

6 QUANTUM PHYSICS

In 1900 the wave theory of light, founded on the electromagnetic theory of Maxwell was unchallenged, and the mechanics of particles, based on Newton's laws of motion had been accepted for hundreds of years. However, the new development of early 1900's upset the certainty of these theories, because they could not be explained within the framework of classical physics.

We shall go back in time to the beginning of the preceding century and consider some of the outstanding problems in physics of that period namely:

- ◆ The problem of black body radiation.
- ◆ The problem of stability of atoms.
- ◆ The problem of atomic spectra.
- ◆ The problem of wave particle duality:
 - Particle properties of waves (photoelectric effect and Compton's effect).
 - Wave properties of particles (diffraction of particles).

Now we describe these problems and we show how they laid the foundation of modern quantum physics.

6.1 Black Body Radiation, Planck's Quantum Hypothesis

One of the observations that were unexplained at the end of the nineteenth century was the spectrum of light emitted by hot objects. At normal temperatures we are not aware of this electromagnetic radiation because of its low intensity. At higher temperatures, there is sufficient infrared radiation that we feel if we are close to the object. At still higher temperatures objects glow with a yellow or whitish color, such as a filament of a light bulb. A major problem facing scientists in the 1890 was to explain blackbody radiation. Two important theoretical curves based on classical ideas were those proposed by Wien and by Rayleigh and Jeans. However neither Wien's nor Rayleigh-Jean's formulations were in accord in experiment: Wien's was accurate for short wavelengths but deviated from experiment at longer wavelengths, whereas the reverse was truth for the Rayleigh-Jeans's theory, see Fig. 6-1. The situation was actually quite desperate before Planck's discovery.

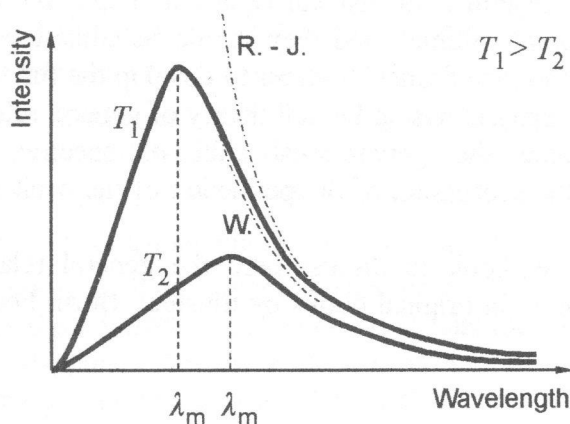


Figure 6-1

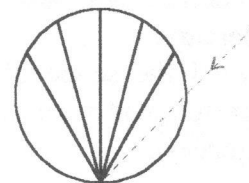


Figure 6-2

At given temperature T a unit area of the hot body surface emits per unit of time an electromagnetic radiation which is distributed to different wavelengths λ along the

function $H_{e\lambda}(\lambda, T)$, which is called the **spectral radiancy**. For the flux of energy within the interval of wavelengths $d\lambda$ we can write

$$dH_e = H_{e\lambda}(\lambda, T)d\lambda; \quad [H_e] = \text{Js}^{-1} \text{m}^{-2}.$$

If the body is irradiated this radiation is partly reflected and partly absorbed. The ratio of absorbed energy to the incoming energy

$$\alpha(\lambda, T) = \frac{dE_{abs}}{dE_{inc}},$$

depends generally on the wavelength and the temperature of the body. A body that would absorb all the radiation falling on it is called a black body. For the black body we have

$$\alpha(\lambda, T) = 1.$$

A model of the black body is shown in Fig. 6-2. To an outside observer a small hole in the wall of the cavity with absorbing interior surface is a black body surface – it absorbs incident radiation almost completely. The radiation emitted from the cavity is independent of the size and shape of the cavity and also independent of the materials of the walls. That is why a black body surface is a suitable standard emitter.

From thermodynamic conclusions can be obtained that the ratio between functions $H_{e\lambda}(\lambda, T)$ and $\alpha(\lambda, T)$ must be for all bodies given by the same universal function

$$f(\lambda, T) = \frac{H_{e\lambda}(\lambda, T)}{\alpha(\lambda, T)}.$$

This function is independent on the material of the body. The law describing correctly the dependence of the function $f(\lambda, T)$ on temperature and the wavelength was deduced in 1900 by Max Planck

$$f(\lambda, T) = \frac{2\pi hc^2}{\lambda^5 \left(e^{\frac{hc}{\lambda kT}} - 1 \right)}, \quad (6-1)$$

where k is the Boltzmann's constant, c is the speed of light and h is the Planck's constant. In quantum physics is also frequently used so called reduced Planck's constant, which is defined as Planck's constant divided by 2π

$$h = 6.626 \times 10^{-34} \text{ Js}; \quad \hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ Js}.$$

The graph showing the dependence of $f(\lambda, T)$ as a function on wavelength of light emitted by a black body is shown in Fig. 6-1. There are also shown corresponding dependencies for Wien's as well as for Rayleigh-Jean's laws.

As it is seen from Fig. 6-1 the graph of $f(\lambda, T)$ versus wavelength is a smooth curve falling to zero for long as well as for short wavelengths and with a maximum at a particular wavelength λ_m , which depends on the temperature of the walls as

$$\lambda_m T = b, \quad (6-2)$$

where $b = 2.898 \times 10^{-3}$ Km. This dependence is known as **Wien's displacement law**. The total power emitted per unit area of the black body can be determined from **Stefan-Boltzmann's law** as

$$H_e = \int_0^{\infty} f(\lambda, T) d\lambda = \sigma T^4; \quad [H_e] = \text{Js}^{-1} \text{m}^{-2},$$

where $\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2} \text{K}^{-4}$ is Stefan-Boltzmann's constant.

Planck then sought a theoretical basis for his formula. He presented a detailed model of the atomic processes taking place at the cavity walls. He assumed that the atoms that make up these walls behave like tiny electromagnetic oscillators each with a characteristic frequency of oscillation. These oscillators emit electromagnetic energy into the cavity. Thus it should be possible to deduce the characteristics of the cavity radiation from those of the oscillators with which it is in equilibrium.

To obtain a correct formula Planck had to do two radical assumptions about the atomic oscillators:

- ♦ An oscillator can not have any energy but only energies given by

$$E = nhf, \quad (6-3)$$

where f is the oscillator frequency, h is Planck's constant and n is a **quantum number**, that can take only integral values. This equation asserts that the oscillator frequency is **quantized**.

- ♦ The oscillators do not radiate energy continuously, but only in "jumps" or **quanta**. These quanta of energy are emitted when an oscillator changes from one to another of its quantized energy states. Thus if n changes by one unit, Eq. 6-3 shows that it is irradiated the amount of energy given by

$$\Delta E = \Delta nhf = hf. \quad (6-4)$$

Thus for the first time in the history of physics the idea was accepted that some physical quantity – energy would not be continuous quantity as had been believed for centuries. Rather it is quantized – it exists only in discrete amounts. The smallest amount of energy possible (hf) is called the quantum of energy.

6.2 Stability of Atoms

The model of atoms proposed by Thomson visualized the atom as a homogeneous sphere of positive charge inside which were negatively charged electrons, a little like plums in a pudding.

Around 1911, Ernest Rutherford performed experiment whose result contradicted Thomson's model of the atom. In this experiment a beam of positively charged alpha particles was directed at a thin foil of gold, see Fig. 6-3. The alpha particles were shown to be ionized helium atoms.

It was expected from the Thompson's model that the alpha particles would not be deflected by the atoms of Au-foil significantly since electrons are much lighter than alpha particles, and the alpha particles would not approach any massive concentration of positive charge to strongly repel them. The experimental results completely contradicted these predictions.

It was found that most of the alpha particles passed through the foil unaffected, as if the foil were mostly empty space. And of those deflected a few were deflected at a very large angles. This could happen, only if the positively charged alpha particles were repelled by a massive positive charge, concentrated in a very small region of space.

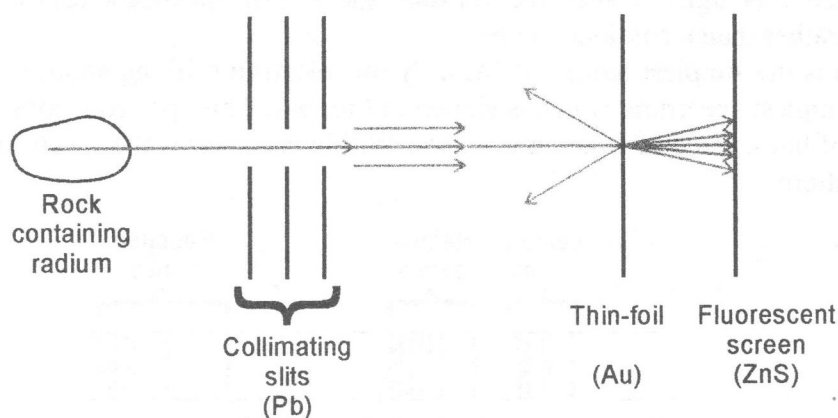


Figure 6-3

Rutherford thus proposed planetary model of the atom that is the atom must consist of tiny but massive positively charged nucleus, surrounded by electrons some distance away. The electrons would be moving in orbits about the nucleus, because if they were at rest they would fall into the nucleus due to electrical attractions.

However, following classical electromagnetic theory due to the orbital motion of electron around nucleus is emitted the electromagnetic radiation. This radiation represents a loss of energy for the moving electron, thus Coulomb's attractive force between the electron and nucleus prevails over centrifugal force and the electron would spiral in toward a nucleus in a very short time (for hydrogen this time is of order of 10^{-9} s).

Thus following classical physics the atoms will not be stable particles. This contradiction between theory and reality was solved by Niels Bohr. He postulated that **electrons move about the nucleus in circular orbits, but that only certain orbits are allowed**. He further postulated that an electron in each orbit would have a definite energy and would move in the orbit without radiating energy (even though this violated classical ideas). He thus called the possible orbits **stationary states**. The postulate concerning the stationary states is

$$mvr_n = n\hbar, \quad (6-5)$$

where m is mass of electron moving in a circle with radius r_n with velocity v , \hbar is the reduced Planck's constant and n is an integer which is called a quantum number of the orbit.

Bohr's second postulate deals with the emission of electromagnetic radiation. This **radiation is emitted only when an electron jumps from one stationary state to another state of lower energy**. When such a jump occurs, a single photon would be emitted whose energy is given by

$$E_m - E_n = hf, \quad (6-6)$$

where E_m refers to the energy of the upper state, E_n is the energy of the lower state and f is the frequency of emitted radiation.

On the base of these postulates Bohr was able to calculate the energies of various stationary states in which a hydrogen atom can exist. As we shall see in the next section the stationary values are in good agreement with experimental results.

6.3 Atomic Spectra – Bohr's Model

The fact that each chemical element is associated with a unique optical spectrum is one of the striking aspects of nature. Rarefied gases excited by electrical discharges also emit light. When this light is analyzed through the slit of spectrometer we can see a line spectrum rather than a continuous one.

Hydrogen is the simplest atom – it has only one electron orbiting about its nucleus. It has also the simplest spectrum, which is shown in Fig. 6-4. This spectrum consists of a number of series of lines, three of which are shown. Within each series the spectrum lines follow a regular pattern.

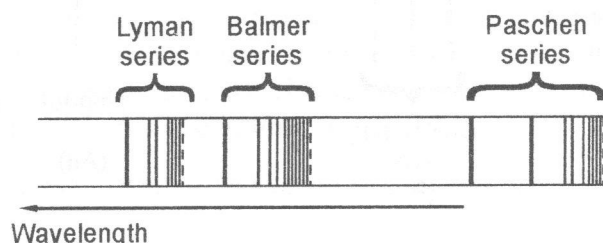


Figure 6-4.

We interpret the spectra in terms of energy levels of atoms. The Rutherford's model was unable to explain why atoms emit line spectra. According to this model, electrons orbit the nucleus and since their paths are curved the electrons are accelerating. Hence they should emit the radiation like any other accelerating charge. Hence since energy is conserved, the electrons own energy must decrease. Hence electrons would be expected to spiral into the nucleus. As they spiraled inward, their frequency would increase gradually and so too would the frequency of radiation emitted.

Thus the Rutherford's model predicts that electromagnetic radiation of a continuous range of frequencies will be emitted whereas experiment shows line spectra.

Clearly Rutherford's model was not sufficient and it was Bohr who modified it by adding the quantum hypothesis expressed in his postulates given by Eq. 6-5 and Eq. 6-6.

Using the Bohr's postulates let us find the frequencies of radiation emitted by hydrogen atom. In order to do it we need to know the energies of various stationary states in which a hydrogen atom can exist.

We assume that the electron in the hydrogen atom moves in a circular orbit of radius r_n centered on its nucleus. We also assume that the nucleus, which is a single proton, is so massive that the center of mass of the system is essentially at the position of the proton. Let us calculate the energy E of such an atom.

For this electron the electrical force of attraction between the negative electron and the positive nucleus is balanced by the centrifugal force, or

$$m_e \frac{v^2}{r_n} = \frac{1}{4\pi\epsilon_0} \frac{Z e^2}{r_n^2}, \quad (6-7)$$

where m_e is the mass of electron and Z is the number of positive charges. Though for the hydrogen atom $Z = 1$ we include Z into our derivation so that we can treat other single electron atoms.

Substituting for v from the Bohr's postulate for stationary states (Eq. 6-5),

$$m_e v r_n = n \hbar$$

we solve for r_n and we find

$$r_n = \frac{\epsilon_0 h^2}{\pi m_e e^2 Z} n^2. \quad (6-8)$$

This equation gives the radii of the possible orbits in the Bohr's model of hydrogen. We see that r_n depends on the square of the quantum number of the orbit. The smallest orbit has $n = 1$ and it has the value of radius $r_1 = 0.529 \times 10^{-10}$ m. For the velocity of electron in this orbit we obtain

$$v_1 = \frac{h}{2\pi r_1 m_e} = \frac{e^2}{2\epsilon_0 h} = 2.18 \times 10^6 \text{ ms}^{-1}.$$

In each of its possible orbits, the electron would have a definite total energy, which equals to the sum of the kinetic and potential energies. The potential energy of the electron is given as

$$E_p = - \int_{\infty}^{r_n} \mathbf{F}_c d\mathbf{r} = - \int_{\infty}^{r_n} \left(- \frac{Z e^2}{4\pi\epsilon_0 r^2} \right) dr = - \frac{Z e^2}{4\pi\epsilon_0 r_n}. \quad (6-9)$$

The negative sign in the expression for Coulomb's force expresses the fact that the charge of electron is negative. The kinetic energy of electron is

$$E_k = \frac{1}{2} m_e v^2 = \frac{Z e^2}{8\pi\epsilon_0 r_n}. \quad (6-10)$$

Substituting for r_n from Eq.6-8 into Eq. 6-9 and Eq.6-10 we obtain for the total energy for an electron in the n -th orbit of radius r_n

$$E_n = - \left(\frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^2} \right) \frac{1}{n^2}. \quad (6-11)$$

For the hydrogen the lowest energy level has $n=1$ and thus for energy we obtain

$$E_{n=1} = - 2.17 \times 10^{-18} \text{ J} = - 13.6 \text{ eV}.$$

Note that the energy has negative value. This has to do with the way we defined the zero for potential energy. For two point charges zero potential energy corresponds to the case when they are infinitely far apart. Thus, an electron with zero kinetic energy that is free from the atom would have $E = 0$, corresponding to $r \rightarrow \infty$ and $n \rightarrow \infty$. Electrons that are part of an atom have $E < 0$. Also it is clear that energy would be required to remove an electron from an atom – this energy is called the **ionization energy**. The ionization energy for hydrogen is $+ 13.6 \text{ eV}$.

It is still useful to show the various possible energy levels as horizontal lines on an energy level diagram. This is shown for hydrogen in Fig. 6-5.

The quantum number n that labels the orbit radii also labels the energy levels. The lowest energy level or energy state is called the **ground state**. The higher states are called **excited states**. Once in an excited state, an electron can jump down to a lower state and give off a photon of radiation. This is, according to the Bohr's model, the origin of the emission spectra of excited gases. The vertical arrows in Fig. 6-5 represent the transition or jumps that correspond to the various spectral lines.

Combining Eqs. 6-11 and 6-6 we can obtain a completely theoretical formula for the frequencies of the lines in the hydrogen spectrum

$$f = \frac{m_e e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{s^2} - \frac{1}{m^2} \right), \quad (6-12)$$

where m and s are quantum numbers of the higher and lower levels of energy. The great success of Bohr's theory is that it gives a model for why atoms emit line spectra and accurately predicts, for hydrogen, the wavelength of the emitted light.

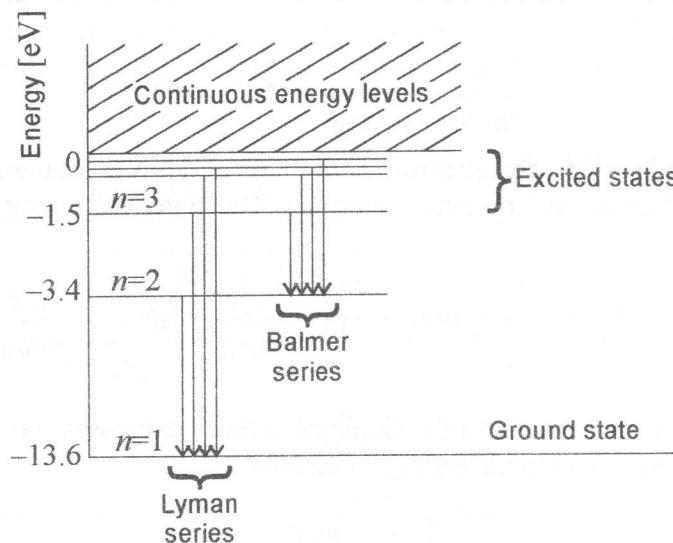


Figure 6-5

6.4 Wave Particle Duality

To most of us there is nothing mysterious or ambiguous about the concept of the particle and wave. The mechanics of particles and the optics of waves are, by tradition, independent subjects, each with its own chain of experiments and hypotheses.

We regard electrons as particles because they possess charge and mass and behave according to the laws of particle mechanics in such a familiar device as television picture tube. However, there is evidence in favour of interpreting a moving electron as a wave manifestation (experiment of Davisson and Germer).

We regard electromagnetic waves as waves because under suitable circumstances they exhibit such characteristics wave behavior as interference. However, under other circumstances electromagnetic waves behave as though they consist of stream of particles (photoelectric and Compton's effect).

The wave particle duality is central to understanding of modern physics so we shall now explore it.

6.4.1 Photoelectric and Compton's Effect

Late in the nineteenth century a series of experiments were performed, which revealed that electrons are emitted from a metal surface when light of sufficiently high frequency falls on it. The emission of electrons by a substance being irradiated with light is known as photoelectric effect.

This effect can be observed using the apparatus shown in Fig. 6-6. The two electrodes are connected to an ammeter and a source of electromotive force. When the photocell is in the dark, the ammeter reads zero. But when light of sufficiently high frequency is shone on the photocathode, the ammeter indicates the current flowing in the circuit.

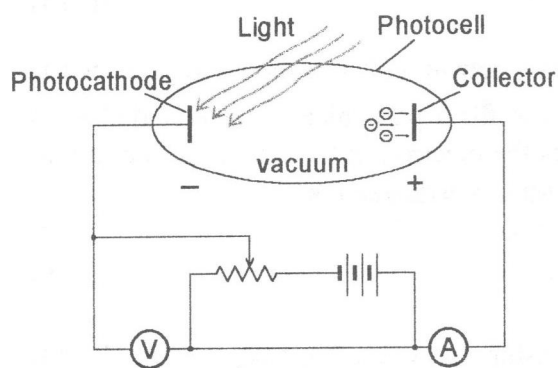


Figure 6-6

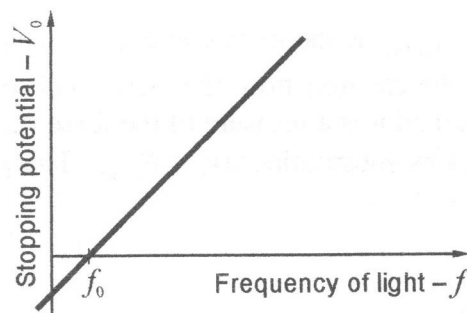


Figure 6-7

That electrons should be emitted when light shines on metal is consistent with the electromagnetic theory, since the electric field of an electromagnetic wave could exert a force on electrons in the metal and thrust some of them out.

With the apparatus that is shown in Fig. 6-6 we can measure the maximum kinetic energy $E_{k,\max}$ of the emitted electrons. This can be done by reversing the terminals so that collector is negative and photocathode is positive. The electrons emitted from the photocathode will be repelled by the negative collector, but if this reverse voltage is small enough, the fastest electrons will still reach collector and there will be the current in the circuit. If the reverse voltage is increased a point is reached where the current reaches zero - no electrons have sufficient kinetic energy to reach collector. This voltage V_0 is called the stopping voltage (potential). A plot of the stopping voltage for various frequencies is shown in Fig. 6-7.

First of the features of the photoelectric effect that particularly puzzled its discoverers is that the maximum energy of emitted electrons is independent of the intensity of light. The wave theory predicts that if the light intensity is increased, the number of electrons ejected and their maximum kinetic energy should be increased because a higher intensity means greater electric field amplitude, and the greater electric field should thrust electrons out with higher speed.

Second of the features of the photoelectric effect equally odd from the point of view of the wave theory is the fact that the maximum energy of emitted electrons depends upon the frequency of the light employed - see Fig. 6-7. According to the wave theory, this effect should occur for any frequency of the light, provided only that the light is intense enough. However, Fig. 6-7 shows, that there exists a characteristic cut-off frequency f_0 . For frequencies less than this, the photoelectric effect disappears, no matter how intense is the illumination.

Third discrepancy between the wave theory and experimental results is that there should be, if the light is feeble enough, a measurable time lag between the impinging of the light on the surface and ejection of the electron. During this interval the electron should be "soaking" energy from the wave until it has accumulated enough energy to escape. However, no detectable time lag has ever been measured.

In 1905 Albert Einstein found that the discrepancies presented could be understood by making an assumption that the light is transmitted as tiny particles called photons. The energy of a single photon is

$$E = hf = \hbar\omega, \quad (6-13)$$

where $\hbar = h/2\pi$ is the reduced Planck's constant and $\omega = 2\pi f$. The rest mass of photons is zero, photons move with the speed of light. Taking into account this concept Einstein's famous formula for the photoelectric effect is

$$hf = A + E_{k,\max}, \quad (6-14)$$

where $E_{k,\max}$ is the kinetic energy of the emitted electron and A is the energy needed to extract the electron from the metal. This quantity A for a particular metal is called work function and it is a measure of the force that holds the electron in the metal. Let us rewrite Eq. 6-14 by substituting $eV_0 = E_{k,\max}$. This yields after rearrangement

$$V_0 = \frac{h}{e} f - \frac{A}{e}. \quad (6-15)$$

Thus Einstein's theory predicts a linear relationship between stopping voltage V_0 and frequency f , which is in complete agreement with experiment, see Fig. 6-8. The slope of the experimental curve is proportional to the Planck's constant.

Compelling confirmation of the concept of the photon as a concentrated bundle of energy was provided in 1923 by Arthur Compton. Compton allowed a beam of X-rays of sharply defined frequency f to fall on different materials. He found that the scattered X-rays had a slightly lower frequency f' than did the incident X-rays, indicating a loss of energy, see Fig. 6-8. This, he showed, could be explained by assumption that the incoming X-ray beam

was not a wave but an assembly of photons of energy $E = h\frac{c}{\lambda}$, and that these photons experienced billiard-ball-like collisions with the free electrons of the scattering material. Compton applied the laws of conservation of energy and momentum to such collisions and found that the predicted energies of scattered photons were in accord with experimental results.

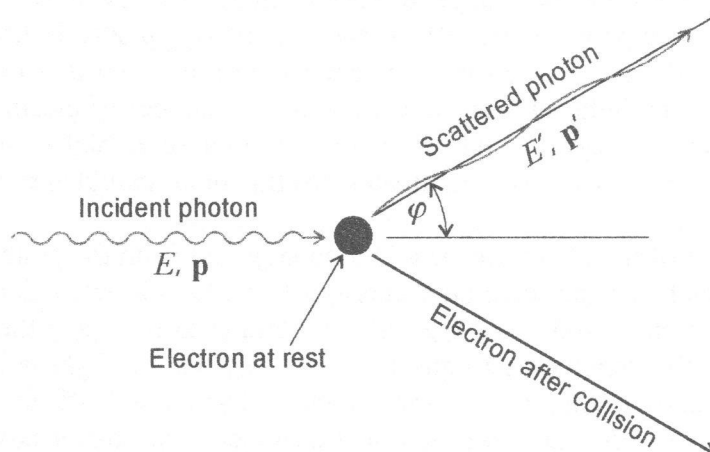


Figure 6-8

Now let us analyze a single photon-electron collision quantitatively. However, we have to note that recoil electrons may have a speed that is comparable with the speed of light and that the photons travel at the speed of light. Thus we must use relativistic formulas for dealing with mass, energy and momentum.

We can write the conservation of energy law for photon-electron collision as

Energy of the incoming photon = energy of the scattered photon + kinetic energy of electron.

$$\frac{hc}{\lambda} = \frac{hc}{\lambda'} + m_0 c^2 \left(\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} - 1 \right).$$

Now let us apply the law of conservation of linear momentum to the collision of Fig. 6-8. We first need an expression for the momentum of a photon. The mass of any particle is given by

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}. \quad (6-16)$$

We know that the photon travels at the speed of light. Since $v = c$ in Eq. 6-16, the denominator is zero. So the rest mass, m_0 , of a photon must also be zero, or its energy $E = mc^2$ would be infinite. The momentum of a photon, see Eq. 5-49, therefore is

$$p = \frac{E}{c}. \quad (6-17)$$

Since energy of the photon $E = h \frac{c}{\lambda}$ we have for its momentum

$$p = \frac{h}{\lambda}. \quad (6-18)$$

Multiplying numerator and denominator by 2π we obtain

$$p = \hbar k, \quad (6-19)$$

where k is the wave number.

Eq. 6-19 is another expression for the momentum of photon. The electron's momentum is

$$\mathbf{p}_e = m\mathbf{v} = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \mathbf{v}. \quad (6-20)$$

We can then write for linear momentum (see Fig. 6-8, triangle p' , p_e and p):

$$p_e^2 = p^2 + p'^2 - 2pp' \cos \varphi, \quad (6-21)$$

where φ is the scattering angle.

Substituting Eq. 6-18 and 6-20 into Eq. 6-21 we obtain

$$\left(\frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}} \right)^2 = \left(\frac{h}{\lambda} \right)^2 + \left(\frac{h}{\lambda'} \right)^2 - 2 \frac{h^2}{\lambda \lambda'} \cos \varphi. \quad (6-22)$$

Carrying out the necessary algebraic steps leads to the expression for so called Compton's shift:

$$\Delta \lambda = \lambda' - \lambda = \frac{h}{m_0 c} (1 - \cos \varphi). \quad (6-23)$$

Compton's measurement of 1923 was consistent with this formula. The wave theory of light predicts no such shift. An incoming electromagnetic wave of frequency f should set electrons in oscillation at frequency f , and such oscillating electrons should reemit electromagnetic waves of this same frequency. Hence the Compton's effect adds to the firm experimental foundation for the photon theory.

6.4.2 Diffraction of particles

For photons the wave properties were discovered first and the corpuscular properties later. For electrons and other particles the order was reversed. In the experiment of Davisson and Germer and in the experiment of G. P. Thomson was shown that the electrons exhibit wavelike properties.

In Thomson's experiment, see Fig. 6-9, the beam of electrons produced in an electron gun was scattered by a thin aluminum foil. It was expected that most of electrons would pass through the foil undeflected. However, the record on the photographic plate situated perpendicular to the incident beam shows a set of concentric circles, which is well known diffraction pattern of light on a circular aperture. As far as light is electromagnetic wave it was shown that electrons have wavelike properties.

Later experiments showed that protons, neutrons and other particles have also wavelike properties.

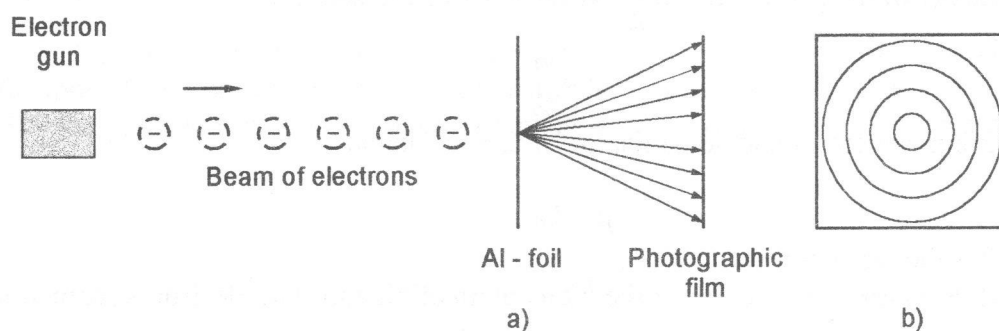


Figure 6-9

6.5 Wave Nature of Matter

As we saw in the preceding sections some experiments show that electromagnetic radiation behaves like a wave, and other indicate that it behaves like a stream of particles. To clarify the situation Niels Bohr proposed the principle of complementarity. It states that to understand any given experiment, we must use either the wave or the photon theory, but not both.

In 1923 Louis de Broglie extended the idea of the wave-particle duality. He argued that if light sometimes behaves like a wave and sometimes like a stream of particles, then those objects in the nature thought to be particles - such as electrons and other material objects - might also have wave properties. De Broglie proposed that the wavelength of a material particle would be related to its momentum in the same way as for a photon. Thus for a particle of a mass m traveling with speed v the wavelength λ is

$$\lambda = \frac{h}{mv}. \quad (6-24)$$

In this expression λ is called de Broglie wavelength. The dual nature of matter is shown in this equation. In the left side there is a wave quantity (wavelength) and on the right side there is a particle quantity (momentum). De Broglie wavelength is incredibly small to be measured and detected.

One of the de Broglie original arguments in favor of wave nature of electrons was that it provided an explanation for Bohr's theory of the hydrogen atom. Each electron orbit in an atom is actually a standing wave. But only certain ones - those that have nodes at the ends are sustained.

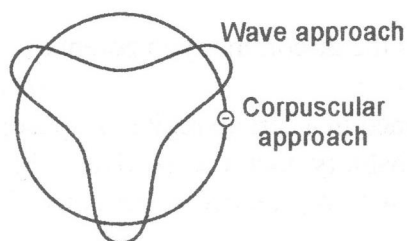


Figure 6-10

All other wavelengths interfere themselves upon reflection and their amplitudes quickly drop to zero. Since electrons move in circles de Broglie supposed that the electron wave must be a circular standing wave that close on itself (see Fig. 6-10). If the wavelength of a wave does not close on itself, destructive interference takes place as the wave travels around the loop and it quickly dies out. Thus the only waves that persist are those for which the circumference of the circular orbit contains a whole number of

wavelengths. The circumference of a Bohr's orbit of radius r_n is $2\pi r_n$ so must have

$$2\pi r_n = n\lambda, \quad \text{where } n = 1, 2, 3, \dots$$

If we substitute for the de Broglie wavelength from Eq. 6-24 we obtain

$$2\pi r_n = n \frac{h}{mv},$$

which is just the quantum condition proposed by Bohr. Thus we have an explanation for the quantized orbits and energy states in Bohr's model: they are due to the wave nature of electron.

There is nothing imaginary about matter waves. They are perfectly real, just as light waves or sound waves are. Shortly after their discovery they were used for example in electron microscopes. The de Broglie wavelengths of fast electrons are shorter than the wavelength of visible light and hence they permit a greater resolution of detail.

6.6 Wave Function

The idea that the stationary states of atoms correspond to standing matter waves was taken by E. Schrodinger in 1926 and used by him as the foundation of wave mechanics, one of several equivalent formulations of quantum physics.

An important quantity in wave mechanics is the wave function $\Psi(x, y, z, t)$, which describes the matter wave. The wave function may be real as well as complex. Max Born first suggested that quantity

$$|\Psi(x, y, z, t)|^2 = \Psi(x, y, z, t) \Psi^*(x, y, z, t), \quad (6-25)$$

at any particular point is a measure of probability that the particle will be near that point. In this expression Ψ^* is imaginary conjugated function to Ψ . More exactly if a volume element $dV = dx dy dz$ is constructed at point x, y, z , the probability $dP(x, y, z, t)$ that the particle will be found in the volume element dV at a given instant of time is

$$dP(x, y, z, t) = |\Psi(x, y, z, t)|^2 dV. \quad (6-26)$$

This interpretation of the wave function provides a statistical connection between the wave and the associate particle. It tells us where the particle is likely to be and not where it is. From Eq. 6-26 we can express the probability density as

$$|\Psi(x, y, z, t)|^2 = \frac{dP(x, y, z, t)}{dV}. \quad (6-27)$$

This quantity is more important than the wave function itself because it tells us where the particle is likely to be. The wave function must fulfill certain conditions:

- it must be unique function of coordinates and time,
- it must be continuous even in the points where there is the discontinuity in potential,
- it must have continuous first derivatives,
- in infinity it must be equal to zero (for a particle confined in a certain region in space),
- it must be normalized, which means that the probability that the particle will be somewhere in the infinite volume V is unity, which represents a certainty. The normalization condition is

$$\int_V |\Psi(x, y, z, t)|^2 dV = 1, \quad (6-28)$$

- it must obey the principle of superposition, or

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2. \quad (6-29)$$

The wave function associated with the motion of the particle can be expressed in following way

$$\Psi(\mathbf{r}, t) = A e^{j(\omega t - \mathbf{k} \cdot \mathbf{r})}, \quad (6-30)$$

where \mathbf{r} is the position vector and \mathbf{k} is the wave vector. This is the wave function in which are included the wave quantities, like ω and \mathbf{k} .

Let us rewrite this wave function to the form in which there will be involved the corpuscular quantities. To do so we use Eq. 6-4

$$E = hf = h \frac{\omega}{2\pi} = \hbar \omega, \quad (6-31)$$

where \hbar is reduced Planck's constant. For momentum we have from Eq. 6-24

$$p = \frac{h}{\lambda}.$$

The magnitude of the wave vector is $|\mathbf{k}| = \frac{2\pi}{\lambda}$. Inserting for wavelength into the previous expression we obtain for momentum

$$\mathbf{p} = \hbar \mathbf{k}. \quad (6-32)$$

Substituting Eqs. 6-31 and 6-32 into Eq. 6-30 we have

$$\Psi(\mathbf{r}, t) = A e^{\frac{j}{\hbar}(Et - \mathbf{p} \cdot \mathbf{r})}. \quad (6-33)$$

This is the expression for the same wave function as expressed by Eq. 6-30, however, in this case the corpuscular quantities for the description of the wave are used.

Now let us have a look what is the connection between the motion of the particle and propagation of the de Broglie wave. We have already defined phase velocity (chapter 2.3)

as $c_f = \frac{\omega}{k}$. We can multiply both numerator and denominator by \hbar . Thus we have

$$c_f = \frac{\hbar \omega}{\hbar k} = \frac{E}{p} = \frac{mc^2}{mv} = \frac{c^2}{v} > c. \quad (6-34)$$

In this expression c is the speed of light and v is the speed of the particle motion. We see that the phase velocity of the de Broglie wave is greater than the speed of light. This conclusion seems to be in contradiction with the second postulate of special theory of relativity. However, the phase velocity is velocity with which travels the phase or certain point on the wave - like crest. This velocity has nothing common with the transport of energy.

Let us also have a look on the expression for the group velocity

$$c_{gr} = \frac{\partial \omega}{\partial k}.$$

The energy of a particle is given as $E = \frac{p^2}{2m} = \hbar \omega$. Taking into account Eq. 6-32 we obtain

$$E = \frac{\hbar^2 k^2}{2m} = \hbar \omega,$$

or

$$\omega = \frac{\hbar k^2}{2m}. \quad (6-35)$$

Using Eq. 6-3 to determine the group velocity we have

$$c_{gr} = \frac{\partial}{\partial k} \left(\frac{\hbar k^2}{2m} \right) = \frac{\hbar k}{m} = \frac{p}{m} = \frac{mv}{m} = v. \quad (6-36)$$

We see that the group velocity of the de Broglie wave is equal to the velocity of the particle.

6.7 The Uncertainty Principle

We have already learned that the particles have also wave properties. A moving particle with a well-defined momentum \mathbf{p} behaves like a wave of wavelength $\lambda = \frac{h}{p}$ and this

relation is valid for all particles. We have also learned that the state of motion of a particle can be described by a complex wave function $\Psi(\mathbf{r}, t)$. It is important to understand that a wave in a quantum mechanics need not look like a sine wave, that is very special case.

Consider now a state of motion of a particle described by the initial wave function $\Psi(\mathbf{r}, 0)$. What we can say about the position and momentum of the particle at time $t = 0$?

We know that the absolute square of the wave amplitude at a point is a measure of the probability that the particle will be in this point. If the initial wave function is such that the amplitude is zero except in a very small region, then we can say that the particle is in this region (at time $t = 0$), that is its position is accurately known. On the other hand if the initial wave function is very much spread out such that its amplitude is approximately constant over a very large region, we can not assign a precise position to the particle: the position at time $t = 0$ is subject to a large uncertainty.

Analogous considerations apply to the momentum variable. Since momentum and wavelength are related by Eq. 6-24 it is intuitively clear that the momentum can not be well defined unless the wavelength is well defined.

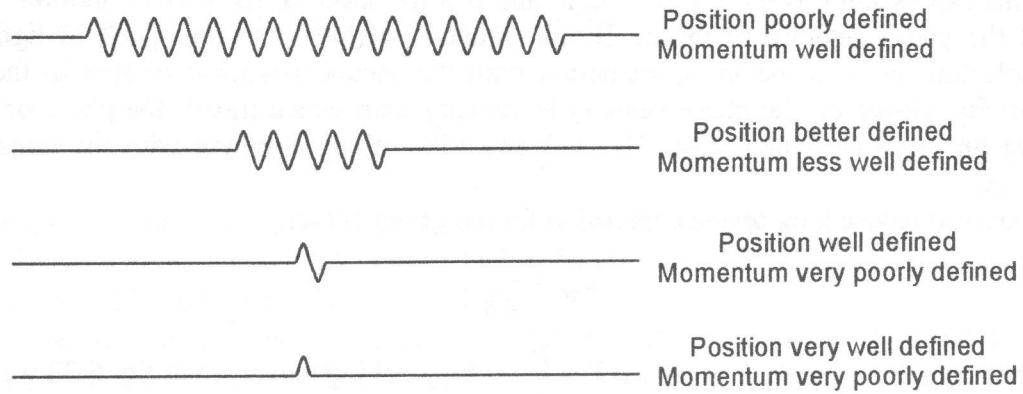


Figure 6-11

For the wavelength to be well defined it is necessary that the wave function exhibits some pattern of periodicity. A long sine wave has a well-defined wavelength. To illustrate our discussion let us see Fig. 6-11. In this figure we have plotted four particular wave trains of finite length. We know that the wave function is in general complex valued function, which fact creates problems when we want to represent it graphically. We can however plot the real part of the function separately and thus we can interpret Fig. 6-11 as showing for example the real part of the wave function only.

It was realized by Heisenberg that whereas there are no limits to the accuracy to which either the momentum or the position can be defined, there is a fundamental limit to the accuracy to which position and momentum can be defined at the same time - that is for the same wave function. This insight finds its expression in the celebrated uncertainty relation formulated by Heisenberg.

We shall now derive these relations through simple intuitive arguments. Looking at the Fig. 6-11 we can see that the better the position is defined the more poorly is the momentum defined. Let us denote the uncertainty in the position x by Δx . As a rough measure of the uncertainty in position we may take the length of the wave train. If the wave train consists of n -full waves we have

$$\Delta x \approx n\lambda = n \frac{h}{p}. \quad (6-37)$$

Now it is clear that the larger the number of full oscillations in the wave train the wavelength is better defined. As a rough measure of a fractional uncertainty in the wavelength we take

$$n = \frac{\Delta \lambda}{\lambda} = \frac{\Delta p}{\frac{h}{p}} = \frac{p}{\Delta p}. \quad (6-38)$$

Combining Eqs. 6-37 and 6-38 we obtain

$$\Delta x \Delta p \approx h. \quad (6-39)$$

However, we have to understand that waves in quantum mechanics need not look like a sine wave (at a given instant of time). In Fig. 6-12 is shown another example of the real part of the complex wave function. It is seen that the position is poorly defined but the momentum is also poorly defined.



Figure 6-12

The correct position - momentum uncertainty relation must therefore be of the form

$$\Delta x \Delta p \geq h. \quad (6-40)$$

This expression is the well-known uncertainty principle, which tells us that the measurement of the position and momentum of the particle simultaneously with unlimited accuracy is impossible.

Another way to formulate this principle is in terms of energy and time. The relation is

$$\Delta E \Delta t \geq h. \quad (6-41)$$

Thus if you try to measure the energy of a particle, allowing yourself a time interval to do so, your energy measurement will be uncertain by an amount ΔE given by $\frac{h}{\Delta t}$.

The limits on measurements imposed by Eq. 6-40 and Eq. 6-41 have nothing to do with the crudity of our measuring instruments. The uncertainty principle represents a fundamental limitation imposed by nature.

6.8 Schrodinger's Equation

We have seen that wave function is a complex valued function of position and time. The important postulate of quantum mechanics is that every definite wave function corresponds to a definite state of motion of the particle. The basic problem of quantum mechanics can be formulated in the following way: supposing that we know the wave function in initial time $\Psi(\mathbf{r}, 0)$, how to find the wave function $\Psi(\mathbf{r}, t)$ for time $t > 0$. This problem was solved by E. Schrodinger. The theory based on the Schrodinger's equation is based on following approximations:

- ◆ Creation and destruction of material particles are assumed not to take place, or the number of each kind of particles remains constant.
- ◆ All relevant velocities are assumed to be sufficiently small so that a non-relativistic approximation is valid.
- ◆ The equation sought must be linear and homogeneous - in this case the wave function obeys the principle of superposition, which is generally valid for the wave processes.
- ◆ The equation sought must be differential equation of the first order with respect to time. In this case the evolution of the wave function as time goes on can be predicted on the knowledge of wave function in initial time.

To obtain the Schrodinger's equation we try to find the simplest linear wave equation satisfied by every plane wave. To do so we suppose that the state of motion of a free particle is described by one-dimensional wave, or

$$\Psi = \Psi_0 e^{-\frac{j}{h}(Et - p_x x)}. \quad (6-42)$$

If we differentiate the wave function with respect to time we obtain

$$\frac{\partial \Psi}{\partial t} = -\frac{j}{\hbar} E \Psi.$$

Thus for energy we have

$$E = \frac{1}{\Psi} \left(j\hbar \frac{\partial \Psi}{\partial t} \right). \quad (6-43)$$

Similarly if we differentiate the wave function twice with respect to the coordinate we obtain

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2} \Psi.$$

For the square of momentum we have

$$p_x^2 = \frac{1}{\Psi} \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right). \quad (6-44)$$

The energy of a free particle moving in x direction is

$$E_K = \frac{p_x^2}{2m}. \quad (6-45)$$

Substituting Eq. 6-43 and Eq. 6-44 into Eq. 6-45 we obtain

$$j\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}. \quad (6-46)$$

This equation is the time-dependent Schrodinger's equation for a free particle moving in one direction. In three dimensions this equation will have following form

$$j\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \Psi. \quad (6-47)$$

Let us now consider motion of the particle in an external field of force derivable from a potential. We shall denote the potential energy of the particle by $V(x)$. The potential is a function of position but not of time. In this case the total energy of the particle is

$$E_K = \frac{p_x^2}{2m} + V(x). \quad (6-48)$$

Substituting Eq. 6-43 and Eq. 6-44 into Eq. 6-48 we obtain

$$j\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi. \quad (6-49)$$

For three-dimensional case we can therefore write

$$j\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \Psi + V(x, y, z) \Psi. \quad (6-50)$$

This equation, in which Δ stands for the Laplacian operator, is the time-dependent Schrodinger's equation.

Let us now treat the special case when potential V does depend on time explicitly (we have already done this assumption when constructing Eq. 6-50). In this case the wave function can be considered as a product of two functions. The first of them $\psi(\mathbf{r})$ will depend on coordinates and the second $\Omega(t)$ will depend on time. Thus we can write

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \Omega(t) \quad (6-51)$$

The original wave function - see Eq. 6-42 - rewritten for three dimensions has following form

$$\Psi = \Psi_0 e^{-\frac{j}{\hbar}(Et - \mathbf{p}\mathbf{r})}.$$

We can rearrange this equation into following form

$$\Psi = \Psi_0 e^{\frac{j}{\hbar}(\mathbf{p}\mathbf{r})} e^{-\frac{j}{\hbar}Et} = \psi(\mathbf{r}) \Omega(t),$$

where

$$\psi(\mathbf{r}) = \Psi_0 e^{\frac{j}{\hbar}(\mathbf{p}\mathbf{r})} \quad \text{and} \quad \Omega(t) = e^{-\frac{j}{\hbar}(Et)}.$$

If we differentiate wave function $\Psi(\mathbf{r}, t)$ with respect to time we obtain

$$\frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = -\psi(\mathbf{r}) \frac{j}{\hbar} E e^{-\frac{j}{\hbar}Et}. \quad (6-52)$$

Substituting this equation into Eq. 6-47 we obtain after little rearrangement

$$\Delta \psi(\mathbf{r}) + \frac{2m}{\hbar^2} E_K \psi(\mathbf{r}) = 0. \quad (6-53)$$

The energy E_K in this equation expresses kinetic energy of the particle. We can write kinetic energy of the particle as the difference between total energy E and potential energy V of the particle, or

$$E_K = E - V \quad (6-54)$$

Substituting Eq. 6-54 into Eq. 6-53 we finally have

$$\Delta \psi(\mathbf{r}) + \frac{2m}{\hbar^2} (E - V) \psi(\mathbf{r}) = 0. \quad (6-55)$$

This equation is called the time-independent Schrodinger's equation. Its time-independent solutions $\psi(\mathbf{r})$ determine, through Eq. 6-51, the space dependence of the solutions $\Psi(\mathbf{r}, t)$ to the Schrodinger's equation.

The functions $\psi(\mathbf{r})$ are called eigenfunctions. The first part of this word, eigen, is the German word for characteristic. The student is cautioned to keep clearly in mind the difference between the eigenfunctions $\psi(\mathbf{r})$ and the wave functions $\Psi(\mathbf{r}, t)$.

Schrodinger's equation forms a fundamental law of nature applying to quantum mechanics in the same sort of way in which Newton's law of motion forms the fundamental law for classical mechanics. As well as the Newton's laws it can not be derived from more general laws. Its justification comes from comparison of predictions based on this equation with experimental facts. From Schrodinger's equation follows the existence of discrete energy levels and this can be therefore understood in terms of wave description of matter.

It should be pointed out that we could not apply the Schrodinger's equation to particles moving with relativistic velocities. It is due to the fact that this equation is consistent with Eq. 6-48, which is incorrect for velocities comparable to the velocity of light. In 1928 Dirac developed a relativistic theory of quantum mechanics utilizing essentially the same postulates as the Schrodinger's theory, except the Eq. 6-48 was replaced by its relativistic analogue

$$E = \sqrt{c^2 p^2 + m_0^2 c^4} + V.$$

6.9 Solutions of Time-Independent Schrodinger's Equation

In this chapter we shall obtain many interesting predictions concerning quantum mechanical phenomena. We know that the properties of time-independent Schrodinger's equation depend, among other things, upon the form of potential energy function $V(\mathbf{r})$. This is as it should be since $V(\mathbf{r})$ determines the force acting on the particle whose behavior is supposed to be described by the solution of the Schrodinger's equation. Our goal therefore will be to find acceptable solutions of the time - independent Schrodinger's equation and we will see that these exist only for certain values of energy. These allowed values of energy are called the **eigenvalues**; a particular potential has a particular set of eigenvalues. Corresponding to each eigenvalue is an eigenfunction, which is a solution to the time-independent Schrodinger's equation for the potential $V(\mathbf{r})$.

We shall restrict ourselves to a single dimension because it simplifies the mathematics. We shall start by treating the simplest possible form of the potential, namely by $V(x) = 0$. Then we shall gradually add complexity to the potential.

6.9.1 The zero potential

The simplest time-independent Schrodinger's equation is the one for the case $V(x) = \text{constant}$. A particle moving under the influence of such a potential is a free particle since the force acting on it is zero. It is seen from the following equation

$$F = -\frac{dV}{dx} = 0. \quad (6-56)$$

As this is true regardless of the value of the constant, we do not lose generality by choosing the arbitrary additive constant that always arises in the definition of a potential energy in such a way as to obtain

$$V(x) = 0. \quad (6-57)$$

We know that in classical mechanics a free particle may be either at rest or moving with constant momentum. In either case its total energy is constant. To find behavior predicted by quantum mechanics for a free particle we solve time-independent Schrodinger's equation (Eq.6-55), setting the potential $V(x)$ to zero. With this form for potential the equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0. \quad (6-58)$$

The solutions are eigenfunctions

$$\psi = A e^{jkx} + B e^{-jkx}, \quad (6-59)$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$. As far as there are no restrictions imposed on the free electron wave number, k can have any arbitrary value. The eigenvalues as a function of k are shown in Fig. 6-13.

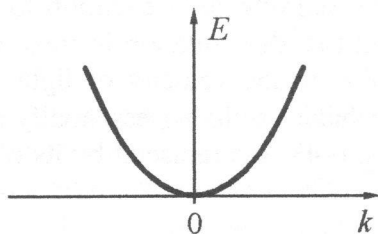


Figure 6-13

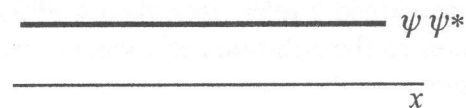


Figure 6-14

For the probability density as a function of coordinate x we obtain $\psi\psi^* = \text{constant}$, see Fig. 6-14. Thus the particle is equally likely to be found anywhere.

A physical example approximating this idealized situation represented by these eigenfunctions would be a proton moving in a highly mono-energetic beam emerging from a cyclotron.

6.9.2 The step potential - energy less than step height

Now we shall study solutions to the time-independent Schrodinger's equation for a particle whose potential energy $V(x)$ has a different constant value in two adjacent regions of the x axis. This is the case of step potential, illustrated in Fig. 6-15.

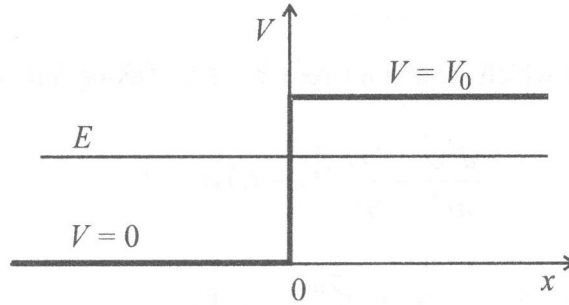


Figure 6-15

We can express this potential as

$$V = V_0 \quad \text{for} \quad x \geq 0$$

$$\text{and} \quad V = 0 \quad \text{for} \quad x < 0. \quad (6-60)$$

We may think of V as an appropriate approximate representation of the potential energy function for a charged particle moving along the axis of a system of two electrodes, separated by a very narrow gap, which are held at different voltages.

Assuming that a particle of a mass m and total energy E is in the region $x < 0$ and that is moving toward the point $x = 0$ at which the potential abruptly changes its value. According to classical mechanics, the particle will move freely in that region until it reaches $x = 0$, where it is subjected force of infinite magnitude. Since the total energy E is constant and smaller than V_0 , classical mechanics says that the particle can not enter the region $x > 0$.

The reason is that in that region

$$E = \frac{p^2}{2m} + V < V \quad \text{or} \quad \frac{p^2}{2m} < 0.$$

Thus the kinetic energy $\frac{p^2}{2m}$ would be negative in the region $x > 0$, which would lead to an imaginary value for the linear momentum in that region. Neither is allowed, nor even make physical sense, in classical mechanics.

To determine the motion of the particle according to quantum mechanics we must find the eigenfunction of the time-independent Schrodinger's equation. For the step potential the x -axis breaks up into two regions. In the region $x < 0$ (left of the step) we have $V = 0$, and the Schrodinger's equation is written as Eq. 6-58. In the region where $x \geq 0$ (right of the step) we have $V = V_0$, and the eigenfunction is a solution to a time-independent Schrodinger's equation which is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0. \quad (6-61)$$

The two equations are solved separately. Then the eigenfunctions valid for the entire range of x is constructed by joining the two solutions together at $x = 0$ in such a way that the eigenfunction and its first derivative are everywhere finite, single valued and continuous.

Consider the differential equation valid for the region in which $V = 0$. Since this is precisely the time-independent Schrodinger's equation for a free particle, we take for its general solution the eigenfunction of Eq. 6-59, or

$$\psi = A e^{jk_1x} + B e^{-jk_1x}, \quad \text{where } k_1 = \sqrt{\frac{2mE}{\hbar^2}}. \quad (6-62)$$

Next consider Eq. 6-61 which is valid for region $x \geq 0$. Taking into account that $V_0 \geq E$ we can write

$$\frac{d^2\psi}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi = 0. \quad (6-63)$$

Denoting
$$k_2 = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}, \quad (6-64)$$

we can write the solution of Eq. 6-63 as

$$\psi(x) = C e^{k_2x} + D e^{-k_2x}. \quad (6-65)$$

The arbitrary constants A , B , C and D of Eqs. 6-62 and 6-65 must be so chosen that the total eigenfunction satisfies the requirements of chapter 6-6. Consider first the behavior of $\psi(x)$ as $x \rightarrow +\infty$. In this region of the x -axis the general form of the $\psi(x)$ is given by Eq. 6-65. Inspection shows that it will generally increase without limit as $x \rightarrow +\infty$, because of the presence of the first term $C e^{k_2x}$. In order to prevent this and keep $\psi(x)$ finite we must set the arbitrary constant of the first term equal to zero

$$C = 0. \quad (6-66)$$

Single valuedness is satisfied automatically by these functions. To study their continuity, we consider the point $x = 0$. At this point the two forms of $\psi(x)$, given by Eqs. 6-62 and 6-65 must join in such a way that $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous. Thus we obtain

$$A + B = D, \quad (6-67)$$

$$A - B = \frac{jk_2}{k_1} D. \quad (6-68)$$

Adding and subtracting Eqs. 6-67 and 6-68 gives

$$A = \frac{D}{2} \left(1 + \frac{jk_2}{k_1} \right), \quad (6-69)$$

$$B = \frac{D}{2} \left(1 - \frac{jk_2}{k_1} \right). \quad (6-70)$$

Thus the eigenfunction for this step potential, and for the energy $E < V_0$ is

$$x < 0: \quad \psi(x) = \frac{D}{2} \left(1 + \frac{jk_2}{k_1} \right) e^{jk_1 x} + \frac{D}{2} \left(1 - \frac{jk_2}{k_1} \right) e^{-jk_1 x}, \quad (6-71)$$

$$x \geq 0: \quad \psi(x) = D e^{-k_2 x}. \quad (6-72)$$

The presence of the one remaining constant D reflects the fact that the time-independent Schrodinger's equation is linear in $\psi(x)$.

Consider now the eigenfunction of Eq. 6-71. Using the relation

$$e^{jkx} = \cos kx + j \sin kx,$$

it is easy to show that the eigenfunction given by Eq. 6-71 for $x < 0$ can be expressed as

$$\psi(x) = D \cos k_1 x - D \frac{k_2}{k_1} \sin k_1 x. \quad (6-73)$$

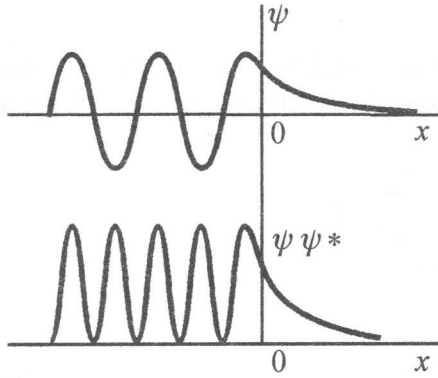


Figure 6-16

In the top part of Figure 6-16 we illustrate the eigenfunction, which is a real function of x if we take D real. In the bottom part of this figure is shown the probability density corresponding to this eigenfunction.

Here we find a feature, which is in sharp contrast to the classical predictions. Although in the region $x \geq 0$ the probability density

$$\psi^* \psi = D e^{-k_2 x} D e^{-k_2 x} = D^2 e^{-2k_2 x} \quad (6-74)$$

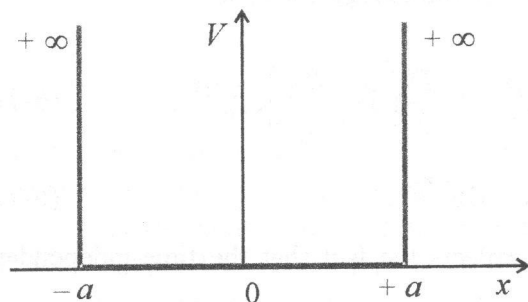
decreases rapidly with increasing x , there is a finite probability of finding the particle in the region

$x > 0$. In classical mechanics it would be absolutely impossible to find the particle in this region. This phenomenon, called penetration of the classically excluded region is one of the most striking predictions of quantum mechanics.

6.9.3 The infinite potential well

In the preceding sections we have treated the motion of the particle in potentials which are not capable of binding them to limited regions of space. Although a number of interesting quantum phenomena showed up, energy quantization did not. The energy quantization can be expected only for potentials, which are capable of binding a particle. In this section we shall discuss the simplest potential having this property, the infinite potential well. We imagine a particle confined within a one dimensional well with infinitely high walls, see Fig. 6-17.

This well has a feature that it will bind a particle with any finite total energy. In classical mechanics, any of these energies are possible. However in quantum mechanics only certain discrete eigenvalues are allowed. This type of potential well is often used in quantum mechanics to represent a situation in which a particle moves in a restricted region of space under the influence of forces which hold it in that region.



The potential well is written as

$$|x| \geq a \quad V \rightarrow \infty, \quad (6-75)$$

$$|x| < a \quad V = 0. \quad (6-76)$$

The problem of a particle confined to a potential well with infinitely high walls is a bit unrealistic but we shall study it for the illustrative purposes.

Figure 6-17

In the region inside the well the general solution to the time-independent Schrodinger's equation can be written in agreement with previous section as

$$\psi(x) = A \sin kx + B \cos kx, \quad (6-77)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}.$$

Let us now find the value of the eigenfunction for $x = \pm a$. We know that in this case the potential V goes to infinity. We can rewrite the time-independent Schrodinger's equation to the form

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}E\psi + \frac{2m}{\hbar^2}V\psi.$$

Dividing by ψ and denoting $\frac{d^2\psi}{dx^2} = \psi''$ we have

$$\frac{\psi''}{\psi} = -\frac{2m}{\hbar^2}E + \frac{2m}{\hbar^2}V. \quad (6-78)$$

As far as for $x = \pm a$ the right side of this equation goes to infinity it means that

$$\psi(a) = \psi(-a) = 0. \quad (6-79)$$

Applying the boundary condition of Eq. 6-79 to eigenfunctions of Eq.6-77 we have

$$x = -a: \quad 0 = -A \sin ka + B \cos ka, \quad (6-80)$$

$$\text{and for } x = +a: \quad 0 = A \sin ka + B \cos ka. \quad (6-81)$$

Addition of the last two numbered equations gives

$$2B \cos ka = 0. \quad (6-82)$$

Due to the fact that $ka \neq 0$ we see that $\cos ka \neq 0$ (supposing that $ka \neq \frac{n\pi}{2}$, where n is odd number). To fulfil Eq. 6-82 we see that B must be equal to zero

$$B = 0. \quad (6-83)$$

However, both constants A and B could not be equal to zero, for then $\psi(x) = 0$ everywhere and the eigenfunction would be of no interest because the particle would not be in the box. Therefore A must be different from zero, or

$$A \neq 0. \quad (6-84)$$

Thus for the points $x = \pm a$ the eigenfunction is

$$\psi = A \sin ka = 0. \quad (6-85)$$

As far as $A \neq 0$ we can write

$$\sin ka = 0. \quad (6-86)$$

The allowed values of k therefore are

$$k = \frac{n\pi}{2a}, \quad \text{where } n \text{ is even number.} \quad (6-87)$$

Knowing the allowed values of k we can write the eigenfunction as

$$\psi_e = A \sin \frac{n\pi}{2a} x. \quad (6-88)$$

We can now subtract Eqs. 6-80 and 6-81. Thus we obtain

$$2A \sin ka = 0. \quad (6-89)$$

Following the same considerations as in the previous case, we finally obtain for eigenfunction

$$\psi_o = B \cos \frac{n\pi}{2a} x, \quad \text{where } n \text{ is odd number.} \quad (6-90)$$

Thus we see that we have obtained two classes of allowed solutions of the time-independent Schrodinger's equation for the particle confined in the well. The number n which figures in Eqs. 6-88 and 6-90 is called the quantum number which is used to label corresponding eigenfunctions.

To determine the constants A and B it is necessary to apply the normalization condition. As an illustrative example we write this condition for eigenfunction given by Eq. 6-88, or

$$A^2 \int_{-a}^{+a} \sin^2 kx dx = 1. \quad (6-91)$$

Solving this integral we obtain

$$A = \pm \frac{1}{\sqrt{a}}. \quad (6-92)$$

The constant B can be obtained in the same way

$$B = \pm \frac{1}{\sqrt{a}}. \quad (6-93)$$

Substituting for A and B into Eqs. 6-88 and 6-90 we obtain for eigenfunction

$$\psi_e = \frac{1}{\sqrt{a}} \sin \frac{n\pi}{2a} x \quad n = 2, 4, 6, \dots \quad (6-94)$$

$$\psi_o = \frac{1}{\sqrt{a}} \cos \frac{n\pi}{2a} x \quad n = 1, 3, 5, \dots \quad (6-95)$$

The probability density is then given by following two equations

$$\psi_e^* \psi_e = \frac{1}{a} \sin^2 \frac{n\pi}{2a} x; \quad \psi_o^* \psi_o = \frac{1}{a} \cos^2 \frac{n\pi}{2a} x.$$

The eigenfunctions for quantum number $n = 1, 2$ and 3 of a particle in infinite square well potential are shown in the left side of Fig. 6-18. On the right side of this figure there is shown the probability density distribution for corresponding eigenfunctions.

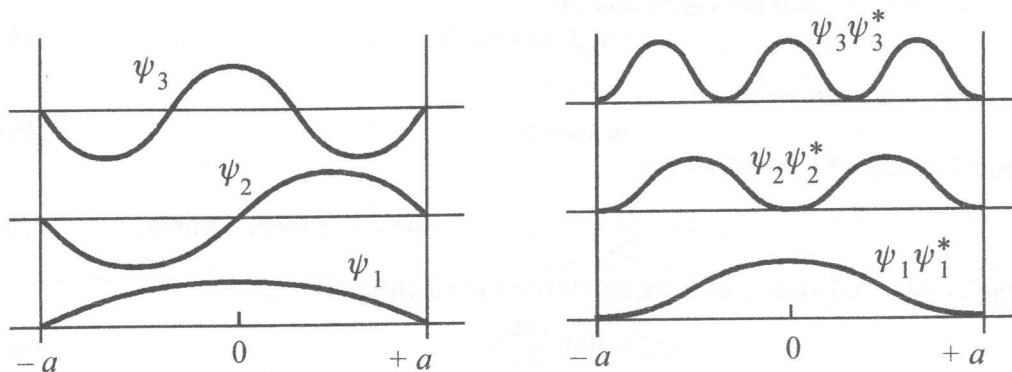


Figure 6-18

We know that the probability density tells us where the particle is likely to be. We see from Fig. 6-18 that the probability density distribution differs for different quantum numbers. Thus for example for the state described by the eigenfunction ψ_1 the particle will be with the biggest probability found in the centre of the well. On the contrary for the state described by the eigenfunction ψ_2 the probability to find the particle in the centre of the well equals to zero. These conclusions are in a sharp contradiction with classical assumptions.

The quantum number n is also used to label the corresponding eigenvalues. Using relation

$k = \sqrt{\frac{2mE}{\hbar^2}}$ and the expression for the allowed values of $k = \frac{n\pi}{2a}$ we find

$$E = \frac{n^2 \pi^2 \hbar^2}{8ma^2}, \quad \text{where } n = 1, 2, 3, 4, \dots \quad (6-96)$$

From this expression we see that only certain values of total energy E are allowed. We say that the total energy of the particle in the box is quantized.

As an example we now determine the energetic spectrum of electron confined inside an infinite potential well for two cases:

- 1) For the well of microscopic dimensions $a = 10^{-10}$ m.
2. For the well of macroscopic dimensions $a = 10^{-2}$ m.

We begin with the well of microscopic dimensions. Substituting for $m_e = 9.1 \times 10^{-31}$ kg, $\hbar = 6.6 \times 10^{-34}$ Js and taking into account the conversion factor $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ we obtain the eigenvalues - allowed values of energy - for quantum numbers changing from 1 to 3:

$$E_1 = 8.5 \text{ eV} \quad E_2 = 34 \text{ eV} \quad E_3 = 76.5 \text{ eV}.$$

Repeating the same operations for the well of macroscopic dimensions we have

$$E_1 = 8.5 \times 10^{-16} \text{ eV} \quad E_2 = 34 \times 10^{-16} \text{ eV} \quad E_3 = 76.5 \times 10^{-16} \text{ eV}.$$

From this example it is seen that if the dimensions of the well are macroscopic (in comparison with the dimensions of the region in which the electron is likely to be) then the difference between energies of two adjacent levels is so small that it can hardly be detected. We can therefore suppose that the energy of electron changes continuously. We also say that in macroscopic world the energy (and other physical quantities) is not quantized. On the other side if the dimensions of the well are comparable with the dimensions of the region in which the electron is likely to be, then the changes of energy on two adjacent levels are detectable and thus we say that the energy is quantized.

The principle of quantization of energy is therefore one of the most remarkable consequences obtained from Schrodinger's equation.

6.9.4 The potential well of a finite height

The problem of a particle confined to a potential well with infinitely high walls is a bit unrealistic. In fact the wells have finite height, see Fig. 6-19. We imagine that the energy E of the particle is smaller than V_0 .

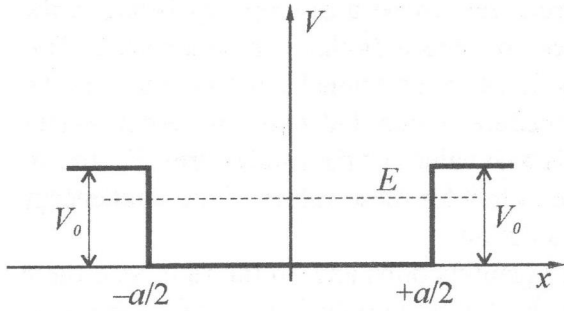


Figure 6-19

This type of well is a good approximation to represent the potential acting on a conduction electron in a block of metal. Figure 6-20 indicates how something like a potential well can be obtained by superimposing the potentials produced by the closely spaced positive ions in the metal.

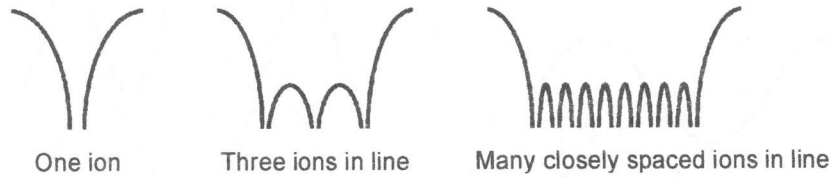


Figure 6-20

To study the problem we have to find the form of eigenfunctions, which are solutions to the time-independent Schrodinger's equation. The problem decomposes itself into three regions: $x < -a/2$ (left of the well), $-a/2 < x < a/2$ (within the well) and $x > a/2$ (right of the well). The general solution of the Schrodinger's equation for the region within the well is

$$\psi = A \sin k_1 x + B \cos k_1 x, \quad (6-97)$$

where k_1 is given by Eq. 6-62.

Now consider the solutions in the regions outside the well. In these regions the general solutions have the forms

$$\psi = C e^{k_2 x} + D e^{-k_2 x} \quad \text{for } x < -a/2 \quad (6-98)$$

and

$$\psi = F e^{k_2 x} + G e^{-k_2 x} \quad \text{for } x > a/2 \quad (6-99)$$

where

$$k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}. \quad (6-100)$$

Now since acceptable eigenfunctions must everywhere remain finite, we can immediately see that we must set $D = F = 0$. Thus we can rewrite eigenfunctions for the regions outside the well as

$$\psi = C e^{k_2 x} \quad \text{for } x < -a/2 \quad (6-101)$$

and

$$\psi = G e^{-k_2 x} \quad \text{for } x > a/2. \quad (6-102)$$

The three forms of Eqs. 6-97, 6-101 and 6-102 involve four arbitrary constants A , B , C and G .

Four more equations involving these constants can be obtained by demanding that $\psi(x)$ and $d\psi/dx$ be continuous at the two boundaries between the regions $x = -a/2$ and $x = a/2$. But we can not allow all four of these constants to be specified by these equations. One of them must remain unspecified. Thus there seems to be a discrepancy between the number of equations to be satisfied and the number of constants that can be adjusted. This problem is resolved by treating the total energy E as an additional constant that can be adjusted as needed. It can be found that this procedure works, but only for certain values of E . That is, there will emerge a certain set of possible values of the total energy E , and so the energy will be quantized to a set of eigenvalues. Only for these values of the total energy does the Schrodinger's equation have acceptable solutions.

On the left side of Fig. 6-23 there are shown the eigenfunctions and on the right side there are shown corresponding probability distributions for the three bound states of a particle in a particular potential well.

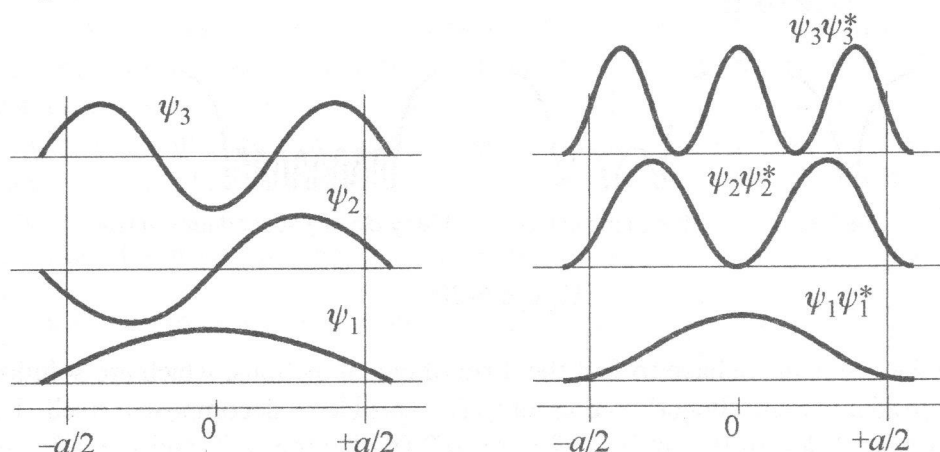


Fig. 6-21

Focusing attention on the probability distribution function that extends into the region outside the well we see that there is a finite probability to find a particle outside the well, that is in a classically excluded region.

6.9.5 The simple harmonic oscillator potential

We have discussed several potentials, which are discontinuous functions of position with constant values in adjacent regions. Now we turn to the more realistic case of potential, which is continuous function of position that is to the potential of simple harmonic oscillator. The simple harmonic oscillator is of tremendous importance in physics. It is used in the study of the vibrations of atoms in diatomic molecules, the acoustic and thermal properties of solids which arise from atomic vibrations, magnetic properties of solids, electrodynamics of quantum systems in which electromagnetic waves are vibrating etc.

We can write the equation for the potential of the simple harmonic oscillator as

$$V = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2. \quad (6-103)$$

Classical mechanics predicts that a particle under the influence of the restoring force $F = -kx$ exerted by the potential of Eq. 6-103 will oscillate in simple harmonic motion with frequency

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (6-104)$$

According to the theory the total energy of the particle can have any value.

Quantum mechanics, based on the solution of the Schrodinger's equation predicts that the total energy E can have only a discrete set of energies

$$E_n = \left(n + \frac{1}{2}\right) hf, \quad \text{where } n = 0, 1, 2, 3, \dots \quad (6-105)$$

where f is the classical oscillation frequency of the particle and n is the quantum number.

From Eq. 6-105 we see that the lowest value of the energy (for $n = 0$) equals to $hf/2$. This is the zero-point energy for the potential, the existence of which is required by the uncertainty principle. The potential and the eigenvalues and the eigenfunctions for three states of simple harmonic oscillator are shown in Fig. 6-22.

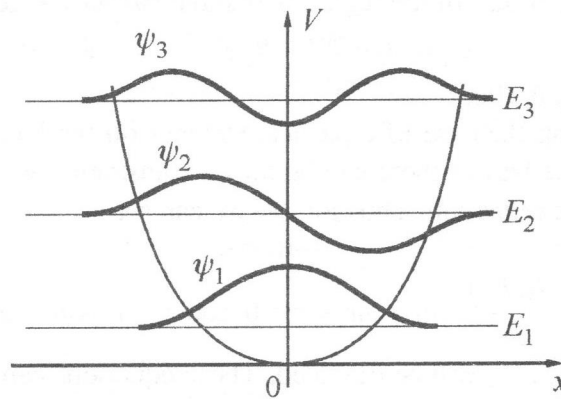


Figure 6-22

6.9.6 The barrier potential

Let us now consider a particle moving in the field of barrier potential, illustrated in Fig. 6-23.

The potential can be written as follows:

$$\begin{aligned} V &= V_0 & \text{for } 0 \leq x \leq a, \\ V &= 0 & \text{for } x < 0 \text{ and for } x > a. \end{aligned}$$

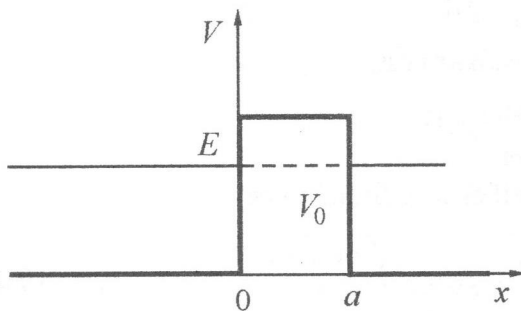


Figure 6-23

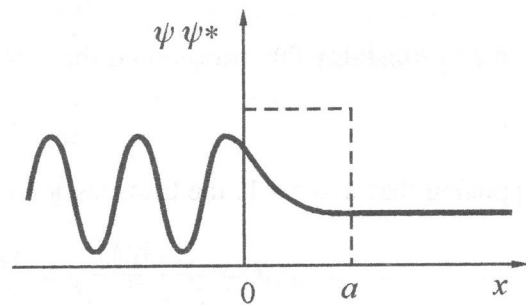


Figure 6-24

We suppose that a particle of a mass m and total energy E is in the region $x < 0$ and it is moving along axis to the right. The height V_0 of the potential barrier is greater than the total energy E of the particle. Due to this fact the classical mechanics says that the particle cannot reach the region $x > a$. However, quantum mechanics predicts that there is a certain probability that the particle will be transmitted through the barrier into the region $x > a$.

To study the problem from the standpoint of quantum mechanics we have to find the eigenfunctions. In analogy with the problem of the step potential we may expect that the Schrodinger's equation breaks up into three separate equations for three regions in which the potential energy is constant, or

$$\begin{array}{ll} x < 0 & \text{left of the barrier,} \\ 0 \leq x \leq a & \text{inside a barrier,} \\ x > a & \text{right of the barrier.} \end{array}$$

In the regions to the left and to the right of the barrier the equations are those for a free particle of total energy E . Their general solutions are

$$\psi_I = A_1 e^{jk_1x} + B_1 e^{-jk_1x}, \quad \text{for } x < 0, \quad (6-107)$$

$$\psi_{III} = A_3 e^{jk_1x} + B_3 e^{-jk_1x}, \quad \text{for } x > a, \quad (6-108)$$

where k_1 is given by Eq. 6-62. In the region within the barrier the general solution is

$$\psi_{II} = A_2 e^{-k_2x} + B_2 e^{k_2x}, \quad \text{for } 0 \leq x \leq a. \quad (6-109)$$

where k_2 is given by Eq. 6-100.

Since we are considering the case of a particle incident on the barrier from the left, in the region to the right of the barrier there can be only a transmitted wave as there is nothing in that region to produce a reflection. Thus for ψ_{III} we can set

$$B_3 = 0. \quad (6-110)$$

In matching $\psi(x)$ and $\frac{d\psi(x)}{dx}$ for points $x = 0$ and $x = a$ four equations in the arbitrary constants A_1, A_2, A_3, B_1, B_2 will be obtained. These equations can be used to evaluate A_2, A_3, B_1 and B_2 in terms of A_1 . The value of A_1 , determines the amplitude of the incident wave, and it can be left arbitrary. The form of the probability density corresponding to the eigenfunction obtained is indicated in Fig. 6-24.

The most interesting result of the calculation is the ratio T of the probability flux transmitted through the barrier into the region $x > 0$, to the probability flux upon the barrier. This ratio is called the transmission coefficient T . The probability flux is proportional to the square of the amplitude of the corresponding wave. Thus the probability flux incident on the barrier is

$$I_{inc} = \frac{\hbar k_1}{m} |A_1|^2.$$

Similar probability flux transmitted through the barrier is

$$I_{trans} = \frac{\hbar k_1}{m} |A_3|^2.$$

Supposing that $k_2 a \gg 1$, the transmission coefficient is found to be

$$T = \frac{16k_1^2 k_2^2}{(k_1^2 + k_2^2)^2} e^{-2k_2 a} = T_0 e^{-\frac{2}{\hbar} \sqrt{2m(V_0 - E)}}. \quad (6-111)$$

This equation makes the prediction, which is, from the point of view of classical mechanics, very remarkable. The particle of mass m and total energy E incident on a potential barrier $V_0 > E$ and finite thickness a , actually has a certain probability, (see Fig. 6-25) of penetrating the barrier and appearing on the other side. This phenomenon is called **barrier penetration**, and the particle is said to **tunnel** through the barrier.

There are many interesting examples of barrier penetration e.g. functioning of the tunnel diode or emission of alpha particles.

6.9.7 The hydrogen atom

Let us now extend what we have learned about an electron trapped in an infinite well to the more realistic case of an electron trapped in an atom. We choose the simplest atom, hydrogen.

The hydrogen atom consists of a single electron bound to its nucleus by the attractive Coulomb's force. The potential energy function $V(r)$ for this system is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (6-112)$$

where r is the distance between electron and atom. This hydrogen atom trap, unlike the one-dimensional well, is three-dimensional. Therefore to find the energetic spectrum of electron we have to solve the time-independent Schrodinger's equation taking into account Eq. 6-112, or

$$\Delta\psi + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0. \quad (6-113)$$

As far as the problem has a spherical symmetry it is convenient to use the spherical coordinates r , ϑ and φ . Thus we can rewrite Eq. 6-113 to the following form, where $\psi = \psi(r, \vartheta, \varphi)$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0 \quad (6-114)$$

Equation 6-114 can be solved by making repeated applications of the technique of separation of variables to split the partial differential equation into a set of three ordinary differential equations, each involving only one coordinate, and then using standard procedures to solve these equations. We therefore suppose that

$$\psi(r, \vartheta, \varphi) = R(r)\Theta(\vartheta)\Phi(\varphi). \quad (6-115)$$

The problem has been therefore reduced to that of solving three ordinary differential equations for $\Theta(\vartheta)$ and $\Phi(\varphi)$ and $R(r)$. In solving these equations we can find that the equation has acceptable solutions only for certain values of m_l . Using these values of m_l in the equation for $\Theta(\vartheta)$, it turns out that this equation has acceptable solutions only for certain values of l . With these values of l in the equation for $R(r)$, this equation is found to have acceptable solutions only if the total energy has one of the values E_n , where

$$E_n = -\frac{mZ^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}, \quad (6-116)$$

where n is the principal quantum number. Comparing this prediction with the predictions of the Bohr's model (see Eq. 6-11) we find that identical allowed energies are predicted by this treatment. It can be also shown that the quantum numbers l and m_l are related to the magnitude L of the orbital angular momentum of the electron and to its component L_z by the relation

$$L = \sqrt{l(l+1)}\hbar, \quad \text{where } l = 0, 1, 2, \dots, n-1 \quad (6-117)$$

$$L_z = m_l \hbar, \quad \text{where } m_l = 0, \pm 1, \dots, \pm l \quad (6-118)$$

Although there are many points at which the Schrodinger's theory corresponds quite closely to the Bohr's model, there are certain striking differences. Thus for example in both

treatments the ground state corresponds to the quantum number $n = 1$ and it has the same value of the total energy. But in the Bohr's model the orbital angular momentum for this state is $L = n\hbar = \hbar$ whereas in quantum mechanics it is $l = \sqrt{l(l+1)}\hbar = 0$ since $l = 0$, where $n = l$ (see Eq.6-117). The results of measurements of atomic spectra show that the quantum mechanical prediction for zeros orbital angular momentum in the ground state is the correct one.

Name	Symbol	Allowed values	Associated with	Number of values
Principal	n	1, 2, 3, ...	Energy	∞
Orbital	l	0, 1, 2, ..., (n-1)	Magnitude of orbital angular momentum	n
Magnetic	m_l	0, ± 1 , ± 2 , ..., $\pm l$	Projection of orbital angular momentum	$2l + 1$
Spin	m_s	$\pm \frac{1}{2}$	Spin angular momentum	2

The Schrodinger's theory is therefore a more detailed description of hydrogen atom than Bohr's model. It is therefore of great practical importance because it forms the foundation of the quantum mechanical treatment of all multielectron atoms, as well as molecules and nuclei. In the previous table are summed up the quantum numbers of the hydrogen atom.

6.10 Magnetic Dipole Moment, Spin

We are going now to discuss the result of some experiments, which measure the orbital angular momentum \mathbf{L} of an atomic electron. These experiments do not actually measure \mathbf{L} directly. Instead they measure a related quantity μ_l - the orbital magnetic dipole moment, by measuring its interaction with a magnetic field applied to the atom. When considering the results of measurements of atomic dipole moments, we shall discover the very important fact, that electrons have an intrinsic angular momentum called spin, and an associated spin magnetic dipole moment.

We know (see Physics I, Eq.16-9) that associated with an electron of mass m and charge e in a circular orbit there is the orbital magnetic dipole moment

$$\mu_l = i\mathbf{S}\mathbf{n}_0. \quad (6-119)$$

When such a dipole is placed in an applied magnetic field \mathbf{B} the dipole will experience a torque (see Physics I, Eq. 16-10)

$$\tau = \mu \times \mathbf{B}, \quad (6-120)$$

tending to align the dipole with the field. Associated with this torque, there is a potential energy of orientation

$$U = -\mu_l \cdot \mathbf{B}. \quad (6-121)$$

If the applied magnetic field is uniform in space, there will be no net translational force acting on the magnetic dipole. But if the field is non-uniform, there will be such a translational force.

In 1922 Stern and Gerlach measured the possible values of the magnetic dipole moment for neutral silver atoms by sending a beam of these atoms through a non-uniform magnetic field. They found that this beam of atoms is split into two discrete components, one

component being bent in the positive z direction and the other bent in the negative z direction. The experiment was repeated using several other species of atoms (for example hydrogen), and in each case investigated it was found that the deflected beam is split into two, or more, discrete components. The results are, qualitatively, direct experimental proof of the quantization of the z component of the magnetic dipole moments of atoms and, therefore of their angular momentum.

This result leads us to the assumption that an electron has an intrinsic (built-in) magnetic dipole moment μ_s , due to the fact that it has an intrinsic angular momentum S called its spin. We also assume that the magnitude S and z component of the spin angular momentum are related to two quantum numbers s and m_s , by quantization relations which are identical to those for angular momentum (see Eqs. 6-117 and 6-118)

$$S = \sqrt{s(s+1)}\hbar, \quad (6-122)$$

$$S_z = m_s \hbar. \quad (6-123)$$

From the experimental observation that the beam of hydrogen atoms is split into two symmetrically deflected components, it is apparent that μ_{s_z} can assume just two values, which are equal in magnitude but opposite in sign. If we make the final assumption that the possible values of m_s differ by one and range from $-s$ to $+s$, as is true of the quantum numbers of m_l and l for orbital angular momentum, then we can conclude that the two possible values of m_s are

$$m_s = -\frac{1}{2}, +\frac{1}{2}, \quad (6-124)$$

and that s has a single value $1/2$.

Credit for the introduction of electron spin is generally given by so called fine structure of certain lines of the optical spectra of hydrogen and the alkali atoms. The splitting of the atomic energy levels could then be understood as due to a potential energy of orientation of the magnetic dipole moment of the electron in the magnetic field that is present in the atom because it contains moving charged particles.

The total angular momentum of an atom can be expressed as

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (6-125)$$

The total angular momentum \mathbf{J} satisfies the quantum mechanical angular momentum conservation law, that is if the atom is in free space so that the external torque act on it, its \mathbf{J} maintains a fixed magnitude J and a fixed z component.

Magnitude and z component of the total angular momentum \mathbf{J} are specified by two quantum numbers j and m_j , according to the usual quantization conditions as

$$J = \sqrt{j(j+1)}\hbar, \quad j = l + \frac{1}{2}, l - \frac{1}{2}, l - \frac{3}{2}, l - \frac{5}{2}, \quad (6-126)$$

$$J_z = m_j \hbar, \quad m_j = -j, -j+1, -j+2, \dots, j-1, j. \quad (6-127)$$

Thus to conclude we can say that although the electron seems to be a „point particle“, four quantum numbers n , l , m_l , and m_s are required to specify its quantum state. Instead of these quantum numbers in spectroscopy we use sometimes quantum numbers n , l , j , and m_j . To describe the quantum state of multielectron atom we use quantum numbers L , S and J . However, it should be pointed out that due to the so called spin-orbit interaction (L - S coupling) the description of multielectron atoms is more complex.

The atomic nucleus can be also considered as a quantum system. Thus for example proton, like the electron has a spin of $1/2$ in units of \hbar .

The spin technology is now currently used in such applications like medical diagnostic imaging. The protons in the various tissues of the human body find themselves in different local magnetic environments. When the body, or part of it, is immersed in a strong magnetic field, these environmental differences can be detected by spin-flip techniques and translated by computer processing into a x-ray-like image.

6.11 Multielectron Atoms, Exclusion Principle

Electrons are identical particles - any electron is exactly the same as any other electron. Nevertheless, in classical physics identical particles can be distinguished from each other by procedures, which do not otherwise affect their behavior, and so it is possible to assign labels to the particles.

In quantum mechanics this can not be done because the uncertainty principle does not allow us to observe constantly the motion of the electrons without changing their behavior. Thus we see that there is a fundamental distinction between the classical and quantum description of a system containing identical particles. An accurate quantum mechanical treatment of these systems must be formulated in such a way that the indistinguishability of identical particles is explicitly taken into account. That is measurable results obtained from accurate quantum mechanical calculations should not depend on the assignment of labels to identical particles.

Since it is the wavefunction that carry the burden of describing quantum mechanical system it must be them to contain a mathematical expression of the qualitative ideas just mentioned. Without going to further details we can say that the condition of indistinguishability of identical particles leads us to two types of wavefunctions - the symmetric and the antisymmetric ones. We can say that the symmetric wave function is unchanged by the exchange of the particle labels, that is $\Psi(1,2) = \Psi(2,1)$. The particles of zero or integral spin are described by the symmetric wavefunctions.

On the other side the antisymmetric wavefunction in multiplied by minus one by an exchange of particle labels, that is $\Psi(1,2) = -\Psi(2,1)$. The system of particles with spin $s=1/2$ (that is the system of electrons) is described by the antisymmetric wavefunctions.

Now we can return to the multielectron atoms namely to the question why all the electrons can not be bound in the same quantum state represented by the intermost shell of the atom. Pauli's explanation of this problem is that the electrons bound in atom must be described by antisymmetric wavefunctions, which vanish, if even two electrons are in the same quantum state. This idea led Pauli to the formulation of his exclusion principle:

In a multielectron atom there can never be more than one electron in the same quantum state.

If this important principle did not hold, all of the electrons in an atom would move to the state of lowest energy and then the entire universe would be radically different.

We group the electron states of multielectron atoms into subshells; each characterized by a given value of quantum numbers n and l , see following table. The interpretation of a periodic table of elements is based on information about the ordering according to energy of the outer filled subshells of multielectron atoms.

The first column of this table identifies the subshells by the quantum numbers n and l . The second column identifies the subshells by giving the spectroscopic notation for n and l . The number gives the values of n , and the letter gives the value of l according to the following scheme:

	$l = 0$	1	2	3	4	5	6	...
spectroscopic notation	s	p	d	f	g	h	i	...

The third column gives the maximum number of electrons that can occupy different states in the same subshell without violating the exclusion principle.

The energy ordering of the outer filled subshells

Quantum numbers n, l	Designation of subshell	Capacity of subshell $2(2l+1)$	Energy
-	-	-	Less negative
6,2	6 d	10	
5,3	5 f	14	
7,0	7 s	2	
6,1	6 p	6	
5,2	5 d	10	
4,3	4 f	14	
6,0	6 s	2	
5,1	5 p	6	
4,2	4 d	10	
5,0	5 s	2	
4,1	4 p	6	
3,2	3 d	10	
4,0	4 s	2	
3,1	3 p	6	
3,0	3 s	2	
2,1	2 p	6	
2,0	2 s	2	
1,0	1 s	2	Lowest energy (most negative)

If the ordering according to energy of the outer filled subshells is being known, it is easy to determine the configuration of any atom in its ground state. In the ground state the electrons must fill all the subshells in such a way as to minimize the total energy of the atom, and yet not exceed the capacity $[2(2l+1)]$ of any subshell. The subshell will fill in order of increasing energy as it is shown in the previous table.

Consider first the hydrogen atom. The single electron occupies the 1s subshell, with its spin either „up“ or „down“. For the He atom both electrons are in the 1s subshell, one spin is up“ and the other is „down“. The configuration of H is written ${}^1\text{H}:1s^1$. The configuration of He is written ${}^2\text{He}:1s^2$.

The superscript on the subshell designation specifies the number of electrons, which it contains. The superscript on the chemical symbol specifies the Z value for the atom.

In the ${}^3\text{Li}$ atom one of the electrons must be in the 2s subshell because the capacity of the 1s subshell is only 2. The configuration of this atom is ${}^3\text{Li}:1s^2 2s^1$.

We can say that it is a major triumph of quantum mechanics that, taking the filling order properly into account we can understand the entire periodic table of the elements.

6.12 Operators, Expectation Values

Every physical theory involves some basic physical concepts and a set of correspondence rules that map the physical concepts onto the mathematical objects that represent them. Once the mathematical version of the problem is formulated, it may be solved by purely mathematical techniques that need not have any physical interpretation. The formal solution is then translated back into the physical world by means of the correspondence rules. Now we are going to establish these correspondence rules.

Certain dynamical variables, which should take on a continuum of values according to classical mechanics, were found by experiment to take on only discrete or quantized values. This is illustrated clearly by atomic spectra. However energy is not always quantized, since a free electron can take on a continuum range of energies. Evidently we need some means of calculating the allowed values of dynamical variables, and it should treat the discrete and continuous cases on an unbiased footing. This is accomplished by the following postulate:

To each dynamical variable corresponds a Hermitian operator whose eigenvalues are the possible values of the dynamical variable.

An operator \hat{A} maps a function Ψ onto functions Φ , that is

$$\Phi = \hat{A} \Psi. \quad (6-128)$$

An operator is fully defined by specifying its action on every function in its domain. A linear operator satisfies following condition

$$\hat{A}(c_1\Psi_1 + c_2\Psi_2) = c_1(\hat{A}\Psi_1) + c_2(\hat{A}\Psi_2). \quad (6-129)$$

We shall be treating only linear operators and so we shall henceforth refer to them simply as operators. To assert the equality of two operators $\hat{A} = \hat{B}$, means that

$$\hat{A}\Psi = \hat{B}\Psi, \quad (6-130)$$

for all functions in the common domain of \hat{A} and \hat{B} . Thus we can define the sum and product of two operators

$$(\hat{A} + \hat{B})\Psi = \hat{A}\Psi + \hat{B}\Psi, \quad (6-131)$$

$$\hat{A}\hat{B}\Psi = \hat{A}(\hat{B}\Psi). \quad (6-132)$$

Both these equations must hold for all Ψ . It follows from this definition that operator of multiplications is necessarily associative

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}. \quad (6-133)$$

But it need not be commutative, $\hat{A}\hat{B}$ being unequal to $\hat{B}\hat{A}$ in general.

If an operator acting on a certain function produces a scalar multiple of the same function

$$\hat{A}\Psi_n = A_n\Psi_n, \quad (6-134)$$

we call the function Ψ_n an eigenfunction and the scalar A_n an eigenvalue of the operator \hat{A} . If \hat{A} is a Hermitian operator, then all its eigenvalues are real. It can be also shown that the eigenfunctions corresponding to distinct eigenvalues of a Hermitian operator must be orthogonal.

The set of eigenvalues A_n of operator \hat{A} is called a spectrum of operator \hat{A} . This spectrum can be purely discrete or continuous. The operator is said to have a degenerate spectrum if to one eigenfunction correspond several eigenvalues.

Following to the postulate that to each dynamical variable corresponds a Hermitian operator we introduce some basic operators. As an operator of coordinate we take the multiplication by coordinate, or

$$\hat{x}\Psi_n = x_n\Psi_n. \quad (6-135)$$

An operator of momentum can be found by differentiating the wave function (see Eq. 6-42) with respect to x

$$\frac{\partial\Psi}{\partial x} = \frac{j}{\hbar}p_x\Psi, \quad \text{which gives} \quad -j\hbar\frac{\partial\Psi}{\partial x} = p_x\Psi. \quad (6-136)$$

We see that the effect of multiplying the function Ψ by the x -component of momentum is the same as the effect of operating on it with the differential operator $-j\hbar\frac{\partial}{\partial x}$. Thus in

accordance with Eq. 6-134 we can consider the differential operator $-j\hbar\frac{\partial}{\partial x}$ as an operator of x -component of linear momentum. An operator of momentum can be thus expressed as

$$\hat{p} = -j\hbar\nabla. \quad (6-137)$$

A similar association can be found between another dynamical quantity energy and differential operator $j\hbar\frac{\partial}{\partial t}$ by differentiating Eq-6-42 with respect to time. After a little rearrangement we obtain

$$j\hbar\frac{\partial\Psi}{\partial t} = E\Psi. \quad (6-138)$$

In agreement with previous considerations we can write an operator of energy as

$$\hat{E} = j\hbar\frac{\partial}{\partial t}. \quad (6-139)$$

We can also show that the time independent Schrodinger's equation can be written in the form of Eq. 6-134. To do this we rewrite Eq. 6-65 to the form

$$\left[-\frac{\hbar^2}{2m}\Delta + V \right] \Psi = E\Psi. \quad (6-140)$$

By comparing Eq. 6-140 with Eq. 6-134 we see that the square bracket is just the operator for the total energy. Thus we can write Schrodinger's equation in the form

$$\hat{H}\Psi = E\Psi, \quad (6-141)$$

where the total energy operator \hat{H} is called the Hamiltonian.

Using the operators we can determine so called expectation values of dynamical variables, which are expressed by corresponding operators. Consider a particle and its associated wave function $\Psi(\mathbf{r}, t)$. In a measurement of the position of the particle in the system described by the wave function, there should be a finite probability of finding it at any x coordinate in the interval from x to $x+dx$, as long as the wave function is nonzero in that interval. Thus we are not able to state that the x coordinate of the particle has a certain definite value. However, it is possible to specify some sort of average position of the particle in the following way. Let us imagine making a measurement of the position of the particle at the instant t . The probability of finding it between x and $x+dx$ is given by Eq. 6-25. Imagine performing this measurement a number of times on identical system described by the same wave function $\Psi(\mathbf{r}, t)$, always at the same value of t , and recording the observed values of x at which we find the particle.

We can use the average of the observed values to characterize the position at time t of a particle associated with the wave function $\Psi(\mathbf{r}, t)$. This average value we call the **expectation value** of the x coordinate at the instant t . We can express the expectation value of x , which is written as \bar{x} , as just the value of the x coordinate weighted by the probability of observing that value, or

$$\bar{x} = \frac{\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) \hat{x} \Psi(\mathbf{r}, t) dV}{\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) dV} = \int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) \hat{x} \Psi(\mathbf{r}, t) dV, \quad (6-142)$$

because the denominator equals to one – see Eq. 6-28. In the same way we can calculate the expectation value of any dynamical variable. As an example let us obtain the expression for the expectation value of the x - component of momentum. Following Eq. 6-142 and with respect to Eq. 6-137 we can write

$$p_x = \int_{-\infty}^{\infty} \Psi^*(x, t) \left(-j\hbar \frac{\partial}{\partial x} \right) \Psi(x, t) dx = -j\hbar \int_{-\infty}^{\infty} \Psi^*(x, t) \left(\frac{\partial \Psi(x, t)}{\partial x} \right) dx. \quad (6-143)$$

We thus obtained an expression, which can be integrated, immediately if we know $\Psi(x, t)$. The procedure, which we have just described, provides us with a powerful method for obtaining the expectation values of any dynamical quantity. We have also seen how to extract from the wave function a wide variety of additional information concerning not only the position of the particle, but also its momentum, energy and all other quantities that characterize its behavior.

6.13 Solid State Physics

A solid consists from atoms packed closely together, and their proximity is responsible for characteristic properties of this state of matter.

Most solids are crystalline in nature or nearly so, though a few, such as glass have no definite ordered structures.

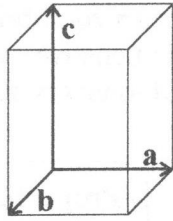
An ideal crystal is constructed by the infinite repetition in space of identical structural units. In the simplest crystals (copper, silver, gold, etc.) the structural unit consists of a single atom. More generally the structural unit contains several atoms or molecules up to perhaps 100 in inorganic crystals and 10^4 in protein crystals. A crystal may be composed of more than one chemical element (as in NaCl). We describe the structure of all crystals in terms of a single periodic lattice, with a group of atoms attached to each lattice point or situated in each elementary parallelepiped. This group of atoms is called the **basis**. The basis is repeated in space to form the crystal.

An ideal crystal is composed of atoms arranged in a lattice defined by three **fundamental translation vectors** $\mathbf{a}, \mathbf{b}, \mathbf{c}$ such that the atomic arrangement looks the same in every respect when viewed from any point \mathbf{r} as when viewed from point with position vector

$$\mathbf{r}' = \mathbf{r} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, \quad (6-144)$$

where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are called the crystal axis and n_1, n_2 and n_3 are arbitrary integers. The set of points \mathbf{r}' specified by Eq. 6-144 for all values of integers and n_1, n_2 and n_3 defines a **lattice**.

The lattice is a regular periodic arrangement of points in space.



The parallelepiped defined by the primitive axes **a, b, c** is called a **primitive cell**, see Fig. 6-25.

Figure 6-25

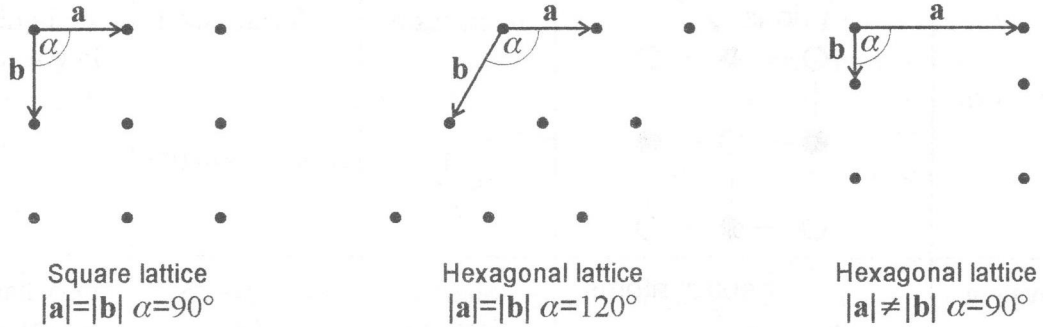


Figure 6-26

There are one, two or three dimensional lattice types. The atoms distributed along the line form one-dimensional lattice. In Fig. 6-26 there are shown different types of two-dimensional lattices. The example of three-dimensional lattices is shown in Fig. 6-27.

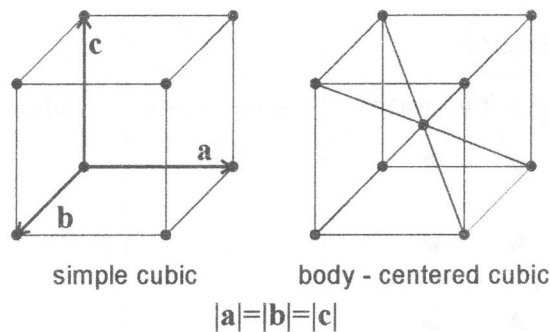


Figure 6-27

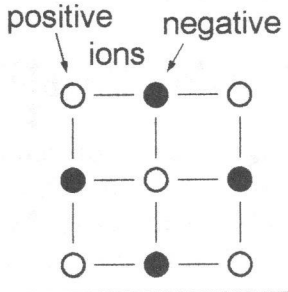
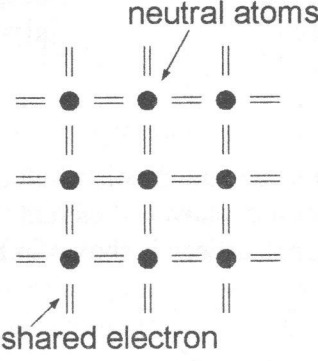
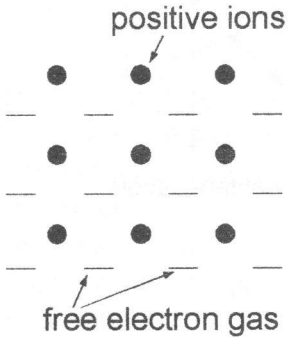

6.14 Crystal Binding

Following character of the forces, which hold the crystal together, we can distinguish four types of crystals:

- ionic,
- covalent,
- metallic,
- molecular (Van der Waals).

Ionic crystals are made up of positive and negative ions. The **ionic bond** is the bond resulting from the electrostatic interaction of oppositely charged ions. Such bonds come into being when atoms which have low ionization energies, and hence lose electrons easily, interact with other atoms which have high electrons affinities.

The former atoms give up electrons to the latter, and they thereupon become positive and negative ions respectively. In an ionic crystal these ions come together in an equilibrium configuration in which the attractive forces between positive and negative ions predominate over the repulsive forces between similar ions. The example of ionic crystal is the crystal of sodium chloride - NaCl.

Crystal	Figure	Interaction	Example	Properties
Ionic		Electrostatic interaction $\approx \frac{1}{r^2}$	Sodium chloride NaCl $E_b \sim 3.3 \text{ eV/atom}$	Hard, soluble in liquids like water
Covalent		Shared electrons	Diamond, Si, Ge $E_b \sim 7.4 \text{ eV/atom}$	Very hard, non soluble, high melting point.
Metallic		Free electron gas	Sodium - Na $E_b \sim 1.1 \text{ eV/atom}$	High electrical and heat conductivity
Molecular		Van der Waals forces $\approx \frac{1}{r^2}$	Sugar, ice, dry ice, CH ₄ $i \sim 0.1 \text{ eV/atom}$	Soft, low melting and boiling point

Crystals of all types are prevented from collapsing under the influence of the cohesive forces present by the action of the Pauli's exclusion principle, which requires the occupancy of higher energy states when electron shells of different atoms overlap and mesh together. The cohesive force in **covalent crystals** arises from the presence of electrons between adjacent atoms. Each atom participating in a covalent bond contributes an electron to the bond, and these electrons are shared by both atoms rather than being exclusive property of one of them as an ionic bond. Diamond is an example of a crystal whose atoms are linked by covalent bond. Each carbon atom has four nearest neighbors and shares an electron pair with each of them. Silicon, germanium, and silicon carbide are among the substances whose crystal structures are the same as that of diamond. We can think of a **metal crystal** as an array of positive charges embedded in a uniform sea of negative charge. The valence (outermost) electrons of the atoms comprising a metal may be common to the entire atomic aggregate, so that a „gas“ of free electrons pervades it. The presence of these free electrons accounts nicely for the high electrical conductivities and other unique properties of metals.

There are many substances whose molecules are so stable that, when brought together, they have no tendency to lose their individuality by joining together in a collective lattice with multiple linkages like these found in ionic and covalent crystals. However, even they can exist as liquids and solids through the action of the attractive Van der Waals intermolecular forces. These forces explain why even two nonpolar molecules can attract each other. Even though the distribution of the electric charges in the nonpolar molecule is symmetric on the average, the electrons themselves are in constant motion and at any given instant one part or another part of the molecule has an excess of them. Thus a nonpolar molecule has a constantly shifting asymmetry of the electric charge. When two nonpolar molecules are close enough, their fluctuating charge distributions tend to shift together, adjacent ends always having opposite signs and always causing an attractive force. This force is named after the Dutch physicist Van der Waals force. Van der Waals forces are present not only between all molecules, but also between all atoms, including those of inert gases which do not otherwise interact. Van der Waals bonds are much weaker than ionic and covalent bonds, and as result **molecular crystals** generally have low melting and boiling points and a little mechanical strength. Ordinary ice and dry ice (solid CO_2) are examples of molecular crystals. The comparison of different types of crystals is shown in the preceding table.

6.15 Band Theory of Solids

The free electron model of metals mentioned in the preceding chapter gave us considerable insight into several electronic properties of metals, yet there are other electronic properties of solids for which the free electron model gives us no help. The model can not to help us to understand why some chemical elements are good conductors of electricity and others are insulators or they form semiconductors. Besides the distinction between the conductivity values of metallic conductors and insulators are striking. The conductivity of pure metals at low temperatures may be of the order $10^6 - 10^7 (\Omega\text{m})^{-1}$ and the conductivity of insulators may be as low as $10^{-10} - 10^{-13} (\Omega\text{m})^{-1}$. The conductivity of semiconductors lies within a wide range $10^{-8} - 10^4 (\Omega\text{m})^{-1}$ and depends for example on temperature, illumination etc. To understand the difference between insulators, semiconductors and conductors we must extend the free electron model to take into account the periodic lattice of the solid.

The crystal field, see Fig. 6-20, can be approximated by a periodic array of potential wells of rectangular shape. This is the one-dimensional „Kronig-Penney“ model of the crystal which is shown in Fig. 6-28. Let us calculate the energy levels of an electron in this periodical potential field. The depth of the well is V_0 .

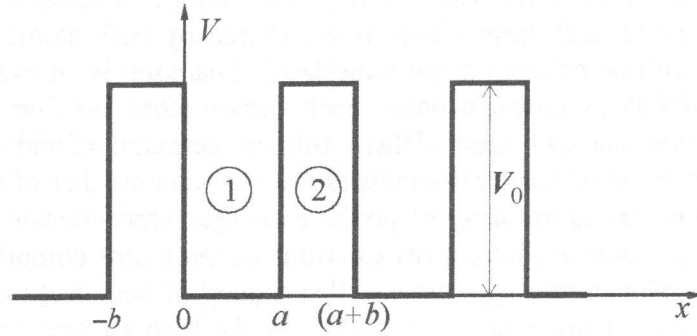


Figure 6-28

We introduce so-called lattice constant $c = a+b$. The potential is periodic in c .

$$V(x) = V(x+c) = V(x+2c) = \dots \quad (6-145)$$

It is reasonable to try for eigenfunction $\psi(x)$ a solution of the form

$$\psi(x) = u(x)e^{jkx}, \quad (6-146)$$

$$\text{where } u(x) = u(x+c) = u(x+2c) = \dots \quad (6-147)$$

This is so called a „Bloch“ function which respects the periodicity of the lattice. To find the energies of electron we use the time independent Schrodinger's equation, see Eq. 6-55. To substitute Bloch function into Schrodinger's equation we determine $\frac{d\psi}{dx}$ and $\frac{d^2\psi}{dx^2}$.

Substituting these into Schrodinger's equation we have

$$\frac{d^2u}{dx^2} + 2jk \frac{du}{dx} + \left[\frac{2m}{\hbar^2} (E - V) - k^2 \right] u = 0. \quad (6-148)$$

From Fig. 6-28 we see that potential V has different values depending on coordinate x .

Thus we can distinguish two different regions of potential.

- 1st region.

$$0 < x < a \quad V = 0 \quad (6-149)$$

We denote the eigenfunction for this region as ψ_1 .

- 2nd region.

$$a \leq x \leq (a+b) \quad V = V_0 \quad (6-150)$$

We denote the eigenfunction for this region as ψ_2 .

Taking the Schrodinger's equation for the first region we have

$$\frac{d^2u_1}{dx^2} + 2jk \frac{du_1}{dx} + \left[\frac{2m}{\hbar^2} E - k^2 \right] u_1 = 0. \quad (6-151)$$

Denoting
$$\frac{2m}{\hbar^2} E = \alpha^2, \quad (6-152)$$

the solution can be written in the form

$$u_1 = A e^{-j(\alpha+k)x} + B e^{j(\alpha-k)x} \quad \text{for } 0 < x < a. \quad (6-153)$$

We now take Schrodinger's equation for the second region, or

$$\frac{d^2 u_2}{dx^2} + 2jk \frac{du_2}{dx} + \left[\frac{2m}{\hbar^2} (E - V_0) - k^2 \right] u_2 = 0. \quad (6-154)$$

We denote

$$\frac{2m}{\hbar^2} (E - V_0) = -\beta^2. \quad (6-155)$$

The eigenfunction for the second region therefore is

$$u_2 = C e^{(-jk+\beta)x} + D e^{-(jk+\beta)x} \quad \text{for } a \leq x \leq (a+b). \quad (6-156)$$

The condition of continuity for u and $\frac{du}{dx}$ yields

$$u_1(0) = u_2(0) \quad u_1(a) = u_2(a) \quad (6-157)$$

$$\frac{du_1(0)}{dx} = \frac{du_2(0)}{dx} \quad \frac{du_1(a)}{dx} = \frac{du_2(a)}{dx}.$$

Taking into account the condition of periodicity we can also write

$$\frac{du_1(a)}{dx} = \frac{du_2(a)}{dx} = \frac{du_1(-b)}{dx} = \frac{du_2(-b)}{dx}. \quad (6-158)$$

Thus we have a set of four conditions for eigenfunction and its derivatives. Substituting functions u_1 and u_2 into these conditions we obtain a homogeneous set of equations for A , B , C and D . This set can be solved if the determinant Δ of these coefficients vanishes. From this condition we obtain

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a+b). \quad (6-159)$$

This is the equation for the energy of electron (this energy figures in the expression for α and β). Let us denote left side of this equation as $f(E)$ or

$$f(E) = \frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a. \quad (6-160)$$

As far as on the right side of Eq. 6-159 there is a function of $\cos k(a+b)$ it is obvious that

$$|f(E)| \leq 1 \quad (6-161)$$

However, it could be shown that for certain values of energy Eq. 6-161 could not be fulfilled. As an example let us imagine that the energy is

$$\alpha a = n\pi. \quad (6-162)$$

We substitute Eq. 6-162 into Eq. 6-160 and thus we obtain

$$f(E) = \pm \cosh \beta b \quad \text{or} \quad |f(E)| \geq 1, \quad (6-163)$$

which is in contradiction with Eq. 6-161.

Thus we can say that the energy derived from condition $\alpha a = n\pi$, that is

$$\sqrt{\frac{2mE}{\hbar^2}} a = n\pi \quad \text{or} \quad E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad (6-164)$$

is forbidden.

We can therefore conclude that for an electron in a periodical potential field certain values of energy are **forbidden**. These ranges are called **forbidden energy bands or gaps**. Between these gaps are **allowed energy bands**.

We can now exhibit our results in a very interesting form by plotting the energy E of electron as a function of wave number k , see Fig. 6-29.

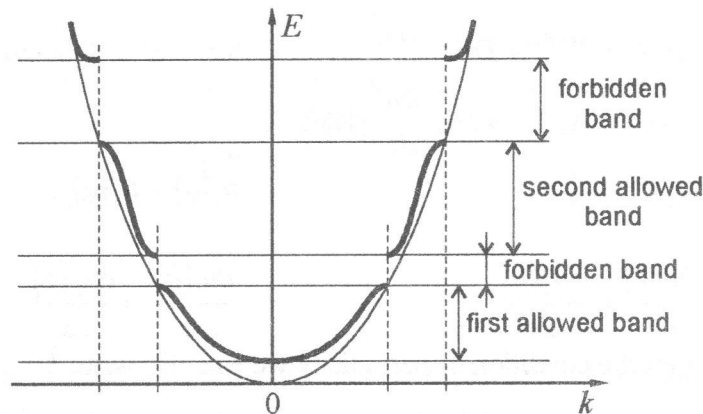


Figure 6-29

We see that for the electron in a periodic potential field the parabola for the free electron, see Fig. 6-13, is replaced by S-shaped parts of a sine curve which are separated from each other by discontinuities in energy - these are forbidden energy gaps.

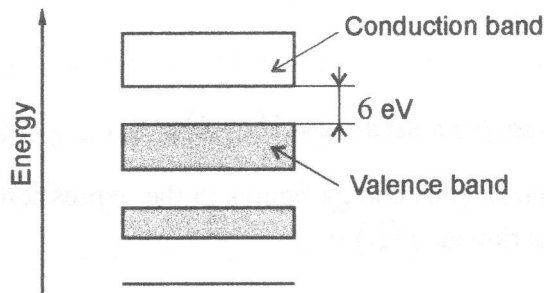


Figure 6-30

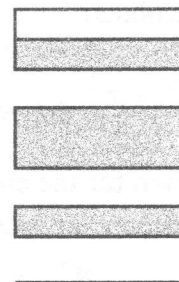


Figure 6-31

The energy band in a solid corresponds to the energy levels in an atom, and an electron in a solid can possess only these energies that fall within these energy bands. Depending on the element the various energy bands in a solid may overlap or may not overlap.

The electrical behavior of a crystalline solid is determined both by its energy-band structure and how electrons normally fill these bands.

To understand the difference between conductors and insulators let us have a look on the schematic electron occupancy of allowed energy bands for an insulator and a conductor. Fig. 6-30 corresponds to the electrical insulator and Fig. 6-31 corresponds to the conductor. The vertical extent of boxes indicates the allowed energy regions, the shaded area indicate the regions filled with electrons.

Fig. 6-30 is a simplified diagram of the energy bands of diamond. The two lower energy bands are completely filled with electrons. The upper band filled with electrons is called valence band. There is a gap of 6 eV between the top of valence band and empty band above it (which is called conduction band). This means that at least 6 eV of additional energy must be provided to an electron if it is to have any kinetic energy, since it can not have any energy lying in the forbidden band. An energy increment of this magnitude can not readily be given to an electron in a crystal by an electric field. An electron moving through a crystal collides with another electron after an average distance 10^{-8} m, and it loses much of the energy it gained from electric field in the collision. Thus we can estimate an electric field if an electron is to gain 6 eV in the path length of 10^{-8} m to be $E \cong 6 \times 10^8$ V/m, which is an immense value. Diamond is therefore a very poor conductor of electricity, and is accordingly classed as an insulator.

Fig. 6-31 is a simplified diagram of the energy bands of sodium. We see that the upper energy band is only partially occupied. When an electric field is set up across a piece of solid sodium, electrons easily acquire additional energy while remaining in their original energy band. The additional energy is in the form of kinetic energy, and the moving electrons constitute an electric current. Sodium is therefore a good conductor of electricity as are other crystalline solids with energy bands that are only partially filled.

There exists however another group of materials, which are called semiconductors.

6.16 Semiconductors

There is an essential difference between a semiconductor, such as germanium and a good conductor such as silver. The conductivity of semiconductors lies in the region of $10^{-8} - 10^4$ $(\Omega\text{m})^{-1}$ and may be strongly dependent on temperature. At absolute zero a pure, perfect crystal of most semiconductors will be an insulator. The characteristic semiconducting properties are brought about by thermal excitation, impurities and lattice defects. Devices based on the properties of semiconductors include transistors, rectifiers, thermistors, photocells etc.

In case of semiconductors we distinguish two kinds of conductivity:

1. **Intrinsic conductivity** - this type of conductivity is exhibited by highly purified semiconductors. In the intrinsic temperature range the electrical properties of a semiconductor are not essentially modified by impurities in the crystal. An electronic band scheme leading to intrinsic conductivity is shown in Fig. 6-32.

At temperature 0 K the conductivity is zero because all states in the conduction band are vacant. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band, where they become mobile. The conduction band is separated from the valence band by the gap E_g . The values of the band gap for 0 K for Si equal to 1.17 eV and for Ge 0.74 eV.

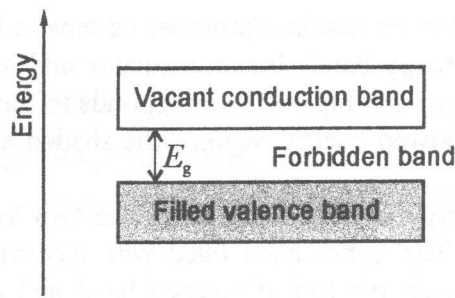


Figure 6-32.

2. Impurity conductivity - certain types of impurities drastically affect the electrical properties of a semiconductor. Thus the addition of boron to silicon in the proportion of 1 boron atom to 10^5 silicon atoms increases the conductivity of pure silicon by a factor of 10^3 at room temperature. The deliberate addition of impurities to a semiconductor is called doping. The semiconductors with impurities are known as deficit semiconductors. There are two types of deficit semiconductors.

Let us incorporate a few arsenic atoms in a silicon crystal. Arsenic atoms have five electrons in their outermost shells, while silicon atoms have four. When an arsenic atom replaces a silicon atom in a silicon crystal, four of its electrons are incorporated into the covalent bonds with its nearest neighbors (see Fig. 6-33). The fifth electron requires little energy to be detached and move about in the crystal. Such a substance is called **n-type** semiconductor, because electric current is carried by negative charges.

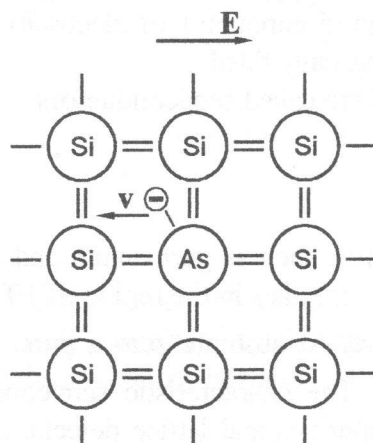


Figure 6-33

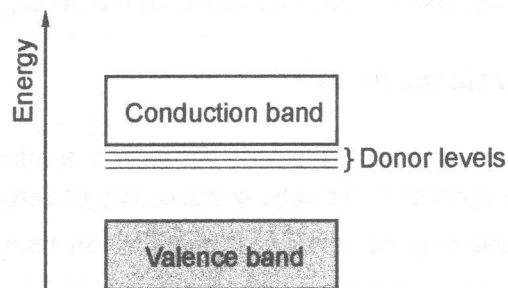


Figure 6-34

The arsenic atom is called a **donor** atom, because it gives up an electron. It can be shown that these impurity atoms give rise to electronic energy levels, which lie within the energy gap E_g close to the lower edge of the conduction band. In this way appear so-called **donor energy levels** (see Fig. 6-34). To raise electrons from these donor levels to the conduction band much smaller energy than the width of the band is required.

If we incorporate gallium atoms in a silicon crystal, a different effect occurs. Gallium atoms have only three electrons in their outer shells, and their presence leaves vacancies called **holes** in the electron structure of the crystal. An electron needs relatively little energy to enter a hole, but as it does it leaves a new hole in its former location (see Fig 6-35). When an electric field is applied across a silicon crystal containing a trace of gallium, electrons move toward the anode by successively filling holes. The flow of current is in this case described with reference to the holes, whose behavior is like that of positive charges since

they move toward the negative electrode. A substance of this kind is called **p-type semiconductor** (p-means positive charges).

The gallium atom is called **acceptor** because it accepts an electron from the valence band. In the case of p-type semiconductors the impurity energy levels are situated slightly above the valence band (see Fig. 6-36).

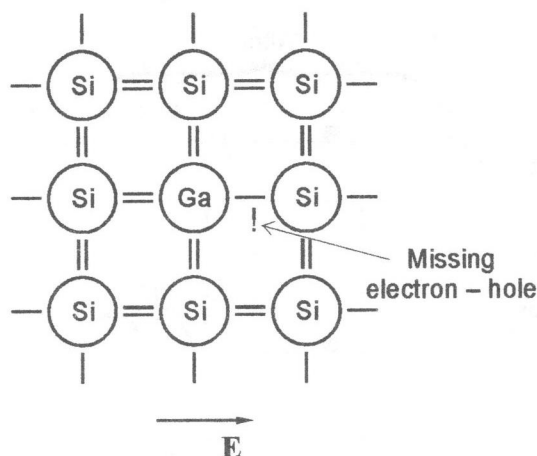


Figure 6-35

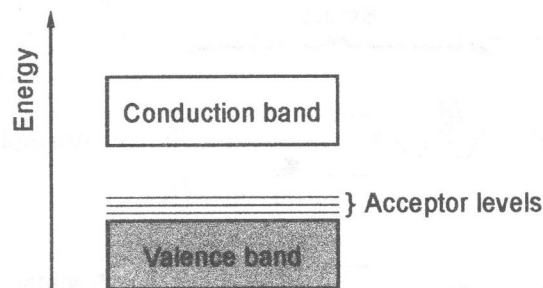


Figure 6-36

A small temperature can raise electrons from the lower valence band to the acceptors levels, leaving few energy levels in the valence band. The electrical conductivity is then caused by the existence of these empty levels.

The unusual properties of n-type and p-type semiconductors have made possible the development of such compact and efficient electronic devices as the transistor.

6.17 Lasers

The word laser is an acronym for Light Amplification by Stimulated Emission of Radiation. To understand the operation of laser we have to learn of stimulated emission.

Let us consider a single isolated atom that can exist in only one of two states of energies E_1 and E_2 . Let us discuss three ways in which this atom can be caused to move from one of its two allowed states to the other.

Fig. 6-37a shows an atom initially in the lower of its two states, with energy E_1 . We also assume that a continuous spectrum of radiation is present. If a photon of energy

$$hf = E_2 - E_1, \quad (6-165)$$

interacts with the atom, the photon will vanish and the atom will move to its upper energy state. We call this process **absorption**.

In Fig. 6-37b the atom is in this upper state and no radiation is present. After a certain mean time, the atom moves of its own accord to the state of lower energy, emitting a photon of energy hf . We call this process a **spontaneous emission**, because it was not triggered by any outside influence. Normally the mean life of excited atoms before spontaneous emission occurs is about 10^{-8} s. However there exist some states in which this mean life is much longer, perhaps as long as 10^{-3} s. We call such states **metastable states**. These states play an essential role in laser operation.

In Fig. 6-37c the atom is again in its upper state, but this time a continuous spectrum of radiation is also present. As in absorption, a photon whose energy is given by Eq. 6-165

interacts with the atom. The result is that the atom moves to its lower energy state and there are now two photons when only one existed before. The emitted photon is in every way identical to the triggering, or stimulating photon. It has the same energy, direction and polarization. In this way is produced the laser light.

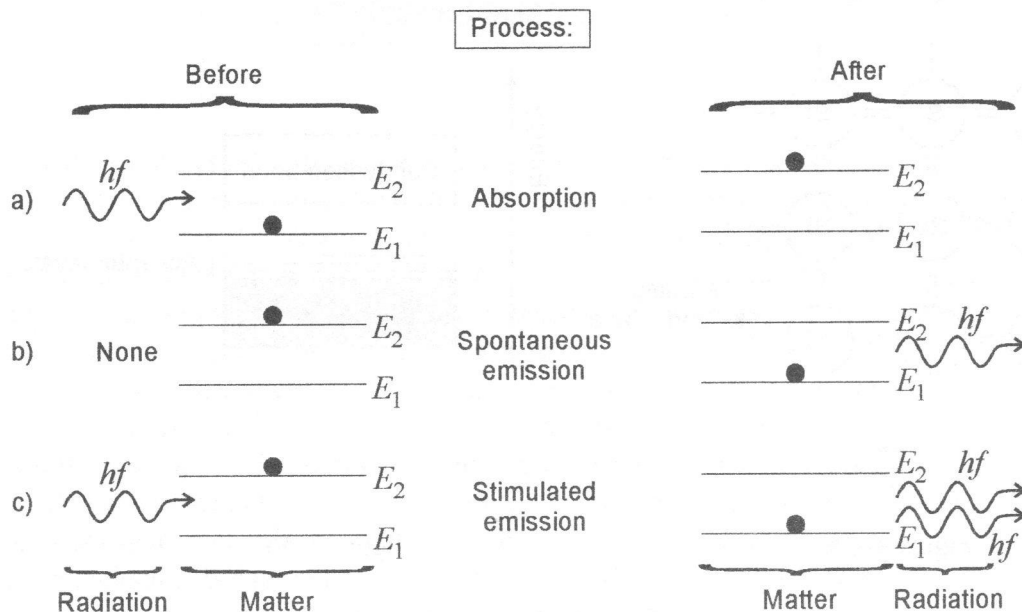


Figure 6-37

Fig. 6-37c describes the stimulated emission of a photon from a single atom. In the usual case, however, many atoms are present. Fig. 6-38a shows the normal thermal equilibrium distribution of atoms between two states and Fig. 6-38b shows an inverted population, obtained by special techniques. To generate a laser light we have to create this population inversion.



Figure 6-38

As an example of laser operation we describe an optically pumped laser. Fig. 6-39 shows schematically how we can set up a population inversion in a lasing material so that laser action can occur.

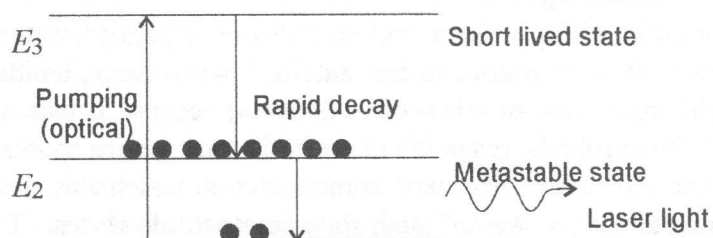


Figure 6-39

We start with essentially all of the atoms of the material in the ground state E_1 . We then supply energy to the system so that many atoms are raised to an excited state E_2 . In optical pumping the energy comes from an intense, continuous spectrum light source that surrounds the lasing material.

From state E_3 many atoms decay rapidly to state E_2 , which must be a metastable state, that is, it must have a relatively long mean-life against spontaneous emission. The state E_2 can then become more heavily populated than state E_1 and we have so called population inversion. A stray photon of the right energy can then trigger an avalanche of stimulated emission from state E_2 and thus we have a laser light.

The elements of a helium-neon gas laser are shown in Fig. 6-40.

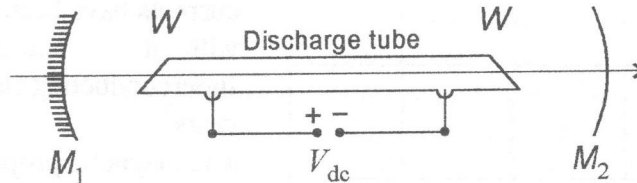


Figure 6-40

The glass discharge tube is filled with an 80%-20% mixture of helium and neon, neon being the lasing medium. The necessary population inversion comes about because of collisions between the helium and the neon atoms. Most stimulated emission photons produced in the discharge tube will not happen to be parallel to the tube axis and will quickly be stopped at the tube walls. Stimulated emissions photons that are parallel to the axis, however, can be made to move back and forth through the discharge tube many times by successive reflection from mirrors M_1 and M_2 . A chain reaction builds up rapidly in this direction, accounting for the inherent parallelism of the laser light. The mirrors M_1 and M_2 are concave with their focal points coinciding at the center of the discharge tube. The mirror M_1 is coated with a dielectric film whose thickness is carefully adjusted to be a perfect reflector at the wavelength of the laser light. The mirror M_2 is coated so as to be slightly „leaky“ so that a small fraction of the laser light can escape at each reflection to form a useful beam. The windows W , which close the ends of the discharge tube, are slanted to minimize loss of light by reflection.

Except of the gas lasers there are semiconductor lasers where incoming current creates light at a pn junction, solid state lasers (the name is given to all non-semiconductor crystal and gas lasers) and dye lasers (which use flowing liquids that are excited by a flash lamp or other lasers).

Lasers emit coherent light - that is light with well-defined frequency, phase and polarisation. This light can be used for many purposes - technological (cutting, welding, blasting) medical (e.g. eye surgery) information processing (audio or video signals) measurements, holography, research purposes (laser initiated thermonuclear fusion) etc.

6.18 Superconductivity

The electrical resistivity of many metals and alloys drops abruptly to zero when a specimen is cooled to sufficiently low temperature, often a temperature in the liquid helium range. Kamerlingh Onnes first observed this phenomenon in 1911. The results of his original measurements on mercury are shown in Fig. 6-41.

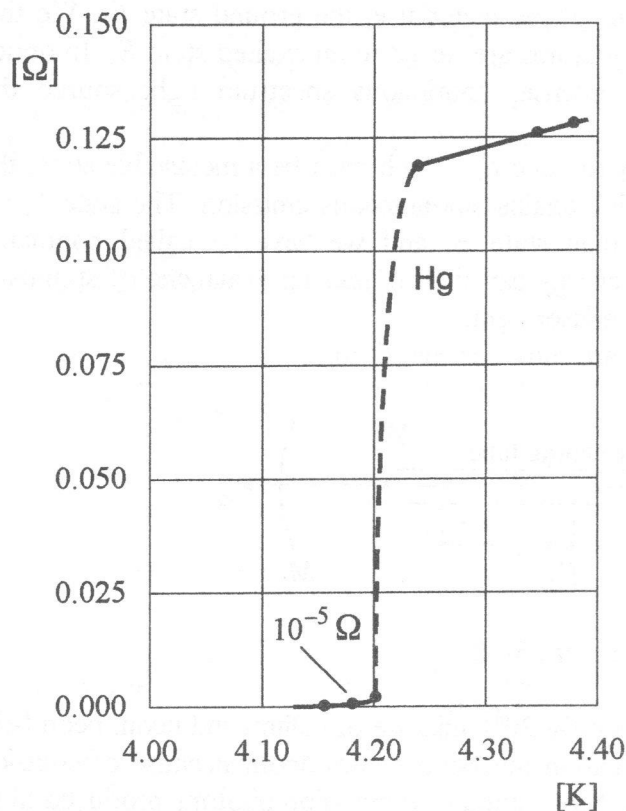


Figure 6-41

Note the narrowness of the temperature interval in which the resistivity change occurs. We say that at a critical temperature T_C the specimen undergoes a phase transition from a state of normal electrical resistivity to a superconducting state.

In the superconducting state the electrical resistivity is so close to zero that persistent electrical currents have been observed to flow without attenuation in superconducting rings for more than years.

The magnetic properties exhibited by superconductors are as dramatic as their electrical properties. It is an experimental fact that a bulk superconductor in a magnetic field will act as a perfect diamagnet, with zero magnetic induction in the interior of a bulk semiconductor.

When a specimen is placed in a magnetic field and is then cooled through the transition temperature, the magnetic flux originally present is ejected from the specimen. This is called the Meissner effect. The sequence of events of this effect is shown in Fig. 6-42.

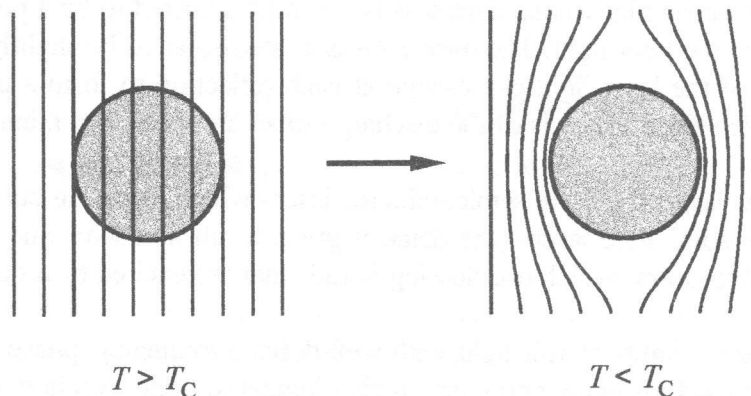


Figure 6-42

We see a sphere in a constant applied magnetic field. Below the transition temperature the lines of induction \mathbf{B} are ejected from the sphere.

However, sufficiently strong magnetic field will destroy superconductivity. The threshold or critical value of the applied magnetic field for the destruction of the superconductivity is denoted by B_C and is function of temperature. At the critical temperature the critical field is zero. The variation of the critical field with temperature is shown in Fig. 6-43. The threshold curve separates the super-conducting state S from the normal state N.

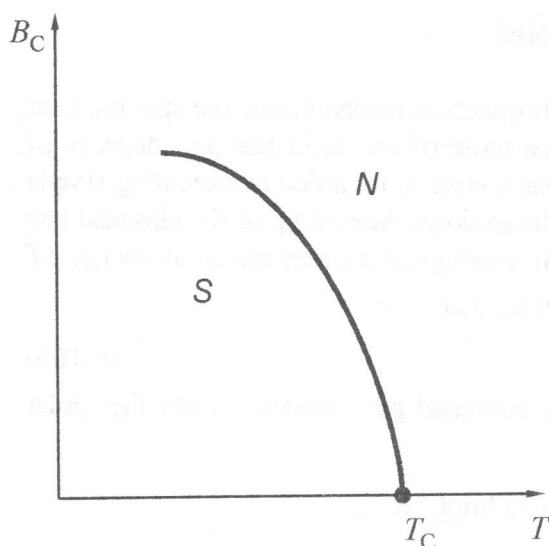


Figure 6-43

According to their behaviour in a magnetic field superconductors can be divided into two types. Superconductors exhibiting a complete Meissner effect (perfect diamagnetism) are called type I superconductor. There are however other materials (alloys for commercial solenoids e.g.) which can be penetrated by the external magnetic field and still remain superconductive. The Meissner effect is therefore said to be incomplete. These are called type II superconductors.

A successful quantum theory of superconductivity was given by Bardeen, Cooper and Schrieffer. The heart of the BCS theory – as it is called, after the initials of its developers – is the assumption that the charge carriers are not single electrons but pairs of

electrons. These Cooper pairs behave like single particles, with properties dramatically different from those of single electrons. Electrons normally repel each other so that some special mechanism is needed to induce them to form a pair. A semiclassical picture that helps in understanding this quantum mechanism is as follows: An electron plows through the lattice, distorting it slightly and thus leaving in its wake a very short-lived concentration of enhanced positive charge. If a second electron is nearby at the right moment, it may well be attracted to this region by the positive charge, thus forming a pair with the first electron. These electron pairs move almost freely through the superconductor.

Another interesting property of superconductors is magnetic flux quantization. Just as electric charge is quantized so is the magnetic flux through a superconducting loop- the flux quantum is equal to $h/2e$ (where h is Planck's constant).

It was also shown that the pairs of electrons in a superconducting current can move ("tunnel") through a thin insulating barrier. A loop of superconducting material with such a barrier or "tunnel junction" can still be superconducting. This is called the Josephson effect. The problem with the technological development of superconductivity has always been the low temperatures that were necessary to maintain it. In 1987, however, new ceramic materials based on yttrium-barium-copper oxide were discovered that become superconducting at temperatures as high as 125 K.

The phenomenon of superconductivity has many practical applications. One of them is for example magnetically levitated train, which was constructed in Japan. This train floats without touching the ground as a result of repulsion between its superconducting magnets and the magnetic field that they induce in the tracks. Josephson junction devices serve as memory and processing elements in digital computers. Another interesting application is a large superconducting ring which is used in Tacoma (USA) to store electrical energy. It takes up to five megawatts during peaks of supply and releases the energy during peaks in demand.

The phenomenon of superconductivity is therefore of great importance in technology because it means that charges can flow through the conductor without thermal losses.

6.19 The Specific Heat of a Crystalline Solid

In this section we present one of the applications of quantum mechanics to the specific heat of a crystalline solid. Following classical ideas one mole of the solid has $3N_0$ degrees of freedom, where N_0 is the Avogadro's number and each atom is regarded as executing simple harmonic oscillations about its lattice site in three dimensions. According to the classical law of equipartition of energy each degree of freedom is assigned an average total energy kT ($\frac{1}{2}kT$ for kinetic and $\frac{1}{2}kT$ for potential energy) so that

$$U_i = 3N_0 kT = 3RT, \quad (6-166)$$

where k is the Boltzmann's constant and R is the universal gas constant. Then the molar heat capacity at constant volume is

$$C_V = \left(\frac{\partial U_i}{\partial T} \right)_V = 3R \approx 25 \text{ Jmol}^{-1} \text{ K}^{-1}.$$

This equation is called Dulong and Petit's law. The molar specific heat of lead, aluminium and carbon as a function of temperature are shown in Fig. 6-44.

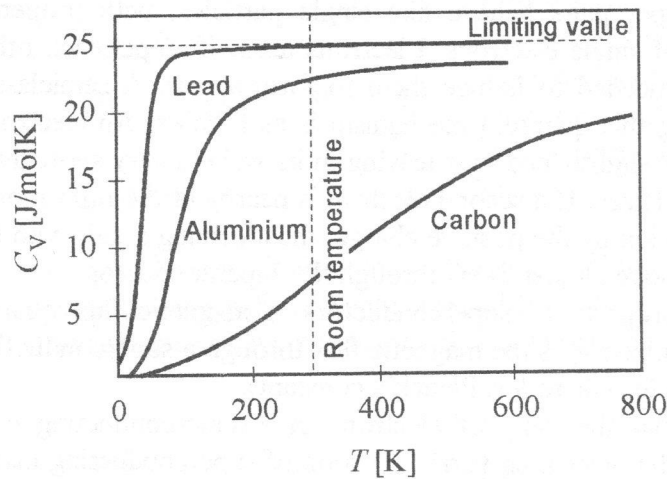


Figure 6-44

As Fig. 6-44 suggests C_V varies with temperature approaching $25 \text{ Jmol}^{-1} \text{ K}^{-1}$ at high enough temperatures. Some substances such as carbon do not reach this limiting value until temperatures well above room temperature. Later experiments showed that the C_V of all solids tends to zero as the temperature decreases. Thus we see that there is a discrepancy between experimental results and results based on classical ideas.

It was A. Einstein who suggested that the kT factor (see Eq. 6-166) from the classical equipartition theorem should be replaced by a factor that takes into account the energy quantization of a simple harmonic oscillator such as Planck had done in the black body radiation problem. Einstein represented a solid body as a collection of simple harmonic oscillators of the same fundamental frequency f and replaced kT by $hf \left(e^{\frac{hf}{kT}} - 1 \right)$. From this

assumption he calculated the molar heat capacity

$$C_V = 3R \left(\frac{hf}{kT} \right)^2 \exp \left[-\frac{hf}{kT} \right], \quad \text{for } hf \gg kT.$$