Lecture 5. The solving of the quantum-mechanical problem for hydrogen atom

eigenstates - собственные значения
eigenfunctions - собственные функции
principal quantum number - главное квантовое число
azimuthal quantum number - орбитальное квантовое число
magnetic quantum number - магнитное квантовое число
quantization - квантование
space quantization - пространственное квантование
angular momentum quantization - квантование орбитального момента
degeneracy - вырождение (кратность вырождения)
degenerate energy levels - вырожденные энергетические уровни
cgs units – система СГС
SI units – система СИ

Goal. To solve the quantum-mechanical problem for hydrogen atom

The Schrodinger equation for hydrogen atom

Let's consider now the solution of the Schrödinger equation for the hydrogen atom. Since the potential function of an electron in a hydrogen atom in **cgs units** has the form $U(r) = -\frac{e^2}{r}$, where e is a charge of electron (and proton), Schrodinger equation is written as:

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

Here ψ is an electron wave function in the reference frame of the proton, m is mass of electron, $\hbar = \frac{h}{2\pi}$, E - full energy of electron, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ - Laplace operator. Since the potential function depends on r, and not on the coordinates separately, it will be convenient to write down the Laplacian in spherical coordinates (r, θ, φ). In it, it looks like this:

$$\Delta\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\phi}\right)$$

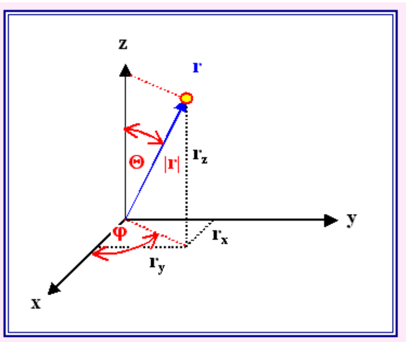


Fig.5.1. Spherical coordinates

Schrodinger equation in spherical coordinates:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\phi}\right) + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

In this equation ψ is function of three variables (r,θ,φ). Divide it into three simpler equations. To do this, we represent the function ψ (r,θ,φ) as the product of three functions: $\psi(r,\theta,\varphi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\varphi)$. These functions will be denoted simply R,Θ,Φ. Then

$$\frac{\partial\psi}{\partial r} = \frac{\partial R}{\partial r}\Theta\Phi, \quad \frac{\partial\psi}{\partial\theta} = \frac{\partial\Theta}{\partial\theta}R\Phi, \quad \frac{\partial\psi}{\partial\phi} = \frac{\partial\Phi}{\partial\phi}\Theta R.$$

After substituting the values of the partial derivatives in the Schrödinger equation we obtain:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\Theta\Phi + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\Theta R + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)R\Phi + \frac{2m}{\hbar^2}\left(E+\frac{e^2}{r}\right)R\Theta\Phi = 0$$

Multiplying equation by $\dfrac{r^2\sin^2\theta}{R\Theta\Phi}$:

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{r}\right) = 0$$

The second term depends only on ϕ. We transfer it into the right-hand side.

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{r}\right) = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad (1)$$

Equality is possible when both sides are equal to some constant value. We denote it m_l^2. Consequently,

$$\frac{\partial^2\Phi}{\partial\phi^2} = -m_l^2\Phi$$

The solutions of this equation are the functions

$$\Phi = A\sin(m_l\phi), \quad \Phi = A\cos(m_l\phi)$$

The angle ϕ may vary from 0 to 2π. Function Φ must be periodic with period 2π. This is possible only if $m_l = 0,\pm1,\pm2,\pm3,...$ Thus, from the solutions of the Schrödinger equation, we obtain the value of one of the quantum numbers (of course, you can get out of it all of them). The number m_l is called the magnetic quantum number.

Further, integrating the square of the modulus of the function Φ from 0 to 2π, and equating the resulting expression 1, we get that

$$A = \frac{1}{\sqrt{2\pi}}.$$

Next, we consider the left-hand side of the equation. It, of course, is m_l^2:

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{r}\right) = m_l^2$$

Divide the equation by $\sin^2\theta$:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{r}\right) = \frac{m_l^2}{\sin^2\theta}$$

After a similar transference of the second term in the right-hand side and indicating of the value, to which the parts is equal, through β, we obtain

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) = \beta$$
$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2mr^2}{\hbar^2}\left(E + \frac{e^2}{r}\right) = \beta$$

Solving of these last two equations yields values l and n, respectively. 3 quantum numbers together fully describe the state of the electron in the hydrogen atom. Module of the total energy of an electron in a stationary state in the hydrogen atom is inversely proportional to n^2. The number n is called the principal quantum number. It can have values from 1 to ∞.

$$E_n = -\frac{me^4}{2\hbar^2}\cdot\frac{1}{n^2}$$

Module of the total energy of an electron in a stationary state in the hydrogen-like atom in SI units is

$$E_n = -\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2}$$

The number l is called the azimuthal quantum number, it determines the angular momentum of the electron and the shape of the electron cloud; can have values from 0 to $n-1$ (n here refers to the energy level at which the electron is considered). The magnetic quantum number m_l determines the projection of the angular momentum on the selected axis in a magnetic field. This projection is $m_l\hbar$.

The charge-cloud model, which is also called the quantum-mechanical model, does not attempt to describe the path of each electron in a fixed orbit. Scientists now describe the possible positions of electrons in terms of probability. Computers can calculate the eigenfunctions of electron and give the points in space that an electron has the highest probability of occupying. These points can be connected to form a three-dimensional shape. Electrons are characterized in terms of the three-dimensional shapes that their probability define. The sum total of the various paths of electrons, traveling at very high speeds, is described as the electron cloud.

Visualizing the hydrogen electron orbitals

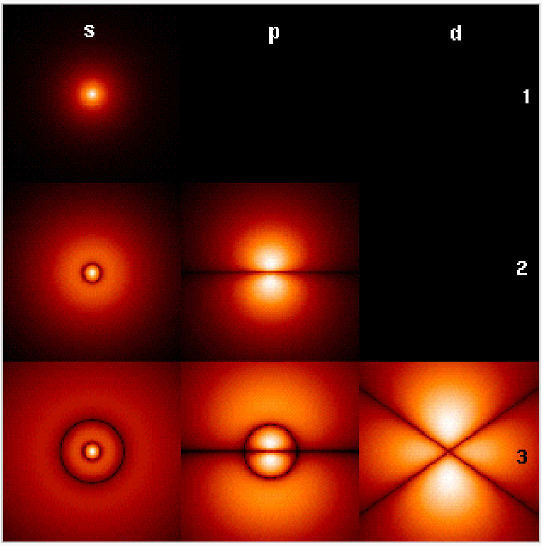
The image to the right shows the first few hydrogen atom orbitals (energy eigenfunctions). These are cross-sections of the probability density that are color-coded (black=zero density, white=highest density). The angular momentum (orbital) quantum number *l* is denoted in each column, using the usual spectroscopic letter code ("s" means *l* = 0; "*p*": *l* = 1; "*d*": *l* = 2). The main (principal) quantum number *n* (= 1, 2, 3, ...) is marked to the right of each row. For all pictures the magnetic quantum number *m* has been set to 0, and the cross-sectional plane is the *xz*-plane (*z* is the vertical axis). The probability density in three-dimensional space is obtained by rotating the one shown here around the *z*-axis.

The "ground state", i.e. the state of lowest energy, in which the electron is usually found, is the first one, the "1s" state (principal quantum level *n* = 1, *l* = 0).

An image with more orbitals is also available (up to higher numbers *n* and l).

Black lines occur in each but the first orbital: these are the nodes of the wavefunction, i.e. where the probability density is zero. (More precisely, the nodes are Spherical harmonics that appear as a result of solving Schrodinger's equation in polar coordinates.)

The quantum numbers determine the layout of these nodes.[6] There are:



Probability densities through the xz-plane for the electron at different quantum numbers (l, across top; n, down side; m=0)

Quantum numbers and degeneracy of the energy levels

The quantum numbers can take the following values:

$n = 1, 2, 3, \ldots$ principal quantum number

$\ell = n-1, n-2, \ldots, 1, 0$ azimuthal quantum number

$m = -\ell, \ldots, \ell.$ magnetic quantum number

$P_l = L = \sqrt{l(l+1)}\hbar$

$L_z = m_l \hbar$

We have Ψ_{nlm_l} *and* E_n

$$\boxed{E_n = -\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2}}$$

System with the different wave functions at the same energy, is called degenerate, and the number of different states with the same energy is called the degeneracy.

$$\sum_{l=0}^{n-1}(2l+1) = n^2$$

Example 5.1

levels	Eigenfunction	n	l	m_l	State	Degeneracy
E_1	Ψ_{100}	1	0	0	$1s$	1
E_2	Ψ_{200}, Ψ_{210}, Ψ_{211}, Ψ_{21-1}	2	0 1	0 $0, \pm 1$	$2s$ $2p$	4
E_3	Ψ_{300}, Ψ_{310}, Ψ_{311}, Ψ_{31-1}, Ψ_{320}, Ψ_{321}, Ψ_{32-1}, Ψ_{322}, Ψ_{32-2}	3	0 1 2	0 $0, \pm 1$ 0 ± 1 ± 2	$3s$ $3p$ $3d$	9

Problems.

1.Rewrite the equation that determines the radial part of the wave function of an electron in the Coulomb field of the nucleus Z in the dimensionless form. An atomic unit of the length (the first Bohr radius) and atomic energy unit (electron coupling energy in the hydrogen atom) can be taken as measure units.

2. What solutions of the time-dependent Schrödinger equation are called as stationary? Show that such solutions are obtained when U does not explicitly depend on time.

3. How the total wave function $\Psi(x,t)$ describing the stationary states will change, if you change the origin of the potential energy by a certain amount ΔU?

4. Find a solution of the time-dependent Schrödinger equation for a free particle, moving with momentum p in the positive direction of the axis x.

5. A particle with a mass m is located in the two-dimensional square potential well with absolutely impenetrable walls $(0 < x < l)$. Find: a) The energy eigenvalues and normalized eigenfunctions of the particle; b) the probability of finding the particle with the lowest energy in the region $l/3 < x < 2l/3$; c) the number of the energy levels in the range $(E, E + dE)$.

Literatures

1. Dzhumagulova K.N. Lecture cource on “Atomic physics”. Almaty: Kazakh University, 2017, p.101.
2. Walter R. Johnson Lectures on Atomic Physics, University of Notre Dame, 2006.
3. Matveev A.N. Atomic physics, M.: High School, 1989.
4. Irodov I.I. Tasks on atomic and nuclear physics. M.: Science , 1984.