

# **Fundamentals of Quantum Physics**

Chapters 6-10 from the textbook  
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## 6. Physics of atoms and molecules

Radiation of isolated atoms in visible part of electromagnetic wave spectrum consists of individual lines. In first approximation the molecular spectrum of gases consists on strips. Solids have continuous spectra.

### 6.1 Spectrum of Hydrogen atom. Frank-Hertz experiment

**First of all it was noticed that the atom's spectrum lines are situated in definite order or series.**

The hydrogen atom is an ideal system for performing precise comparisons of theory with experiment. The emission spectrum of hydrogen includes four prominent lines that occur at visible wavelengths of 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm, respectively. In 1885 Johann Balmer found that the wavelengths of these and less prominent lines can be described by the simple empirical equation:

$$\omega = R \left( \frac{1}{2^2} - \frac{1}{m^2} \right)$$

where  $\omega$  is angular frequency,  $R$  is Rydberg constant ( $R=1.07 \cdot 10^{16} \text{ s}^{-1}$ ),  $m=3,4,5$ . The first line of the Balmer series, with wavelength 656.3 nm, corresponds to  $m=3$  in the above equation. The line at 486.1 nm corresponds to  $m=4$ , and so on. Later, in addition to the Balmer series of spectral lines, a series in far ultraviolet and infrared regions were subsequently discovered, described by similar equations.

Angular frequencies of every hydrogen spectrum line can be calculated from equation:

$$\omega = R \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$

here  $n$  is an integer number equal or greater than 1,  $m$  is an integer greater than  $n$ .

It should also be noted, that each line in the absorption spectrum of a given element coincides with a line in the emission spectrum of the element.

### 6.2 Rutherford's model of atom

In 1911 Ernest Rutherford (1871–1937) and his students Hans Geiger and Ernest Marsden performed a critical experiment which led to formulation of the planetary model of an atom. In this experiment, a beam of positively charged **alpha particles** was projected against a thin metal foil, as shown in Figure 6.1.

The results of the experiment were astounding. Most of the alpha particles passed through the foil as if it were empty space, but a few particles deflected from their original direction of travel were scattered through large angles. Some particles were even deflected backwards, reversing their direction of travel. Such large deflections were not expected on the basis of Thomson's model, used earlier. Rutherford explained these results by assuming that the positive charge in an atom was concentrated in a region that is small relative to the size of the atom. He called this concentration of positive charge the **nucleus** of the atom. Any electrons belonging to the atom were assumed to be in the relatively large volume outside the nucleus.

In order to explain why electrons in this outer region of the atom were not pulled into the nucleus, Rutherford viewed them as moving in orbits about the positively charged nucleus in the

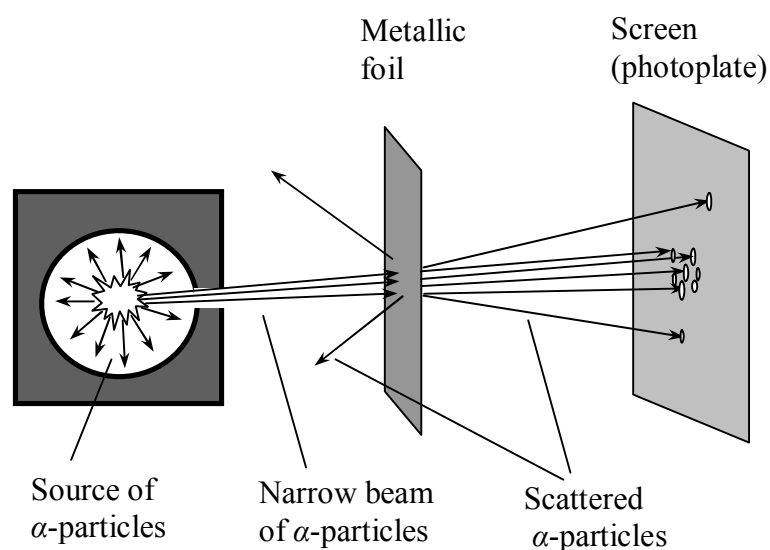


Figure 6.1

same way that planets orbit the Sun. Alpha particles themselves were later identified as the nuclei of helium atoms.

There are two basic difficulties with Rutherford's planetary model.

1. An atom emits waves of certain discrete characteristic frequencies of electromagnetic radiation and no others; the Rutherford model is unable to explain this phenomenon.
2. The electrons in Rutherford's model undergo a centripetal acceleration as they orbit a nucleus. According to Maxwell's theory of electromagnetism, centripetally accelerated charges revolving with frequency  $\nu$  should radiate electromagnetic waves of the same frequency. Unfortunately, this classical model leads to disaster when applied to the atom. As the electron radiates energy, the radius of its orbit steadily decreases and its frequency of revolution increases. This leads to an ever-increasing frequency of emitted radiation and a rapid collapse of the atom as the electron spirals into the nucleus.

### 6.3 Bohr's postulates. Frank-Hertz experiment

In 1913 Bohr developed a model of the simplest atom, hydrogen, in an attempt to explain why the atom was stable and why do atoms of a given element emit only certain spectral lines. His model of the hydrogen atom contains some classical features, as well as some revolutionary postulates that could not be justified within the framework of classical physics.

**The postulates of Bor's theory are following**

1. Only certain electron orbits are stable. These are orbits in which atom doesn't emit energy in the form of electromagnetic radiation. The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum:

$$L = m \vartheta_n r_n = n\hbar .$$

The allowed orbits are those for which the electron's orbital angular momentum  $L$  about the nucleus is proportional to  $\hbar$  (pronounced "h bar"), where  $\hbar = \frac{h}{2\pi}$  (Plank's constant  $h$  over  $2\pi$ ),  $n$  is number of orbit,  $r$  is radius of orbit,  $\vartheta_n$ -electron's velocity on orbit of number  $n$ .

2. Radiation is emitted by the hydrogen atom when the electron "jumps" from a more energetic initial state to a less energetic state. The "jump" can't be visualized or treated classically. In particular, the frequency  $\nu$  of the radiation emitted in the jump is related to the change in the atom's energy and is *independent of the frequency of the electron's orbital motion*. The angular frequency of the emitted radiation is given by formula:

$$\omega_{mn} = \frac{E_m - E_n}{\hbar}$$

where  $E_m$  is energy of initial state on  $m^{\text{th}}$  level and  $E_n$  is energy of final state on  $n^{\text{th}}$  level. Existence of discrete energetic levels was confirmed by Frank-Hertz's experiment.(Fig.6.2)

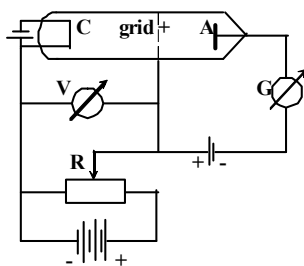


Fig. 6.2

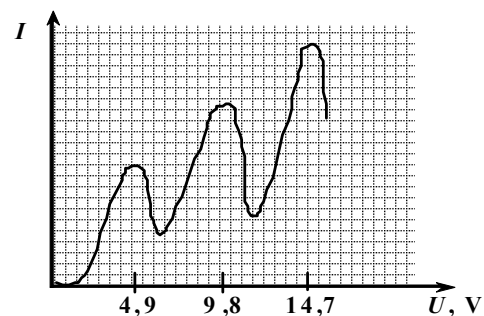


Fig.6.3

The tube with mercury vapor (the pressure in the tube was about 1mm Hg) has three electrodes-cathode C, positively charged grid, anode A (collecting electrons). As is shown on Fig. 6.3, the current  $I$  in anode-cathode circuit increase with increasing the voltage  $U$  until it reaches  $U=4.9\text{V}$ .

Then it drops sharply and begin to increase again. The repeated current maxima take place at  $U=9.8\text{V}$ ,  $14.7\text{V}$ , etc. Such regularity is explained by the fact that atoms can absorb energy only by portion  $\Delta E=E_2-E_1$ ,  $\Delta E$  is the difference of between stationary levels  $E_2$  and  $E_1$ .

## 6.4 Bor's model of Hydrogen

With these assumptions, we can calculate the allowed energies and emission angular frequency (wavelengths) of the hydrogen atom.

1) We know from the first postulate that orbital angular momentum  $L = m\mathcal{G}_n r_n = n\hbar$ .

2) Energy of the atom remains constant, and classical mechanics can be used to describe the electron's motion. From Newton's second law for the electron on a stable orbit we obtain

$$\frac{m\mathcal{G}^2}{r} = \frac{e}{4\pi\epsilon_0 r^2} \quad (Z=1, \text{ for hydrogen})$$

3) thus  $\frac{nh}{mr} = \mathcal{G}$

4) after substitution of  $\mathcal{G}$ , we find radius  $r$  and energy  $E$  of hydrogen atom on level number  $n$

$$r_n = \frac{4\pi\epsilon_0}{me^2} n^2 \hbar^2, \quad E_n = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}.$$

Difference between energies  $E_m$  and  $E_n$  of levels  $m$  and  $n$  is  $\Delta E = \frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$ .

This equation and Bohr postulate show that if the electron jumps from one orbit with quantum number  $m$  to a second orbit with quantum number  $m$ , it emits a photon angular frequency

$$\omega = R' \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$

Comparing this formula and Balmer's formula we see that Rydberg's constant  $R' = \frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^3}$ .

## 6.5 Merits and demerits of Bohr theory

Bohr's theory successfully predicts the wavelengths of all the observed spectral lines of hydrogen and hydrogen-like atoms, which has one electron, rotating around nucleus. But attempts to extend the Bohr theory to more complex, multi-electron atoms, were unsuccessful.

Bohr's theory was not able to explain why the angular momentum of the electron was restricted to these discrete values. Ten years later, de Broglie, one of quantum mechanics creator, gave a direct physical way of interpreting this condition. He assumed that an electron orbit would be stable (allowed) only if it contained an integral number of electron wavelengths.

**Quantum mechanics is in agreement with classical physics when the energy differences between quantized levels are very small.** This principle, first formulated by Bohr, is called the **correspondence principle**.

### Problem

During bombardement of hydrogen atom by electrons only one line in hydrogen spectrum is observed. Find the energy range for these electrons

**Strategy.**

Angular frequencies of every hydrogen spectrum line can be calculated from Balmer's formula for series of spectral lines:  $\omega = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$ . Energy, which is needed to transfer atom of hydrogen from one state to another is determined by formula:  $\hbar\omega = R\hbar\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$

### Solution

1) Energy, which is needed to transfer atom of hydrogen to the first excited state (n=1, m=2):

$$\hbar\omega = R\hbar\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 10.2 \text{ eV.}$$

2) Energy, which is needed to transfer atom of hydrogen to the second excited state (n=1, m=3)

$$\hbar\omega = R\hbar\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 12.1 \text{ eV.}$$

Hence, atom of hydrogen will have only one spectrum line if bombarding electrons will have energy  $W$  in range:  $10.2 \text{ eV} \leq W \leq 12.1 \text{ eV}$ .

## 7. Elements of quantum mechanics

### 7.1. De Broglie hypothesis

Light has dual (wave-particle) properties and can be described by equations derived in previous section:

$$\varepsilon_{ph} = \hbar\omega = h\frac{c}{\lambda} - \text{photon energy}$$

$$p_{ph} = \frac{\hbar\omega}{c} = \frac{h}{\lambda} - \text{photon linear momentum.}$$

To explain Bohr's postulates, in 1924 de Broglie suggested, that if **the photons have wave and particle characteristics, then all forms of matter have** dual (particle-wave) nature. He hypothesised that *all* material particles with momentum  $p$  should have a characteristic wavelength  $\lambda = h/p$  in analogy to photon wavelength. As the momentum of a particle of mass  $m$  and speed  $\vec{v}$  is  $\vec{p} = m\vec{v}$ , **de Broglie wavelength** of a particle is

$$\lambda = \frac{h}{p} = \frac{h}{m\vec{v}}$$

According to de Broglie, electrons, just like light, have a dual particle-wave nature.

Experiments performed in 1927 by Davisson and Germer (Fig. 7.1.a), Thomson and independently by Tartakovsky (Fig. 7.1.b) confirmed the wave properties of electrons.

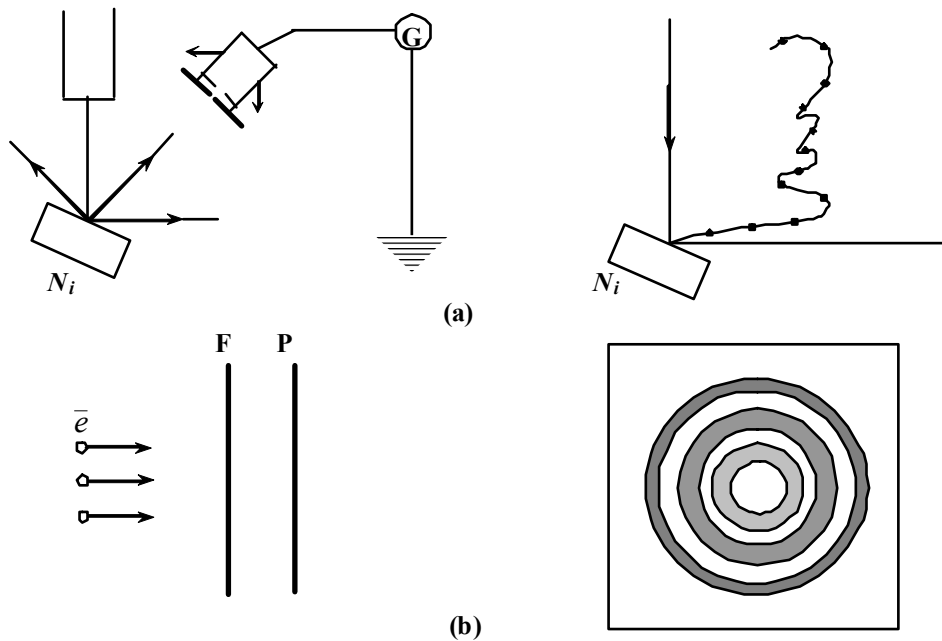


Fig.7.1

Davisson and Germer performed extensive diffraction measurements (experimental setup is shown in the left panel of Fig.7.1a) on electrons reflected from single-crystal *Ni* targets. Measuring the current through the galvanometer G they obtained information on the intensity of electron reflection, which appeared to have maxima at some values of incidence angle, which are characteristic for wave diffraction. This result proved the wave nature of electrons and confirmed de Broglie relation  $\lambda=h/p$ . The same year, G.P. Thomson and P.S. Tartakovsky also observed electron diffraction patterns by passing electrons through very thin gold foils F (Fig.7.1b, left panel) and result was similar to the result of X-ray diffraction. Diffraction patterns have since been observed for helium atoms, hydrogen atoms, and neutrons. Hence, the universal nature of matter waves has been established.

A practical devices that relies on the wave characteristics of electrons are the **electron microscope, the semiconductor electronics (electronic chips, etc).**

## 7.2. Heisenberg uncertainty principle

In classical mechanics there is no fundamental barrier to a refinement of the apparatus or experimental procedures and to improve the experimental precision thus eliminating uncertainty of the measured quantity. In other words, classical mechanics, in principle, allows making a measurement with arbitrarily small uncertainty. Quantum theory predicts, however, that uncertainties can not be eliminated in principle. In 1927, Werner Heisenberg introduced this notion, which is now known as the **uncertainty principle**:

**If a measurement of the particle's position is made with precision  $\Delta x$  and a simultaneous measurement of linear momentum is made with precision  $\Delta p_x$ , then the product of the two uncertainties can never be smaller than  $\hbar/2$ :**

$$\Delta x \cdot \Delta p_x \geq \hbar/2.$$

Another form of the uncertainty relationship sets a limit on the accuracy with which the energy  $E$  of a system can be measured in a finite time interval  $\Delta t$ :

$$\Delta E \cdot \Delta t \geq \hbar/2.$$

It can be inferred from this relationship that the energy of a particle in a stationary state cannot have a definite value but has a finite energy width inversely proportional to lifetime during

which an electron resides in this state. In spectroscopy this results in a finite natural linewidth of atomic spectra which can not be explained within Bohr's theory.

When an electron is viewed as a particle, the uncertainty principle tells us that (a) its position and velocity cannot both be known precisely at the same time and (b) its energy can be uncertain for a period given by  $\Delta t = \hbar / E$

The meaning of Heisenberg uncertainty principle is clarified by the next example (see figure 7.2). If the particle is dissipated on a slit with the width  $\Delta x$ , additional linear momentum component  $\Delta p_x$  can appear and the particle can be deflected from its original direction of motion.

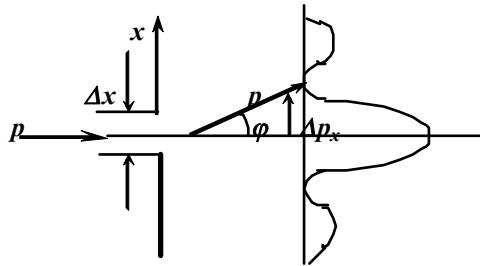


Fig. 7.2

Then:

1)  $\Delta p_x = p \sin \phi$  (as result of diffraction on slit)

2)  $\Delta x \sin \phi = \lambda$  (The first minimum or the edge of the first maximum)

3)  $\lambda = \frac{h}{p} = \frac{h}{\Delta p_x} \sin \phi$

4)  $\Delta x \sin \phi = \frac{h}{\Delta p_x} \sin \phi$  (after substitution step 3 into step

2)

5) As result we have:  $\Delta p_x \Delta x = h$

The last formula is in accordance with formulation of the Heisenberg uncertainty principle for momentum and position. Thus, the notion of particle's trajectory has limited application. At some circumstances the motion of particle can be viewed as particle follows defined trajectory. Example of such situation is electron's path in cathode ray tube.

### 7.3 Wave function. Shroedinger equation

The Schrödinger wave equation represents a key element in quantum mechanics. **It's as important in quantum mechanics as Newton's laws in classical mechanics.** Each particle is represented by a wave function that depends both on position and on time.

In general case the Shroedinger's equation is written in form:

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

The Shroedinger's equation for stationary (time independent) case has the following form:

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

here  $m$  is mass of micro particle;  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is Laplacian differential operator;  $x, y, z$

are coordinates of micro particle;  $\psi$  is the wave function;  $E$  is energy of the particle,  $U$  is potential energy of the particle,  $i = \sqrt{-1}$ .

The above equations are the differential equations of second order. Solving Schrödinger's equation (this mathematical procedure is beyond the scope of this course) determines the wave function  $\psi$ . The wave function and derivative of wave function are finite, one valued, continuous.

Once a quantity  $\psi$  is found,  $|\psi|^2$  can be calculated. The value of  $|\psi|^2$  gives information on the **probability** (per unit volume) of finding the particle in any given region  $dV$ . Probability  $dP = |\psi|^2 dV$ . The condition of probability normalization follows from definition of wave

function  $\int_{-\infty}^{\infty} \psi \psi^* dV = 1$ . Here  $\psi^*$  is the function conjugated to  $\psi$ . This condition shows that presence of particle somewhere in space is reliable event and it's probability have to be equal one.

To understand the sense of quantity  $|\psi|^2$ , we return to experiment involving coherent light passing through a double slit.

1. First, recall that the intensity of a light beam is proportional to the square of the electric field strength  $E$  associated with the beam:  $I \sim E^2$ . According to the wave model of light, there are certain points on the viewing screen where the net electric field is zero as a result of destructive interference of waves from the two slits. Because  $E$  is zero at these points, the intensity is also zero, and the screen is dark there. Likewise, at points on the screen at which constructive interference occurs,  $E$  is large, as is the intensity; hence, these locations are bright.

2. Consider the same experiment when light is viewed as having a particle nature. The number of photons reaching a point on the screen per second increases as the intensity (brightness) increases. Consequently, the number of photons that strike a unit area on the screen each second is proportional to the square of the electric field, or  $N \sim E^2$ . From a probabilistic point of view, a photon has a high probability of striking the screen at a point at which the intensity (and  $E^2$ ) is high and a low probability of striking the screen where the intensity is low.

When describing particles rather than photons,  $|\psi|$  rather than  $E$  plays the role of the amplitude. Using an analogy with the description of light, we make the following interpretation of  $|\psi|$  for particles: If  $|\psi|$  is a wave function used to describe a single particle, the value of  $|\psi|^2$  at some location at a given time is proportional to the probability per unit volume of finding the particle at that location at that time. Adding up all the values of  $|\psi|^2$  in a given region gives the probability of finding the particle in that region.

#### 7.4. Hydrogen atoms in quantum mechanics

One of the first great achievements of quantum mechanics was the solution of the wave equation for the hydrogen atom. In case of hydrogen atom it has the following form:

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left( E + \frac{e^2}{r} \right) \psi = 0$$

where  $r$  is coordinate of electron in hydrogen atom and potential energy of electron in the field of nucleus is  $U = -\frac{e^2}{r}$ . The details of the solution are far beyond the scope of this course, but we'll describe its properties and implications for atomic structure.

According to quantum mechanics, the energies of the allowed states are in exact agreement with the values obtained by the Bohr theory, when the allowed energies depend only on the principal quantum number  $n$ :

$$E = -\frac{me^4}{\pi^2 \hbar^2} \cdot \frac{1}{n^2}.$$

The wave function found from the Shroedinger's equation for Hydrogen atom appears to depend not only on the principal quantum number  $n$  but also on quantum numbers  $l$  and  $m$ :  $\psi = \psi_{nlm}$ . The quantum number  $l$  is called the **orbital quantum number**, and  $m$  is called the **orbital magnetic quantum number**.

The value of  $n$  (*general quantum number*) is integer.

The value of  $l$  (*orbital quantum number*) can range from 0 to  $n - 1$  in integer steps.

The value of  $m$  (*magnetic quantum number*) can range from  $-l$  to  $+l$  in integer steps.

From these rules, it can be seen that for a given value of  $n$ , there are  $n$  possible values of  $l$  while for a given value of  $l$  there are  $2l+1$  possible values of  $m$ . For example, if  $n = 1$ , there is only 1



value of  $l$ :  $l=0$ . For  $l=0$  one has  $2l+1=1$  and there is only one value of  $m$ , which is  $m=0$ . If  $n=2$ , the value of  $m$  may be 0 or 1; if  $l=0$ , then  $m=0$ , but if  $l=1$ , then  $m$  may be 1, 0, or -1.

### 7.5. Pauli exclusion principle

To explain an unusual results obtained in Stern–Gerlach experiment with Ag atom in inhomogeneous magnetic field (the separation of atomic flow in two parts only), the spin magnetic quantum number  $s$ , has to be introduced. The results of this experiment indicates that spin angular momentum  $s$  has two opposite directions and magnitude equal to  $+1/2$  or  $-1/2$ .

The Stern–Gerlach experiment involves sending a beam of particles through magnetic field and observing their deflection (Fig.7.3) in homogenous ( $H \neq 0$ ,  $dH/dz=0$ ) and inhomogeneous magnetic field ( $H \neq 0$ ,  $dH/dz \neq 0$ ) from the direction of beam without magnetic field ( $H=0$ ).

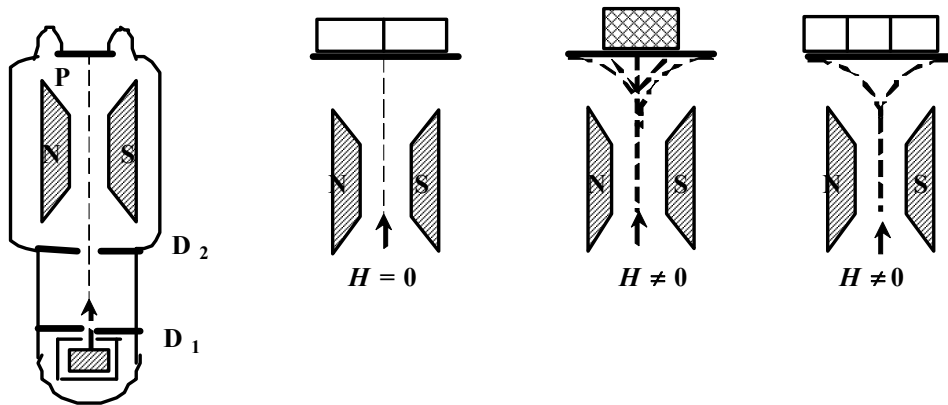


Fig. 7.3

Thus, there are four quantum numbers, which are characteristics of electron state in atom. And in general, for a given value of  $n$  there are  $2n^2$  states with distinct values of  $l$  and  $m$  and  $s$ .

The question, how many electrons in an atom can have a particular set of quantum numbers was answered by Pauli in 1925 in a powerful statement known as the **Pauli exclusion principle**:

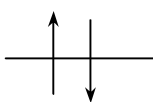
**No two electrons in an atom can ever have the same set of values for the set of quantum numbers  $n$ ,  $l$ ,  $m$  and  $s$ .**

The Pauli exclusion principle explains the electronic structure of complex atoms as a succession of filled levels with different quantum numbers increasing in energy, where the outermost electrons (so called valence electrons) are primarily responsible for the chemical properties of the element.

If this principle weren't valid, every electron would end up in the lowest energy state of the atom and the chemical behaviour of the elements would be grossly different.

Totality of electrons with the same number  $n$  forms the shell of electrons (it is denoted **K**, **L**, **M**, **N**...), which subdivides into subshells (denoted **s**, **p**, **d**, **f**...). Subshells differs by the number  $l$ .

As a general rule, the order of filling an atom's subshell by electrons is as follows: **once one subshell is filled, the next electron goes into the vacant subshell that is lowest in energy. If the atom were not in the lowest energy state available to it, it would radiate energy until it reached that state. A subshell is filled when it contains  $2(2l+1)$  electrons (Figure 7.4).**



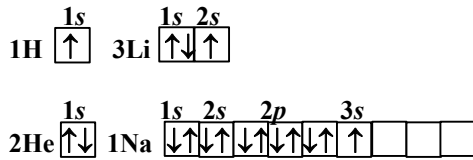


Figure 7.4

**As result one gets periodic system of elements.**

The first element in the periodic table, *Hydrogen* has only one electron, which, in its ground state, can be described by either of two sets of quantum numbers: 1, 0, 0, + 1/2 or 1, 0, 0, -1/2 . The electronic configuration of this atom is often designated as  $1s^1$ . The notation  $1s^1$  refers to a state for which  $n = 1$  and  $l = 0$ , and the superscript indicates that one electron is

present in this level.

Neutral *helium* has two electrons. In the ground state, the quantum numbers for these two electrons are 1, 0, 0, +1/2 and 1, 0, 0, -1/2. No other possible combinations of quantum numbers exist for this level, and we say that the K shell is filled. The helium electronic configuration is designated as  $1s^2$ .

Neutral *lithium* has three electrons. In the ground state, two of these are in the 1s subshell and the third is in the 2s subshell, because the latter is lower in energy than the 2p subshell. Hence, the electronic configuration for lithium is  $1s^2 2s^1$ .

The eleventh element, Na has completely filled shells K and L and one electron in subshell 3s. Its electron configuration is:  $1s^2 2s^2 2p^6 3s^1$ . The outer 3s electron is weakly connected with other electrons. So the properties of Na are similar to the properties of Li with configuration  $1s^2 2s^1$ .

**7.6. Molecular spectra**

Cohesion (chemical bonding) between atoms in molecules may be homeopolar or heteropolar. It depends on electron configuration in molecule. Chemical bonding of first type can be covalent or atomic. Chemical bonding of second type is ionic. Ionic molecules are created as result of transformation of interacting atoms into ions with opposite electrical charge. Typical ionic molecules are NaCl ( $\text{Na}^+\text{Cl}^-$ ), CsCl ( $\text{Cs}^+\text{Cl}^-$ ). Homeopolar bonding is created by electron pairs with antiparallel spins.

The most simple of such molecules is molecule of Hydrogen. It was shown that at rapprochement of atoms with anti parallel spins molecule energy increases at  $r \rightarrow r_0$  (Fig. 7.5). At rapprochement of atoms with antiparallel spins molecule energy decreases and such joining up is profitable.

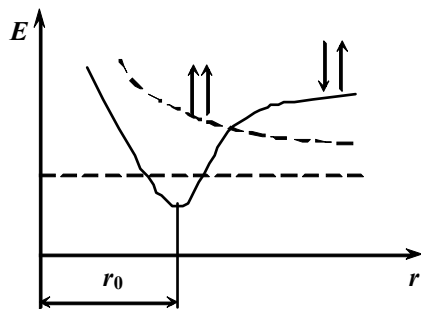


Figure 7.5

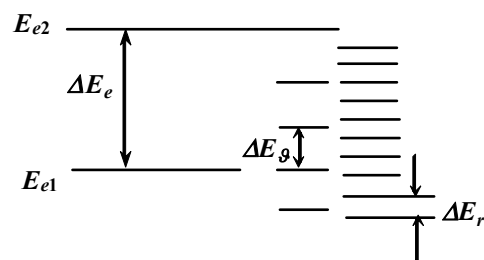


Figure 7.6

Molecular spectrum is conditioned by: energy of electron shell  $E_e$ , energy of vibrational motion of atoms  $E_g$ , energy of rotational motion of atoms  $E_r$ :

$$E = E_e + E_g + E_r .$$

From quantum mechanics it is known that energy of vibrational motion  $E_g = \left(g + \frac{1}{2}\right)\hbar\omega$ . Here  $g$  is vibrational quantum number ( $g=1, 2, 3\dots$ ) and energy of rotational motion  $E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I} = \frac{\ell(\ell+1)}{2I}$ , where  $I$  is moment inertia of molecule,  $\omega$  is atom's angular velocity around rotation center of molecule;  $L=I\omega$  is molecule's angular momentum. Spectrum of molecule is shown on Fig.7.6. Molecular spectra are composed from groups of closely spaced energy levels

$$\Delta E_r \ll \Delta E_g \ll \Delta E_e.$$

The nearest levels correspond to rotational degrees of freedom. Vibrational motions require larger amounts of energy to be given to molecule.

### Problem.

Consider behaviour of electron in potential one-dimensional box (Figure 7.7), if potential box has rectangular walls and motion of electron is limited by the walls of box at  $x=0$  and  $x=l$ . The potential energy  $U=0$  for  $0 \leq x \leq l$  and  $U=\infty$  for  $0 > x > l$ . Find the wave function  $\psi$ , the energy spectrum  $E$ , difference  $\Delta E$  between energies  $E_m$  and  $E_n$  of levels  $m$  and  $n$ .

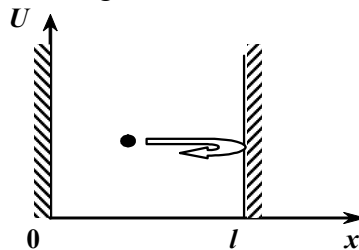


Figure 7.7

### Strategy.

As the potential energy  $U=0$  for  $0 \leq x \leq l$  and  $U=\infty$  for  $0 > x > l$ , the electron can not get outside box's borders and so on the borders of box  $\psi(0)=0$  and  $\psi(l)=0$ . Write and solve one-dimensional Shroedinger's equation for stationary (time independent) case.

### Solution

1) One-dimensional Shroedinger's equation for stationary (time independent) case, if  $U=0$  has the form:

$$\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2} + E\psi = 0, \text{ or } \quad \psi'' + \frac{2m}{\hbar^2} E\psi = 0$$

2) Denote  $\omega^2 = \frac{2m}{\hbar^2} E$ , then  $\psi'' + \omega^2\psi = 0$

3) From the theory of oscillation solution of such equation is well known and can be expressed by formula:  $\psi = \psi_0 \sin(\omega x + \alpha)$ .

4) If  $\psi(0)=0 \rightarrow \alpha=0$  and  $\psi(l) = \psi_0 \sin \omega l = 0$ , then has to be  $\omega l = \pm \pi n$

5)  $\omega^2 = \frac{2m}{\hbar^2} E$ , so  $\omega^2 = \frac{\pi^2 n^2}{l^2} = \frac{2mE_n}{\hbar^2}$

6) As result we obtain the energy of  $n$ -level:  $E_n = \frac{\pi^2 \hbar^2}{2l^2} n^2$

7) Difference  $\Delta E$  between energy levels  $E_m$  and  $E_n$  is  $\Delta E = E_m - E_n$

8) After substitution one finds:  $\Delta E = \frac{\pi^2 \hbar^2}{2ml^2} ((n+1)^2 - n^2) = \frac{\pi^2}{2ml^2} \hbar^2 (2n+1) \approx \frac{\pi^2}{ml^2} \hbar^2 \cdot n$

9) The wave function  $\psi = \psi_0 \sin \omega x = \psi_0 \sin \frac{\pi n}{l} x = \sqrt{\frac{2}{l}} \sin \frac{\pi n}{l} x$  for three values of  $n$  are shown on figure 7.8.  $\psi_0 = \sqrt{\frac{2}{l}}$  due to normalizing condition for the wave function (see Sect.7.3).

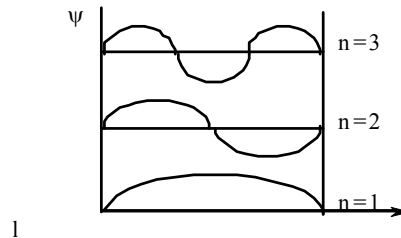


Figure 7.8

## Conclusions

Results of solution:

1. Energy of electron is quantized and depends on dimensions of box, mass of particle, number  $n$  (principal quantum number).
2. Wave function and square of wave function depend on dimensions of box, coordinate  $x$  and number  $n$ . One can see from fig. 7.8 that the probability distribution of finding the particle in particular position is non-uniform.

## 8. Absorption, spontaneous and induced radiation

### 8.1. Spontaneous and induced radiation. Principle of detailed equilibrium

The processes of light absorption are stimulated processes in all cases. As was predicted by Einstein, the processes of radiation may be either spontaneous or stimulated (induced).

An atom will emit radiation only at certain frequencies that correspond to the energy separation between the various allowed states. Consider an atom with many allowed energy states, labeled  $E_1, E_n, E_m$ , as shown in figure 8.1.

1. When light is incident on the atom, only those photons can be absorbed by the atom whose energy  $\hbar\omega$  equals the energy separation  $\Delta E$  between two levels. A schematic diagram representing this **stimulated absorption process** is shown in figure 8.1. At ordinary temperatures, most of the atoms in a sample are in the ground state. If a body containing many

atoms is illuminated with a light beam containing all possible photon frequencies (that is, a continuous spectrum), only those photons of energies  $E_2 - E_1, E_3 - E_1, E_4 - E_1$ , and so on, can be absorbed.

2. As a result of this absorption, some atoms are raised to various allowed higher energy levels, called **excited states**. Once an atom is in an excited state, there is a constant probability that it will jump back to a lower level by emitting a photon, as shown in Figure 8.1. This process is known as **spontaneous emission**. Typically, an atom will remain in an excited state for only about  $10^{-8}$  s.

3. **From the thermodynamic principle of detailed equilibrium** a third process that take place in lasers is important. It is **stimulated emission**. Suppose an atom is in the excited state  $E_2$ , and a photon with energy  $\hbar\omega = E_2 - E_1$  is incident on it. The incoming photon increases the probability

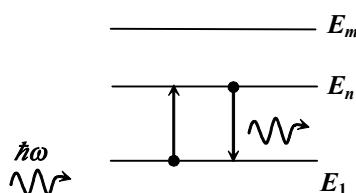


Fig.8.1

that the excited atom will return to the ground state and thereby emit a second photon having the same energy  $\hbar\omega$ .

The two identical photons result from stimulated emission: the incident photon and the emitted photon. *The emitted photon is exactly in phase with the incident photon.* These photons can stimulate other atoms to emit photons in a chain of similar processes. The many photons produced in this fashion are the source of the intense, coherent (in phase), monochromatic radiation in a laser.

Stimulated emission has following features:

1. Frequency of stimulated emission coincides with induced radiation frequency.
2. Direction of stimulated emission and its polarization are the same as induced radiation.
3. Probability  $P_{mn}$  of stimulated emission transitions from energy level  $m$  to the energy level  $n$  is proportional to the flow of induced radiation,  $u_\omega$ :  $P_{mn} = B_{mn}u_\omega$ , here  $B_{mn}$  is called Einstein coefficient.
4. It follows from equilibrium of transitions probability  $n \rightarrow m$  and  $m \rightarrow n$ , that:

$$P_{mn} = P_{nm}.$$

Number of stimulated transitions  $N^{st}$  is :

$$\boxed{N_{mn}^{(st)} = P_{mn} N_m = B_{mn} u_\omega N_m}$$

$$\boxed{N_{nm}^{(st)} = P_{nm} N_n = B_{nm} u_\omega N_n}$$

The two processes are equally probable. When light is incident on a system of atoms, there is usually a net absorption of energy, because when the system is in thermal equilibrium, **there are many more atoms in the ground state than in excited states.**

If the situation can be inverted so that there are more atoms in an excited state than in the ground state, a net emission of photons can result. This is one of conditions to create the such type of light source as Laser.

## 8.2. Lasers

Lasers (an acronym for **light amplification by stimulated emission of radiation**) are modern devices, which are used in different areas of science, industry, medicine.

To produce the laser's radiation it is necessary:

1. to create a material with special system of energy levels, one of which is to be metastable energy level;
2. to create **population inversion of energy levels** in material (medium of radiation), the fundamental principle involved in the operation of a laser;
3. to ensure the situation, when absorption coefficient of medium  $\mu < 0$ .

**One of the first solid state lasers that exhibits stimulated emission of radiation is ruby laser.** Figure 8.2 is an energy-level diagram for the  $\text{Cr}^{+++}$  atom in ruby crystal.

The amplification corresponds to a creation of photons in the system. To ensure the amplification, the system must be in a state of population inversion, that is, more atoms in an excited state than in the ground state. The excited state of the system must be a *metastable state*, which means its lifetime must be long ( $\tau_m \sim 10^{-3}$  s) compared with the otherwise usually short lifetimes of excited states ( $\tau_e \sim 10^{-8}$  s). When that is the case, stimulated emission will occur before spontaneous emission.

The scheme of laser head is shown on Figure 8.3. The emitted photons must be confined within the system long enough to allow them to stimulate further emission from other excited atoms. This is achieved by the use of reflecting mirrors at the ends of the system. One end is totally reflecting, and the other is slightly transparent to allow the laser beam to escape.

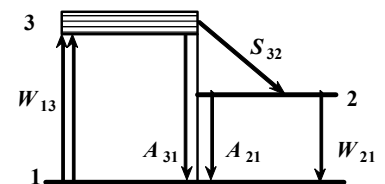


Figure 8.2

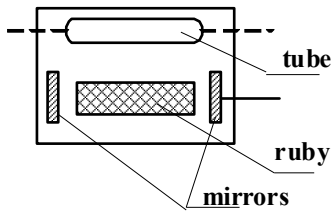


Figure 8.3

The tube emits the light and it raise atom of  $\text{Cr}^{+++}$  in ruby to excited states. Atoms are excited to state 3 from the ground state 1 (see fig. 8.2). When atom makes a transition to metastable state 2, it stimulates emission by excited atoms. This results in the production of coherent light with a wavelength of 693.4 nm. Figure 8.2 summarizes the steps in the production of a laser beam and figure 8.4 shows the block-scheme of laser technological automatic setting.

Here :

- 1. is laser head,
  - 2,3 are power units,
  - 4 is indication system of laser radiation parameters,
  - 5 is system of laser beam control,
  - 6 is object of laser treatment,
  - 7 is two coordinate table,
- Efficiency of the first solid state lasers was about 0,5%. Modern semi-conducting lasers have the greatest efficiency which can reach 35%.

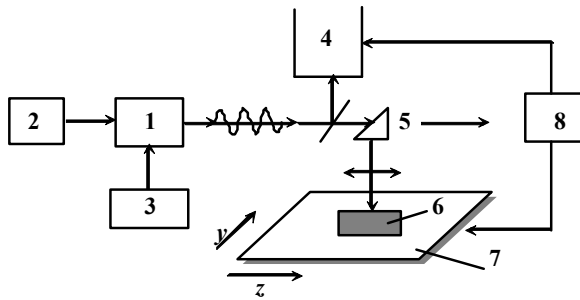


Figure 8.4

**General applications of lasers** are: medicine, biology, technology of material treatment (laser heat treatment and laser shock wave treatment), measurements of distances between objects and object's dimensions, laser's communications, holograms (based on interference and diffraction, the principles are shown in fig.8.4).

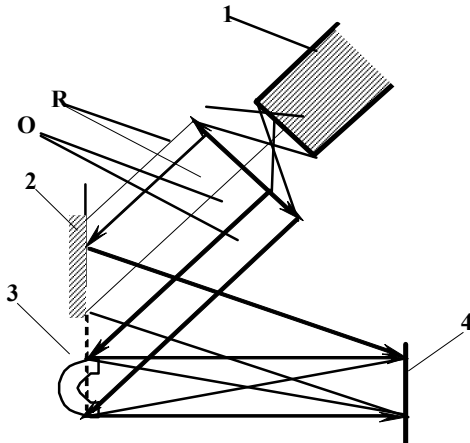


Figure 8.4 a. Recording a hologram: 1 – laser, 2 – mirror, 3 – object, 4 – photographic plate. A hologram is made by splitting a laser beam into two beams (R-reference beam, O-object beam) and then reuniting them on the film

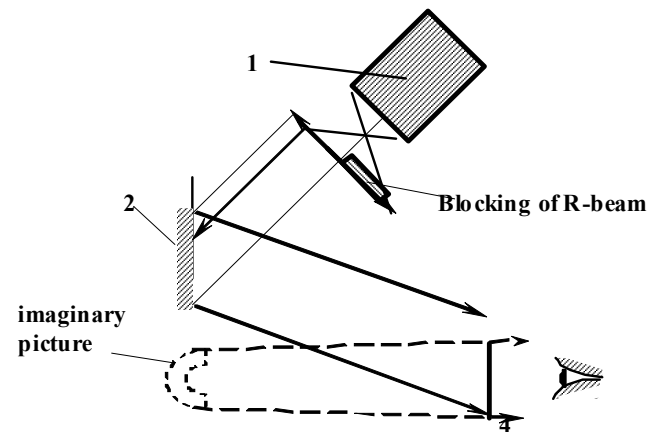


Fig.8.4b Recovery of object's image from photographic plate 4

In future lasers will serve as sources of power energy to initiate nuclear fusion processes (called laser nuclear synthesis).

## 9. Solid state physics

### 9.1. Chemical bonding and internal structure of solids

Solids maintain constant form and volume.

Principal types of chemical bonding and forces of interaction between atoms are:

### 1. ionic, 2. covalent (homopolar), 3. metallic, 4. Van der Waals bonding.

The ionic and covalent bonds are "strong" ones. In comparison with this type of bond the metallic bond is weak. The Van der Waals is the weaker bond. The nature of bond is determined by type of interaction between electrons and nuclei in substance.

There are two types of solid substances: crystals and amorphous substance.

Crystals have regular external form and periodical disposition of its particles. The periodical disposition of particles (atoms) is called crystal lattice, particles equilibrium positions are called sites. The distance between sites is called period of crystal lattice. There is a special classification of lattice types, called syngonies, which differ one from another by number of symmetry elements. Some examples (rotation around axis, reflection in plane, etc) are shown in figure 9.1.

The most perfect syngony is cubic, which has the greatest number of symmetry elements. Solid crystals are distinguished by the sort of atoms and types of chemical bonding as well as forces of interaction between atoms.

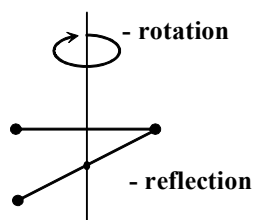


Figure 9.1

Symmetry is ability of figure to be self dual after some operations of spatial displacement. The cubic syngony is the most perfect one.

The smallest element of crystal lattice is elementary cell. Any crystal can be constructed by translation of elementary cell.

The main peculiarity of physical properties of crystals is anisotropy (its properties are different in different directions).

Ideal crystals would exhibit a perfect periodicity of atoms in crystal lattice. Real crystals, however, have some amount of crystallographic defects which are deviations from regular pattern in atomic distribution.

One distinguishes between point defects, which are vacancies, interstitial atoms or impurity atoms, and line defects, which are edge dislocation and screw dislocations. Planar and bulk defects are also possible in real crystals. Vacancy is a lattice site unoccupied by atom. It causes a distortion of crystal field as the neighboring atoms are shifted towards the vacancy. Interstitial defect occurs when atom occupies position not in the lattice site but in between the atoms in their lattice sites. Interstitial defects and vacancies can be created in pair when an atom jumps out its site. During the crystal growth, atoms of the different chemical nature can be incorporated into the lattice. As different atoms have different radii, this also produces a local distortion, being a substitutional defect. Edge dislocations are the imperfect atomic planes terminated inside crystal and screw dislocations can be visualised as a displacement of atoms, at which one can move from one atomic plane to another along the helical path around the dislocation line without jumping to other plane but as if going up the stairs.

The presence of crystallographic defects greatly influences mechanical, electrical and optical properties of crystals. To avoid creation of defects, special conditions have to be maintained during the crystal growth which can be assured only in scientific or industrial laboratory with controlled temperature, pressure and chemical composition of the medium. Growth from the liquid phase and vapour phase epitaxy are the modern methods used for creating crystals with 99.9999% purity and perfectness or to introduce, if needed, the desired impurity in predetermined proportion.

## 9.2. Fundamentals of quantum theory of specific heat. Phonons

### 9.2.1 Heat capacity of ideal gas and solids in classical physics.

For ideal gas molar specific heats of gases at constant pressure  $C_p = C_V + R$ , here  $C_V$  is molar specific heat of gases at constant volume,  $R$  is universal gas constant.

It follows from thermodynamics that the molar specific heat at constant volume can be calculated from the internal energy function as  $C_V = \left( \frac{\partial U}{\partial T} \right)_V$ . From classical physics for one kilomole of any solid molar capacity  $C = C_p \approx C_V = 3R$  (*Dulong-Petit law*). **This law is valid at relatively high temperatures ( $T \geq \theta_D$ ,  $\theta_D$  is characteristic Debye temperature).** At low temperature the heat capacity decreases with temperature decreasing and approach to zero at 0 K. Classical physics is unable to explain this experimental fact.

### 9.2.2 Quantum theory of specific heat. Phonons

According to the quantum theory of heat capacity suggested by Einstein a crystal is the system of  $3N$  oscillators, which have the same angular frequency of oscillations  $\omega$ .  $N$  is number of atoms in this crystal.

In quantum mechanics the oscillator's energy is equal  $\epsilon = \left( n + \frac{1}{2} \right) \hbar \omega$ ,  $n=0,1,2,3\dots$

Considering the distribution of oscillation by energy states and Einstein's simplifications one can get the following formula for internal energy of crystal:

$$U = \frac{3N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

As  $C_V = C = \frac{\partial U}{\partial T}$  after differentiation we obtain  $C = \frac{3N\hbar\omega}{\left( e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} e^{\frac{\hbar\omega}{kT}} \cdot \frac{\hbar\omega}{k} \cdot \frac{1}{T^2}$

Let us discuss two cases:

1) High temperature (when  $\hbar\omega \ll kT$ ).

Using series expansion, ( $e^x \approx 1 + x$  - Maclaurin's formula,  $x = \frac{\hbar\omega}{kT}$ ) we obtain from the above formula the impression of heat capacity at high temperature

$$C = \frac{3N\hbar\omega}{\left( \frac{\hbar\omega}{kT} \right)^2} \cdot \frac{\hbar\omega}{k} \cdot \frac{1}{T^2} \cdot k,$$

which yields, after crossing

$$C = 3Nk.$$

For one kilomole:

$$\boxed{C_{1\text{ kmol}} = 3N_A k = 3R}.$$

Thus we come to *Dulong-Petit law again*. *The Dulong -Petit law is hold true ,when temperature  $T > \theta$  and  $\hbar\omega_{\max} = k\theta$*

2) low temperature (when  $\hbar\omega \gg kT$ ).

In that case it follows from the initial formula for molar specific heat that  $C = \frac{3N\hbar^2\omega^2}{kT^2} \cdot e^{-\frac{\hbar\omega}{kT}}$ .

An exponent multiplier changes faster than  $T^2$ . So when the temperature approaches zero, expression tends to zero by the exponential law. This is in qualitative agreement with well known experiments.



Limitation of Einstein theory of heat capacitance is in quantitative discrepancy of  $C(T)$  dependence with the experiments, when  $T < \theta$ . This discrepancy was explained by Debye, who improved Einstein's theory.

### 9.2.3 Phonons

The oscillations of crystal lattice can be represented as gas of special particles – phonons.

This is in analogy with electromagnetic radiation, which are treated as special particles – photons.

In contrast to the particle of light (photon), the phonon is quasi-particle, because it exists only in crystal. It's energy  $\varepsilon_{ph} = \hbar\omega_s$ , where  $\omega_s$  is angular frequency of sound wave .Linear pulse of

phonon  $p_{ph} = \frac{\hbar\omega}{c_s}$ .  $c_s$  is velocity of sound in crystal. Wavelength of the sound wave  $\lambda_s = \frac{2\pi c_s}{\omega}$ .

Concept of phonons is used in description of crystal properties, such as heat conductivity, heat capacity, thermo-e.m.f.

## 9.3. Energy bands in crystals

One of the most important theories of solid state physics is band theory. It explains different physical properties of materials, such as conductivity and superconductivity, behavior of semiconductors at doping, temperature dependence of conductivity of semiconductors, principle of p-n junction rectification, etc.

The fundamentals of band theory are formation mechanism and arrangement of energy bands, energy distribution of electrons in solids, notion of Fermi level.

### 9.3.1. Energy bands in crystals and classification of solids on metals, semiconductors and insulators.

If identical atoms are very far apart, they do not interact, and their electronic energy levels can be considered to be those of isolated atoms. Hence, the energy levels are exactly the same. As the atoms come close together, they essentially become one quantum system, and the Pauli exclusion principle demands that the electrons be in different quantum states for this single system.

The exclusion principle manifests itself as a changing or splitting of electron energy levels (see Fig. 9.2) that were identical in the widely separated atoms, and in solids with very

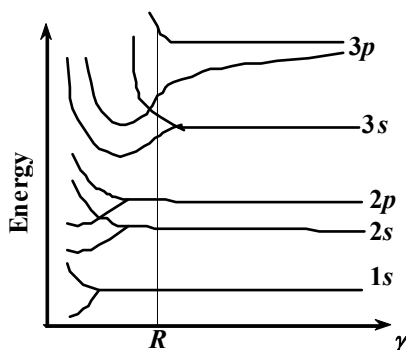


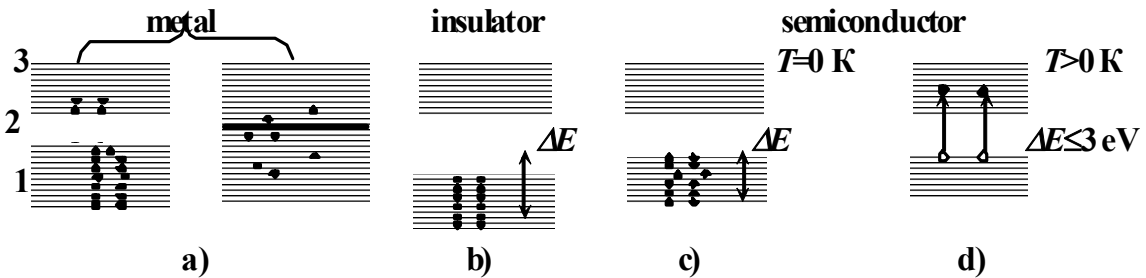
Figure 9.2

large number of atoms we obtain a large number of levels so closely spaced that they may be regarded as a continuous **band** of energy levels, as in Figure 9.3. An electron can have any energy within an allowed energy band, but cannot have an energy in the **band gap**  $\Delta E$ , or the region between allowed bands. In practice we are only interested in the band structure of a solid at some equilibrium separation of its atoms  $R$ , and so we remove the distance scale on the  $x$ -axis and simply plot the allowed energy bands of a solid as a series of horizontal bands, as shown in Figure 9.3

It is possible to gain a qualitative understanding of whether a solid is a conductor, an insulator, or a semiconductor by considering only the structure of the upper or upper two

energy bands and whether they are occupied by electrons.

Depending on band filling, all materials are classified as metals, semiconductors and insulators



**Figure 9.3** 1–valence band; 2 – forbidden band (energy gap); 3 – conduction band

(dielectrics). Important case is that shown in Figure 9.3 a where the highest energy band is partially filled only. The other important case, where the highest occupied band is completely filled, is shown in Figure 9.3 b. Notice that this figure the highest filled band (called the **valence band**) is shown also and the next higher band (called the **conduction band**) is empty. The energy band gap (forbidden band), which varies with the material of solid, is also indicated as the energy difference  $E_g$  between the top of the valence band and the bottom of the conduction band.

**A conductor has a highest-energy occupied band which is *partially filled*, and in an insulator, has a highest-energy occupied band which is *completely filled* with a large energy gap between the valence and conduction bands.** Semiconductors have smaller value of energy gap than dielectrics ( $<3$  eV). At some conditions, when temperature  $T > 0$  the electrons can jump into the empty conduction band and produce current carriers.

### 9.3.2. Electrons in metals. Fermi level

In quantum physics the description of particle state differs from the classical one considerably. In solid state theory the quantum statistics are used to determine number of micro particles  $N$  per quantum state. If the total number of quantum states is  $G$  and  $G \gg N$  then the classical statistics (Boltzmann's distribution) can be used. When number of micro particles in solid  $N$  is approximately equal number of states  $G$  quantum statistics is used. In such case the states of micro particles are discrete. Two types of quantum statistics are known, namely Bose-Einstein and Fermi-Dirac statistics. Electrons are the micro particles with half-integer spin. They are described in metals by Fermi-Dirac quantum statistics and electrons (as other particles with half-integer spin) are called fermions. For fermions the distribution function of particles by energy states  $f(\epsilon)$  is determined from formula

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon - E_F}{kT}} + 1}$$

Here  $f(\epsilon)$  is Fermi-Dirac function;  $E_F$  is Fermi energy,  $f(E) = \frac{n(E)}{g(E)}$ ;  $n(E)$  is the concentration of electrons with energy  $E$ ;  $g(E)$  is the density of states in unit interval of energy. The definition of Fermi-Dirac function:

**Fermi Dirac function** is average concentration of micro particles with energy  $E$  in unit state for interval of energy  $[E, E+dE]$ .

In figure 9.4 Fermi-Dirac function is shown for temperatures  $T=0$  K (figure 9.4 a) and  $T>0$  K (figure 9.4 b).

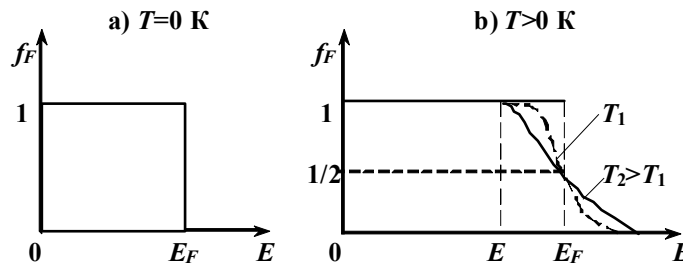


Figure9.4

When the temperature  $T=0$  K then the distribution function takes one of two values

$$f(E) = \begin{cases} 1 & \text{if } E \leq E_F \\ 0 & \text{if } E > E_F \end{cases}$$

This means that all levels with energies up to  $E_F$  are filled by electrons and

Fermi energy is maximum energy which electron has at temperature 0 K.

When the temperature increases electrons jumps onto higher energy levels and their distribution on energy states is changed (Fig.9.4b). Function  $f_F$  “spreads” and a “tail” of occupied states where energy of electrons is larger than  $E_F$  is apparent). In normal conditions concentration of electrons in excited states is very small (for 300 K it aggregates less than 1% of total electron concentration in metal).

### 9.3.3. Superconductivity .Explanation of superconductivity

**Classical physics can not explain phenomenon of superconductivity, when below the temperature, called critical temperature, electrical resistance of material (metal, alloy, ceramic) drops to zero (see Figure 9.5).**

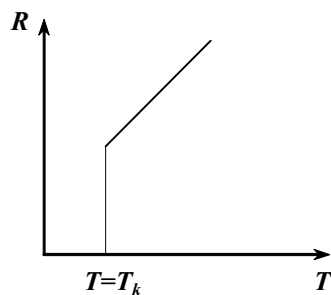


Figure 9.5

In experiment, the sharp decrease of electric resistance for temperature  $T < T_c$  can be studied by two methods:

1. By switching superconductor in series with conductor. Then the drop voltage on superconductor become zero at moment of transition into superconducting state.
2. By inserting superconducting coil into magnetic field normal to it. Current, induced in coil, will flow during very long time without damping (in one of fundamental experiments it existed for more than two years).

Superconductors are ideal diamagnetics, and magnetic field does not penetrate into depth of superconductor. Strong

magnetic field destroys superconductivity of material. Value of breaking magnetic field  $B_c$  depends on temperature. If  $T=T_c$  then  $B_c=0$  (Figure 9.6).

Superconductivity is a phenomenon, in which quantum effects become apparent on macroscopic scales. Theoretical explanation of superconductivity of metals and alloys based on quantum theory has been proposed in works of Bogoliubov and Bardeen, Cooper and Schrieffer.

In accordance with this theory at some conditions electrons in solids are bound into superconducting pairs (Figure 9.7)

It conditioned by phonon interchanging between electrons (corresponding diagram is shown in the upper part of the figure). This interchange of phonon (quantum of lattice vibration) is visualized below the diagram. Each of two electrons passing through the lattice make ions to shift from their equilibrium positions. This produce effective attraction of electrons (electrons repel each other but are attracted to ions shifted by other electron).

Electrons have opposite spins in such state and electrical charge of superconducting pair is  $2e$ . Such electron pairs (Cooper pair) moves without dispersion on vibrations of crystal lattice.

So resistance of material is zero in the temperature region  $T < T_c$ .

Superconducting pairs are destroyed at temperature increase to value  $T > T_c$ . Then the material pass to normal state (with usual electrical resistance).

Alloys  $Nb_3Ge$ ;  $Nb_3Si$ ;  $SnGe$ ,  $ZrSn$ , compounds  $YBa_2Cu_4O_7$ ; are superconductors with different  $T_c$  – from 10 K till 98 K, the highest  $T_c$  so far discovered is 139 K for  $Hg_{0.2}Tl_{0.8}Ca_2Ba_2Cu_3O$  compound.

Ordinary ferromagnetic-core electromagnets are limited to fields of around 2 T, higher fields require high current densities which lead to the melting of wires. Nowadays, conventional superconductors, especially  $Nb_3Sn$  alloy, are used to create ultra high magnetic fields up to 20 teslas, which a metallic conductor in normal (non-superconducting) state is unable to create because of energy leak to Joule heating. For the same reason the superconducting magnet consumes much less power. Strong magnetic fields have many applications, for example, in magnetic resonance imaging (MRI) used in medical diagnostics. Structure of chemical compounds can be determined with nuclear magnetic resonance equipment (NMR, uses strong magnetic field) very precisely. Modern accelerators of charged particles use magnetic field to control the trajectory of high-energy particles. In state-of-art Large Hadron Collider the niobium-titanium magnets operating at 1.9 K produce field of 8.3 T. The solenoid superconducting magnets designed for the ITER fusion reactor use niobium-tin ( $Nb_3Sn$ ) as a superconductor producing a field of 13.5 teslas. Without this solenoid hot plasma would not be confined inside the ITER reactor for time enough to allow fusion of Hydrogen nuclei, which, hypothetically, will become a source of energy for the future.

If in a circuit two superconductors are separated by normal metal, persistent current occurs. This system, referred to as Josephson junctions is extremely sensitive to magnetic field and is used in superconducting quantum magnetometers (SQUID) to measure magnetic fields with unmatched precision.

Other expected applications of superconductors will be transmission of energy without losses and fast-acting electronic switch. The latter can become main logical elements of future computer designs, in which bit will be realized as element in normal or superconducting state (superconducting qubit).

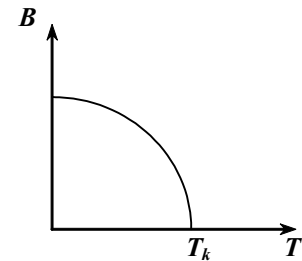


Figure 9.6

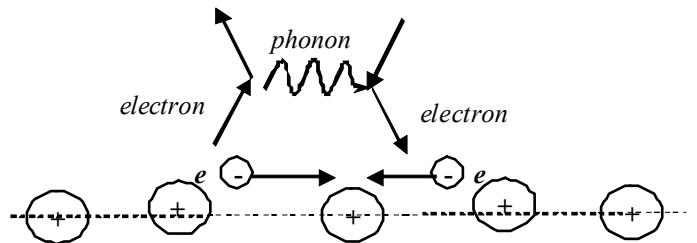


Figure 9.7

## 10. Conductivity of semiconductors. Contact phenomena

1 normal state  
0 superconduction state

## 10.1 Donors and acceptors. Electrons and holes

Semiconductors are the class of substances which conductivity depends on temperature, pressure, radiation, concentration of impurities and presence of defects.

The typical semiconductors are elements like Si, Ge, P, Se, Te and their different compounds, for example:

$A^{III}B^{V}$	GaP, GaAs, GaSb, InSb,	} Semiconductors
$A^{II}B^{VI}$	CdTe, CdS, CdSe	
$A^{IV}B^{VI}$	$Cd_xHg_{1-x}Te$	
$A^VB^{VI}$	$Bi_2Te_3$ , BiSe, BiSb	

**The conductivity of pure semiconductors is called intrinsic conductivity, the conductivity, caused by impurities is called extrinsic conductivity.**

In the figure 10.1 the concept of electrons and holes in conduction and valence bands and the concept of an electron and a hole in a simpler, more graphic way as the presence or absence of an outer-shell electron at a particular location in a crystal lattice is shown.

In pure semiconductors at low temperature all electrons are localized on the valence bonds (Figure 10.1 c) and current carriers are absent. For this reason the conductivity of semiconductors at low temperature is very low as for insulators. In energy representation this corresponds to Figure 10.1 a, at low temperature the thermal energy of electrons is insufficient to allow jumps into the higher conduction band. At high enough temperature the thermal motion can break off bonding and free an electron. The unfilled bond, left by electron becomes positively charged (charge  $+e$ ) and is called "hole" (figure 10.1 d). Another electron can jump in this free place. As result the hole begin to travel in crystal too. This case corresponds to figure 10.1 b with equal numbers of electrons in conduction band and holes in valence band.

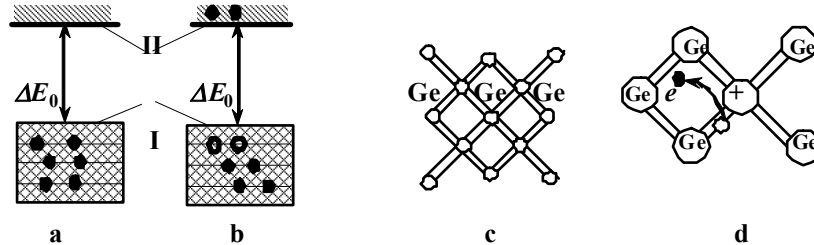


Figure 10.1

When small amounts of impurities are added to a semiconductor such as silicon (about one impurity atom per  $10^7$  silicon atoms), both the band structure of the semiconductor and its resistivity are modified.

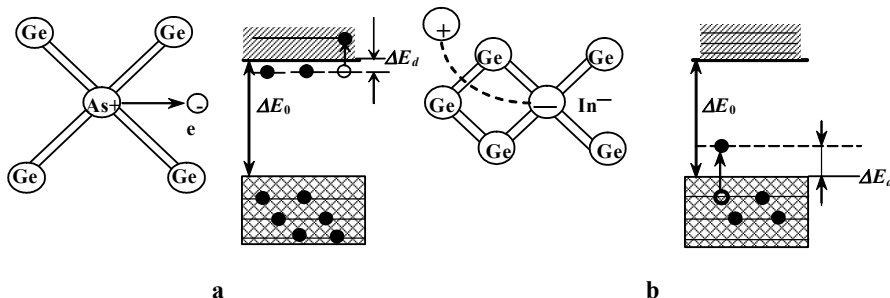


Figure 10.2

The process of adding impurities, called **doping**, is important in making devices having well-defined regions of different resistivity. For example, when an atom containing five outer-shell electrons, such as arsenic, is added to a semiconductor such as silicon, four of the arsenic

electrons form shared bonds with atoms of the semiconductor and one is left over. (Figure 10.2 a)

This extra electron is nearly free of its parent atom and has an energy level that lies in the energy gap, just below the conduction band. Such a pentavalent atom in effect donates an electron to the structure and hence is referred to as **donor atom**. Because the spacing between the energy level of the electron of the donor atom and the bottom of the conduction band is very small (typically, about 0.05 eV), only a small amount of thermal energy is needed to cause this electron to move into the conduction band. Recall that the average thermal energy of an electron at room temperature is  $3k_B T/2$  about 0.04 eV). Semiconductors doped with donor atoms are called **n-type semiconductors**, because the charge carriers are electrons, the charge of which is *negative*.

If a semiconductor is doped with atoms containing three outer-shell electrons, such as aluminum, or indium, the three electrons form shared bonds with neighbouring semiconductor atoms, leaving an electron deficiency—a hole—where the fourth bond would be if an impurity-atom electron was available to form it. The energy level of this hole lies in the energy gap, just above the valence band. An electron from the valence band has enough energy at room temperature to fill that impurity level, leaving behind a hole in the valence band. Because a trivalent atom, in effect, accepts an electron from the valence band, such impurities are referred to as **acceptor atoms**. A semiconductor doped with acceptor impurities is known as a **p-type semiconductor**, because the majority of charge carriers are positive charged holes.

## 10.2. Intrinsic and extrinsic conductivity of semiconductors. Temperature dependence of conductivity in semiconductors. Photoinduced conductivity

The intrinsic conductivity  $\sigma$  is characterized by simultaneous appearance of two types carriers -electrons and holes:  $\sigma_i = e(\mu_n n + \mu_p p)$ . Here  $\mu_n$  is mobility of electrons,  $n$  is concentration of electrons,  $\mu_p$  is mobility of holes and  $p$  is concentration of holes.

The extrinsic conductivity is described by formula:  $\sigma_p = e\mu_p p_a$  or by formula:  $\sigma_n = e\mu_n n_d$ . The first is used, when carriers are holes, created due to acceptor atoms and the second, when the carriers are the electrons of donors.

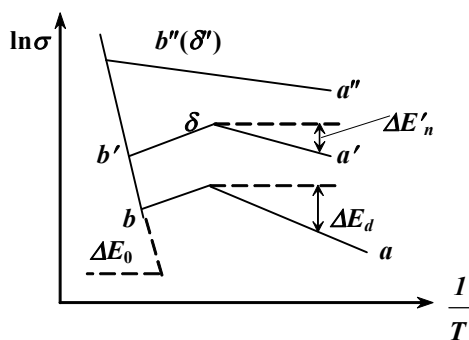


Figure 10.3

The temperature dependence of conductivity divides into three regions (Figure 10.3), which are qualitatively differed and corresponds to different temperatures.

For *n*-type semiconductor it is explained in the next way:

- 1) At low temperature the conductivity increases with temperature increasing (because the number of electrons passing from donor levels to the conduction band increases.) This is a region of impurity conductance.
- 2) When all donors are ionized, the concentration is remained constant and mobility of carriers decreases, so conductivity decreases too (this is region of exhaust).
- 3) The third region is conditioned by appearance of intrinsic conductivity due to transition of electrons from valence into conduction band.

The formula for temperature dependence of conductivity is:  $\sigma = \sigma_0 e^{-\frac{\Delta E_0}{2kT}}$  (intrinsic region of conductivity);  $\sigma = \sigma_{10} e^{-\frac{\Delta E_d}{2kT}}$  (extrinsic region, or impurity conductivity). Here  $\Delta E_0$  is energy gap width of semiconductor and  $\Delta E_d$  is energy of impurity level.

Temperature dependence of conductivity for *p*-type semiconductor is explained in like manner. Only the region of impurity conduction is explained by increasing of electrons jumping from valence band to the acceptor's levels.

From the dependence  $\ln \sigma \left( \frac{1}{T} \right)$  we can obtain the width band (gap) of semiconductor  $\Delta E_0$  and energy of impurity levels  $\Delta E_d$  (or  $\Delta E_a$ ).

**Photoconductivity** is connected with transition of electrons from donor levels to conduction band, or transition of electrons from valence band to acceptor levels under light action. The light is considered as the flow of photons. Photoconductivity takes place, when energy of photon  $h\nu > \Delta E_d$  (for impurity semiconductor) or  $h\nu > \Delta E_0$  (for intrinsic conductivity). As result the conductivity of semiconductor increases under irradiation.

### 10.3 Contacts phenomena. p– n junction

Contact phenomena are these which take place on the border between two different metals, or metal and semiconductor or two semiconductors with p- and n-types of conductivity.

p– n junction is the region, depleted by free carriers of current, which is created on the border of semiconductors of p and n-type of conductivity. In n-type semiconductor concentration of free electrons is many orders of magnitude greater than in p-region and vice versa. After p- and n-regions are connected diffusion processes tend to establish an equilibrium distribution of carriers across the border.

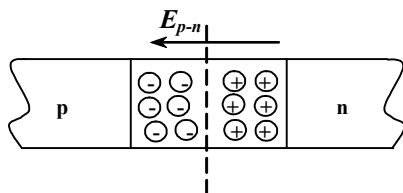


Figure 10.4

Mobile donor electrons from the n-region nearest the junction move to p-region (the figure 10.4.) leaving behind immobile positive ions. At the same time, holes from the p-region nearest the junction diffuse to the n-region and leave behind a region of fixed negative ions. As a result, an internal electric field  $E_{p-n}$  of the order  $10^4 - 10^6$  V/cm is created within the depletion region.

This field sweeps mobile charge out of the depletion

region. Internal electric field creates an internal potential energy difference  $e\Delta\phi$ , that prevents further diffusion of holes and electrons across the junction and thereby ensures zero current in the junction when no external potential difference is applied .

**p-n junction is the principal element of all modern semiconductor electronics.**

**Semiconductor diodes use the ability of p–n junction to pass current in only one direction.**

In Figure 10.5 the physical reason of such an unidirectional conduction is illustrated.

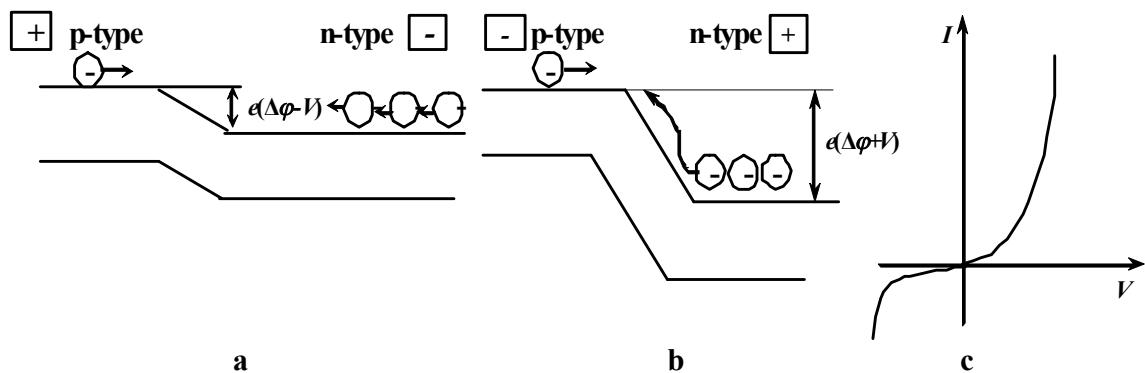


Figure 10.5

If an external voltage  $V$  is applied to the junction such that the *p* side is connected to the positive terminal of a voltage source as in Figure 10.5 a, the internal potential difference  $e\Delta\phi$  across the junction decreases, resulting in a current that increases exponentially (positive  $V$  values in Figure

10.5 c) with increasing forward voltage, or *forward bias*. In *reverse bias* (where the *n* side of the junction is connected to the positive terminal of a voltage source, Figure 10.5 b), the internal potential difference  $\Delta\phi$  increases with increasing reverse bias. This results in a very small reverse current that quickly reaches a saturation value (negative  $V$  values in Figure 10.5 c).

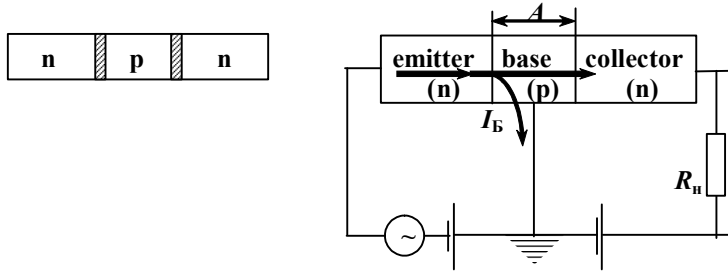


Figure 10.6

The transistors are the semiconductor devices consisting on two p-n junction and bias (very narrow region) between them (Figure 10.6). Its invention in 1948 totally revolutionized the world of electronics. Another types of semiconductor devices are semistor, dinistor, thyristor differ one from another by number and peculiarities of p-n junctions. An **integrated circuit** is a collection of interconnected transistors, diodes, resistors, and capacitors fabricated on a single piece of silicon known as a chip. State-of-the-art chips easily contain several million components in  $1\text{cm}^2$ .

### Problem

Calculate the forbidden gap width of semiconductor thermoresistor, if at voltage measurement by scheme shown on figure 10.7 potential drop on thermo resistor decreased by half, when the temperature increased from  $17^\circ\text{C}$  to  $27^\circ\text{C}$  (intrinsic region of conductivity). Potential drop on thermo resistor at  $17^\circ\text{C}$  is  $U_1=0,9\text{ V}$ . E.m.f. of battery  $E=1\text{ V}$ . Internal resistance of battery  $r=2\text{ Ohm}$ .

### Strategy.

Recollect 1. Ohm's law for scheme drawn on figure 10.7.

2. Band structure of semiconductors and the formula for temperature dependence of their conductivity.

### Solution

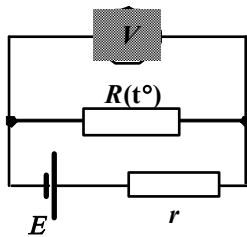


Figure 10.7

1) From Ohm's law  $U_1 = \frac{\varepsilon}{R_2 + r} R_1$  and  $U_2 = \frac{\varepsilon}{R_2 + r} R_2$ .

2) Ratio  $\frac{R_1}{R_2} = e^{\frac{\Delta E}{2k} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]} = e^{\frac{\Delta E}{2k} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]}$  (from temperature dependence of semiconductor's resistance).

3) As ratio  $\frac{U_1}{U_2} = \frac{R_1(R_2 + r)}{R_2(R_1 + r)} = \alpha$

4) ratio  $\frac{R_1}{R_2} = \frac{R_1}{r}(\alpha - 1) + \alpha$

5) From steps 2) and 4)  $\frac{\Delta E}{k} \left( \frac{T_2 - T_1}{T_1 T_2} \right) = \ln \left( \frac{R_1}{r}(\alpha - 1) + \alpha \right)$

6) From step 1) one has  $R_1 = \frac{U_1 r}{\varepsilon - U_1}$

7) then  $\Delta E = \frac{k T_1 T_2}{T_1 - T_2} \ln \left[ \frac{U_1(\alpha - 1)}{\varepsilon - U_1} + \alpha \right]$



and after calculation one finds  $\Delta E \approx 1,6 \text{ eV}$ .