

## Quantum mechanics

In the previous chapter we have already seen that in case of an atomic electron we can not speak about trajectory, and we have seen the wave-particle nature of electron. In 1924 de-Broglie suggested to describe the atomic electron by using its wave nature. In 1926 Schrödinger wrote his famous equation to describe the motion of the electron. This is the basic equation of quantum mechanics. In this equation he used a so called wave function to describe the state of the electron. The Greek letter psi is used, and in general  $\Psi(x, y, z, t)$ , or in one dimension  $\Psi(x, t)$ .  $\Psi$  usually represents a complex function in the mathematical sense.

### What is the meaning of the wave function $\Psi$ for a particle?

The wave function describes the distribution of the particle in space. It is related to the probability of finding the particle in various regions. If we imagine a volume element  $dV$  around a point, the probability that the particle will be found in that volume element is measured by  $|\Psi|^2 dV$ . The so called probability density is  $\rho = |\Psi|^2$ . We can say only where the particle is likely to be, not where it is.

### How is the wave function $\Psi$ determined for a given problem?

The wave function can be obtained by the solution of the Schrödinger equation for the given physical situation. The time dependent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \Delta \Psi + V(\vec{r})\Psi = -\frac{\hbar}{i} \cdot \frac{\partial \Psi}{\partial t},$$

where  $m$  is the mass of the particle and  $V$  is the potential energy. In all the situations we will meet here, the space and time variables can be grouped separately and the consequence that

$\Psi(\vec{r}, t)$  can be written in the form:  $\Psi(\vec{r}, t) = \varphi(\vec{r}) \cdot e^{-\frac{i}{\hbar} E t}$ . In these cases the solution is called stationary solution. Considering this separated solution we can obtain the time independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \Delta \varphi + V(\vec{r})\varphi = E \cdot \varphi, \text{ or in one dimension } -\frac{\hbar^2}{2m} \frac{d^2 \varphi}{dx^2} + V(x)\varphi = E \cdot \varphi.$$

It turned out for some system that acceptable solutions exist only when some physical quantity for example the energy of the system has certain special values that is quantized.

### Quantum mechanical description of the motion of a free particle.

We begin with a quantum-mechanical analysis of a free particle that moves along a straight line without being acted on any force. In this case the potential energy is zero  $V = 0$ , so the

Schrödinger equation in one dimension:  $-\frac{\hbar^2}{2m} \frac{d^2 \varphi}{dx^2} = E \cdot \varphi$ .

$$\frac{d^2 \varphi}{dx^2} = -\frac{2mE}{\hbar^2} \cdot \varphi$$

$$E = \frac{1}{2} m v_x^2 = \frac{p_x^2}{2m}, \text{ so } p_x^2 = 2mE$$

$$\frac{d^2\varphi}{dx^2} = -\frac{p_x^2}{\hbar^2} \cdot \varphi$$

$$\frac{d^2\varphi}{dx^2} = -\left(\frac{p_x}{\hbar}\right)^2 \cdot \varphi$$

The solution of this equation:  $\varphi(x) = Ae^{i\frac{p_x}{\hbar}x}$

The time dependent function from the stationary solution:  $\tau(t) = e^{-\frac{i}{\hbar}Et}$ .

The wave function for the free particle:  $\Psi(x,t) = Ae^{i\frac{p_x}{\hbar}x} \cdot e^{-\frac{i}{\hbar}Et} = Ae^{-\frac{i}{\hbar}(Et - p_x x)}$

$$\Psi(x,t) = Ae^{-\frac{i}{\hbar}(Et - p_x x)}$$

We know from electrodynamics the wave function of a monochromatic plane wave:

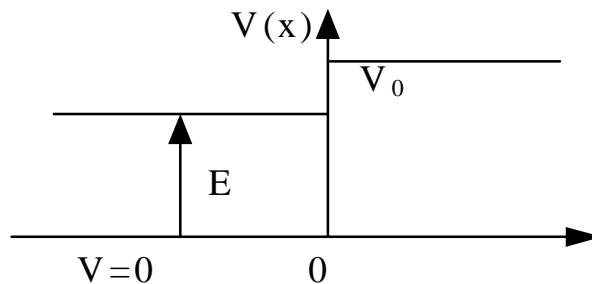
$$\Psi(x,t) = Ae^{-i(\omega t - k_x x)}$$

Comparing the two equations:  $\frac{E}{\hbar} = \omega$ ,  $E = 2\pi f \frac{h}{2\pi}$ , and  $E = h \cdot f$ . This is just the Einstein, Planck formula for the energy of a quantum.

$\frac{p_x}{\hbar} = k_x$ ,  $\frac{2\pi p_x}{h} = \frac{2\pi}{\lambda}$ , so  $\lambda = \frac{h}{p_x}$  which is the so called de-Broglie hypothesis. So we obtained these two very important formulas.

### Travelling through a potential step

Suppose that the particle is moving in a region where there is a potential step. We discuss one dimension stationary state. The wave function:  $\Psi(x,t) = \varphi(x) \cdot e^{-\frac{i}{\hbar}Et}$ . Consider the potential step as it is shown on the next figure:



$V(x) = 0$ , if  $x < 0$ , and  $V(x) = V_0$ , if  $x > 0$ .  $E$  is the energy of the particle, and  $E < V_0$ . The energy of the particle is less than the height of the potential step. Like the situation in case of a free electron in a conductor. In this case due to classical mechanics the particle cannot be to the right of the origin, because the kinetic energy would be negative, which is impossible. So  $x > 0$  is a classically forbidden region.

We do not go into details, in quantum mechanics we have to solve the adequate Schrödinger equation in both region and write the probability density in the right side region:

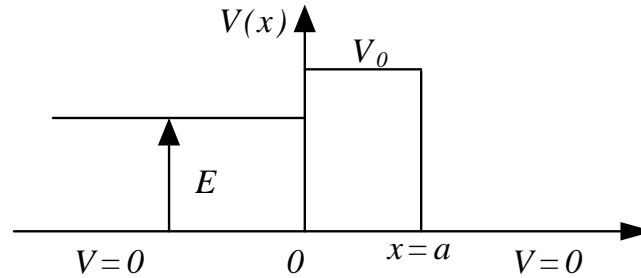
$$\rho_2(x) = |\varphi_2(x)|^2 \sim e^{-\frac{\sqrt{8m(V_0 - E)}}{\hbar}x}$$

The function is not zero inside the potential step (this region is forbidden for Newtonian

mechanics), and exponentially decreases with the distance. So a particle that is initially to the left of the potential step has some probability of being found to the right side. How great this probability is depends on the distance and the particle's energy and the height of the potential step.

### Tunnelling through a rectangular potential barrier

Suppose that the potential step has a finite size, denote it by  $a$ . See the next figure:



There are three different potential energy regions. Solving the suitable Schrödinger equations can be obtained the probability density in the right side region:

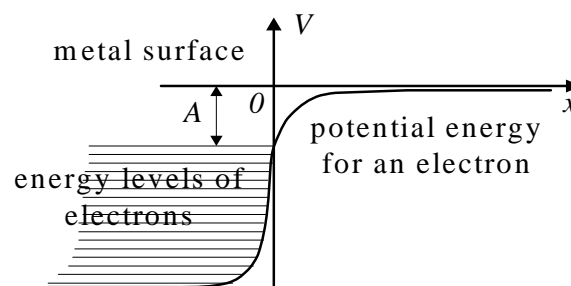
$$\rho(a) = |\varphi(a)|^2 \sim e^{-\frac{\sqrt{8m(V_0-E)} \cdot a}{\hbar}} \neq 0.$$

So there is a finite probability of finding the particle whose energy is smaller than the height of the potential barrier to go through the potential barrier. This effect is really a quantum mechanical effect and is called tunnel effect.

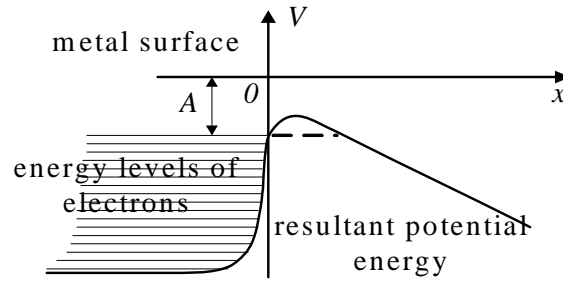
### Application of tunnel effect

Tunnelling has a number of practical applications, some of considerable importance.

1. When you twist two copper wires together or close the contacts of a switch, current passes from one conductor to the other despite a thin insulator oxide layer between them. The electrons go through this thin insulating layer by the tunnel effect. If there are only a few atomic layers between the two conductors the tunnelling probability is enough for conducting.
2. Another example is the cold electron emission. Consider a free electron in a metal.



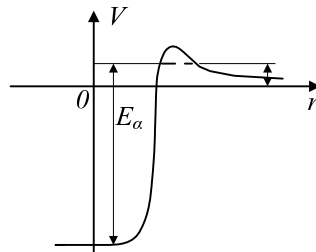
$A$  is the so called work function we have already seen at the photoelectric effect. This amount of energy is needed for the electron on the highest energy level to escape from the metal. This energy may be transferred by heating, or by absorption of a photon. But the electron may also escape by applying a strong external electric field. The potential energy distribution is shown on the next figure.



The resultant potential energy distribution is similar to a potential barrier, and its size is denoted by the dotted line. Some electron in the metal can go through the barrier.

3. The scanning tunnelling microscope (STM) uses electron tunnelling to create images of surfaces down to the scale of individual atoms. An extremely sharp conducting needle is brought very close to the conductor surface, within 1 nm, and moved by piezoceramics with high resolution. The space between the surface and the tip forms a potential energy barrier. If the tip is close enough to the surface, electrons from the sample can tunnel through this barrier from the surface to the tip, forming a tunnelling current. The tunnelling current is measured. The tunnelling current has an exponential function of the distance between the tip and the surface, so we can get the surface topography.  $I_{\text{tunnelling current}} \sim Ue^{-kd}$ .  $U$  is the voltage between the surface and the tip, and  $d$  is the distance
4. The radioactive alpha decay

Tunnelling is also important effect in nuclear physics. The emission of alpha particles from unstable nuclei also carried out by tunnelling. The alpha particle can escape only by tunnelling, because its energy in the nucleus is less than the height of the potential barrier. Depending on the barrier height and width for a given kind of alpha-emitting nucleus, the tunnelling probability can be low or high.



### The quantum mechanical model of the Hydrogen atom

We are looking for only the stationary solution. Use the time-independent Schrödinger equation, and the potential energy function of the proton electron electrostatic interaction.

$$V = -k \frac{e^2}{r}$$

Here  $k$  is the Coulomb constant and  $e$  is the elementary charge,  $r$  is the electron proton distance.

$$-\frac{\hbar^2}{2m} \Delta \varphi + V(\vec{r})\varphi = E \cdot \varphi$$

$$-\frac{\hbar^2}{2m} \Delta \varphi - k \frac{e^2}{r} \varphi = E \cdot \varphi.$$

Due to the spherically symmetric potential-energy function, the hydrogen-atom problem can be solved in spherical coordinates  $(r, \vartheta, \varphi)$ . The Schrödinger equation with this potential-

energy function can be solved exactly. The solution gives the possible energy values of the electron and the wave functions.

Without details in the process of finding solutions, we find the wave functions and the corresponding energy levels. These are:

$$E_n = -E^* \cdot \frac{1}{n^2}, \text{ where } E^* = \frac{mk^2e^4}{2\hbar^2} = 2,18 \cdot 10^{-18} \text{ J} = 2,18 \text{ aJ}$$

The number  $n$  is called principal quantum number. So the energy of the electron is quantized and this result is the consequence of Schrödinger equation. Although the energies of the hydrogen atom states can be described by the single quantum number  $n$ , the wave functions describing these states require three quantum numbers.

Principal quantum number:  $n = 1, 2, 3, \dots$

Orbital quantum number:  $l = 1, 2, 3, \dots, n - 1$

Orbital magnetic quantum number  $m = -l, -l + 1, \dots, 0, \dots, l - 1, l$

The orbital quantum number is a measure of the magnitude of the angular momentum associated with the quantum state; it is also a quantized quantity. The orbital magnetic quantum number is related to the orientation in space of this angular momentum vector. That is, only certain discrete values of the magnitude and components of orbital angular momentum are permitted.

The possible values of the magnitude  $L$  of orbital angular momentum  $\vec{L}$  are:

$$L = |\vec{L}| = \hbar\sqrt{l(l+1)}, \text{ where } l = 1, 2, 3, \dots, n - 1$$

The permitted values of the component of  $\vec{L}$  in a given direction, say the  $z$ -direction:

$$L_z = \hbar m, \text{ where } m = -l, -l + 1, \dots, 0, \dots, l - 1, l.$$

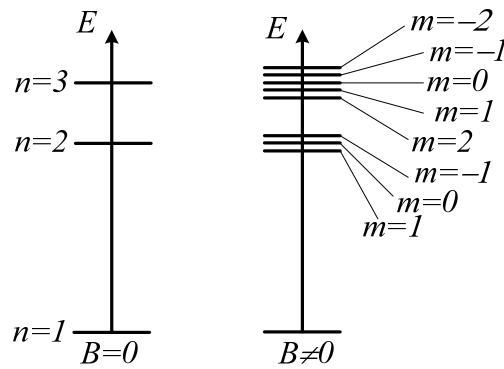
This quantum number can be zero or a positive or negative integer up to, but no larger in magnitude than  $l$ . This quantum number is also called magnetic quantum number.

We recall that angular momentum quantization was put into the Bohr model as an ad hoc assumption with no fundamental justification, with Schrödinger equation it comes out automatically.

### The electron spin

In 1896 Zeeman discovered that in the presence of a magnetic field, some spectral lines were split into groups of closely spaced lines. The Zeeman effect is the splitting of atomic energy levels when the atoms are placed in a magnetic field. This effect confirms experimentally the quantization of angular momentum.

The orbiting electron around the nucleus is equivalent to a current loop. The current loop has a magnetic dipole moment. We do not go into details; the magnetic dipole moment is proportional with orbital angular momentum. The orbital angular momentum is quantized, so magnetic dipole moment is also quantized. In magnetic field there is an interaction with magnetic dipole momentum and this interaction splits the energy levels. Without a magnetic field these states all have the same energy.



Due to experience the number of the new spectral lines is limited by the so called selection rules.  $\Delta m = 0, \mp 1$ . So we can say there are allowed transitions; and forbidden transitions.

Due to experience the ground state splits into two lines. In this case  $n = 1$ ,  $l = 0$ ,  $m = 0$ , so it was impossible to explain this effect by the Zeeman splitting. In 1926 Goudsmidt and Uhlenbeck, proposed that the electron might have some additional spin angular momentum, and it is also quantized.

The spin momentum  $\vec{S}$ . Its magnitude  $|\vec{S}| = \hbar\sqrt{s(s+1)}$ , where  $s = \frac{1}{2}$ , so  $|\vec{S}| = \hbar\frac{\sqrt{3}}{2}$ .

The permitted values of the component of  $\vec{S}$  in a given direction, say the  $z$ -direction:

$S_z = \hbar m_s$ , where  $m_s = \pm\frac{1}{2}$ , the so called spin magnetic quantum number. With the

introduction of spin the splitting of the ground state can be explained.

$n = 1$ ,  $l = 0$ ,  $m = 0$ ,  $m_s = \pm\frac{1}{2}$ .

The Stern Gerlach experiment proved the existence of the spin.