

## Quantum Mechanics and its mathematical tools

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### 1. INADEQUACY OF THE CLASSICAL PHYSICS AND THE OLD QUANTUM THEORY

In the beginning of the twentieth century there appeared some phenomena which were non-explainable using the classical physics. Let me recall some of them.

**1. Radiation of the black body.** The *black body* is an isolated matter which only emits radiational energy in form of electromagnetic waves. The dependence of the energy of the emitted waves on the wave length could not be explained on the ground of classical physics. Max Planck made calculations which suggested that the shape of the wavelength–energy curve could be explained when one assumes that the radiation is emitted only in quanta. It means that the admitted energies are

$$E = n \cdot \hbar\omega = n \cdot h\nu, \quad n = 1, 2, \dots,$$

where  $\omega = \frac{\nu}{2\pi}$  is the angular velocity,  $\nu$  is the frequency (see (2.4) and  $\hbar = \frac{h}{2\pi}$  is an universal constant such that the **Planck constant**

$$h \approx 6.62 \cdot 10^{-27} \text{erg} \cdot \text{s}.$$

(Recall that erg is a CGS unit of energy,  $\text{erg} = g \cdot \text{cm}^2/\text{s}^2 = 10^{-7} J \cdot \text{s} = 10^{-7} N \cdot m \cdot \text{s}$ , where Joule  $J$  and the Newton  $N$  are SI unit of energy and force.)

Therefore these portions of the electromagnetic radiation could be interpreted as particles, namely the *photons*, with the mass  $m = 0$ . According to the Einstein equation (3.3),  $E = c^2 p^2$ , also the absolute momentum  $|p|$  should be quantized,  $|p| = \frac{E}{c} = \frac{\hbar\omega}{c} = \hbar|k|$ . The principal quanta of energy and momenta should satisfy the relation

$$(1.1) \quad E = \hbar\omega, \quad p = \hbar k$$

where  $k$  is the wave vector.

**2. The Compton scattering and the photoelectric phenomenon.** The *Compton's experiment* of scattering of the light (electromagnetic waves) on electrons revealed that the photons of light behave like particles, equipped with momentum, energy and with zero mass.

The *photoelectric phenomenon* appears when a monochromatic light with fixed frequency  $\omega$  is directed to a metal's surface. If the energy  $\hbar\omega$  of the quanta of the photons is greater than some threshold energy  $W$  then the surface emits electrons with kinetic energy  $T = \hbar\omega - W$ . This kinetic energy does not depend on the radiation intensity. This also confirms the corpuscular nature of the light.

**3. The Davisson–Germer experiment.** In the textbook version of this experiment a flow of *electrons* passes through two near and small holes. On a screen behind the holes a diffraction picture formed by electrons appears. In the original experiment a bundle of electrons was reflected from a nickel crystal surface and the effect was the same, even when the bundle's intensity was so low that the electrons were passing separately. This suggests that sometimes electrons behave rather like waves (not like particles).

**4. The Stern–Gerlach experiment.** In this experiment a bundle of electrons was divided into two subbundles when passing through a constant magnetic field. Since the interaction of charged particles with the magnetic field is realized through

the component  $M_z$  in the direction of the magnetic field of the angular momentum of the particle, the experiment suggests that the angular momentum of electrons is also quantized. Moreover, as we shall see it below, the electron besides the angular momentum has a kind of ‘internal angular momentum’ called the *spin*.

**5. The Franck–Hertz experiment and the Balmer–Ritz classification of the spectral lines.** In the *Franck–Hertz experiment* it was confirmed that electrons lose discrete portions of energy in collisions with photons.

The *Balmer–Ritz classification* says that the frequencies of the emitted or absorbed photons in interaction with the hydrogen atom satisfy the following rule

$$(1.2) \quad \omega = N \left( \frac{1}{m^2} - \frac{1}{n^2} \right), \quad m, n = 1, 2, \dots,$$

where  $N$  is a normalizing constant. For  $m = 2$  it is called the *Balmer series* and was discovered in 1885 by Balmer.

**6. The atoms’ stability.** When one assumes that the electron in an atom moves along a circular (or elliptical orbit) around its kernel then one arrives to a contradiction, because then the electron should lose its energy. Indeed, by the Maxwell equations it should generate a varying magnetic field  $B$  which, on order, should generate a varying electric field  $E$ ; hence an electromagnetic wave should be emitted. After a very short time ( $\sim 10^{-9}s$ ) the electron should fall into the kernel. This evidently contradicts with the observed atoms’ stability.

The **old quantum theory** was created by de Broglie, Bohr and others in order to explain the above facts using some simple assumptions and rules.

One of these assumptions stated that with a particle, like the electron, one should associate a wave, called the *de Broglie wave*, of the form

$$(1.3) \quad \text{const} \cdot e^{-i(Et - px)/\hbar}$$

where  $E$  and  $p$  are the energy and the momentum of the particle.

The rules are the following **Bohr rules**:

1. The angular momentum of the electron is an integer multiple of  $\hbar$ ,

$$(1.4) \quad M = n\hbar, \quad n = 1, 2, \dots$$

2. The electron in an atom has only discrete energies  $E_n$  and a jump from an energy level  $E_n$  to an energy level  $E_m$  is associated with an electromagnetic radiation with the angular velocity  $\omega_{nm}$  defined by the formula

$$(1.5) \quad \hbar\omega_{nm} = |E_n - E_m|.$$

**Theorem 1.1.** *Assuming the above rules formula (1.2) follows.*

*Proof.* For an electron, with the mass  $m$  and the electric charge  $-e$ , which moves along a circular trajectory of radius  $r$  (with center at the proton with the charge  $+e$ ) with an angular velocity  $\omega$  (and the linear velocity  $v = r\omega$ ) we have the following formulas (the *Coulomb’s rule* and the third component of the angular momentum):

$$\frac{e^2}{r^2} = mr\omega^2, \quad M_z = m\omega r^2.$$

Since  $M_z = n\hbar$  (by rule 1) we get the possible values of the radius

$$r = r_n = r_0 \cdot n^2, \quad r_0 = \hbar^2/me^2.$$

The energy of the electron consists of the kinetic energy  $T = \frac{1}{2}m(r\omega)^2$  and of the potential energy  $U = -\frac{e^2}{r}$ . We find

$$E = T + U = E_n = -\frac{e^2}{2r_0} \cdot \frac{1}{n^2}.$$

Application of rule 2 gives the thesis of the theorem.  $\square$

The above calculations were successful, but there remained too many open questions. So this theory did not developed further. The old quantum theory was subsequently replaced by mathematically more rigorous theory called the Quantum Mechanics.

## 2. BASICS OF QUANTUM MECHANICS

We begin with underlining the fact that Quantum Mechanics is a completely mathematical theory. Physicists, like Heisenberg, Planck, Schrödinger and others, constructed a mathematically rigorous theory whose theorems turned out to be in agreement with the physical observations. The latter fact decided that the theory survived.

The main mathematical tools were: the probability theory and the linear algebra of eigenvalues and eigenvectors of linear operators (including elements of the representation theory). The functional analysis came into the game later, when a rigorous treatment of unbounded differential operators was needed.

Let us present the main postulates of Quantum Mechanics.

**P0** The states of the physical system are defined via so called the **wave functions** (or the *state functions*) which are complex valued functions on the configuration space

$$\psi : Q \rightarrow \mathbb{C}.$$

The physical quantities, like energy, momentum, position, are defined via certain linear differential operators  $\hat{A} = \hat{A}(x, \partial_x)$ , called the **observables**, which act on the wave functions.

For example, if  $d = \dim Q = 1$  then the *position operator*  $\hat{x}$  acts as the multiplication by the argument

$$(\hat{x}\psi)(x) = x\psi(x)$$

and the ‘momentum operator’  $\hat{A} = -i\partial_x$  acts as the differentiation

$$\hat{A}\psi(x) = -id\psi/dx.$$

Important assumption is that:

*the observables are symmetric operators, i.e.*

$$\int_Q (\hat{A}\varphi)(x)\bar{\psi}(x)dx = \int_Q \varphi(x)\overline{\hat{A}\psi(x)}dx.$$

Then one can associate with such observable  $\hat{A}$  its collection of eigenvalues  $\lambda_n$  and eigenfunctions  $u_n(x)$ . By the symmetry the eigenfunctions are pairwise orthogonal,  $\int u_m u_n = 0$  for  $m \neq n$ . We assume also that  $\int u_n \bar{u}_n = 1$ . (Often the eigenvalues are not discrete, but at this stage we skip such subtleties).

**P1** The only possible results of measurement of a physical quantity represented by an observable  $\hat{A}$  are the eigenvalues  $\lambda_n$  of this operator. After the measurement the system switches to the state  $\psi = u_n$  represented by the corresponding eigenfunction.

**P2** If the physical system is in a state represented by an eigenfunction  $\psi(x) = u_n(x)$  then the observation result is the corresponding eigenvalue  $\lambda_n$ , i.e.  $\hat{A}\psi = \lambda_n\psi$ .

**P3** The average of many observations of the physical observable  $\hat{A}$  in the same state  $\psi$  equals

$$(2.1) \quad \langle \hat{A} \rangle_\psi = \frac{\int (\hat{A}\psi)(x)\bar{\psi}(x)dx}{\int \psi(x)\bar{\psi}(x)dx}.$$

**P4** The probability of obtaining  $\lambda_n$  as a result of measurement of the physical quantity  $\hat{A}$  in a state  $\psi$  equals

$$(2.2) \quad P(\lambda_n) = \left| \int \psi(x)\bar{u}_n(x)dx \right|^2.$$

It is the same as the probability  $P(u_n)$  that we are in the eigenstate  $u_n$ .

**Remark 2.1.** Introducing the Hermitian product  $(\varphi, \psi) = \int_Q \varphi(x)\bar{\psi}(x)dx$  we equip the space of states with the structure of a pre-Hilbert space, which is completed to the Hilbert space

$$(2.3) \quad \mathcal{H} = L_2(Q).$$

Then the symmetry condition means  $(\hat{A}\varphi, \psi) = (\varphi, \hat{A}\psi)$ . Later usually we shall assume that the state functions are normalized,  $\|\psi\|^2 = (\psi, \psi) = 1$ . Then  $\langle \hat{A} \rangle_\psi =$

$(\hat{A}\psi, \psi)$ . Moreover,  $P(\lambda_n) = |(\psi, u_n)|^2$ .

If  $\psi(x) = \sum a_n u_n(x)$ ,  $a_n \in \mathbb{C}$ , then  $\sum |a_n|^2 = 1$ ,  $P(\lambda_n) = P(u_n) = |a_n|^2$  and  $\langle \hat{A} \rangle_\psi = \sum \lambda_n |a_n|^2$ . Here we see the probabilistic aspect of the above postulates.

For example,  $\langle \hat{x} \rangle_\psi$  can be interpreted as  $\mathbb{E}x$ , the expectation value of the ‘random variable’  $x$  with the probability distribution defined by  $|\psi(x)|^2 dx$ .

Of course, there appears the problem of definition of the operators associated with the very concrete physical quantities. Here we have two rules.

The first rule is called the **correspondence rule** which stated the following:

*relations satisfied by physical quantities in the classical mechanics hold true after replacing the corresponding quantities by corresponding quantum operators.*

**Example 2.1.** If  $\hat{x}, \hat{y}, \hat{z}$  are the position operators and  $\hat{p}_x, \hat{p}_y, \hat{p}_z$  are the momentum operators, the the *angular momentum operators* are following

$$(2.4) \quad \hat{M}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{M}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{M}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$

The energy operator of a particle, i.e. the *Hamiltonian*, equals

$$(2.5) \quad \hat{H} = \hat{E} = \frac{1}{2m}\hat{p}^2 + U(\hat{x}).$$

**Remark 2.1.** For the physicists of the beginning of the twentieth century the correspondence rule was quite natural. But from the mathematical point of

view it is not that obvious. The problem is that the algebra of operators is not a commutative algebra. So the problem of ordering of product of observables appears. One could define the  $z$ -th component of the angular momentum operators as  $\hat{p}_y \hat{x} - \hat{p}_x \hat{y}$ , which is wrong.

The problem of a proper definition of a ‘homomorphism’ from the algebra  $C^\infty(T^*Q)$  of smooth functions on the phase space  $T^*Q$  to the algebra of differential operators is called the *quantization problem*. It is one of most important problem in the modern mathematical physics (see [Ber], [BS]).

The another rule is the famous **indeterminacy principle** which is crucial for the Quantum Mechanics’ philosophy. Suppose that we are dealing with two observations  $\mathcal{A}$  and  $\mathcal{B}$  (of some physical quantities). After applying any of the observations the state of the physical system changes. But the changes infected by these observations may be not harmonious. It may turn out that  $\mathcal{A}\mathcal{B} \neq \mathcal{B}\mathcal{A}$ , the result of two observations may depend on the order in which the observations are made.

This non-commutativity of the observations is easily translated into the mathematical language. It means the non-commutativity of the corresponding observable operators, the *commutator*

$$[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}$$

is nonzero. For example, if eigenfunctions  $u_n$  of the operator  $\hat{A}$  are no longer eigenfunctions of the operator  $\hat{B}$  and  $\psi$  is a given state then application of the observation  $\mathcal{B}\mathcal{A}$  (firstly  $\mathcal{B}$  and next  $\mathcal{A}$ ) switches the system to some state  $u_m$  (with the probability  $\left| (\hat{B}\psi, u_n) \right|^2$ ), whereas the observation  $\mathcal{A}\mathcal{B}$  switches the system to some eigenfunction of  $\hat{B}$ .

Moreover, on the basis of the old quantum theory we can even estimate qualitatively the value of the above commutator for some specific operators  $\hat{A}$  and  $\hat{B}$ . It should be either zero, if the operators commute, or of the order  $\hbar$ , if the corresponding physical quantities are complementary.

By definition, two classical quantities are **complementary** when their product is measured in  $g \cdot m^2/s$ . For example, the pairs:  $x$  and  $p_x$ ,  $t$  and  $E$ ,  $\varphi$  and  $M_z$  are complementary; here  $\varphi = \arg(x + iy)$  is the angle in the  $xy$  coordinates.

The physicists express the non-commutativity in the form of the following **Heisenberg’s indeterminacy principle**

$$(2.6) \quad \Delta x \cdot \Delta p_x \geq \hbar, \quad \Delta t \cdot \Delta E \geq \hbar, \quad \Delta \varphi \cdot \Delta M_z \geq \hbar.$$

(To be correct, one should write  $\Delta x \cdot \Delta y \geq \text{const} \cdot \hbar$ , etc. See Theorem 2.1 below. But the above form looks simpler and is traditional.) The meaning of the inequalities (2.6) is that the product of discrepancies of quantum measurement of, say the position  $x$  and the corresponding momentum  $p_x$ , is always separated from zero. If one knows an exact position of an electron then one can say nothing about its momentum and vice versa.

Therefore we postulate  $[\hat{x}, \hat{p}_x] = \alpha \hbar$ , where  $\alpha$  is a constant to be found. Since  $[\hat{x}, \partial_x] \psi = x \psi'_x - (x\psi)' = -\psi$  it should be  $\hat{p}_x = -\alpha \hbar \partial_x$ . The operator  $-\alpha \hbar \partial_x$  has the eigenfunctions of the form

$$u_p = \text{const} \cdot e^{-px/\alpha \hbar}$$

with the eigenvalues  $p$ . But the de Broglie wave of a particle with momentum  $p$  equals  $\sim e^{ipx/\hbar}$  (see (1.3)). It follows that  $\alpha$  should equal  $i$  and hence

$$(2.7) \quad \hat{p}_x = -i\hbar\partial_x, \quad \hat{p}_y = -i\hbar\partial_y, \quad \hat{p}_z = -i\hbar\partial_z.$$

Knowing this we get the **Hamiltonian operator**, called also the **Schrödinger operator**,

$$(2.8) \quad \hat{H} = \hat{E} = -\frac{\hbar^2}{2m}\Delta + U(\hat{x})$$

(see (2.5)) where  $x = (x_1, \dots, x_d)$  and the *Laplacian*  $\Delta = \partial_{x_1}^2 + \dots + \partial_{x_d}^2$ .

Using and the fact that the quantities  $t$  (the time) and  $E$  (the energy) are complementary, we get  $\hat{E} = \text{const} \cdot i\hbar\partial_t$ . But the de Broglie wave  $e^{-i(Et-px)/\hbar}$  has the energy  $E$ , which should be the eigenvalue of  $\hat{E}$ . So

$$(2.9) \quad \hat{E} = i\hbar\partial_t.$$

Moreover, we obtain the following **Schrödinger equation**

$$(2.10) \quad i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

which describes the evolution of the wave function  $\psi(x) = \psi(x, t)$  in time.

**Example 2.2.** For a free particle, i.e. with  $U(x) \equiv 0$ , the de Broglie wave  $\psi = e^{-i(Et-px)/\hbar}$  satisfies  $i\hbar\frac{\partial\psi}{\partial t} = E\psi$  and  $\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = \frac{p^2}{2m}\psi$ . The classical formula  $E = \frac{p^2}{2m}$  follows.

The following theorem provides a probabilistic interpretation of the Heisenberg's indeterminacy principle. For the operator  $\hat{x}$  in a normalized state  $\psi$  we define its mean value as  $\langle\hat{x}\rangle_\psi = \langle\hat{x}\rangle = (\hat{x}\psi, \psi)$  and its *standard deviation* as

$$\Delta\hat{x} = \langle\hat{x} - \langle\hat{x}\rangle\rangle_\psi^{1/2} = ((\hat{x} - \langle\hat{x}\rangle)\psi, \psi)^{1/2}.$$

Analogously we define  $\Delta\hat{p}_x = \Delta\hat{p}$ .

**Theorem 2.1.** *We have*

$$\Delta\hat{x} \cdot \Delta\hat{p} \geq \frac{1}{2}\hbar$$

and the equality take place when the wave function can be reduced to the *Gaussian function*

$$(2.11) \quad \psi(x) = \frac{1}{\sqrt{2\pi\sigma}}e^{-x^2/2\sigma^2}$$

by a translation of  $x$  and multiplication by the oscillating factor  $e^{i\lambda x}$ .

*Proof.* By shifting of the variable  $x$  we can assume that  $\langle\hat{x}\rangle = 0$ . The identity

$$-i\hbar\partial_x (e^{i\lambda x}\psi) = e^{i\lambda x}(\lambda\hbar - i\hbar\partial_x)\psi$$

shows that the shifting of the variable  $p$  corresponds to the multiplication of the state function by an oscillating factor. Therefore assume that also  $\langle\hat{p}\rangle = 0$ . Thus  $\Delta^2\hat{x} = (\hat{x}^2\psi, \psi)$  and  $\Delta^2\hat{p} = (\hat{p}^2\psi, \psi)$ .

By the Schwartz inequality we get

$$\Delta^2\hat{x} \cdot \Delta^2\hat{p} = \|\hat{x}\psi\|^2 \cdot \|\hat{p}\psi\|^2 \geq |(\hat{x}\psi, \hat{p}\psi)|^2 = |(\hat{p}\hat{x}\psi, \psi)|^2.$$

The number in the right-hand side of the latter inequality is estimated from below by

$$|\operatorname{Im}(\hat{p}\hat{x}\psi, \psi)|^2 = \frac{1}{4} |(\hat{p}\hat{x}\psi, \psi) - (\psi, \hat{p}\hat{x}\psi)|^2 = \frac{1}{4} |([\hat{p}, \hat{x}]\psi, \psi)|^2.$$

As  $[\hat{p}, \hat{x}] = i\hbar$  this equals  $\frac{1}{4}\hbar \|\psi\|^2 = \frac{1}{4}\hbar$ .

The Schwartz inequality becomes an equality when  $\hat{p}\psi = \mu\hat{x}\psi$  for a constant  $\mu$ . The modulus of a complex number equals its imaginary part when the real part vanishes. So the inequality from the thesis of Theorem 2.1 is an equality when

$$0 = 2 \operatorname{Re}(\hat{x}\psi, \hat{p}\psi) = (\mu + \bar{\mu})(\hat{x}\psi, \hat{p}\psi).$$

Thus  $\mu = i\nu$  is imaginary and the equation

$$-i\hbar\psi' = i\nu\psi$$

gives  $\psi = \text{const} \cdot e^{-\nu x^2/\hbar}$ . □

**Remark 2.2.** The Gaussian probability distribution  $\frac{1}{\sqrt{2\pi}\sigma} \exp(-x^2/2\sigma^2)dx$  has the standard deviation  $\sigma$ , which is interpreted as  $\Delta x$  appearing in inequalities (2.6). Let the wave function be  $\psi(x) = (2\pi\Delta x^2)^{-1/4} \exp(-x^2/4\Delta x^2)$ .

Recall that the eigenfunction of the momentum operator  $\hat{p}_x$  are  $u_p = \text{const} \cdot e^{ipx/\hbar}$ . Recall also that the probability of falling into the state  $u_p$  after measuring the momentum is  $P_\psi(p) = |\varphi(p)|^2$ , where

$$(2.12) \quad \varphi(p) = (\psi, u_p) = \text{const} \cdot \int \psi(x) e^{-ipx/\hbar} dx.$$

Standard calculations show that  $\varphi(p) = \text{const} \cdot \exp(-p^2\Delta x^2/\hbar^2)$  and hence

$$|\varphi(p)|^2 = \text{const} \cdot \exp(-p^2/2(\hbar/2\Delta x)^2) = \text{const} \cdot \exp(-p^2/2\Delta p_x^2).$$

We see that  $\Delta x \cdot \Delta p_x = \frac{\hbar}{2}$ .

The transformation (2.12) is the well known *Fourier transformation*, normalized accordingly to the quantum mechanics aims. Therefore the indeterminacy principle has pure mathematical meaning that, if a function  $\psi$  is well localized in the position space then its Fourier transform is weakly localized in the momentum space, and vice versa.

**Remark 2.3.** (*The Newtonian equations*) The Schrödinger equation (2.10) with the initial condition  $\psi|_{t=0} = \psi_0$  has the solution  $\psi_t = e^{-i\hat{H}t/\hbar}\psi_0$ , where  $U(t) = e^{-i\hat{H}t/\hbar}$  is the evolution operator. This is called the *Schrödinger image*. In the further sections we show that it is a unitary operator and that  $U(t)^* = U(-t) = U(t)^{-1}$ .

Recall that we are interested in the quantities  $(\hat{A}\varphi, \psi)$  which are the amplitudes of transition from a state  $\varphi$  to a state  $\psi$ . When the states evolve we deal with the quantities

$$(\hat{A}\varphi_t, \psi_t) = (\hat{A}U(t)\varphi, U(t)\psi) = (U(-t)\hat{A}U(t)\varphi, \psi).$$

But the latter quantity can be interpreted as  $(\hat{A}(t)\varphi, \psi)$ , where

$$(2.13) \quad \hat{A}(t) = U(-t)\hat{A}U(t).$$

It means that the physical observable evolves, while the states remain constant. This interpretation of evolution is called the *Heisenberg image*. Of course, the Schrödinger image and the Heisenberg image are equivalent.

It is easy to check that the evolving operators  $\hat{A}(t)$  satisfy the equations

$$(2.14) \quad i\hbar \frac{d}{dt} \hat{A}(t) = [\hat{A}(t), \hat{H}], \quad \hat{A}(0) = \hat{A};$$

(at least at the formal level). Taking the operators  $\hat{x}$  and  $\hat{p}_x$  as  $\hat{A}$  and  $\hat{H} = \frac{1}{2m}\hat{p}_x^2 + U(\hat{x})$ , we obtain the equations

$$\frac{d\hat{x}}{dt} = \hat{p}_x, \quad \frac{d\hat{p}_x}{dt} = -\frac{\partial U}{\partial x}(\hat{x}).$$

These are the Newtonian equations.

### 3. BOUNDED STATES AND FREE STATES

This section is devoted to study the eigenvalues, denoted by  $E$  (the energy), and the eigenfunctions  $u_E = u_E(x)$  of the Schrödinger operator (2.8). We begin with the following observation.

**Proposition 3.1.** *If the eigenfunction  $u_E$  is in the Hilbert space  $\mathcal{H} = L_2(Q)$  and  $\|u_E\| = 1$ , then the probability distribution  $|u_E(x)|^2 dx$  is stationary, i.e. does not change with time.*

*Proof.* We have  $\hat{H}u_E = Eu_E$ , hence  $\psi_t = U(t)u_E = e^{-i\hat{H}t/\hbar}u_E = e^{-iEt/\hbar}u_E$ . It follows  $|\psi_t(x)|^2 = |e^{-iEt/\hbar}u_E(x)|^2 = |u_E(x)|^2$ .  $\square$

The eigenfunctions  $u_E$  which belong to the Hilbert space  $\mathcal{H}$  are called the **bounded states**. It means that the particle is localized, or bounded, in a fixed region of the phase space. The amplitude of the wave function is fixed, only its *phase* (i.e. the argument) changes.

The equation

$$(3.1) \quad \hat{H}\psi = E\psi$$

is called the **stationary Schrödinger equation**.

**Example 3.1.** (*Infinite potential well*) This example can be found in any textbook on Quantum Mechanics.

The potential energy function  $U(x)$  is 0 for  $|x| < 1$  and  $+\infty$  otherwise. The stationary Schrödinger equation (3.1) with  $\psi = u$  means the following

$$u''(x) = -k^2u(x), \quad |x| < 1, \quad u(x) \equiv 0, \quad |x| \geq 1,$$

where  $k^2 = \frac{2mE}{\hbar^2} > 0$ . (It is easy to see that the case  $E < 0$  is not realized.) So we get the following boundary value problem

$$u'' + k^2u = 0, \quad u(1) = u(-1) = 0.$$

Its solutions are

$$u_{2l}(x) = A \sin(l\pi x), \quad u_{2l+1}(x) = B \cos((l + 1/2)\pi x).$$

The corresponding values  $k_n$  of  $k$  are  $k_{2l} = 2l \cdot \frac{\pi}{2}$  and  $k_{2l+1} = (2l + 1) \cdot \frac{\pi}{2}$ . Thus  $k_n = n\pi/2$  and the corresponding eigenvalues (energies of bounded states) are

$$E_n = \frac{\pi^2 \hbar^2}{8m} n^2.$$

This example suggests that the eigenvalues corresponding to the bounded states are discrete in the spectrum of the Hamiltonian operator.



But we know at least one operator, namely  $\hat{p}_x = -i\hbar\partial_x$ , for which the eigenvalues are not discrete and the eigenfunctions are not quadratically integrable. Here the eigenfunctions are  $u_p = e^{ipx/\hbar}$  (and do not belong to  $\mathcal{H}$ ) and the corresponding eigenvalues  $p$  fill the whole real line. The states  $u_p(x)$  correspond to a state of a particle which moves with constant velocity  $v = p/m$ ; its momentum is fixed but its position is completely unknown.

Similar situation may occur (and occurs) for the Schrödinger operator  $\hat{H}$ . The eigenstates  $u_E(x)$  such that

$$u_E(x) \sim \text{const} \cdot e^{ipx/\hbar} \quad \text{as } |x| \rightarrow \infty$$

are called the **free states**. Also linear combination of such states is called a free state.

**Example 3.2.** (*Finite potential well*) The potential energy equals

$$U(x) = 0 \quad \text{for } |x| < 1, \quad U(x) = V \quad \text{for } |x| > 1.$$

The stationary Schrödinger equation (3.1) leads to the equations

$$(3.2) \quad u''(x) + \frac{2Em}{\hbar^2}u(x) = 0, \quad |x| < 1,$$

$$(3.3) \quad u''(x) + \frac{2(E-V)}{\hbar^2}u(x) = 0, \quad |x| > 1.$$

The bounded states should satisfy  $|u(x)| \rightarrow 0$  as  $|x| \rightarrow \infty$ . Therefore it should be  $\frac{2(E-V)}{\hbar^2} = -K^2 < 0$ . Then

$$u(x) = C_1 e^{-Kx} \quad \text{for } x > 1, \quad u(x) = C_2 e^{Kx} \quad \text{for } x < -1.$$

The potential is an even function of  $x$  and hence the eigenfunction can be divided into even and odd. For even solutions we have  $C_1 = C_2 = C$  and for odd solutions we have  $C_1 = -C_2 = C$ .

Consider the domain  $|x| < 1$ . The case  $E < 0$  is not physical and it can be checked that it is not realized. So  $0 < E < V$ , e.g. for bounded states. Denoting  $k_0^2 = 2Em/\hbar^2$  we get the even solutions  $D \cos k_0 x$  and the odd solutions  $D \sin k_0 x$ ; below we put  $D = 1$ .

The eigenfunctions should be of class  $C^1$  which implies the gluing conditions

$$\cos k_0 = C e^{-K}, \quad k_0 \sin k_0 = K C e^{-K},$$

e.g. in the even case. The resulting equation  $k_0 \tan k_0 = K$ , where  $k_0$  and  $K$  depend on  $E$ , has finitely many solutions  $E = E_n$ . In the odd case the corresponding equation takes the form  $k_0 \cot k_0 = -K$  and also has only finitely many solutions.

Consider the case  $E > V$ . Then  $u(x) = C_1 e^{ikx} + C_2 e^{-ikx}$ ,  $k^2 = 2(E-V)m/\hbar^2$ , for  $|x| > 1$  in the even case. The gluing conditions

$$\cos k_0 = C_1 e^{ik} + C_2 e^{-ik}, \quad -k_0 \sin k_0 = ikC_1 e^{ik} - iC_2 e^{-ik}$$

are satisfied by some constants  $C_{1,2}$ . Analogously one finds odd free states.

It follows that the (physical) spectrum of the Hamiltonian operator consists of finitely many points in the interval  $(0, V)$  (the *discrete spectrum*) and of the infinite interval  $[V, \infty)$  (the *continuous spectrum*). Moreover, for each  $E > V$  the corresponding eigenspace is two dimensional; we say that the continuous spectrum is of multiplicity 2.

## 4. BOUNDED STATES FOR THE HYDROGEN ATOM

The classical Hamiltonian of the electron in the hydrogen atom takes the form

$$H = \frac{p^2}{2m} + U(r), \quad U(r) = -\frac{e^2}{r},$$

where  $r = \sqrt{x^2 + y^2 + z^2} = |q|$ .

Writing  $q = re_r$  (where  $e_r$  is a unit vector) we get  $\dot{q} = \dot{r}e_r + r\dot{e}_r = \dot{r}e_r + r\dot{\psi}e_\psi$  (where  $\psi$  is the polar angle in the plane spanned by  $q$  and  $\dot{q}$  and  $e_\psi$  is a unit vector in this plane orthogonal to  $e_r$ ). Therefore  $p^2 = m\dot{q}^2 = p_r e_r + p_t e_\psi$ , where  $p_r = m\dot{r}$  is the radial part of the momentum and  $p_t = mr\dot{\psi} = \frac{|M|}{r}$  is the tangential part of the momentum; here  $M = q \times p$  is the angular momentum. Therefore

$$p^2 = p_r^2 + p_t^2, \quad p_t^2 = M^2/r^2.$$

The corresponding quantum mechanical operator takes the form

$$(4.1) \quad \hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{M}^2}{2mr^2} - \frac{e^2}{r},$$

where  $\hat{p}_r^2 + \hat{M}^2/r^2$  is a corresponding splitting of the operator  $-\hbar^2\Delta$ . The following result is proved in the next subsection.

**Theorem 4.1.** *In the spherical coordinates  $r, \varphi, \theta$  (such that  $x = r \sin \theta \cos \varphi$ ,  $y = r \sin \theta \sin \varphi$ ,  $z = r \cos \theta$ ) we have*

$$(4.2) \quad \hat{p}_r^2 = -\hbar^2 \cdot r^{-2} \partial_r r^2 \partial_r = -\hbar^2 \cdot (\partial_r^2 + 2r^{-1} \partial_r),$$

$$(4.3) \quad \hat{M}^2 = -\hbar^2 \cdot \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}$$

and  $\hat{M}^2$  commutes with the Schrödinger operator  $\hat{H}$  and with  $\hat{r}$ .

Moreover, the operator  $\hat{M}^2$ , acting on  $L_2(\mathbb{S}^2, \sin \theta d\varphi d\theta)$ , has the eigenvalues

$$(4.4) \quad \hbar^2 \cdot l(l+1), \quad l = 0, 1, 2, \dots$$

each of multiplicity  $2l+1$  and with eigenfunctions

$$(4.5) \quad Y_{l,m}(\varphi, \theta) = \text{const} \cdot e^{-im\varphi} (\sin \theta)^{|m|} z_{l,|m|}(\cos \theta), \quad m = -l, -l+1, \dots, l-1, l,$$

where  $z_{l,|m|}(w)$  are polynomials such that the functions  $P_l^{|m|}(w) = (1-w^2)^{|m|/2} z_{l,|m|}(w)$  are the so-called Legendre functions of the first kind.

Since  $d^3x = r^2 dr \cdot \sin \theta d\varphi d\theta$  we can represent the Hilbert space  $\mathcal{H} = L_2(\mathbb{R}^3)$  as the following tensor product

$$(4.6) \quad \mathcal{H} = L_2(\mathbb{R}_+, r^2 dr) \otimes L_2(\mathbb{S}^2, \sin \theta d\varphi d\theta).$$

The space  $L_2(\mathbb{S}^2)$  is split into the subspaces  $\mathbb{C} \cdot Y_{l,m}$  and the space  $\mathcal{H}$  is split into subspaces  $L_2(\mathbb{R}_+, r^2 dr) \cdot Y_{l,m}$  which are invariant with respect to the operator  $\hat{H}$  (by the commutativity of  $\hat{H}$  and  $\hat{M}^2$ ). Therefore the eigenfunctions for  $\hat{H}$  should be of the form

$$\psi = u(r) Y_{l,m}(\varphi, \theta),$$

where the function  $u$  satisfies the following 1-dimensional Schrödinger equation

$$(4.7) \quad \left\{ -\frac{\hbar^2}{2m} \frac{1}{r^2} \partial_r r^2 \partial_r + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{r} \right\} u(r) = Eu(r).$$

**Remark 4.1.** When one puts  $u(r) = \chi(r)/r$  then the above equation takes the form  $-\frac{\hbar^2}{2m}\chi'' + \frac{\hbar^2 l(l+1)}{2mr^2}\chi + U(r)\chi = E\chi$ , which recalls the classical Hamiltonian. The factor  $1/r$  is ‘quantum mechanical’.

We seek solutions  $u(r)$  to equation (4.7), with  $E = -|E_n| < 0$ , which belong to  $L_2(\mathbb{R}_+, r^2 dr)$ . It means that  $|u(r)|r^2$  and  $|u'(r)|r^2$  are integrable.

The physicists use the following normalizations

$$\rho = \alpha_n r, \quad u(r) = u_{n,l}(\rho), \quad |E_n| = me^4/(2\hbar^2 \lambda_n^2),$$

where

$$\alpha_n^2 = 8m|E_n|/\hbar^2.$$

They find the equation

$$(4.8) \quad \left\{ \frac{1}{\rho^2} \partial_\rho \rho^2 \partial_\rho - \frac{l(l+1)}{\rho^2} - \frac{1}{4} + \frac{\lambda_n}{\rho} \right\} u_{n,l}(\rho) = 0.$$

The following lemma is proved by direct calculations.

**Lemma 4.1.** *As  $\rho \rightarrow \infty$  equation (4.8) has two independent solutions of the form*

$$u_1(\rho) \sim \rho^{\lambda_n-1} e^{\rho/2}, \quad u_2(\rho) \sim \rho^{-\lambda_n-1} e^{-\rho/2},$$

*and as  $\rho \rightarrow 0$  it has two meromorphic independent solutions of the form*

$$u_3(\rho) \sim \rho^l, \quad u_4(\rho) \sim \rho^{-l-1}.$$

*Moreover, the solutions are analytic functions of  $\rho$  in  $\mathbb{C} \setminus 0$ .*

Since we look for bounded states, we must choose the solution  $u_2$  near infinity. Also the solution  $u_4$  near zero is ‘bad’ because its derivative is not square integrable with respect to the measure  $\rho^2 d\rho$ . Therefore the solution  $u_{n,l}(\rho)$  should be an integer function. Moreover, the function  $u_{n,l}(\rho)\rho^{-l}e^{\rho/2}$  should be integer and of polynomial growth; so, it should be a polynomial denoted by  $L(\rho) = L_{n,l}(\rho)$ , called the *Laguerre polynomial*. Thus

$$u_{n,l}(\rho) = \text{const} \cdot \rho^l e^{-\rho/2} L_{n,l}(\rho),$$

where the polynomial  $L$  satisfies the *Laguerre equation*

$$\rho L'' + (2l + 2 - \rho) L' + (\lambda_n - l - 1)\rho = 0.$$

Assuming  $L(\rho) = \sum a_k \rho^k$  we find the recurrent relations

$$(k(k+1) + 2(l+1)(k+1)) a_{k+1} = (k+l+1 - \lambda_n) a_k.$$

Since  $a_j = 0$  for large  $j$  we get that

$$\lambda_n = n$$

is integer and

$$k + l + 1 \leq n.$$

It is a condition for the eigenvalues of the Schrödinger operator, because

$$(4.9) \quad E_n = -\frac{me^4}{2\hbar^2} \frac{1}{n^2}, \quad n = 1, 2, \dots$$

We can formulate the following result, which explains the Balmer–Ritz classification of the spectral lines in formula (2.1) in Subsection 2.

**Theorem 4.2.** *The point spectrum of the hydrogen atom Hamiltonian consists of the points (4.9). Each such eigenvalue has multiplicity  $n^2$  and the corresponding eigenfunctions take the form*

$$u_{n,l,m}(r, \varphi, \theta) = \text{const} \cdot e^{im\varphi} (\sin \theta)^{|m|} z_{l,|m|}(\cos \theta) \rho^l e^{-\rho/2} L_{n,l}(\rho),$$

$$\rho = \alpha_n r, \quad \alpha_n = 2me^2/(\hbar^2 n).$$

*Proof.* It remains to calculate the multiplicity. For fixed  $n$  the number  $l$  can take the values  $0, 1, \dots, n-1$  and for fixed  $n$  and  $l$  the number  $m$  can take  $2l+1$  values. Thus the multiplicity equals  $\sum_{l=0}^{n-1} (2l+1) = n^2$ .  $\square$

The continuous spectrum of the hydrogen atom operator is discussed in Chapter 3 (Section 3) below.

## 5. THE ANGULAR MOMENTUM AND THE REPRESENTATION THEORY OF $so(3)$

The components of the angular momentum operator can be written as linear vector fields:

$$\hat{M}_x = -i\hbar(y\partial_z - z\partial_y) \sim -i\hbar A_x q, \quad \hat{M}_y \sim -i\hbar A_y q, \quad \hat{M}_z \sim -i\hbar A_z q,$$

where  $q = (x, y, z)$  and

$$(5.1) \quad A_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad A_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \quad A_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

are antisymmetric matrices, generating the Lie algebra  $so(3)$ . The algebra  $so(3)$  is the Lie algebra of the group  $SO(3)$  if rotations in  $\mathbb{R}^3$  and is isomorphic with  $\mathbb{R}^3$  equipped with the vector product as the commutator.

The commutation relations for the components of  $\hat{M}$  and of  $A$  are following

$$(5.2) \quad \begin{aligned} [\hat{M}_x, \hat{M}_y] &= i\hbar \hat{M}_z, & [\hat{M}_y, \hat{M}_z] &= i\hbar \hat{M}_x, & [\hat{M}_z, \hat{M}_x] &= i\hbar \hat{M}_y, \\ [A_x, A_y] &= -A_z, & [A_y, A_z] &= -A_x, & [A_z, A_x] &= -A_y. \end{aligned}$$

**Proposition 5.1.** *The angular momentum operator realizes a representation of the Lie algebra  $so(3)$  in the Hilbert space  $\mathcal{H} = L_2(\mathbb{R}^3)$ , e.g. modulo the factor  $-i\hbar$ .*

Interesting question is whether this representation of the Lie algebra arises from a representation of the Lie group  $SO(3)$  (or maybe  $O(3)$ ) in  $\mathcal{H}$  by means of unitary operators. As we shall see, this is true for the model of the hydrogen atom presented in the previous subsection, but in a more adequate model of the electron there exist so-called *spin representations* which do not arise from any representation of the Lie group  $SO(3)$ .

**5.1. Representation of  $so(3)$  in  $L_2(\mathbb{S}^2)$ .** Let us calculate the Laplacian in the spherical variables (following the V. Arnold's book [Arn]). Denoting the spherical coordinates  $(x_1, x_2, x_3) = (r, \varphi, \theta)$  and the orthogonal frame  $(e_1, e_2, e_3) = (e_r, e_\varphi, e_\theta)$ , we write the metric as follows

$$ds^2 = dr^2 + r^2 \sin^2 \theta d\varphi^2 + r^2 d\theta^2 = E_1 dx_1^2 + E_2 dx_2^2 + E_3 dx_3^2.$$

Since  $\langle dx_i, e_i \rangle = dx_i/ds = 1/\sqrt{E_i}$  we have

$$dr(e_r) = 1, \quad d\varphi(e_\varphi) = 1/(r \sin \theta), \quad d\theta(e_\theta) = 1/r.$$

With a vector field  $A = A_1(x)e_1 + A_2(x)e_2 + A_3(x)e_3$  one associates two differential forms

$$\omega_A^1 = (A, \cdot), \quad \omega_A^2 = \det(A, \cdot, \cdot).$$

In fact, we have

$$\begin{aligned} \omega_A^1 &= \sum A_i \sqrt{E_i} dx_i, \\ \omega_A^2 &= A_1 \sqrt{E_2 E_3} dx_2 \wedge dx_3 + A_2 \sqrt{E_3 E_1} dx_3 \wedge dx_1 + A_3 \sqrt{E_1 E_2} dx_1 \wedge dx_2. \end{aligned}$$

We have the following formulas:  $df = (\nabla f, \cdot) = \omega_{\nabla f}^1$ , which defines the *gradient* of a function

$$\text{grad } f = \sum \frac{1}{\sqrt{E_i}} \frac{\partial f}{\partial x_i} e_i = \frac{\partial f}{\partial r} e_r + \frac{1}{r \sin \theta} \frac{\partial f}{\partial \varphi} e_\varphi + \frac{1}{r} \frac{\partial f}{\partial \theta} e_\theta,$$

and  $d\omega_A^2 = \text{div } A \cdot VOL = \text{div } A \cdot \sqrt{E_1 E_2 E_3} dx_1 \wedge dx_2 \wedge dx_3$ , which defines the *divergence* of a vector field

$$\text{div } A = \frac{1}{\sqrt{E_1 E_2 E_3}} \left\{ \frac{\partial}{\partial x_1} (A_1 \sqrt{E_2 E_3}) + \frac{\partial}{\partial x_2} (A_2 \sqrt{E_3 E_1}) + \frac{\partial}{\partial x_3} (A_3 \sqrt{E_1 E_2}) \right\}.$$

Since the *Laplacian* of a function  $f$  equals  $\Delta f = \text{div grad } f$  the previous formula, with  $A_j = E_j^{-1/2} \partial f / \partial x_j$ , gives

$$\begin{aligned} \Delta f &= \frac{1}{\sqrt{E_1 E_2 E_3}} \left\{ \frac{\partial}{\partial x_1} \left( \sqrt{\frac{E_2 E_3}{E_1}} \frac{\partial f}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( \sqrt{\frac{E_3 E_1}{E_2}} \frac{\partial f}{\partial x_2} \right) \right. \\ &\quad \left. + \frac{\partial}{\partial x_3} \left( \sqrt{\frac{E_1 E_2}{E_3}} \frac{\partial f}{\partial x_3} \right) \right\} \\ &= \frac{1}{r^2 \sin \theta} \left\{ \frac{\partial}{\partial r} \left( r^2 \sin \theta \frac{\partial f}{\partial r} \right) + \frac{\partial}{\partial \varphi} \left( \frac{1}{\sin \theta} \frac{\partial f}{\partial \varphi} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) \right\}. \end{aligned}$$

Therefore  $\Delta = \Delta_r + \frac{1}{r^2} \Delta_t$ , where the radial  $\Delta_r$  and the tangential  $\Delta_t$  parts are equal

$$\Delta_r = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right), \quad \Delta_t = \frac{1}{r^2} \left\{ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right\}.$$

The operators  $\Delta_r$  and  $r^2 \Delta_t$  commute and it follows that the tangential part should equal the square of the angular momentum divided by  $-\hbar^2 r^2$ :

$$(5.3) \quad \hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2 = -\hbar^2 r^2 \Delta_t$$

Hence we have proved first part of Theorem 4.1.

We note also the expression of the third component in the spherical coordinates:

$$(5.4) \quad \hat{M}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

which follows directly from the formula  $\tan \varphi = y/x$ . The other components have more complicated expressions:  $\hat{M}_x = i\hbar \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right)$  and  $\hat{M}_y = i\hbar \left( -\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right)$ .

**Lemma 5.1.** *The operator  $\hat{M}^2$  commutes with the components  $\hat{M}_x, \hat{M}_y, \hat{M}_z$ .*

*Proof.* The commutation of  $\hat{M}^2$  with  $\hat{M}_z$  follows directly from their expressions in formulas (5.3) and (5.4).

It follows also from the commutation relations (5.2). Indeed, we have

$$\begin{aligned} [\hat{M}^2, \hat{M}_z] &= [\hat{M}_x^2, \hat{M}_z] + [\hat{M}_y^2, \hat{M}_z] \\ &= \hat{M}_x[\hat{M}_x, \hat{M}_z] + [\hat{M}_x, \hat{M}_z]\hat{M}_x + \hat{M}_y[\hat{M}_y, \hat{M}_z] + [\hat{M}_y, \hat{M}_z]\hat{M}_y \\ &= i\hbar(-\hat{M}_x\hat{M}_y - \hat{M}_y\hat{M}_x + \hat{M}_y\hat{M}_x + \hat{M}_x\hat{M}_y) = 0. \end{aligned}$$

(The operator  $\hat{M}^2$  is also called the *Casimir operator* of the representation.)  $\square$

Since the operators  $\hat{M}^2$  and  $\hat{M}_z$  commute and are symmetric, they can be simultaneously diagonalized, e.g. in the space  $L_2(\mathbb{S}^2)$ . The eigenfunctions of the operator  $\hat{M}_z$  with eigenvalues  $\lambda = \hbar m$  are

$$u_m(\varphi, \theta) = \text{const}(\theta) \cdot e^{im\varphi}$$

and it is clear that  $m$  should be integer. The common eigenfunctions of  $\hat{M}^2$  with eigenvalues  $\hbar^2\beta$  and  $\hat{M}_z$  should take the form

$$Y_{\beta,m}(\varphi, \theta) = e^{im\varphi} \tilde{P}_{\beta,m}(\theta)$$

where  $\tilde{P} = \tilde{P}_{\beta,m}$  satisfies the equations  $\left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) - \frac{m^2}{\sin^2\theta} \right\} \tilde{P} = -\beta\tilde{P}$ . The substitution

$$w = \cos\theta,$$

i.e.  $\tilde{P}(\theta) = P(w)$ , leads to the *Legendre equation*

$$(5.5) \quad \frac{d}{dw} \left\{ (1-w^2) \frac{d}{dw} \right\} P + \left( \beta - \frac{m^2}{1-w^2} \right) P = 0.$$

Of course,  $P(w)$  should be finite in the closed interval  $[-1, 1]$ .

The only singularities of the function  $P$  can appear at the endpoints of this interval.

**Lemma 5.2.** *Near  $w = 1$  we have two independent solutions to (5.5) of the form*

$$P^{(1)} = (1-w)^{|m|/2}(a_0 + a_1(1-w) + \dots), \quad Q^{(1)} = (1-w)^{-|m|/2}(a_0 + a_1(1-w) + \dots)$$

*and near  $w = -1$  we have two independent solutions of the form*

$$P^{(-1)} = (1+w)^{|m|/2}(a_0 + a_1(1+w) + \dots), \quad Q^{(-1)} = (1+w)^{-|m|/2}(a_0 + a_1(1+w) + \dots).$$

*If  $m = 0$  then the solutions  $Q^{(1)}$  and  $Q^{(-1)}$  take another form (with logarithm).*

Of course, our solution should equal  $P^{(1)}$  near  $w = 1$  and  $P^{(-1)}$  near  $w = -1$ ; it is a condition for the eigenvalue  $\hbar^2\beta$ . So,

$$P_{\beta,m}(w) = (1-w^2)^{|m|/2} z(w)$$

where the function  $z(w)$  satisfies the equation

$$(1-w^2)z'' - 2((1+|m|)wz' + (\beta - |m|)(|m| + 1)w)z = 0$$

and is an integer function of  $w \in \mathbb{C}$ . The Taylor expansion  $z = \sum a_k w^k$  implies the recurrent relations

$$(k+1)(k+2)a_{k+2} = \{(k+|m|)(k+|m|+1) - \beta\} a_k.$$

If all  $a_k \neq 0$ , then  $a_{k+2} \sim a_k$  and the function  $z(w)$  were not integer. So some coefficient before  $a_k$  in the above formula must vanish. We have

$$\beta = l(l+1)$$

for a nonnegative integer

$$l \geq |m|.$$

The obtained solutions  $z_{l,|m|}(w)$  are polynomials such that the functions  $P_l^{|m|} = (1-w^2)^{|m|/2} z_{l,|m|}$  are the so-called *Legendre functions of the first kind* (see [BE1, BE2]). In fact, we have  $z_{l,|m|}(w) = \frac{d^{|m|}}{dw^{|m|}} P_l(w)$  where  $P_l(w)$  are the standard *Legendre polynomials* with the generating function  $\sum_{l=0}^{\infty} P_l(w) \zeta^l = (1-2\zeta w + \zeta^2)^{-1/2}$  (see [Sch]).

If  $k = l - |m|$  is odd then we have  $a_0 = 0$  and the Legendre polynomial is an odd function of  $w$ . If  $k$  is even, then  $a_0 \neq 0$ ,  $a_1 = 0$  and we have an even Legendre polynomial.

Therefore we have proved the second statement of Theorem 4.1.  $\square$

**Remark 5.1.** For fixed integer  $l \geq 0$  the spherical functions  $Y_{l,m} = \text{const} \cdot e^{im\varphi} P_l^{|m|}(\cos \theta)$ ,  $m = -l, -l+1, \dots, l$ , generate a subspace of  $L_2(\mathbb{S}^2)$  which supports an irreducible representation of the Lie algebra  $so(3)$  (see also Subsection 3 below). But these representations of the Lie algebra can be integrated to representations of the Lie group  $SO(3)$ .

Indeed, the rotation by the angle  $\alpha$  around the  $OZ$ -axis corresponds to the operator  $\exp(i\alpha \hat{M}_z / \hbar)$  which acts on the wave function  $Y_{l,m}$  by multiplication by the number  $e^{im\alpha}$ .

**5.2. Interaction with the magnetic field.** The energy levels of the bounded states of an electron in the hydrogen atom depend only on the number  $l$ , but not on  $m$ . In order to see that the states with different  $m$ 's are physically different one must embed the hydrogen atom in a constant magnetic field. Then the energy levels  $E_n$  become separated. Therefore we need to have a formula for the Hamiltonian operator of the electron in presence of a magnetic field.

**Proposition 5.2.** *The classical Hamiltonian in this situation is following*

$$(5.6) \quad H = \frac{1}{2m} \left( p - \frac{e}{c} A \right)^2 + e\varphi,$$

where  $A$  is the vector potential and  $\varphi$  is the scalar potential defined by  $B = \nabla \times A$ ,  $E = -\frac{1}{c} \frac{\partial A}{\partial t} - \nabla \varphi$ .

*Proof.* The equations of motion with the Hamilton function (5.6) take the form

$$\dot{q} = H'_p = \frac{1}{m} \left( p - \frac{e}{c} A \right), \quad \dot{p} = -H'_q = \frac{e}{mc} \left( p - \frac{e}{c} A, \nabla A \right) - e \nabla \varphi.$$

So  $p = m\dot{q} + \frac{e}{c} A$ . Since  $(\dot{q}, \nabla A)_j = \sum_i \dot{q}_i \frac{\partial A_i}{\partial q_j} = \sum_i \dot{q}_i \left( \frac{\partial A_i}{\partial q_j} - \frac{\partial A_j}{\partial q_i} \right) + \sum_i \frac{\partial A_j}{\partial q_i} \dot{q}_i = (\dot{q} \times B)_j + \sum_i \frac{\partial A_j}{\partial q_i} \dot{q}_i$  and  $\frac{dA_j}{dt} = \sum_i \frac{\partial A_j}{\partial q_i} \dot{q}_i + \frac{\partial A_j}{\partial t}$ , we get  $m\dot{q} + \frac{e}{c} \dot{q} \times B = \frac{e}{c} \dot{q} \times B - e \nabla \varphi$ . This means exactly that  $m\ddot{q} = eE + \frac{e}{c} \dot{q} \times B$ , which agrees with the classical notions of the electromotoric and Lorentz forces (see formula (2.3) in Section 1).  $\square$

**Lemma 5.3.** *When  $B = \text{const}$  the vector potential can be taken in the form  $A = \frac{1}{2} B \times q$ . In particular, for an electron in the hydrogen atom in presence of a constant magnetic field  $B$  the Hamiltonian (5.6) takes the form  $H = \frac{1}{2m} \left( p - \frac{e}{2c} B \times q \right)^2 - \frac{e^2}{|q|}$ .*

Then for small  $e/c$  the approximate contribution to the energy arising from the interaction with the magnetic field equals

$$-\frac{e}{c}(\dot{q}, A) = \frac{e}{2c}(\dot{q}, q \times B) = -\frac{e}{2mc}(q \times m\dot{q}, B) = -\frac{e}{2mc}(M, B)$$

where  $M$  is the angular momentum of the electron. Assuming  $B$  is directed along the  $OZ$  axis (with length  $B$ ) we have the the quantum mechanical Hamiltonian

$$(5.7) \quad \hat{H} = -\frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{r} - \frac{e}{2m_e c}B\hat{M}_z$$

where  $m_e$  is the electron's mass (in order to avoid confusion with the index  $m$  in the eigenvalues of  $\hat{M}_z$ ). Since the operator  $\hat{M}_z$  commutes with  $\Delta$  and  $\frac{1}{r}$  the operator (5.7) has the same eigenfunctions as the pure hydrogen Hamiltonian operator (4.1), i.e. the functions  $u_{n,l,m}$  defined in Theorem 4.2. But the eigenvalues corresponding to these eigenfunctions do not equal  $E_n$  (defined in Theorem 4.2). The following result is known as the *Zeeman effect*.

**Theorem 5.1.** *The energies of the bounded states for the operator (5.7) equal*

$$(5.8) \quad E_{n,m} = E_n + m\Delta E, \quad \Delta E = \frac{e\hbar B}{2m_e c}, \quad |m| < n.$$

**Remark 5.2.** If the electron is moving with constant velocity  $v$  along a circular orbit of radius  $r$  then we can associate with it the current  $j = \rho v$ , where  $\rho$  is the charge's density equal  $\frac{e}{2\pi r}$ ; thus  $|j| = \frac{e|v|}{2\pi r}$ . Here the classical contribution to the energy is the average of the contribution along the orbit and equals  $-\frac{e}{2c} \int (q \times v, B) = -(\mu, B)$ , where

$$\mu = \frac{|j|}{c} \cdot \text{area} \cdot \vec{n} = \frac{e}{2m_e c} M.$$

The vector  $\mu$  is the *magnetic moment* (of the current generated by the electron) which is parallel to the unit vector  $\vec{n}$  orthogonal to the orbit's plane and area is the area bounded by the circuit. This is a physical interpretation of the Hamiltonian (5.7).

The value  $|\mu| = \frac{e\hbar}{2m_e c}$  is called the *Bohr magneton*.

**5.3. Spin.** Theorem 5.1 implies, in particular, that the first level  $E_1$  is not split (because then  $l = 0$  and  $m = 0$ ). But observations did not confirm this. This level was split into two sublevels. Explanation of this phenomenon lies in considering new representations of the Lie algebra  $so(3)$ . We begin with some algebraic stuff and then apply it to the quantum physics.

Introduce the operators

$$\hat{M}_\pm = \hat{M}_x \pm i\hat{M}_y, \quad A_\pm = A_x \pm iA_y.$$

Together with  $\hat{M}_z$  (respectively, with  $A_z$ ) they satisfy the following commutation relations

$$(5.9) \quad [\hat{M}_z, \hat{M}_\pm] = \pm\hbar\hat{M}_\pm, \quad [\hat{M}_+, \hat{M}_-] = 2\hbar\hat{M}_z$$

(and similar relations are satisfied by  $A$ 's). We can say that the matrices  $A_z, A_+, A_-$  generate the complex Lie algebra  $sl(2, \mathbb{C})$ , which is isomorphic with the complex Lie algebra  $so(3, \mathbb{C}) = so(3) \otimes \mathbb{C}$ , and the operators  $\hat{M}_z, \hat{M}_+, \hat{M}_-$  define a representation



of  $sl(2, \mathbb{C})$ . Recall that the Lie algebra  $sl(2, \mathbb{C})$  consists of  $2 \times 2$  matrices with zero trace.

**Theorem 5.2.** *Any finite dimensional irreducible representation of the Lie algebra  $sl(2, \mathbb{C})$  is equivalent to  $\mathbb{C}^{2l+1}$ ,  $l = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ , with a basis  $\{\psi_m\}_{m=-l, -l+1, \dots, l-1, l}$  such that*

$$\hat{M}_z \psi_m = m \hbar \psi_m$$

and  $\hat{M}_\pm$  are defined below. Moreover here  $\hat{M}^2 = \hbar^2 l(l+1)I$ .

*Proof.* Let  $(\psi_j)$  be a basis of a space of irreducible representation generated by  $\hat{M}_\pm$  and  $\hat{M}_z$  and such that  $\hat{M}_z \psi_j = \lambda_j \psi_j$ .

Fix an element  $\psi_j$  and consider the vector  $\varphi = \hat{M}_+ \psi_j$ . Then (5.9) implies that  $\hat{M}_z \varphi = \hat{M}_+ \hat{M}_z \psi_j + \hbar \hat{M}_+ \psi_j = (\lambda_j + \hbar) \varphi$ . Thus  $\varphi$  is an eigenvector of  $\hat{M}_z$  with the eigenvalue  $\lambda_j + \hbar$ . Analogously we find that the vector  $\hat{M}_- \psi_j$  is an eigenvector of  $\hat{M}_z$  with the eigenvalue  $\lambda_j - \hbar$ .

Since we consider an irreducible representation we can numerate the vector  $\psi_j$  such that

$$\hat{M}_+ \psi_j = \text{const} \cdot \psi_{j+1} \text{ (if } \hat{M}_+ \psi_j \neq 0 \text{) and } \hat{M}_- \psi_j = \text{const} \cdot \psi_{j-1} \text{ (if it is nonzero).}$$

Since the operator  $-\hat{M}_z$  is generated by infinitesimal rotations around the  $OZ$  axis in the negative direction, the spectra of  $\hat{M}_z$  and  $-\hat{M}_z$  are the same. It follows that the spectrum of  $\hat{M}_z$  equals  $\{m\hbar : m = -l, -l+1, \dots, l-1, l\}$ , where  $l\hbar$  is the maximal eigenvalue. We see also that  $l \in \frac{1}{2}\mathbb{Z}$  is a half-integer or integer.

To compute the operator  $\hat{M}^2$  we firstly note that it is proportional to the identity,  $\hat{M}_2 = \mu \cdot I$  (as commuting with the whole representation). By (5.9) we have  $\hat{M}_2 = \hat{M}_- \hat{M}_+ + \hat{M}_z^2 + \hbar \hat{M}_z$ . Since  $\hat{M}_+ \psi_l = 0$  we get  $\hat{M}_2 \psi_l = 0 + \hbar^2 l^2 \psi_l + \hbar^2 l \psi_l$ . Therefore  $\mu = \hbar^2 l(l+1)$ .  $\square$

**Definition 5.1.** The representation described in Theorem 5.2 are called the **spin  $l$  representations**.

**Example 5.1.** The integer spin representations are the representations obtained in Subsection 2 above. They are subrepresentations of  $so(3)$  in  $L_2(\mathbb{S}^2)$  and also in  $\mathcal{H} = L_2(\mathbb{R}^3) = L_2(\mathbb{S}^2) \otimes L_2(\mathbb{R}_+, r^2 dr)$ . Recall that they arise from unitary representations of the group  $SO(3)$ .

The spin 0 representation is the trivial 1-dimensional and all the operators  $A_\pm, A_z$  are equal zero.

The spin 1 representation is the representation  $\rho$  in  $\mathbb{R}^3$  such that  $\rho(A_\pm) = A_\pm$  and  $\rho(A_z) = A_z$ .

The spin  $\frac{1}{2}$  representation is realized in  $\mathbb{C}^2$ . We have

$$\hat{M}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{M}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

and  $\hat{M}_x = \frac{\hbar}{2} \sigma_x$ ,  $\hat{M}_y = \frac{\hbar}{2} \sigma_y$ ,  $\hat{M}_z = \frac{\hbar}{2} \sigma_z$ , where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are the so-called **Pauli matrices**.

The latter representation does not arise from a representation of the Lie group  $SO(3)$ . Indeed, the matrix  $A_z$  corresponds to the vector field  $\frac{\partial}{\partial \varphi} = \frac{i}{\hbar} \hat{M}_z$  and the

matrix  $e^{\alpha A_x}$  is a matrix of rotation by the angle  $\alpha$  around the  $OZ$  axis. In particular,  $e^{2\pi A_x} = I$  (identity matrix). But

$$e^{\alpha i \hat{M}_z / \hbar} = \begin{pmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{pmatrix}$$

and  $\exp(2\pi \hat{M}_z / \hbar) = -id$ .

In fact, the spin  $\frac{1}{2}$  representation of the algebra  $so(3)$  arises from a genuine representation of a larger group than  $SO(3)$ . It is the group

$$SU(2) = \{A : AA^* = 1, \det A = 1\} = \left\{ \begin{pmatrix} a & -\bar{c} \\ c & -\bar{a} \end{pmatrix} : |a|^2 + |c|^2 = 1 \right\}$$

of unitary  $2 \times 2$  matrices. The group  $SU(2)$  covers two times the group  $SO(3)$ ; hence the both groups have the same Lie algebra. Topologically  $SU(2)$  is the 3-dimensional sphere  $\mathbb{S}^3$  and  $SO(3)$  is the real 3-dimensional projective space  $\mathbb{RP}^3$  and the covering  $SU(2) \rightarrow SO(3)$  is the same as the antipodal points identification.

One can say that the spin  $\frac{1}{2}$  representation arises from ‘2-valued representation’ of the group  $SO(3)$ .

As we mentioned in the beginning of this subsection physical experiments demonstrate realization of the spin  $\frac{1}{2}$  representation for the electron in the hydrogen atom. On the other hand, we do not know any natural way to include this representation into our standard Hilbert space  $L_2(\mathbb{R}^3)$ . The physicists found the following solution to this problem.

Instead of acting in the space  $L_2(\mathbb{R}^3)$  we should act in the Hilbert space

$$(5.10) \quad \mathcal{H} := L_2(\mathbb{R}^3) \otimes \mathbb{C}^2 \simeq L_2(\mathbb{R}^3) \oplus L_2(\mathbb{R}^3),$$

which consists of vector-valued functions  $\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$ . Moreover, the Hamilton operator should take the form

$$(5.11) \quad \hat{H} = \left( -\frac{\hbar^2}{2m_e} \Delta - \frac{e^2}{r} \right) \otimes id - \frac{e}{2m_e c} B (\hat{M}_z \otimes id + \hbar \cdot id \otimes \sigma_z).$$

It means that the operators  $-\frac{\hbar^2}{2m_e} \Delta - \frac{e^2}{r}$  and  $\hat{M}_z$  act on the both components  $\psi_1$  and  $\psi_2$  in the same way, while the operator  $\sigma_z$  multiplies  $\psi_1$  by 1 and  $\psi_2$  by  $-1$ .

It means that the electron has some ‘internal’ discrete degrees of freedom and the operator  $\hat{S} = \frac{\hbar}{2} \sigma_z$  is the **spin operator** acting only on these internal discrete variables. One would like to interpret this classically as a kind of rotation of the electron around some (undetermined) axis. But this is not accurate interpretation because the coefficient before  $id \otimes \sigma_z$  is  $\hbar$  (not  $\frac{\hbar}{2}$ ), as it follows from physical experiments.

Anyway, the operator (5.11) acts diagonally and has the eigenfunctions  $u_{n,l,m} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  and  $u_{n,l,m} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  with the eigenvalues which differ from the eigenvalues from Theorem 5.1 by  $\pm \frac{e\hbar}{2m_e c} B$ . Therefore we have the following

**Theorem 5.3.** *The energy levels of the bounded states of the operator (5.11) are following*

$$E_{n,m,\pm} = E_n + (m \pm 1)\Delta E, \quad |m| < n,$$

where  $E_n$  and  $\Delta E$  were defined before.

The phenomenon of having internal spin by elementary particles is common. If a particle has spin  $l$ , then the corresponding Hilbert space is

$$\mathcal{H} = L_2(\mathbb{R}^3) \otimes \mathbb{C}^{2l+1}$$

and the angular momentum operator is replaced by the operator  $\hat{M} + \hat{S}$ , where  $\hat{M} \simeq \hat{M} \otimes id$  acts in the usual (differential) way and  $\hat{S} \simeq id \otimes \hat{S}$  acts in algebraic way.

**Remark 5.3.** The above *Zeeman effect* observed in the discrete spectrum of the hydrogen atom is not end of the story. There exists the so-called *Lamb shift* which says that the energy levels take the form

$$E_{nj} = E_n \left\{ 1 + \frac{\alpha^2}{n} \left( \frac{1}{j + 1/2} - \frac{3}{4n} \right) \right\},$$

where  $j + \frac{1}{2}$  is the maximal eigenvalue of the operator  $\hat{M} + \hat{S}$  and

$$(5.12) \quad \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

is the so-called *fine structure constant*. This shift arises when one takes into account the effect of interaction of the electron with the electromagnetic radiation caused by his movement along the orbit.

Very precise calculation of the Lamb shift and its agreement with experiments in the 1950's was a great success of the quantum electrodynamics.

**Remark 5.4.** (*The group Spin(n)*) There exists a generalization of the twofold covering of the group  $SO(3)$  to higher dimensions.

Firstly we note that the Pauli matrices  $\sigma_x, \sigma_y, \sigma_z$  satisfy the following *anticommutation relations*

$$\{\sigma_x, \sigma_x\} = \{\sigma_y, \sigma_y\} = \{\sigma_z, \sigma_z\} = 2, \quad \{\sigma_x, \sigma_y\} = \{\sigma_y, \sigma_z\} = \{\sigma_z, \sigma_x\} = 0,$$

where  $\{A, B\} = AB + BA$  is the *anticommutator*. Mathematicians say that they generate the Clifford algebra  $Cl(\mathbb{R}^3)$ .

By definition, for a real vector space  $V$  of dimension  $n$  equipped with a scalar product  $Q(x, y)$  (which we assume standard  $Q(e_i, e_j) = \delta_{ij}$ ), the *Clifford algebra*  $Cl(V)$  is an algebra generated by 1 and the basic vectors  $e_i$  with the relations

$$\{e_i, e_j\} = 2Q(e_i, e_j).$$

In the Clifford algebra  $Cl(V)$  we define the 'conjugation'  $x \rightarrow \bar{x}$  by

$$e_{i_1} \dots e_{i_k} \rightarrow (-1)^k e_{i_k} \dots e_{i_1}.$$

Define the group

$$Pin(V) = \{g \in Cl(V) : g\bar{g} = 1, gVg^{-1} = V\}.$$

This group acts in natural way on the space  $V$  by means of orthogonal transformations; so we have a homomorphism  $\pi : Pin(V) \rightarrow O(V)$ . The group  $Spin(V) = \pi^{-1}(SO(V))$  is called the **spinor group** and is twofold covered over the group  $SO(V)$  :

$$Spin(V) \xrightarrow{2:1} SO(V).$$

Indeed, the transformations  $x \rightarrow gxg^{-1}$  and  $x \rightarrow g'xg'^{-1}$  of  $V$  are the same when  $g' = \lambda g$  (because they induce the same automorphisms of the Clifford algebra). But the second condition in the definition of the group  $Pin(V)$  implies that  $\lambda^2 = 1$ .

When  $V$  is the standard  $\mathbb{R}^n$  we use the notation  $Spin(n)$ .

The 2-valued mapping from  $SO(V)$  to  $Spin(V)$  can be defined directly. For example, if  $e_x \rightarrow \cos \varphi \cdot e_x - \sin \varphi \cdot e_y$ ,  $e_y \rightarrow \sin \varphi \cdot e_x + \cos \varphi \cdot e_y$  is a rotation in the  $OXY$  plane in  $V = \mathbb{R}^3$ , then we associate with it the element

$$g = \cos(\varphi/2) \cdot 1 - \sin(\varphi/2)\sigma_x\sigma_y = \begin{pmatrix} \cos \frac{\varphi}{2} + i \sin \frac{\varphi}{2} & 0 \\ 0 & \cos \frac{\varphi}{2} - i \sin \frac{\varphi}{2} \end{pmatrix}$$

from the Clifford algebra  $Cl(\mathbb{R}^3)$ .

We have  $Spin(2) = SU(1) \simeq \mathbb{S}^1$  (with twofold covering over  $SO(2) \simeq \mathbb{S}^1$ ),  $Spin(3) \simeq SU(2)$  and  $Spin(4) \simeq SU(2) \times SU(2)$ .

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