

TALLINN UNIVERSITY OF TECHNOLOGY

Institute of Physics

QUANTUM MECHANICS

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I think I can safely say that nobody understands quantum mechanics.

(Richard Feynman)

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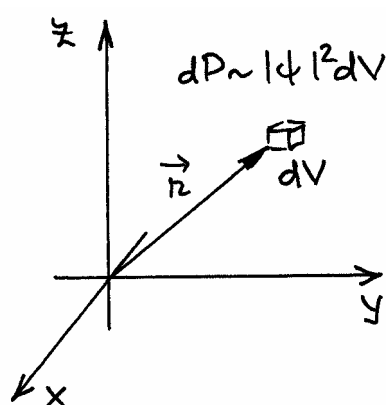
1. Schrödinger equation

In the first paragraphs let us remind some basics concepts of quantum mechanics, treated in the bachelors course of modern physics (introduction to quantum mechanics). In microworld classical physics (Newtonian mechanics) is not applicable, since microparticles are at the same time particles in the usual sense and waves (matter waves), having certain wavelength and frequency. Therefore we must use different concepts and different „rules of play“, and also the mathematics used is somewhat different from that studied in calculus.

1.1 Wave function. We start with single microparticle. Its state is described by the wave function

$$\Psi = \Psi(\vec{r}, t),$$

which is determined in finite region of space or infinite space, depends on time and has in general complex values ($\Psi \in C$). In our course we use mainly the old fashioned name – wave function, but Ψ is also called state function or probability amplitude.



The physical meaning of the wave function is the following: its square of modulus $|\Psi(\vec{r}, t)|^2$ is proportional to the probability to find our particle at certain moment of time t in the small element of volume dV

$$dP \sim |\Psi(\vec{r}, t)|^2 dV.$$

Therefore the wave function itself is not directly measurable quantity, but its square of module is. One can compare probabilities in different places. It also follows that wave functions $\Psi(\vec{r}, t)$ and $\Psi'(\vec{r}, t) = A\Psi(\vec{r}, t)$, where A is some

numerical constant, describe the same physical state (they give the same ratio of probabilities).

1.2 Normalization of the wave function. For Ψ there are two possibilities – integral over the square of modulus (we integrate over the whole space or region where the wave function is nonzero) is finite or it is infinite.

1. In the first case we can normalize the integral to unit. In other words we consider only these wave functions, which satisfy

$$\int |\Psi(\vec{r}, t)|^2 dV = 1.$$

(We simplify our notations and write space integrals as $\int dV$ not $\iiint dx dy dz$ and also omit the boundaries, if these are not necessary.)

Now the wave function gives us the probability of finding particle in certain volume element dV

$$dP = |\Psi(\vec{r}, t)|^2 dV,$$

since the sum of all probabilities equals to 1

$$\int dP = 1 = \int |\Psi(\vec{r}, t)|^2 dV .$$

The square of modulus of wave function gives us probability density

$$\rho(\vec{r}, t) = \frac{dP}{dV} = |\Psi(\vec{r}, t)|^2 .$$

Problem 1.1 Prove, that if the integral $\int |\Psi'(\vec{r}, t)|^2 dV = a$ is finite the wave function can be normalised to unit.

2. In the second case we have

$$\int |\Psi(\vec{r}, t)|^2 dV \rightarrow \infty$$

(example: free particle, described by the de Broglie wave). One can compare probabilities in different places, but not directly calculate them. In that case wave functions usually are normed to δ -function (see next paragraph).

1.3 Conditions on wave functions. All wave functions must satisfy the following conditions – the wave function is finite, unique and continuous function, the first space derivatives are continuous. The first ones (finite, unique and continuous) follow from the physical meaning of wave function since it gives probability, the last one is purely mathematical, since wave function is calculated from the differential equation (Schrödinger equation) which contains second order space derivatives. It should be mentioned that these conditions are very important, because only these solutions which satisfy above given conditions have physical meaning.

1.4 Schrödinger equation. The basic equation in quantum mechanics is the Schrödinger equation. Its general form is the following

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

where $U(\vec{r}, t)$ is the potential function of a given particle (potential energy), M is a mass of particle and Δ is the Laplace operator (in rectangular coordinates $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$). It is also called time dependent Schrödinger equation.

If we treat physical problems in quantum mechanics, we at first must solve the Schrödinger equation for a given potential and then analyse the physical content of a given wave function. Later we see, that it gives us also the results which one may obtain in experiments.

It should be noted that quantum mechanics is a normal physical theory which describes processes in nonrelativistic microworld. Sometimes it is stated, that the quantum mechanics is not satisfactory theory, since it gives only probabilities and for that reason it seems that the behaviour of microparticle is chaotic and for that reason not deterministic. But it is not so, the probabilistic behaviour is characteristic to microparticles, but on the other hand it is deterministic, since the wave function is determined uniquely if the initial conditions are given. As we already mentioned,

microparticles are at the same time particles (corpuscles) and waves, and these qualities need different concepts.

1.5 Continuity equation. From the Schrödinger equation it follows the continuity equation for probability density $\rho = |\Psi(\vec{r}, t)|^2$

$$\frac{\partial \rho}{\partial t} + \text{div } \vec{j} = 0 \quad ,$$

where the vector quantity

$$\vec{j} = \frac{i\hbar}{2M} (\text{grad } \Psi^* \cdot \Psi - \Psi^* \cdot \text{grad } \Psi)$$

is called the probability current density.

Problem 1.2. Derive the continuity equation.

In the case of electrically charged particles we can obtain charge density and current density. If the electrical charge, carried by particle, is q then the charge density is

$$\rho_l = q\rho$$

and current density is

$$\vec{j}_v = q \vec{j} .$$

Example. One dimensional de Broglie wave (free particle with the momentum p)

$$\Psi(x, t) = A e^{-\frac{i}{\hbar}(Et - px)} .$$

Now $\rho = |A|^2$ (probability density is constant) and probability current density is

$$j = \frac{i\hbar}{2M} \left(\frac{d\Psi^*}{dx} \Psi - \Psi^* \frac{d\Psi}{dx} \right) = \frac{p}{M} |\Psi|^2 = \frac{p}{M} |A|^2 .$$

Since $p = M v$, we get

$$j = v |A|^2 ,$$

which describes the particle, moving with the velocity v , or flux of moving particles.

1.6 Schrödinger equation for stationary states. If $U = U(\vec{r})$, the Schrödinger equation simplifies, since the time dependence may be eliminated.

Indeed, in

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

it is possible to separate the variables. Writing

$$\Psi(\vec{r}, t) = f(t) \psi(\vec{r}) ,$$

we have

$$i\hbar \frac{df(t)}{dt} \psi(\vec{r}) = -\frac{\hbar^2}{2M} f(t) \Delta \psi(\vec{r}) + U(\vec{r}) f(t) \psi(\vec{r}) .$$

Dividing both sides by $f\psi$ we get the equation where the variables (time and coordinates) are separated

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2M} \frac{1}{\psi(\vec{r})} \Delta \psi(\vec{r}) + U(\vec{r}) .$$

If we equalize both sides to some constant E , the left side gives

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E ,$$

which after simple integration gives

$$f(t) = e^{-\frac{i}{\hbar} E t} .$$

The right side gives us the Schrödinger equation for stationary states (also known as time independent Schrödinger equation)

$$-\frac{\hbar^2}{2M} \Delta \psi(\vec{r}) + U(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) .$$

Constant E is the total energy of a given particle. On the other hand the latter equation is the eigenvalue problem

$$\hat{H} \psi(\vec{r}) = E \psi(\vec{r}) .$$

of the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta + U(\vec{r}) .$$

For each solution for stationary states there is the following solution for the general Schrödinger equation

$$\Psi(\vec{r}, t) = e^{-\frac{i}{\hbar} E t} \psi(\vec{r}) .$$

The function $\psi(\vec{r})$ is also called wave function and it has the same probability interpretation as $\Psi(\vec{r}, t)$

$$\rho = |\Psi(\vec{r}, t)|^2 = |\psi(\vec{r})|^2 \quad \text{otherwise} \quad \rho = |\Psi(\vec{r}, t)|^2 = |\Psi(\vec{r}, 0)|^2 .$$

The probability density does not depend on time, therefore the probability is time independent – stationary.

1.7 Superposition principle. The general Schrödinger equation is linear concerning the wave equation Ψ

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2M} \Delta \Psi(\vec{r}, t) + U(\vec{r}, t) \Psi(\vec{r}, t) .$$

We can write it symbolically as

$$\hat{A}\Psi = 0.$$

The superposition principle means that if Ψ_1 and Ψ_2 are two arbitrary solutions, then their arbitrary linear combination

$$\Psi = a_1\Psi_1 + a_2\Psi_2$$

is also a solution of a given Schrödinger equation.

However, it is a common property of linear equations, in quantum mechanics it has a totally different meaning comparing classical physics. If for example Ψ_1 and Ψ_2 are two stationary states corresponding to different energies

$$\Psi_1(\vec{r}, t) = e^{-\frac{i}{\hbar}E_1 t} \psi_1(\vec{r}), \quad \Psi_2(\vec{r}, t) = e^{-\frac{i}{\hbar}E_2 t} \psi_2(\vec{r}),$$

where $\hat{H}\psi_1(\vec{r}) = E_1\psi_1(\vec{r})$ ja $\hat{H}\psi_2(\vec{r}) = E_2\psi_2(\vec{r})$, then the possible physical state is also their linear combination

$$\Psi(\vec{r}, t) = c_1\Psi_1(\vec{r}, t) + c_2\Psi_2(\vec{r}, t).$$

The physical meaning of a given solution (see next paragraph) is the following: in state $\Psi(\vec{r}, t)$ the energy is not uniquely fixed, measuring energy we get both values, sometimes E_1 , sometimes E_2 , probabilities of both results depend on c_1 ja c_2 .

Comments:

1. In the stationary case the general solution of the time dependent Schrödinger equation is the arbitrary linear combination

$$\Psi(\vec{r}, t) = \sum_n c_n e^{-\frac{i}{\hbar}E_n t} \psi_n(\vec{r}).$$

2. In paragraph 13 the above given Schrödinger equation is generalized to the case where an external electromagnetic field is present.

3. Phase transformations. The wave equation is not determined uniquely. Even if normed, the functions

$$\Psi(\vec{r}, t) \quad \text{and} \quad e^{i\alpha} \Psi(\vec{r}, t)$$

(where $\alpha \in R$) give the same probability density. Therefore these transformations in ordinary quantum mechanics are not physically interesting, but as we see later, analogical phase transformations where the phase factor $\alpha = \alpha(\vec{r}, t)$ is a function of space and time are very important in modern particle physics.

4. Microparticles have dualistic properties – they are at the same time both – particles and waves. Free particle is described with the help of de’Broglie wave (one dimensional case), which one can represent in two equivalent forms

$$\Psi(x, t) = e^{-\frac{i}{\hbar}(Et - px)} \equiv e^{-i(\omega t - kx)},$$

(particle side is characterized by energy and momentum, wave side by frequency and wave number). It satisfies the free particle equation

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi(x,t)}{\partial x^2} .$$

De'Broglie wave cannot be interpreted as a classical wave: it has complex values and is not a solution of classical wave equation.

Classical wave equation is

$$\frac{1}{v^2} \frac{\partial^2 \Psi(x,t)}{\partial t^2} = \frac{\partial^2 \Psi(x,t)}{\partial x^2} ,$$

where v is a velocity of a given wave.

Problem. Prove that 1) de'Broglie wave is not a solution of classical wave equation; 2) de'Broglie wave must be function having the complex values, since its real part

$$\varphi(x,t) = \text{Re} \Psi(x,t) = \cos(\omega t - kx)$$

does not satisfy the Schrödinger equation.

2. Operators

The mathematics of quantum mechanics is based on operators.

2.1. Operator, linear operator, eigenvalue problem. To each physical quantity A corresponds some linear operator \hat{A} (what is operator and linear operator – see comments at the end of the paragraph). For each operator the most important problem is the eigenvalue problem

$$\hat{A}\varphi_n = a_n\varphi_n .$$

Eigenvalues $a_1, a_2, \dots, a_n, \dots$ are the possible measurable quantities of A . The set of all eigenvalues is called the spectrum of a given operator. That may be discrete, continuous or both. Eigenfunctions $\varphi_1, \varphi_2, \dots, \varphi_n, \dots$ describe states, where the values of A are correspondingly $a_1, a_2, \dots, a_n, \dots$

In the following we mostly treat the cases where the eigenvalues are different and discrete, and to each eigenvalue there is only one eigenfunction, or several eigenfunctions.

All the measurable physical quantities are expressed by the real numbers, therefore we need operators, where all eigenvalues are real numbers.

2.2 Hermitean operators. All operators which correspond to some physical quantity are Hermitean. In order to define Hermitean operators, we introduce the bilinear form (scalar product) of functions.

Bilinear form of functions φ ja ψ is the following integral

$$\langle \varphi | \psi \rangle = \int \varphi^* \psi dV .$$

We use the Dirac notation, where $\psi \equiv |\psi\rangle$ is the “ket”-vector and $\langle \varphi| = \varphi^*$ is the “bra”-vektor (bracket).

Conjugated operator. For each \hat{A} we may write down an integral

$$\langle \varphi | \hat{A}\psi \rangle = \int \varphi^* \hat{A}\psi dV ,$$

which is the bilinear form of φ and $\hat{A}\psi$.

For each operator \hat{A} there also exists an operator \hat{B} , which satisfies

$$\langle \hat{B}\varphi | \psi \rangle = \langle \varphi | \hat{A}\psi \rangle \quad \text{or} \quad \int (\hat{B}\varphi)^* \psi dV = \int \varphi^* (\hat{A}\psi) dV .$$

Operator \hat{B} is a conjugated operator for \hat{A} and is denoted $\hat{B} = \hat{A}^+$.

Hermitean operator. Hermitean operator is operator which equals to its conjugated operator (is therefore selfconjugated)

$$\hat{A}^+ = \hat{A} .$$

Hermitean operator \hat{A} therefore satisfies

$$\langle \hat{A}\varphi | \psi \rangle = \langle \varphi | \hat{A}\psi \rangle , \quad \text{or} \quad \int (\hat{A}\varphi)^* \psi dV = \int \varphi^* (\hat{A}\psi) dV .$$

Example. Momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$ is Hermitean. We assume that both functions $\psi(x)$ and $\varphi(x)$ vanish in infinity, we after integrating by parts, obtain

$$\begin{aligned} \langle \varphi | \hat{p}\psi \rangle &= \int_{-\infty}^{+\infty} \varphi^* (-i\hbar \frac{d\psi}{dx}) dx \equiv -i\hbar \int_{-\infty}^{+\infty} \varphi^* \frac{d\psi}{dx} dx = -i\hbar \varphi^* \psi \Big|_{-\infty}^{+\infty} + i\hbar \int_{-\infty}^{+\infty} \frac{d\varphi^*}{dx} \psi dx = \\ &= i\hbar \int_{-\infty}^{+\infty} \frac{d\varphi^*}{dx} \psi dx \equiv \int_{-\infty}^{+\infty} (-i\hbar \frac{d\varphi}{dx})^* \psi dx = \langle \hat{p}\varphi | \psi \rangle . \end{aligned}$$

2.3 Eigenvalues and eigenfunctions of Hermitean operators.

Theorem 1. Eigenvalues of Hermitean operators are real numbers.

Proof. Let us have some Hermitean operator \hat{A} with its eigenvalues a_n and corresponding eigenfunctions φ_n

$$\hat{A}\varphi_n = a_n\varphi_n \quad \text{or} \quad |\hat{A}\varphi_n\rangle = a_n|\varphi_n\rangle .$$

Eigenvalue problem for complex conjugated eigenfunction $\varphi_m^* = \langle \varphi_m |$ is

$$(\hat{A}\varphi_m)^* = a_m^* \varphi_m^* \quad \text{or} \quad \langle \hat{A}\varphi_m | = a_m^* \langle \varphi_m | .$$

Taking the scalar product of the first equation with $\varphi_m^* = \langle \varphi_m |$ we get

$$\langle \varphi_m | \hat{A}\varphi_n \rangle = a_n \langle \varphi_m | \varphi_n \rangle .$$

Taking similarly the scalar product of the second equation with $\varphi_n = |\varphi_n\rangle$ we get

$$\langle \hat{A}\varphi_m | \varphi_n \rangle = a_m^* \langle \varphi_m | \varphi_n \rangle .$$

Since \hat{A} is Hermitean, the last expression may be written as

$$\langle \hat{A}\varphi_m | \varphi_n \rangle = \langle \varphi_m | \hat{A}\varphi_n \rangle = a_m^* \langle \varphi_m | \varphi_n \rangle .$$

From the above given equations we get the result that

$$(a_n - a_m^*) \langle \varphi_m | \varphi_n \rangle = 0 .$$

At first we assume, that $m = n$. Then we get

$$(a_n - a_n^*) \langle \varphi_n | \varphi_n \rangle = 0 .$$

Since $\langle \varphi_n | \varphi_n \rangle \equiv \int |\varphi_n|^2 dV \neq 0$, we have

$$a_n^* = a_n ,$$

which proves that eigenvalues of Hermitean operator are real numbers.

Theorem 2. Eigenfunctions of Hermitean operator form an orthonormal system of functions.

We treat three different possibilities.

a) We assume that eigenvalues are discrete numbers and different, and for each eigenvalue a_n correspond only one eigenfunction φ_n . Since the eigenvalues are real numbers, we have

$$(a_n - a_m) \langle \varphi_m | \varphi_n \rangle = 0 .$$

If we now take $m \neq n$, we have

$$\langle \varphi_m | \varphi_n \rangle = 0 ,$$

which means that different eigenfunctions are orthogonal. For the same eigenfunctions we have $\langle \varphi_n | \varphi_n \rangle \neq 0$, therefore the eigenfunctions may be normed to one - $\langle \varphi_n | \varphi_n \rangle = 1$.

In conclusion $\langle \varphi_m | \varphi_n \rangle = \delta_{mn}$ or $\int \varphi_m^* \varphi_n dV = \delta_{mn}$.

b) Eigenvalues are discrete, but to one eigenvalue a_n there corresponds k different eigenfunctions $\varphi_{n1}, \varphi_{n2}, \dots, \varphi_{nk}$. It is obvious, that all k eigenfunctions are orthogonal to other eigenfunctions. In order to get orthonormed set of eigenfunctions, one must in addition to orthonorme eigenfunctions, corresponding to a_n . We do not give the general proof, but as an example analyse the case of two different eigenfunctions.

We assume, that for some eigenvalue there exists two eigenfunctions which in general are independent, but not orthogonal: therefore we have functions φ_1 and φ_2 , and assume that $\langle \varphi_1 | \varphi_2 \rangle = d \neq 0$. We demonstrate, that we can form two orthogonal functions ψ_1 and ψ_2 (which afterwards may be normed to 1). At first we take $\psi_1 = \varphi_1$ and try to find an orthogonal function using linear combination $\psi_2 = a\varphi_1 + b\varphi_2$. Demanding $\langle \psi_1 | \psi_2 \rangle = 0$, we have

$$\langle \varphi_1 | a\varphi_1 + b\varphi_2 \rangle = a\langle \varphi_1 | \varphi_1 \rangle + b\langle \varphi_1 | \varphi_2 \rangle = 0 .$$

If we choose $b = -a\langle \varphi_1 | \varphi_1 \rangle / d$, ψ_1 and ψ_2 are orthogonal. (Of course that procedure is not

unique, but there are always two orthogonal eigenfunctions.)

c) Eigenvalues are continuous. One example is free particle. Its energy and momentum spectrum is continuous. The eigenvalue problem is the same, as in the previous cases, but a is continuous

$$\hat{A}\varphi_a = a\varphi_a, \quad \hat{A}\varphi_{a'} = a'\varphi_{a'}.$$

One can similarly prove that

$$\langle \varphi_a | \varphi_{a'} \rangle = 0, \quad \text{if } a \neq a'.$$

The problem is that integral

$$\langle \varphi_a | \varphi_a \rangle = \int |\varphi_a|^2 dV \rightarrow \infty,$$

i.e. it is not finite, since eigenfunctions do not vanish in infinity.

Now the eigenfunctions are normed to the Dirac δ -function

$$\langle \varphi_a | \varphi_{a'} \rangle = \delta(a - a'), \quad \text{or} \quad \int \varphi_a^* \varphi_{a'} dV = \delta(a - a').$$

Normalization in finite volume. In the continuous case one may use the trick, which makes the continuous spectrum discrete. We divide the whole space to cubes which sides have length L . We assume that L is always much bigger than are the linear dimensions of our physical system and for that reason we consider wave functions only in one cube. To connect wave functions in different cubes usually periodical initial conditions are used.

Example. Let us consider the free particle moving on x-axis and try to normalize the eigenfunctions of momentum operator. The x-axis is divided to line segments with the length L .

The eigenfunctions of the momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$ are

$$\varphi_p(x) = e^{\frac{i}{\hbar} p x}.$$

If there are no restrictions, the momentum spectrum is continuous $-\infty \leq p \leq +\infty$.

But now, dividing the x-axis and using periodical initial conditions we must have

$$\varphi_p(x) = \varphi_p(x + L).$$

Now we get discrete eigenvalue spectrum, since from the above given we get

$$e^{\frac{i}{\hbar} p L} = 1,$$

and therefore

$$p = \frac{2\pi \hbar}{L} n, \quad n = 0, \pm 1, \pm 2, \dots$$

If we choose quite large L the difference between momentum values for n and $n+1$ may be small (practically continuous).

Wave functions are normed on finite length L , therefore there are no problems with infinities.

Taking $\tilde{\varphi}(x) = A e^{\frac{i}{\hbar} p x}$, we get

$$\langle \tilde{\varphi} | \tilde{\varphi} \rangle = \int_0^L |\tilde{\varphi}(x)|^2 dx = |A|^2 \int_0^L dx = |A|^2 L .$$

If we choose $A = 1/\sqrt{L}$ the wave function is normed to 1.

2.4 Completeness of eigenfunctions of Hermitean operators. Eigenfunctions form a complete set of functions. In other words it means that if we had some orthonormal system of eigenfunctions $\varphi_1, \varphi_2, \dots, \varphi_n, \dots$ of some Hermitean operator \hat{A} , then an arbitrary function ψ is expanded as a sum (sequence)

$$\psi = \sum_n c_n \varphi_n ,$$

where c_n are some numerical coefficients, obtained as

$$c_n = \langle \varphi_n | \psi \rangle .$$

Geometrical interpretation: eigenfunctions φ_n is treated as a set of orthogonal unit vectors of some vector space and c_n are treated as coordinates of ψ .

Let us assume, that ψ is presented as

$$\psi = \sum_n c_n \varphi_n \quad \text{or} \quad |\psi\rangle = \sum_n c_n |\varphi_n\rangle .$$

To get c_m we find a scalar product with $\varphi_m^* = \langle \varphi_m |$ and use the orthonormality of φ_n

$$\langle \varphi_m | \psi \rangle = \sum_n c_n \langle \varphi_m | \varphi_n \rangle = \sum_n c_n \delta_{mn} = c_m .$$

In other words

$$c_m = \int \varphi_m^* \psi dV .$$

Completeness of eigenfunctions. If we put c_n back, we get

$$\psi = \sum_n \langle \varphi_n | \psi \rangle \varphi_n ,$$

or using bra and ket vectors

$$|\psi\rangle = \sum_n |\varphi_n\rangle \langle \varphi_n | \psi \rangle .$$

From the above given we see, that eigenfunctions must satisfy

$$\sum_n |\varphi_n\rangle\langle\varphi_n| = I.$$

The latter is the completeness condition. It may be written as

$$\sum_n \varphi_n^*(\vec{r}') \varphi_n(\vec{r}) = \delta(\vec{r} - \vec{r}')$$

(prove it).

Example. Fourier' integral. 1-dimensional case. Let us have some continuous function $f(x)$. Fourier' integral is defined as

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) e^{ikx} dk,$$

where $g(k)$ is similarly calculated from $f(x)$

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx.$$

In quantum mechanics it has the following interpretation: functions $\exp(ikx)$ are the eigenfunctions of momentum operator (and form a full system of functions), therefore every continuous function $f(x)$ may be presented as Fourier integral. If we put $g(k)$ back, we get (which is also one possible definition of δ -function)

$$\int_{-\infty}^{+\infty} e^{-i(k-k')x} dx = 2\pi \delta(k - k').$$

2.5 Physical meaning. Let us give the physical meaning of sequence

$$\psi = \sum_n c_n \varphi_n,$$

where ψ is a state function (wave function) of some particle and φ_n are eigenfunctions of operator \hat{A} corresponding to some physical quantity A (energy, momentum, etc).

If we perform measurements of A , the results are equal to the eigenvalues a_1, \dots, a_n, \dots . The probability of results depends on c_1, \dots, c_n, \dots . Namely –

we get a_1 with probability $|c_1|^2$,
 a_2 with probability $|c_2|^2$,
 (and so on).

The sum of probabilities is equal to unity

$$\langle\psi|\psi\rangle = 1 = \sum_{m,n} c_m^* c_n \langle\varphi_m|\varphi_n\rangle \equiv \sum_{m,n} c_m^* c_n \delta_{mn} = \sum_n |c_n|^2.$$

If, for example, our measurements give only one value a_n of A then we have $\psi = \varphi_n$, in other cases the value of A is not uniquely determined. If we have the state ψ , which is expressed as

$$\psi = c_1\varphi_1 + c_2\varphi_2$$

and A is, for example energy, then the measurements of energy give us as a result two values: a_1 or a_2 . a_1 has probability $|c_1|^2$, a_2 has probability $|c_2|^2$. It means that in microworld there exist states where the energy (or some other physical quantity) is not uniquely determined. Such states are more common than the states with a fixed energy.

Comments, appendices:

1. Operator, linear operator. Let us have some set of functions X . Operator is a prescription, using which for every function $f \in X$ is set in correspondence some other function $g \in X$ (from the same set of functions, in other words it is a function of functions). We denote it as \hat{A} and write

$$g = \hat{A}f .$$

In quantum mechanics we use only linear operators. By definition, linear operator satisfies the following two conditions

$$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2 ,$$

$$\hat{A}(af) = a \hat{A}f ,$$

where $f_1, f_2, f \in X$ and $a \in C$ is some number (real or complex).

The sum and product of operators. Sum

$$(\hat{A} + \hat{B})f = \hat{A}f + \hat{B}f ,$$

product

$$\hat{A}\hat{B}f = \hat{A}(\hat{B}f) .$$

2. δ -function. 1-dimensional case. δ -function (Dirac δ -function) is defined as follows

$$\delta(x) = 0 \quad \text{if} \quad x \neq 0, \quad \delta(x) \neq 0 \quad \text{if} \quad x = 0$$

and

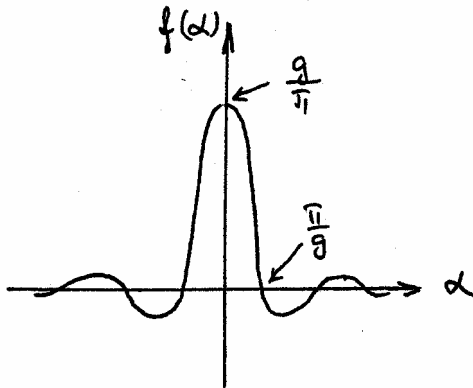
$$\int_a^b \delta(x) dx = 1 \quad \text{if} \quad x = 0 \in [a, b] .$$

From the definition it follows, that for arbitrary function $f(x)$

$$\int_a^b f(x) \delta(x) dx = f(0) ,$$

and

$$\int_a^b f(x) \delta(x-c) dx = f(c) \quad \text{kui} \quad c \in [a, b].$$



δ-function as integral.

Since

$$\int_{-\infty}^{+\infty} \frac{\sin(g\alpha)}{\pi\alpha} d\alpha = 1,$$

δ-function is expressed as limit

$$\delta(\alpha) = \lim_{g \rightarrow \infty} \frac{\sin(g\alpha)}{\pi\alpha}.$$

Since

$$\frac{\sin(g\alpha)}{\pi\alpha} = \frac{1}{2\pi} \int_{-g}^{+g} e^{i\alpha\beta} d\beta,$$

we have

$$\delta(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\alpha\beta} d\beta.$$

δ-function as a limit. In the following we also use the definition of δ-funktsiooni as the following limit

$$\delta(x) = \lim_{A \rightarrow \infty} \frac{\sin^2(Ax)}{\pi Ax^2}.$$

3. Uncertainties of measurements (uncertainty principles)

In a microworld it is common that not all physical quantities are exactly measurable and for that quantities we have some uncertainty relations. It appears that the problems of exact measurements are connected with operators.

If operators of two physical quantities A and B - \hat{A} and \hat{B} commute

$$[\hat{A}, \hat{B}] = 0 ,$$

($\hat{A}\hat{B} = \hat{B}\hat{A}$, i.e. for each ψ we have $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$), the physical quantities A ja B are at the same time(simultaneously) exactly measurable. But if operators do not commute

$$[\hat{A}, \hat{B}] = i\hat{C} ,$$

(\hat{C} is some nonzero Hermitean operator) A and B are not simultaneously measurable, and we have certain restrictions on measurements, called uncertainty principles.

3.1 Simultaneous measurements, exact values of observables. If

$$[\hat{A}, \hat{B}] = 0 ,$$

we prove, that A ja B are simultaneously measurable.

If we assume, that measurements of A ja B give simultaneously certain exact values a and b , then operators commute. Mathematically it means, that there exists such state function (wave function) ψ , for which

$$\hat{A}\psi = a\psi \quad \text{and} \quad \hat{B}\psi = b\psi .$$

Therefore, operators have common eigenfunctions. Now it is easy to demonstrate that $\hat{A}\hat{B} = \hat{B}\hat{A}$ (prove it!).

And vice versa, if

$$[\hat{A}, \hat{B}] = 0 ,$$

\hat{A}

$$\hat{A}\psi_a = a\psi_a$$

and demonstrate that these are also eigenfunctions of operator \hat{B} . Let us apply operator \hat{B}

$$\hat{B}(\hat{A}\psi_a) = a(\hat{B}\psi_a) .$$

Since operators commute, we have $\hat{B}(\hat{A}\psi_a) = \hat{A}(\hat{B}\psi_a)$, and therefore

$$\hat{A}(\hat{B}\psi_a) = a(\hat{B}\psi_a).$$

Now we see that $\hat{B}\psi_a$ is the eigenfunction of operator \hat{A} with the eigenvalue a , and therefore

$$\hat{B}\psi_a \sim \psi_a.$$

We can find a constant b , that

$$\hat{B}\psi_a = b\psi_a.$$

Therefore each eigenfunction of \hat{A} is at the same time also eigenfunction of \hat{B} . Therefore the quantities have simultaneous observables a and b .

3.2 Mean values of physical quantities. The mean value of physical quantity in the state, described by wave function ψ , is calculated from

$$\langle A \rangle = \int \psi^* \hat{A} \psi dV.$$

Proof. Using eigenfunctions of \hat{A} we have an expansion

$$\psi = \sum_n c_n \varphi_n.$$

Since $|c_n|^2$ is probability, that we obtain the result a_n ($n = 1, 2, \dots$), the mean value is calculated as

$$\langle A \rangle = \sum_n a_n |c_n|^2.$$

From the above given $\langle A \rangle = \langle \psi | \hat{A} \psi \rangle \equiv \langle \psi | \hat{A} | \psi \rangle = \int \psi^* \hat{A} \psi dV$. If we replace one ψ and use $c_n^* = \langle \varphi_n | \psi \rangle^* = \langle \psi | \varphi_n \rangle$ we have

$$\begin{aligned} \langle A \rangle &= \langle \psi | \hat{A} \psi \rangle \equiv \left\langle \psi \left| \hat{A} \left(\sum_n c_n \varphi_n \right) \right. \right\rangle = \left\langle \psi \left| \sum_n c_n a_n \varphi_n \right. \right\rangle = \\ &= \sum_n a_n c_n \langle \psi | \varphi_n \rangle = \sum_n a_n |c_n|^2. \end{aligned}$$

3.3 Uncertainty relations. Let us assume that

$$[\hat{A}, \hat{B}] = i\hat{C}$$

and derive uncertainty formulas for measurements of quantities A ja B . It is obvious, that the deviations of mean value is not usable, since its mean value is zero, therefore we consider the mean value of its square, which we define as follows (root mean square deviation)

$$\langle (\Delta A)^2 \rangle = \int \psi^* (\hat{A} - \langle A \rangle)^2 \psi dV ,$$

$$\langle (\Delta B)^2 \rangle = \int \psi^* (\hat{B} - \langle B \rangle)^2 \psi dV .$$

For these quantities one can prove the following general result

$$\langle (\Delta A)^2 \rangle \langle (\Delta B)^2 \rangle \geq \left(\frac{1}{2} \langle C \rangle \right)^2 ,$$

which means the root mean square deviations cannot be simultaneously equal to zero and therefore we have no exact simultaneous values of observables A and B .

Proof. We present the simpler version, assuming that the mean values of A ja B are equal to zero

$$\langle A \rangle = \langle B \rangle = 0 .$$

Now the root mean square deviations are

$$\langle (\Delta A)^2 \rangle = \langle A^2 \rangle = \int \psi^* \hat{A}^2 \psi dV \quad \text{ja} \quad \langle (\Delta B)^2 \rangle = \langle B^2 \rangle = \int \psi^* \hat{B}^2 \psi dV .$$

Let us take the nonnegative integraal, where α is some real parameter

$$J(\alpha) = \int |(\alpha \hat{A} - i\hat{B})\psi|^2 dV \geq 0 .$$

Since \hat{A} ja \hat{B} are Hermitean, one may write

$$\begin{aligned} J(\alpha) &= \int ((\alpha \hat{A} - i\hat{B})\psi)^* (\alpha \hat{A} - i\hat{B})\psi dV = \\ &= \int \psi^* (\alpha \hat{A} + i\hat{B})(\alpha \hat{A} - i\hat{B})\psi dV = \\ &= \int \psi^* (\alpha^2 \hat{A}^2 - i\alpha(\hat{A}\hat{B} - \hat{B}\hat{A}) + \hat{B}^2)\psi dV = \\ &= \int \psi^* (\alpha^2 \hat{A}^2 + \alpha \hat{C} + \hat{B}^2)\psi dV . \end{aligned}$$

(We have used the commutation relation for \hat{A} and \hat{B} ,)

Using mean values it is

$$J(\alpha) = \alpha^2 \langle (\Delta A)^2 \rangle + \alpha \langle C \rangle + \langle (\Delta B)^2 \rangle .$$

Since $J(\alpha) \geq 0$, the coefficients must satisfy

$$4 \langle (\Delta A)^2 \rangle \langle (\Delta B)^2 \rangle \geq \langle C \rangle^2 ,$$

which is our uncertainty relation.

Example. Let us have operators (coordinate and momentum)

$$\hat{A} = \hat{x} \equiv x \quad ja \quad \hat{B} = \hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x}.$$

We have

$$[x, \hat{p}_x] = i\hbar,$$

therefore $\hat{C} = \hbar$. Uncertainty relation is

$$\langle (\Delta x)^2 \rangle \langle (\Delta p_x)^2 \rangle \geq \frac{\hbar^2}{4}.$$

Usually it has simpler expression, if we define

$$\Delta x = \sqrt{\langle (\Delta x)^2 \rangle} \quad and \quad \Delta p_x = \sqrt{\langle (\Delta p_x)^2 \rangle},$$

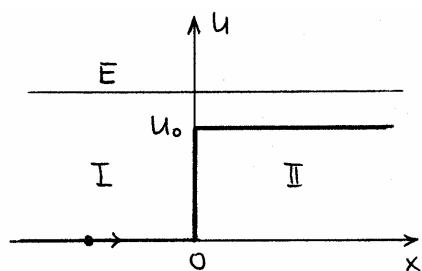
then we have

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}.$$

(Similar expressions we have also for y- ja z-coordinates and corresponding momenta.)

4. Potential barriers, tunnel effect

4.1 Potential barrier (E > U). Consider the following potential energy



$$U = \begin{cases} U_0, & x \geq 0, \\ 0, & x < 0. \end{cases}$$

Let us consider the flux of particles moving from the left to right and analyse their behaviour if the energy of particles E is higher than U_0 .

For classical particles we know that all particles moving from left (region I) continue their moving in the region II, but for microparticles the behaviour of particles is different, some particles always reflect back and do not reach the II region.

We find the solutions of the Schrödinger equation in regions I and II and then apply the continuity of solutions for $x = 0$.

Region I. Since $U = 0$, the Schrödinger equation may be written as

$$\psi'' + k^2 \psi = 0 ,$$

where $k^2 = 2ME / \hbar^2$. General solution is

$$\psi_I(x) = e^{ikx} + Be^{-ikx} .$$

e^{ikx} describes particles moving from left to right. We assume that the initial flux of particles moving toward the barrier is known and take the coefficient before it equal to one ($A = 1$) and the flux of particles moving towards the barrier is equal to k/M . The second term Be^{-ikx} describes the particles that are reflected back. The flux of reflected particles is equal to $k|B|^2 / M$.

Region II. Now $U = U_0$, and the Schrödinger equation is

$$\psi''(x) + k'^2 \psi(x) = 0 ,$$

where $k'^2 = 2M(E - U_0) / \hbar^2$. Special solutions are

$$e^{ik'x} \quad ja \quad e^{-ik'x} .$$

Since in the region II there are particles moving from left to right, the general solution is

$$\psi_{II}(x) = Ce^{ik'x} .$$

In order to find the general solution to our problem, we must use the continuity conditions, which means that $\psi_I(0) = \psi_{II}(0)$, $\psi'_I(0) = \psi'_{II}(0)$.

Using these conditions we after some algebra get that

$$B = \frac{k - k'}{k + k'} , \quad C = \frac{2k}{k + k'} .$$

Therefore the general solution is

$$\psi(x) = \begin{cases} e^{ikx} + \frac{k-k'}{k+k'} e^{-ikx}, & x < 0, \\ \frac{2k}{k+k'} e^{ik'x}, & x \geq 0. \end{cases}$$

The main result we obtained is that $B \neq 0$ and therefore some particles indeed reflect at $x = 0$ back.

Let us calculate the flux of particles. The flux of particles, moving towards the barrier (incident particles) is

$$j_i = \frac{i\hbar}{2M} (\psi \frac{d\psi^*}{dx} - \psi^* \frac{d\psi}{dx}) = \frac{\hbar k}{M}.$$

The flux of reflected particles and particles moving to region II are correspondingly

$$j_p = \frac{\hbar k}{M} |B|^2, \quad j_e = \frac{\hbar k'}{M} |C|^2.$$

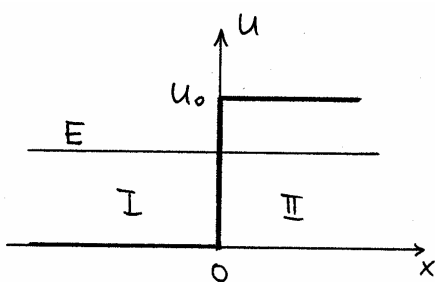
If we define the reflection coefficients and transition coefficients (R and L) as

$$R = \frac{j_p}{j_i} = |B|^2, \quad L = \frac{j_e}{j_i} = \frac{k'}{k} |C|^2,$$

it is possible to verify that

$$R + L = 1.$$

4.2 Potential barrier ($E < U$). Barrier is the same, but now we assume that $E < U_0$. The classical particles must reflect at $x = 0$ back, since classical particles can move only in regions where $E \geq U$. Microparticles have some probability to move in regions where $E < U$ (in regions where kinetic energy is negative!).



Region I. The general solution is the same as in the previous case

$$\psi_I(x) = e^{ikx} + B e^{-ikx}.$$

Region II. Schrödinger equation is

$$\psi'' - \kappa^2 \psi = 0,$$

where $\kappa^2 = 2M(U_0 - E)/\hbar^2$. Special solutions are $e^{\kappa x}$ and $e^{-\kappa x}$. Since the solution must exist in the region $0 \leq x < \infty$, the first one is not applicable, since in $x \rightarrow \infty$ case $e^{\kappa x} \rightarrow \infty$, the second solution is applicable, since it is finite. Therefore the general solution is

$$\psi_{II}(x) = Ce^{-\kappa x}.$$

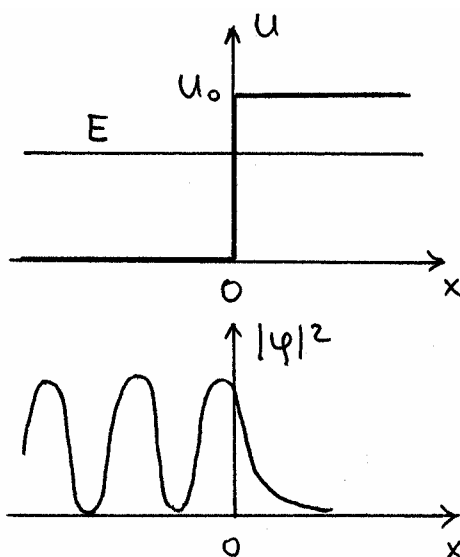
Applying the conditions $\psi_I(0) = \psi_{II}(0)$, $\psi'_I(0) = \psi'_{II}(0)$, we get B and C

$$B = \frac{k - i\kappa}{k + i\kappa}, \quad C = \frac{2k}{k + i\kappa}$$

and the general solution is

$$\psi(x) = \begin{cases} e^{ikx} + \frac{k - i\kappa}{k + i\kappa} e^{-ikx}, & x < 0, \\ \frac{2k}{k + i\kappa} e^{-\kappa x}, & x \geq 0. \end{cases}$$

The result is physically very interesting. The fact, that particles reflect back is obvious, but the fact that $C \neq 0$ is shocking, because it is possible to obtain particles inside the barrier (which is forbidden to classical particles). Probability density of finding particles inside the barrier is



$$|\psi_{II}(x)|^2 = \frac{4k^2}{k^2 + \kappa^2} e^{-2\kappa x}.$$

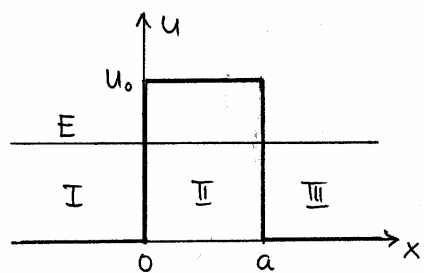
The probability density is increasing exponentially.

Probability distribution $|\psi|^2$ graph. On the left side there is the interference picture of particles (waves) moving towards the barrier and reflected particles.

It appears, that finally all particles reflect back, since the reflection coefficient is equal to 1. Indeed, the simple calculation gives (prove!)

$$R = \frac{j_p}{j_l} = |B|^2 = B^* B = 1.$$

4.3 Tunnel effect (tunneling). Consider the next potential barrier



$$U = \begin{cases} U_0, & 0 \leq x \leq a, \\ 0, & x < 0, x > a. \end{cases}$$

Let us consider the flux of particles moving in the region I from left to right (toward the barrier) with energy E that is less than U_0 ($E < U_0$). Since the width of barrier is finite there is nonzero transition probability and some particles may move to the region III. That effect is called the tunnel effect or tunneling. Of course, in classical physics there is no tunneling, since all classical particles must reflect back at $x = 0$.

In order to prove tunneling we find general solutions for each region and then apply the continuity conditions for $x = 0$ and $x = a$. Region I

$$\psi_I(x) = e^{ikx} + B e^{-ikx}.$$

Region II

$$\psi_{II}(x) = C e^{\kappa x} + D e^{-\kappa x}.$$

(Since $0 \leq x \leq a$ both special solutions must be used). Region III

$$\psi_{III}(x) = F e^{ikx}.$$

Continuity conditions

$$1 + B = C + D, \quad C e^{\kappa a} + D e^{-\kappa a} = F e^{ika},$$

$$ik(1 - B) = \kappa(C - D), \quad \kappa(C e^{\kappa a} - D e^{-\kappa a}) = ikF e^{ika},$$

gives solutions

$$B = \frac{(k^2 + \kappa^2) sh(\kappa a)}{(k^2 - \kappa^2) sh(\kappa a) - 2ik\kappa ch(\kappa a)},$$

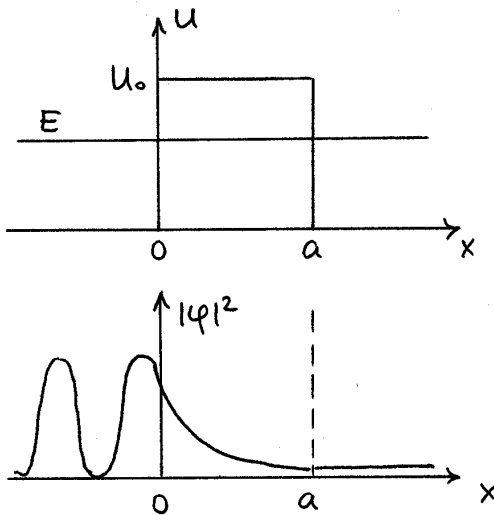
$$F = \frac{2ik\kappa e^{-ika}}{(k^2 - \kappa^2) sh(\kappa a) + 2ik\kappa ch(\kappa a)}.$$

Since $F \neq 0$ there exists tunneling, particles have nonzero probability to „go through“ barrier.

Transition coefficient

$$L = \frac{j_e}{j_i} = |F|^2 = F^* F = \frac{4k^2 \kappa^2}{(k^2 - \kappa^2)^2 \operatorname{sh}^2(\kappa a) + 4k^2 \kappa^2 \operatorname{ch}^2(\kappa a)} .$$

It depends on $\kappa = \frac{\sqrt{2M(U_0 - E)}}{\hbar}$ and a .



The general solution is quite complicated and we therefore consider the simpler, specific case where $\kappa a \gg 1$. Then $\operatorname{sh}^2 \kappa a \approx \operatorname{ch}^2 \kappa a \approx e^{2\kappa a} / 4$ and we get

$$L = |F|^2 = \frac{16k^2 \kappa^2}{(k^2 + \kappa^2)^2} e^{-2\kappa a} .$$

Transition probability decreases exponentially

$$L \approx e^{-2\kappa a} ,$$

Calculating $R = |B|^2$, it is possible to verify that

$$R + L = 1 .$$