates–momentum space. Obviously:

$$dZ = \frac{dxdydzdp_x dp_y dp_z}{dx^0 dy^0 dz^0 dp_x^0 dp_y^0 dp_z^0} = \frac{dVdp_x dp_y dp_z}{h^3}.$$
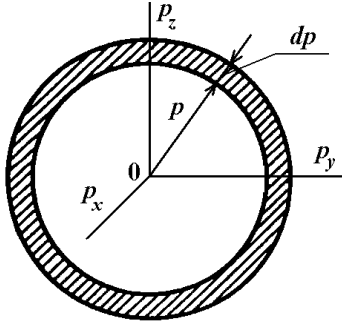
$$(1.17)$$

Fig.1.3 The spherical layer in the momentum space

The number of elementary phase cells inside the unit volume of coordinates space corresponding to an elementary volume of the momentum space can be written as follows:

$$dz = \frac{dZ}{dV} = \frac{dp_x dp_y dp_z}{h^3}. \quad (1.18)$$

Let us find the value of dz inside a spherical layer of momentum-space (Fig.1.3) between two spheres with radii p and $p + dp$. It is clear that $dp_x dp_y dp_z = 4\pi p^2 dp$ and.

$p^2 = 2mE_k = 2mE$. The kinetic energy of the particle E_k equals the total energy E, because the potential energy of a free particle is zero. According (1.4):

$$dp = \left(\frac{m}{2E}\right)^{\frac{1}{2}} dE \quad (1.19)$$

Substituting (1.19) in (1.18) we get

$$dz = \frac{2\pi(2m)^{3/2}}{h^3} E^{1/2} dE. \quad (1.20)$$

Let us find the number of elementary phase cells inside the unit energy interval. This quantity is known as **the density of states.**

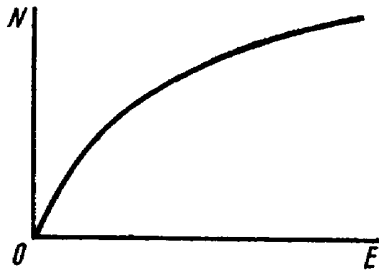$$N(E) = \frac{dz}{dE} = \frac{2\pi(2m)^{3/2}}{h^3} E^{1/2}. \quad (1.21)$$

Fig.1.4 Dependence of the state density on the free electron energy

This parabolic law describing the density of states of free electrons as function of energy is shown in Fig.1.4.

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1.3 Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = i\hbar\frac{\partial\psi}{\partial t}. \tag{1.22}$$

The Schrödinger equation describes the wave properties of particles. The motion of particles is represented by ψ - function (complex function of coordinates and time). m – mass of the particle, i –imaginary unit, U – force field, ∇^2 – the Laplas operator:

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}. \tag{1.23}$$

If U is stationary, the solution of the Schrödinger equation consists of two multipliers. The first multiplier depends on coordinates and the second depends on time.

$$\psi(x, y, z, t) = \psi(x, y, z)e^{-i(E/\hbar)t}. \tag{1.24}$$

Substituting (1.24) in (1.22), we get the *stationary Schrödinger equation*:

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - U)\psi = 0, \tag{1.25}$$

E is the total energy. The square module of ψ defines the probability dP of finding the particle inside the volume dV: $dP = \psi*\psi\, dV$. Normalization condition has the form:

$$\int \psi^*\psi dV = 1. \tag{1.26}$$

As a result of solution of the Schrödinger equation, we get the set of proper energies and proper functions. In general, it is a very tiresome task. We discuss some rather simple situations.

1.3.1 Free Electrons

Let the particle move in a positive direction of x-axis. The potential energy is zero and the Schrödinger equation can be written as:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0. \tag{1.27}$$

It is the equation of free oscillations. The solution can be written in the form:

$$\psi(x) = Ae^{i\alpha x}\cdot e^{i\omega t}, \tag{1.28}$$

$$\alpha = \sqrt{\frac{2m}{\hbar^2}E}. \tag{1.29}$$

It follows from (1.29):

$$E = \frac{\hbar^2}{2m}\alpha^2, \tag{1.30}$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} = k, \tag{1.31}$$

Taking into account (1.1), we arrive to the well-known dependence (1.4) of energy on the wave number k:

$$. E(k) = \frac{\hbar^2 k^2}{2m} \tag{1.32}$$

Thus, the spectrum of allowed energies of a free electron is continuos.

1.3.2 Step Potential Barrier

Let a free electron fall on the step barrier U (Fig.1.5). Three possible situations are under consideration: 1) $E > U$; 2) $E = U$; 3) $E < U$. The Schrödinger equation has the form:
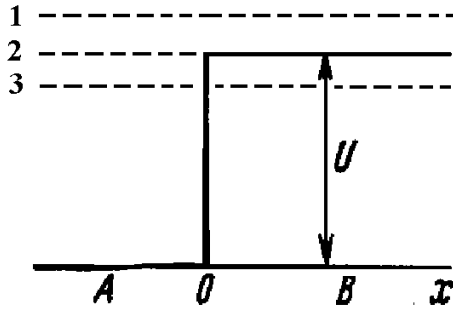
$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0, \tag{1.33}$$

$$k = \frac{1}{\hbar} \sqrt{2mE_k} \tag{1.34}$$

k is a wave number.

In region A, $E_\kappa = E$, $\psi = \psi_1$, In region B, $E_\kappa = E - U$, $\psi = \psi_2$. Hence:

$$\frac{\partial^2 \psi_1}{\partial x^2} + k_1^2 \psi_1 = 0; \tag{1.35}$$

Fig.1.5 *The step barrier*

$$\frac{\partial^2 \psi_2}{\partial x^2} + k_2^2 \psi_2 = 0, \tag{1.36}$$

$$k_1 = \frac{1}{\hbar} \sqrt{2mE} \tag{1.37}$$

$$k_2 = \frac{1}{\hbar} \sqrt{2m(E-U)} \tag{1.38}$$

The general solution of equation (1.35) and (1.36) can be written as follows:

$$\psi_1 = A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}; \tag{1.39}$$

$$\psi_2 = A_2 e^{ik_2 x} + B_2 e^{-ik_2 x}. \tag{1.40}$$

The refraction index R (analogously to optics) is defined as the ratio of the fluxes of probability i.e. as the ratio of squares of amplitudes of reflected and falling waves:

$$R = \frac{|B_1|^2}{|A_1|^2}. \tag{1.41}$$

The barrier transmission coefficient D is defined as the ratio of fluxes of transmitted and falling waves:

$$D = \frac{|A_2|^2}{|B_2|^2} \cdot \frac{k_2}{k_1} \tag{1.42}$$

The coefficient R is the probability of reflection on the interface between two regions and the coefficient D is the probability of penetration in the second region. Obviously:

$$R + D = 1, \tag{1.43}$$

.Continuity condition on the interface is:

$$\left(\psi_1\right)_{x=0} = \left(\psi_2\right)_{x=0}; \tag{1.44}$$

$$\left(\frac{\partial \psi_1}{\partial x}\right)_{x=0} = \left(\frac{\partial \psi_2}{\partial x}\right)_{x=0}. \tag{1.45}$$

For the sake of simplicity, let A=1. The barrier is not limited from the right side, it means $B_2 = 0$. Hence:

$$1 + B_1 = A_2; \quad ik_1 - ik_1 B_1 = ik_2 B_2. \tag{1.46}$$

$$B_1 = \frac{k_1 - k_2}{k_1 + k_2}; \tag{1.47}$$

$$A_2 = \frac{4k_1}{k_1 + k_2}. \tag{1.48}$$

Let us find R and D for the situations shown in Fig.1.5. 1) If $E > U$, then

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2; \tag{1.49}$$

$$D = \frac{4k_1 k_2}{\left(k_1 + k_2\right)^2}; \tag{1.50}$$

$$R + D = 1 \tag{1.51}$$

Hence, we get the result that differs from the classical one: some particles can be reflected. The less k_2, (i.e $E - U$), the greater R.

2) If $E = U$, then $k_2 = 0$ and $R = 1$, $D = 0$. In other words, the wave is totally reflected.

3) If $E < U$, then k_2 is imaginary in accordance to (1.38). Let us introduce the real quantity:

$$k = \frac{1}{\hbar}\sqrt{2m(U - E)}, \tag{1.52}$$

Then:

$$k_2 = ik. \tag{1.53}$$

$$R = \left|\frac{k_1 - ik}{k_1 + ik}\right|^2 = \frac{(k_1 - ik)(k_1 + ik)}{(k_1 + ik)(k_1 - ik)} = 1; \tag{1.54}$$

$$D = R - 1 = 0. \tag{1.55}$$

$$\psi_2 = A_2 e^{ikx} = A_2 e^{-kx}. \tag{1.56}$$

The probability to find the particle in the region B at the locality x is:

$$\psi_2 \psi_2^* = |A_2| e^{-2kx} = |A_2| e^{-\frac{2}{\hbar}\sqrt{2m(U-E)}x}. \tag{1.57}$$

This resultant does not contradict equation (1.55) if we take into account that some particles after having propagated in the region B, again enter the region A. The exponential factor in (1.57) increases very fast when x grows. For example if $U-E=1eV$ and $x=10$ Å, it is about 10^{-8}.

1.3.3 Rectangular Barrier
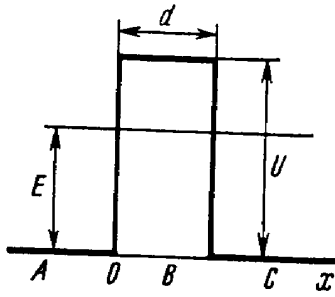

Fig.1.6 *Rectangular barrier*

Fig. 1.7 *An arbitrary potential barrier*

The motion of an electron is analogues the one just discussed. Let us resume that outside the barrier, the potential energy is zero. Inside the barrier, the potential energy is U (Fig.1.6).

We can write the Schrödinger equation for regions *A*, *B*, *C* then using continuity condition will find *R* и *D*. The wavelength in the regions *A* and *C* is the same. We get for *E*⟨*U* (having in mind $A_1 = 1$) after simple calculations:

$$D = |A_3|^2 = A_3 A_3^*$$
(1.58)

When E<U,

$$D = D_0 e^{-\frac{2}{\hbar}\sqrt{2m(U-E)}d}$$
(1.59)

When the quantity (*U*–*E*) increases, the quantity *D* decreases. Practically when *d*>150 Å, $D \approx 0$ for any *U*–*E* >0. Thus, the particles can pass through the thin barrier if the total energy *E* is less than the potential energy *U*. This phenomenon is called the ***tunnel effect.***
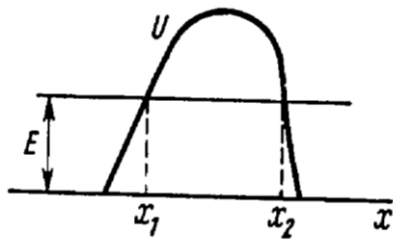
If the barrier is not rectangular, the expression (1.59) transforms in:

$$D = D_0 e^{-\frac{2}{\hbar}\sqrt{2m}\int_{x_1}^{x_2}\sqrt{(U-E)}dx}.$$
(1.60)

The magnitudes of x_1 and x_2 depend on *E* and the barrier form (Fig.1.7). For different barriers, the expressions for *D* are different. The quantity *D* can be calculated with the help of (1.60), if the function $U - E = f(x)$ is known. The quantity D_0 is about a unit.

1.3.4 Deep Rectangular Well

The deep rectangular well is shown in Fig.1.8. In the regions *A* and *C,* the potential energy equals *U*; in the region *B,* the potential energy is zero. Let us take into consideration the particles, which are located in the region *B*. Assume that $U = \infty$. Let *a* be the width of the well, and *E* be the total energy of the particle.

The depth of the well is infinite. Thus the particle can not leave the well. It means that in the region *A* and *C*, ψ = 0. The function ψ is continuos, and we have:

$$\psi(0) = \psi(a) = 0$$
(1.61)

Inside the well, the Schrödinger equation can be written as:

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0,$$
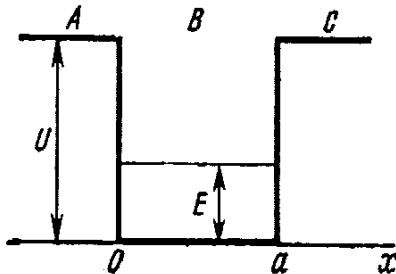(1.62)

$$k = \frac{1}{\hbar}\sqrt{2mE}.$$
(1.63)

Fig.1.8. The rectangular well

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The solution of (1.62):
$$\psi(x) = A_0 \sin(kx + \alpha). \qquad (1.64)$$
Condition (1.61) can be satisfied by proper choice of constant k и α.
If $x = 0$,
$$\psi(0) = 0 \qquad (1.65)$$
It leads to $\alpha = 0$. If $x = a$:
$$\psi(x) = A_0 \sin ka = 0, \qquad (1.66)$$
It follows that:
$$ka = n\pi, \qquad (1.67)$$
$n = 1, 2, 3, ...$, hence:
$$E = \frac{h^2}{8ma} n^2 \qquad (1.68)$$
From equation (1.68), it follows that boundary condition of the task is true only for discrete quantities of energy.

The proper functions $\psi_n(x)$ and proper energies are shown in Fig.1.9:
$$\psi_n = A_0 \sin \frac{\pi}{a} \pi x. \qquad (1.69)$$
The energy levels and squares of the wave functions (the probability density of finding an electron inside the potential well) are shown in Fig.1.10. It can be seen that if $n = 1$, the probability is maximal when $x = a/2$; if $n = 2$ there are two maximums (at $x = a/4$ and at $x = 3a/4$); if $n = 3$ – three maximums and so on.

When quantity n is great, the number of maximums is also great and the particle having the great energy can be located in the vicinity of the walls of the potential well. This circumstance can be of very importance for some problems of semiconductors and dielectrics.

1.4 Atoms. Filling of Electron Shells

In the first approximation, an atomic electron can be assumed to move in the central symmetrical field. Four quantum numbers characterize the electron:
1) principal $n = 1, 2, 3, 4, ...$;
2) orbital (angular) $l = 0, 1, 2, ..., (n - 1)$;
3) magnetic $m = 0, \pm 1, ..., \pm l$;
4) spin s $= +1/2, -1/2$.
The energy depends on n. The angular momentum of an electron depends on the quantum number l as follows:
$$p_l = \hbar\sqrt{l(l+1)} \qquad (1.70)$$

Magnetic quantum number m can be only integer. It describes the projections of angular momentum into given direction. The spin quantum number describes (in $\hbar$ units) the intrinsic angular momentum of an electron. It can be oriented parallel or anti-parallel in respect to the angular momentum.

The set of electrons having the same principal quantum number n is called the **layer.** The layers are subdivided into shells, which have the different quantum numbers l. The following notation is convenient.

The magnitude of n	1	2	3	4	5	6	7

Notation		K	L	M	N	O	P	Q

Inside the layer, the electrons with different angular numbers l build up the shells.

The magnitude of l	0	1	2	3	4	5
Notation	s	p	d	f	g	h

$s = \pm \frac{1}{2}$.

In accordance with the exclusion principle, in a single quantum state characterized by four quantum numbers, only one (or none) particle can be found . In a state characterized by three quantum numbers n, l, and m, not more than two electrons with anti-parallel spins can be found.

The number of states with different m in the interval from $-l$ to $+l$ is $2l+1$.

Hence, the maximal number of electrons inside the shell:

$$N_l = 2(2l+1). \tag{1.71}$$

$$N_n = \sum_{l=0}^{n-1} N_l = 2[1+3+\ldots+(2n+1)] = 2n\frac{1+2n-1}{2} = 2n^2. \tag{1.72}$$

Thus, we can find two electrons in K–layer, eight electrons in L–layer, eighteen electrons in M–layer l and so on. There are: two electrons in s–shell, six electrons in p–shell, ten electrons in d–shell and so on. In single atoms, s–levels are not degenerated but all the other levels are degenerated. It means that for given n and l i.e. for given E, there are $g = (2l + 1)$ different quantities of m, in other words the possible number of electrons is g. Hence, the degeneration factor g (not taking the spin into consideration) equals 3 for p-level. Thus, p-level is three times degenerated. For d-level $g = 5$. Thus, d-level is five times degenerated.

When occupying the shells, the electrons have the tendency to fill the lowest energy levels. Thus the occupation begins from the first layer. Then the second layer is filled and so on.

Unfortunately, the interaction between electrons violates this simple scheme. The first, for given n, the shells are filled in accordance with l, i.e. at first s–shell is filled, then p–shell, d–shell and so on. The second, $4s$–shell is lower than $3d$–shell, $5s$–shell is lower than $4d$–shell, and $6s$–shell is lower not only than $5d$-shell but even $4f$-shell.

The symbolic notation is used for electron states in atoms. For example, the electron configuration of the eleventh element of periodic table sodium:
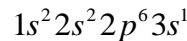
$$1s^2 2s^2 2p^6 3s^1$$

$3s$-electron is bound to atom not so strong as the others. It is called the optic or valence electron. For electrons of $_{14}Si$

Fig.11. The potential well of an isolated atom

$1s^2 2s^2 2p^6 3s^2 3p^2$. Numbers 11 and 14 correspond to number of electrons in neutral atoms. The sum of the upper indices corresponds to the number of electrons in the shells and is identical with the number of chemical element in the periodical table.

The potential well of an atom and energy levels of electrons are had shown in Fig.1.11.
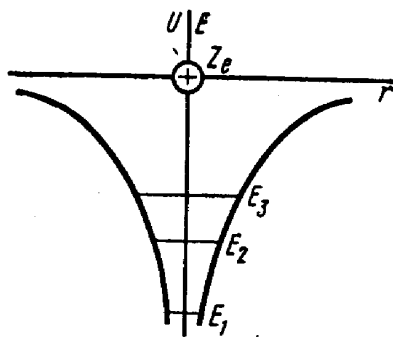
Thus, the state of electrons in atoms is discrete. It is characterized by four quantum numbers. The shells and levels are compound in accordance with these quantum quantities. The energy levels can be shown as horizontal lines inside the potential well of the atom (see Fig.1.11).