Quantum Mechanics of Molecular and Low-Dimensional Systems

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Introduction

The book includes a short summary of mathematical foundations of quantum mechanics, presents exactly solvable traditional problems of non-relativistic quantum mechanics in $d = 1, 2, 3$ dimensions, such as harmonic oscillator, potential barrier, Hydrogen atom, etc., which can be found in any standard textbook in quantum mechanics. Along with it, at the end of each section of this book, the readers can found a set of problems they can solve either numerically or analytically to master their practical skills.The peculiarity of this book is that we have concentrated our attention on *bound states* – atoms, molecules, quantum dots – almost ignoring the scattering problems, typical for nuclear physics or quantum optics. Thus for deep and comprehensive understanding of quantum mechanics the readers are advised to address standard textbooks in quantum mechanics, such as [LL65, CTDL97]. The goal of this book is to provide for a general understanding of the behaviour of micro-world objects – from atoms and molecules to metallic clusters, semiconductor devices and biopolymers, – and give practical skills of calculating ground states of such systems, their energy spectra, and emission frequencies. This skills are essential for both the remote diagnostics and the control of quantum systems. They are also of great importance for calculation of chemical reactions rate. An important part of this book is the calculation of thermodynamic characteristics of quantum systems, based on quantum mechanics and quantum statistics methods. The methods of quantum statistical mechanics are essential for the calculation of energy effect of chemical reactions, heat capacity of molecules, relaxation of atomic clusters, work of different nano-engines and information processing systems.

An almost ideal goal of microphysics would be an exhaustive numeric simulation based on the solution of the Schrödinger equation taken together with statistical simulation of fluctuating environment. Such simulation, even in its simplest form, is available only for very simple chemical reactions, and demands huge computational resources. The techniques of such calculations, commonly known as *ab initio* (lat. *from first principles*) methods, viz. full solution of the Schrödinger equation for the electronic density, is being actively developed at different supercomputer centres as well as on cloud platforms. Numerous amount of research papers in physical chemistry, nano- and bio-electronics, molecular biology, metallurgy and other fields is devoted to *ab initio* methods. Nevertheless, we designed our introductory course to stimulate students for their own research work in this field. We hope it will provide for routine calculations of molecular spectra and thermodynamics of chemical reactions for practical chemists, as well as we hope it will be useful for quantum engineers to simulate new nanoscale devices before construction.

Chapter 2

Foundations of quantum mechanics

2.1 Physical background and basic concepts of quantum mechanics

Quantum mechanics has emerged as an attempt to describe the observed properties of atoms and molecules, the classical description of which in the framework of the Newtonian mechanics and the Maxwellian electrodynamics leads to a contradiction with experiment. In classical physics, the behaviour of an object is described in terms of the *dynamical variables* – the coordinates and their time derivatives. Providing the coordinates and their time derivatives

$$(q_1(t), q_2(t), \ldots, q_n(t), \dot{q}_1(t), \dot{q}_2(t), \ldots, \dot{q}_n(t)) \tag{2.1}$$

are known at some instant of time $t = 0$ one can evaluate their values at any later time instant $t' > 0$: this defines the trajectory of a system in phase space. The number n, the dimension of the system, may be either finite or infinite. In the former case we deal with a system of a finite number of particles, e.g. that in classical mechanics; in the latter case we deal with continuous fields, e.g. in electrodynamics.

The contradictions arise when we attempt to apply classical mechanics and classical Maxwellian electrodynamics to an *atom*. According to classical electrodynamics, the electrons, moving cyclically in the field of atomic nucleus, would have lost all their energy and fall on the nucleus. This never happens – the atom is stable.

This contradiction has been lifted by the assumption, that the laws of physics working at microscopic scales of about $R \leq 10^{-6}$ cm are different from that working at large scales of about $R \geq 10^{-4}$ cm, and the notion of a *trajectory*, which is intimately related to the *continuity* of motion, is no longer valid at microscopic scales. To explain the observed atomic spectra, it was assumed that the microscopic quantum objects possess only the *states*, the transitions between which we can observe performing different manipulations with quantum objects – the *measurements*.

By *measurement* we understand any interaction between a classical and a quantum object, aimed to gain some *information* about the quantum object. The role of the observer in such settings is restricted to registration of the measurement results. The task of quantum mechanics is the prediction of the results of the next measurements, provide the results of previous measurements are known.

The process of quantum measurement has an essential peculiarity: it always affects the state of the measured quantum system. If during the measurement certain coordinates of the electron were fixed, then, strictly speaking, the electron does not have any velocity at the instant of measurement: $\lim\limits_{\Delta t \to 0} \dfrac{\Delta x}{\Delta t}$ does not exist. The upcoming measurements of the electron coordinates will result in different values with certain probabilities. To find these probabilities is the task of quantum mechanics.

The subjects of quantum mechanics are both the physical phenomena at microscopic level, viz. chemical reactions, interaction of atoms with light, and the macroscopic phenomena, such as magnetism, superconductivity and superfluidity, which cannot be explained within classical physics.

Quantum mechanics admits the classical mechanics as a limiting case of non-rigid measurements, the effect of which upon the measured system is infinitely small.

The very term *quantum mechanics* was coined in 1901 by Max Planck, when he was studying thermal radiation of a closed furnace (black-body radiation) and found that the experimentally observed spectrum can be derived from the assumption that light is irradiated by atoms in discrete portions – *quanta*, rather than continuously. The energy of one such *quantum* is proportional to the frequency of light:

$$E = \hbar\omega, \quad \hbar = 1.0545717 \cdot 10^{-27}\mathrm{erg} \cdot \mathrm{sec} = 1.0545717 \cdot 10^{-34}\mathrm{J} \cdot \mathrm{sec} \tag{2.2}$$

The proportionality coefficient $\hbar$ has got a name of Planck's constant (slashing of h, as well as of any other letter, denotes the division by 2π, i.e., $h = 2\pi\hbar$).

The energy density of the black-body radiation, being in thermodynamic equilibrium with a system of oscillators, the solid body is represented by, is equal to

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\bar{\varepsilon} = \frac{8\pi\nu^2}{c^3}k_B T, \tag{2.3}$$

where c is the speed of light, $\bar{\varepsilon}$ is the mean energy of oscillator with frequency ν. More detailed story of the theory equilibrium black-body radiation can be found e.g. in [Bor51]. In the state of thermodynamic equilibrium $\bar{\varepsilon} = k_B T$, where $k_B = 1.38 \cdot 10^{-16}\mathrm{erg/K}$ is the Boltzmann constant. Thus, in classical theory, according to the Rayleigh-Jeans law (2.3), the radiation energy density should quadratically increase with the frequency – this is so-called UV-disaster. The experiment shows quite opposite behaviour: the radiation energy density displays a maximum at certain frequency, which depends on the temperature T, and falls off above and below this frequency. To explain the observed result, it was suggested by Max Planck that the energy of oscillators cannot take *arbitrary* values, but should be equal to $E_n = nh\nu \equiv n\varepsilon_0, n = 0, 1, 2, \ldots$, where $\varepsilon_0 = h\nu$ is the minimal fixed value of energy, acceptable at frequency ν. The mean energy of such system of oscillators is given by

$$\bar{\varepsilon} = -\frac{d}{d\beta}\ln\sum_{n=0}^{\infty} e^{-n\beta\varepsilon_0} = \frac{d}{d\beta}\ln\left(1 - e^{-\beta\varepsilon_0}\right) = \frac{\varepsilon_0}{e^{\beta\varepsilon_0} - 1}, \quad \beta = (k_B T)^{-1}. \tag{2.4}$$

The radiation energy density for such a system

$$\rho(\nu) = \frac{8\pi\nu^3 h}{c^3}\frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \tag{2.5}$$

posses the necessary maximum.

The concept of light quanta was shaped to its final form when the quantum of light with wavelength λ was associated with the momentum

$$\boldsymbol{p} = \hbar\boldsymbol{k}, \quad k = \frac{2\pi}{\lambda}. \tag{2.6}$$

This assignment enabled Albert Einstein to explain the photoelectric effect – emission of electrons from metallic surface irradiated by light. The speed of the emitted electrons, first

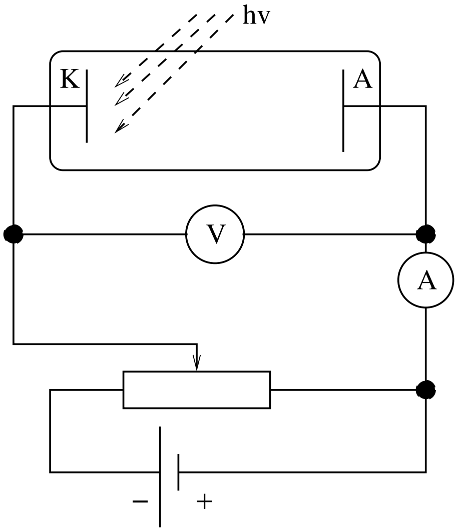

Figure 2.1: The scheme of the setup for studying the photoelectric effect. By means of a potentiometer the retarding voltage was changed, and it was determined at what voltage the photocurrent stopped. Thus, the minimum energy that light can transfer to an electron was determined.

measured in the experiments of Alexander Stoletov in 1888-1890, was shown to be dependent solely on the light frequency, but not on its intensity. Having the frequency fall down below certain minimal value the photoelectric effect was stopped completely. The explanation of the photoelectric effect is based on the energy and momentum conservation laws for an electron colliding with a quantum of light:

$$\hbar\omega + E = \hbar\omega' + E', \quad \hbar\boldsymbol{k} + \boldsymbol{P} = \hbar\boldsymbol{k}' + \boldsymbol{P}'. \tag{2.7}$$

In this way the light was proved to behave like a particle in photoelectric effect. The energy of the absorbed photon is harnessed to surmount the work function of the electron W in a given metal and to give kinetic energy to the emitted electron. The maximal allowed kinetic energy of the emitted electron is equal to

$$T = \hbar\omega - W. \tag{2.8}$$

For the explanation of the photoelectric effect Albert Einstein was awarded by the Nobel Prize in 1921.

To explain the stability of atoms with respect to the radiation energy losses the following postulates have been put forward by Niels Bohr:

1. The negative electron moves around the positive nucleus in a circular orbit.
2. The allowed electron orbits satisfy the first quantization condition: in the n-th orbit, the angular momentum L_n of the electron is an integer multiple of $\hbar$:

$$mv_n r_n = n\hbar. \tag{2.9}$$

3. An electron is allowed to make transitions from one orbit with energy E_n to another orbit with E_m. When an atom absorbs a photon, the electron makes a transition to a higher-energy orbit. When an atom emits a photon, the electron transits to a lower-energy orbit. Electron transitions with the simultaneous photon absorption or photon emission take place instantaneously. Their frequencies are subjected to second quantization condition:

$$|E_m - E_n| = h\nu_{mn}, \tag{2.10}$$

where ν_{mn} is the frequency of either an emitted or an absorbed photon.

Taking into account the equality of the Coulomb attraction of an electron to nucleus and the centripetal force acting on electron, we get for either of orbits

$$\frac{mv_n^2}{r_n} = \frac{e^2}{r_n^2} \Rightarrow r_n = \frac{e^2}{mv_n^2}, \tag{2.11}$$

from where the radii of stationary orbits and their energies are derived:

$$r_n = \frac{n^2\hbar^2}{me^2}, \quad E_n = -\frac{me^4}{2\hbar^2 n^2}. \tag{2.12}$$

The value of r_n for the hydrogen atom at $n=1$ is referred to as the *Bohr radius*

$$r_1 = a_0 = \frac{\hbar^2}{me^2} = 0.52918 \times 10^{-8}\text{cm}. \tag{2.13}$$

The corresponding energy level

$$E_1 = -\frac{me^4}{2\hbar^2} = -\frac{e^2}{2a_0} \equiv -R_\infty = -13.6075\text{eV} \tag{2.14}$$

is known as the Ridberg constant ($1\text{eV} = 1.602 \times 10^{-12}\text{erg}$).

It was experimentally found at the beginning of the 19th century, that the hydrogen atom posses discrete line emission spectrum, and the distribution of radiation frequencies can be described by the law

$$\nu_n = cR\left(\frac{1}{k^2} - \frac{1}{n^2}\right), \tag{2.15}$$

where integer k labels the series, c is the speed of light. $k = 1$ corresponds to the Lyman series, lying in ultraviolet spectrum, $k = 2$ corresponds to the Balmer series, lying in visual spectrum, $k = 3$ corresponds to the Paschen series, lying in infrared spectrum. Thus, the experimentally observed spectra are described by the transitions between the discrete energy levels given by (2.12). The experimental value of the Rydberg constant in Eq.(2.15) is $R = 1.09737 \cdot 10^5\text{cm}^{-1}$.

It was found out, that already known elementary particles, under certain experimental conditions, also behave like waves. The experiments on electron scattering by crystals, performed by L.Germer and C.Davisson in 1925, and also by J.Thomson in 1927, the maxima of refracted electron density have been observed exactly at the angles that satisfy the Wulff-Bragg condition

$$2d\sin\theta = n\lambda, \quad n = 0, 1, 2, \ldots, \tag{2.16}$$

obtained earlier for the X-rays with wavelength λ. For the case of scattered electrons the wavelength turned to be

$$\lambda = \frac{h}{\sqrt{2m_e E}}, \tag{2.17}$$

where m_e is electron mass, and E is its energy. The Wulff-Bragg condition (2.16) is easy to explain at the assumption that the electrons reflected from different layers of crystal behave like waves. If it is the case, the maxima of intensity take place when the difference of the paths of waves, reflected from different layers, is equal to an integer number of wavelenghts, see Fig. 2.2.

Thus for a *particle* we can introduce a *wavelength* equal to the product of inverse momentum to the Planck constant:

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

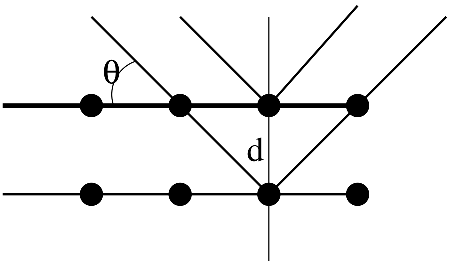

Figure 2.2: Reflection of waves from different layers of a crystal lattice

This wavelength, referred to as de Broglie wavelength, was named after French physicist Louis de Broglie, who was the first to assign a plane wave with energy $E = \hbar\omega$ and momentum $p = \hbar k$ to any free particle moving in x direction:

$$\psi(x,t) = e^{\imath(kx-\omega t)}.$$

In 1929 Louis de Broglie was awarded by the Nobel Prise "for his discovery of the wave nature of electrons."

In other experiments, electrons emitted by cathode ray tube passing through an opaque screen with two slits create an interference pattern behind the screen, which is not the sum of the intensities of electron fluxes that passed through the first and second slits separately. There are areas on it where the waves passing through the first and second slit extinguish each other. Thus, in this experiment, the electron behaves like a wave passing through both slits and destructively interfering with itself after that. Interestingly, similar experiments on a *single electron* have been performed rather recently, in 1977.

Since two arbitrary characteristics of a quantum system – say, the particle position and its velocity, – cannot, in general, be measured simultaneously, it is important to consider a *complete set of commutative observables.* The *complete set of commutative observables* is such a set of physical observables, attributed to a physical system, that can be measured simultaneously; so that any other observables, that are not the functions of the former, cannot be simultaneously measured.

Another important feature of quantum mechanics, which cannot be found in classical physics, is that the same physical objects – electrons, photons, protons and many others, – shows either a wave-like behaviour, or a particle-like behaviour, depending on the experimental conditions. This means the physical object remains the same, but its description is being changed. Such properties, immanent to an object, but manifested alternatively, depending on the experimental conditions, are usually referred to as *complementary properties*, a term coined by Dutch physicist Niels Bohr.

Exercises

1. An electron is accelerated by electric field with the potential 250V. Find de Broglie wavelength of the electron.

Solution

The momentum of the electron is related to its wave-number as

$$p = \hbar k, \quad k = \frac{2\pi}{\lambda}.$$

The momentum of electron, in non-relativistic approximation, is related to its energy as

$$p = \sqrt{2mE} = \sqrt{2mUe}.$$

From the momentum we express the de Broglie wavelength of the electron

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mUe}}$$

From where we get

$$\lambda = \frac{6.626 \cdot 10^{-27}\text{erg} \cdot \text{sec}}{\sqrt{2 \times 9.1 \cdot 10^{-28}\text{g} \times 250\text{V} \times 1.602 \cdot 10^{-12}\frac{\text{erg}}{\text{eV}}}} = 7.7 \cdot 10^{-9}\text{cm}$$

2. Hydrogen atom undergoes a transition from L to state K, emitting a quantum of light. Find the frequency of emitted light in cm^{-1}.

Solution

Hydrogen atom energy levels are determined by the formula

$$E_n = -R\frac{1}{n^2}, \quad \text{where } R = 13.6\text{eV}.$$

The energy change in L-K transition is equal to

$$\Delta E = R(1/1 - 1/4).$$

The energy is proportional to the frequency of light quantum by the Planck constant:

$$\Delta E = h\nu.$$

From the latter equation it follows that

$$\nu = \frac{\Delta E}{h}[\text{Hz}] = \frac{\Delta E}{hc}[\text{cm}^{-1}].$$

Substitution of numeric values gives

$$\nu = \frac{0.75 \times 13.6\text{eV} \times 1.602 \cdot 10^{-12}\text{erg/eV}}{6.626 \cdot 10^{-27}\text{erg} \cdot \text{sec}} = 2.5 \cdot 10^{15}\text{Hz} = 82478\text{cm}^{-1},$$

where frequency in Hz is converted to cm^{-1} by dividing by the speed of light c.

2.2 Mathematical machinery of quantum mechanics

2.2.1 Wave function

In classical mechanics, provided all coordinates and velocities are given, one gets a complete description of physical system (2.1). In quantum mechanics only the *probability* of finding a system in one or the other state can be strictly defined. To give some physical interpretation to wave-like properties of particles, i.e., to give physical interpretation of de Broglie waves, it was suggested that the state of a particle is described by certain complex-valued function of coordinates

$$\Psi = \Psi(q, t), \tag{2.18}$$

the amplitude of which defines the probability to find a given particle at a given spatial point, and the phase of which ensures the possibility of the interference phenomena. By definition, the wave function (2.18) is a function which contains *complete* information about a particle.

The probability to find a particle within the volume Δq is equal to squared modulus of wave function multiplied by this volume:

$$\Delta P = \overline{\Psi(q,t)}\Psi(q,t)\Delta q. \tag{2.19}$$

(The over-line stands for complex conjugation.) The wave function (2.18) is subjected to a natural normalisation condition

$$\int \overline{\Psi(q,t)}\Psi(q,t)dq = 1, \tag{2.20}$$

which states the probability to find a particle in either of states is exactly one.

The knowledge of wave function enables to determine the result of an arbitrary measurement made upon the system, rather than the measurement of coordinates only. In the most general form, the average value of an experimentally measurable physical observable A can be written as

$$\langle A \rangle = \int \overline{\Psi(q)}A(q,q')\Psi(q')dqdq', \tag{2.21}$$

where $A(q,q')$ is certain integral operator, related to the measuring process of A.

Since the wave function enters any expressions for physical observables only in combination $\bar{\Psi}\Psi$, rather than Ψ alone, it is evident that the wave function is defined only up to a phase multiplier. The phase shift

$$\Psi \to e^{\imath\alpha}\Psi \tag{2.22}$$

does not change the physical content of the theory.

2.2.2 The superposition principle

The basic postulate of the quantum theory is the *principle of superposition of quantum states.* It declares:

Let certain measurement being performed on a quantum system in a state with wave function $\Psi_1(q)$ always yield the result 1, and let the same measurement performed on the quantum system in a state with wave function $\Psi_2(q)$ always yield the result 2. Then, any linear combination of wave functions

$$\Psi(q) = c_1\Psi_1(q) + c_2\Psi_2(q), \tag{2.23}$$

with c_1 and c_2 being arbitrary complex numbers, also describes certain admissible state of the same quantum system.

The superposition principle provides for linearity of the equations of quantum mechanics. It enables the mapping between the states of quantum system and the vectors of an abstract linear space of states – the *Hilbert space* (see the mathematical supplement on page 131). Following the Dirac notation, we denote vectors of this space as $|\psi\rangle$ (ket-vector), and vectors of the conjugated space as $\langle\psi|$(bra-vector)– from *Engl. bracket.* One must distinguish between the vector $|\psi\rangle$ and its particular representation in a given basis. We use $\psi(x) \equiv \langle x|\psi\rangle$ for coordinate representation of vector ψ, and $\tilde{\psi}(k) \equiv \langle k|\psi\rangle$ for the representation of the same vector in the eigenbasis of the momentum operator.

The probabilistic interpretation of quantum mechanics leads to the following conclusion. Let a quantum system consist of two parts described by their wave functions, $\psi_1(q_1)$ and $\psi_2(q_2)$, respectively. Then, the wave function of the *combined* system is the product of its parts wave functions:

$$\psi(q_1,q_2) = \psi_1(q_1)\psi_2(q_2).$$

In case of *non-interacting* system the factorisation above survives with the time evolution.

2.2.3 Observables and Operators

The physical observables in classical mechanics – like energy, momentum, angular momentum, and others – are the functions of dynamical variables, $f = f(p(t), q(t))$. The physical observations in quantum mechanics yield concrete values for some states only – for all other states they give different results with different probabilities. If for certain quantum state $|\psi_n\rangle$ the measurement of physical quantity f gives the same result with certainty, we will say this quantity has a definite value f_n in this state, and we will refer such state as an *eigenstate of physical quantity* f.

Let a physical quantity f (energy, momentum, spin, etc.) can take a set of values $\{f_n\}_n$, either finite or infinite. Let the quantum state in which the quantity f has the value f_n be $|\psi_n\rangle$, then there is an operator $\hat{f}$, corresponding to the quantity f, such that $|\psi_n\rangle$ is an eigenstate of $\hat{f}$ with the eigenvalue f_n:

$$\hat{f}|\psi_n\rangle = f_n|\psi_n\rangle. \tag{2.24}$$

By *operator* we understand any mapping of a linear space into itself. We use either the notation $|\psi'\rangle = \hat{f}|\psi\rangle$ or $|\psi\rangle \xrightarrow{f} |\psi'\rangle$ to denote such mappings.

Provide there is an orthonormal set of basic functions $\psi_i(q)$,

$$\int \overline{\psi_n(q)}\psi_m(q)dq = \langle\psi_n|\psi_m\rangle = \delta_{mn}, \tag{2.25}$$

we can write the normalisation condition

$$1 = \langle\Psi|\Psi\rangle \equiv \int \overline{\Psi(q)}\Psi(q)dq$$

for any function $\Psi(q)$ written in this basis

$$\Psi(q) = \sum_n a_n\psi_n(q), \tag{2.26}$$

as

$$\sum_n |a_n|^2 = 1. \tag{2.27}$$

This means a_n is the probability amplitude of finding the system in the state $|\psi_n\rangle$ if it was initially prepared in the state Ψ. These amplitudes are equal to the projections of the state vector Ψ onto the basic vectors ψ_m:

$$a_m = \int \overline{\psi_m(q)}\Psi(q)dq = \langle\psi_m|\Psi\rangle. \tag{2.28}$$

The measurements (observations) performed on a quantum system, prepared each time in the same quantum state $|\Psi\rangle$, will generally yield different results. For this reason, it is natural to define the mean value of physical observable f in a quantum state Ψ as

$$\langle f\rangle = \sum_n f_n|a_n|^2. \tag{2.29}$$

In case of continuous spectrum of the observable f, similarly we have:

$$\Psi(q) = \int a_f\psi_f(q)df, \quad \int \overline{\psi_f(q)}\psi_{f'}(q)dq = \delta(f - f'). \tag{2.30}$$

The values of experimentally observed physical quantities are always *real*. This imposes certain restriction on properties of *operators*, which correspond to physical observables. For the mean value of any observable physical quantity (2.29) the equality

$$\langle\overline{f}\rangle = \langle f\rangle,$$

where the over-line means complex conjugation, should hold. This constraints the properties of operators $\hat{f}$, which correspond to physical observables:

$$\langle f\rangle = \int \overline{\Psi(q)}(\hat{f}\Psi(q))dq = \int \Psi(q)\overline{(\hat{f}\Psi(q))}dq = \int \overline{\Psi(q)}(\hat{f})^{\dagger}\Psi(q)dq = \langle \overline{f}\rangle.$$

In other words, the operators corresponding to physical observables should be Hermitian:

$$\hat{f} = (\hat{f})^{\dagger}. \tag{2.31}$$

Similar relations can be derived in matrix formalism, considering ψ as a vector (possibly an infinite-dimensional vector):

$$\langle f\rangle = \overline{\psi_m} f_{mn}\psi_n = \psi_m \overline{f_{mn}\psi_n} = \overline{\psi_m f_{nm}}\psi_n = \overline{\psi_m} f^{\dagger}_{mn}\psi_n \to f_{mn} = \overline{f_{nm}}.$$

In vector notation we will always use the Einstein's summation agreement: *the summation is implied over all pairs of matching indices*, unless something else is not explicitly specified.

> By definition, an operator $\hat{f}^{\dagger}$ is referred to as the Hermitian conjugation of the operator $\hat{f}$, if for all a, b in the same Hilbert space $\mathcal{H}$, where acts the operator $\hat{f}$, the equality
>
> $$(a, \hat{f}b) = (\hat{f}^{\dagger}a, b)$$
>
> holds.
>
> The same can be written in matrix notation:
>
> $$\overline{a_m} f_{mn} b_n = \overline{{f^{\dagger}}_{nm} a_m} b_n = \overline{a_m}\,\overline{{f^{\dagger}}_{nm}} b_n,$$
>
> from where it follows that
>
> $${f^{\dagger}}_{nm} = \overline{f_{mn}},$$
>
> with the definition of the scalar product $(a, b) \equiv \overline{a_n} b_n$ being implied.
>
> Depending on the properties of operators with respect to Hermitian conjugation we imply the following terminology:
>
> - An operator $\hat{f}$ is called *Hermitian* operator if $\hat{f} = \hat{f}^{\dagger}$.
> - An operator $\hat{f}$ is called *anti-Hermitian* operator if $\hat{f} = -\hat{f}^{\dagger}$.
> - An operator $\hat{f}$ is called *unitary* operator if $\hat{f}\hat{f}^{\dagger} = \hat{1}$.
>
> The condition $\hat{f} = \hat{f}^{\dagger}$ provides the eigenvalues of operator $\hat{f}$ to be real. It is sufficient, but not a necessary condition.

The hermiticity of operators, corresponding to physical observables, has an important physical consequence: the eigenfunctions, corresponding to different eigenvalues of a Hermitian operator are always orthogonal to each other. Indeed, considering the equation (2.24), which defines the n-th eigenvalue of operator $\hat{f}$, together with the conjugated equation for the m-th eigenvalue, we can multiply one of them by $\overline{\psi_m}$, and the other by ψ_n. This gives

$$\langle\psi_m|(\hat{f}|\psi_n\rangle = f_n|\psi_n\rangle),$$
$$(\langle\psi_m|\overline{\hat{f}} = \langle\psi_m|\overline{f_m})|\psi_n\rangle.$$

Subtracting one equation from the other we get

$$\langle\psi_m|\hat{f}|\psi_n\rangle - \langle\psi_m|\hat{f}^{\dagger}|\psi_n\rangle = \langle\psi_m|f_n - f_m|\psi_n\rangle. \tag{2.32}$$

Since the left-hand side of this equation is zero, we infer the orthogonality condition $\langle\psi_m|\psi_n\rangle = \delta_{mn}$ holds.

Referring the reader to special textbooks in linear algebra [Gel89] and functional analysis [KF12] for more mathematical details of operator theory, we just mention few basic properties of linear operators.

Linear operators can be added and multiplied:

$$(\hat{f}+\hat{g})|\psi\rangle = \hat{f}|\psi\rangle + \hat{g}|\psi\rangle, \qquad \hat{f}\hat{g}|\psi\rangle \equiv \hat{f}(\hat{g}|\psi\rangle).$$

In general case $\hat{f}\hat{g} \neq \hat{g}\hat{f}$. That is why it is reasonable to define a *commutator* of two operators $\hat{f}$ and $\hat{g}$:

$$[\hat{f},\hat{g}] \equiv \hat{f}\hat{g} - \hat{g}\hat{f} \tag{2.33}$$

and their *anti-commutator*:

$$\{\hat{f},\hat{g}\} \equiv \hat{f}\hat{g} + \hat{g}\hat{f}. \tag{2.34}$$

The operation of Hermitian conjugation, acting on operator products, as well as on matrix products, reverses the order of the multipliers:

$$(\hat{f}\hat{g})^\dagger = \hat{g}^\dagger \hat{f}^\dagger. \tag{2.35}$$

If two operators commute to each other $\hat{f}\hat{g} = \hat{g}\hat{f}$, i.e., if their commutator vanishes, the corresponding physical variables can be measured simultaneously. All operators of physical variables, which pertain to a given physical system and commute to each other form the *complete set of commuting observables*, i.e., the physical quantities simultaneously meaningful for the given physical system.

2.2.4 Observable and non-observable quantities

Quantum mechanics is essentially different from classical mechanics by the presence of two different types of quantities *observable* and *non-observable*. Observable quantities, or *observables*, are the quantities which can be put into correspondence to Hermitian operators, and which can be measured in physical experiments. Coordinate, momentum, angular momentum are observable. The quantities which cannot be experimentally measured are referred to as *non-observable*. The phase of wave function, the particle's momentum at fixed coordinate, a coordinate between two measurements are non-observable quantities, since there are no experiments to measure them.

Quantum mechanics predicts the probabilities of different experimental results, but not the results themselves. The probabilistic character of the predictions of quantum mechanics is of principle nature – it is not a result of our ignorance of any hidden parameters of quantum systems. It has been proved by John Bell, there exists no classical theory containing *hidden variables*, unknown to us, that can fully reproduce all results of quantum mechanics [Bel66].

2.2.5 The uncertainty principle

The correspondence principle, i.e., the coincidence of the results of quantum mechanics to the results of classical mechanics in the limit $\hbar \to 0$, demands the wave function to be of the form

$$\Psi = a e^{\frac{\imath}{\hbar}S}, \tag{2.36}$$

with S being the action functional of corresponding classical system. The application of the principles of Hamiltonian mechanics to the action functional S leads to the following equation for the momentum operator $\hat{\boldsymbol{p}}$:

$$\hat{\boldsymbol{p}} = -\imath\hbar\frac{\partial}{\partial \boldsymbol{x}}, \quad \hat{\boldsymbol{p}}\Psi(\boldsymbol{x},t) = \boldsymbol{p}\Psi(\boldsymbol{x},t). \tag{2.37}$$

The simplest case of a free particle with the energy E moving in the direction $\boldsymbol{p}$ corresponds to de Broglie wave

$$\Psi(\boldsymbol{x},t) \sim e^{\frac{\imath}{\hbar}(\boldsymbol{px}-Et)}. \tag{2.38}$$

The momentum operator (2.37) is the generator of the group of translations, acting in the coordinate space.

It is easy to see, that the momentum operator does not commute with the coordinate operator. Indeed, since in coordinate representation the operator of coordinate is just a multiplication by this coordinate, and the momentum operator is proportional to the differentiation with respect to the same coordinate, we have:

$$\hat{x}\Psi(\boldsymbol{x},t) = x\Psi(\boldsymbol{x},t), \quad \hat{p}_x\Psi(\boldsymbol{x},t) = -\imath\hbar\frac{\partial}{\partial x}\Psi(\boldsymbol{x},t). \tag{2.39}$$

Hence

$$[\hat{x},\hat{p}_x]\Psi = x\left(-\imath\hbar\frac{\partial}{\partial x}\right)\Psi + \imath\hbar\frac{\partial}{\partial x}x\Psi = \imath\hbar\Psi,$$

from where it follows that

$$[\hat{x},\hat{p}_x] = \imath\hbar. \tag{2.40}$$

In view of the non-commutativity of the momentum and the coordinate operators (2.40), the eigenvalues of these operators cannot be measured simultaneously. The product of errors of their measurements is bounded from below by the Planck constant:

$$\langle(\Delta x)^2\rangle\langle(\Delta p_x)^2\rangle \geq \frac{\hbar^2}{4}. \tag{2.41}$$

The proof of this statement is given below.

Let us consider the operators describing the deviation from the mean

$$\Delta F \equiv \hat{F} - \langle\hat{F}\rangle \tag{2.42}$$

(where $\hat{F}$ is any operator corresponding to a physical observable). Then, given the commutation relation is known for some operators $\hat{F}$ and $\hat{G}$ (the hats over the operators will be dropped hereafter where it does not lead to a confusion)

$$[F,G] = \imath K, \tag{2.43}$$

the commutation relation for the *deviations* from the mean of these operators takes the form

$$[\Delta F,\Delta G] = \imath K. \tag{2.44}$$

Let us construct a functional, depending on a single real variable $\alpha = \overline{\alpha}$, defined as

$$I(\alpha) = \int |(\alpha\Delta F - \imath\Delta G)\Psi(q)|^2\, dq \geq 0. \tag{2.45}$$

After straighforward algebraic manipulations we get:

$$\begin{aligned} I(\alpha) &= \int [(\alpha\Delta F - \imath\Delta G)\Psi][(\alpha\overline{\Delta F} + \imath\overline{\Delta G})\overline{\Psi}]dq = \\ &= \int \overline{\Psi}(\alpha\Delta F^\dagger + \imath\Delta G^\dagger)(\alpha\Delta F - \imath\Delta G)\Psi dq = \\ &= \int \overline{\Psi}(\alpha^2(\Delta F)^2 + (\Delta G)^2)\Psi dq - \imath\alpha\int\overline{\Psi}[\Delta F,\Delta G]\Psi dq = \\ &= \alpha^2\langle(\Delta F)^2\rangle + \langle(\Delta G)^2\rangle + \alpha\langle K\rangle. \end{aligned}$$

The equation which defines the extremum of $I(\alpha)$ is

$$\frac{\partial I(\alpha)}{\partial\alpha} = 0\bigg|_{\alpha=\alpha_0} = 2\alpha_0\langle(\Delta F)^2\rangle + \langle K\rangle. \tag{2.46}$$

The maximum of $I(\alpha)$ is achieved at the point α_0, such that

$$\alpha_0 = -\frac{\langle K\rangle}{2\langle(\Delta F)^2\rangle}, \qquad \frac{\partial^2 I(\alpha)}{\partial\alpha^2}\bigg|_{\alpha=\alpha_0} > 0.$$

Substituting the extremal value α_0 into the definition of the functional (2.45), we get

$$\frac{\langle K\rangle^2}{4\langle(\Delta F)^2\rangle} + \langle(\Delta G)^2\rangle - \frac{\langle K\rangle^2}{2\langle(\Delta F)^2\rangle} \geq 0,$$

from where it follows that

$$\langle(\Delta F)^2\rangle\langle(\Delta G)^2\rangle \geq \frac{\langle K\rangle^2}{4}. \tag{2.47}$$

In the above considered case, when F is the coordinate and G is the momentum, the commutator K in the commutation relation (2.47) is just the Planck constant $\hbar$ – in this way the desired uncertainty relation (2.41) is proved.

The uncertainty relation is an essential restriction, which is introduced by quantum mechanics into the description of physical world. The higher is accuracy in the measurement of a position of the particle, the higher is the uncertainty in its momentum; the higher is the precision of momentum measurement, the more uncertain we are about its position. This relation has been generalized by Niels Bohr in 1927 to a more general *principle of complementarity*:

Gaining experimental information about some characteristics describing microobjects is inevitably accompanied by the loss of information on some other characteristics, *complementary* to the former.

Exercise

A typical size of atom is about $d = 1 \cdot 10^{-8}$ cm. Using the Heisenberg uncertainty principle estimate the typical velocity of electrons in atom.

Solution

$$\Delta x\Delta p \geq \frac{\hbar}{2} \Rightarrow \Delta v \geq \frac{\hbar}{2m\Delta x}$$

from where we get

$$\Delta v \geq \frac{1.05\cdot 10^{-27}\mathrm{erg}\cdot\mathrm{sec}}{2\times 9.1\cdot 10^{-28}\mathrm{g}\times 10^{-8}\mathrm{cm}} \approx 5.8\cdot 10^{7}\frac{\mathrm{cm}}{\mathrm{sec}}.$$

2.3 The Schrödinger equation

Since the momentum operator in quantum mechanics has the form

$$\hat{\boldsymbol{p}} = -\imath\hbar\frac{\partial}{\partial\boldsymbol{x}},$$

it is reasonable to assume that due to the Lorentz invariance, after the substitution of the energy-momentum vector $(E, -\boldsymbol{p})$ by appropriate operator, the energy operator should be

$$\hat{H} = \imath\hbar\frac{\partial}{\partial t}. \tag{2.48}$$

The energy operator – the Hamiltonian $\hat{H}$ – determines the time evolution of the wave function:

$$\imath\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{2.49}$$

The Hamiltonian of a free massive particle, in analogy to classical mechanics, is

$$H = \frac{\boldsymbol{p}^2}{2m} \to \hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \equiv -\frac{\hbar^2}{2m}\Delta. \tag{2.50}$$

For a massive particle moving in an external potential field $U(x)$ the Hamiltonian takes the form

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + U(\boldsymbol{x}).$$

The corresponding evolution equation for the wave function was first written by Erwin Schrödinger in 1926, and is known as the *Schrödinger equation*:

$$\imath\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\Delta + U(\boldsymbol{x})\right)\Psi(x,t). \tag{2.51}$$

The Schrödinger equation determines time evolution of the wave function, and the stationary states – the quantum states with definite energy. The solution of the Schrödinger equation requires the knowledge of boundary conditions.

For stationary states the time dependence of the wave function can be factorised:

$$\imath\hbar\frac{\partial}{\partial t}\Psi(x,t) = E\Psi(x,t) \Rightarrow \Psi(x,t) = e^{-\frac{\imath}{\hbar}Et}\psi(x). \tag{2.52}$$

The equation, which determines the stationary states of the energy E is also referred to as the (stationary) Schrödinger equation:

$$\left(\frac{\hbar^2}{2m}\Delta + [E - U(x)]\right)\psi(x) = 0. \tag{2.53}$$

Exercises

1. Find normalised eigenfunctions of the momentum operator $\hat{p} = -\imath\hbar\frac{\partial}{\partial x}$ acting on an infinite domain $\mathbb{R} = (-\infty, \infty)$.

Solution

The eigenfunctions can be obtained from the solution of eigenequation

$$-\imath\hbar\frac{\partial}{\partial x}\psi(x) = k\psi(x), \tag{2.54}$$

where $\psi(x)$ are the eigenfunctions to be determined, k are the eigenvalues the eigenfunctions correspond to. The solutions to equation (2.54) have the form

$$\psi_k(x) = Ce^{-\frac{i}{\hbar}kx}, \tag{2.55}$$

where C is a constant of integration. Since $\hat{p}$ is Hermitian operator, its eigenvalues are real. The integration constant C is to be determined from the normalisation condition

$$\int_{-\infty}^{\infty} \overline{\psi_{k'}(x)}\psi_k(x)dx = \delta(k' - k). \tag{2.56}$$

Substituting eigenfunctions (2.55) into normalisation condition (2.56) we get

$$\psi_k(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}kx}. \tag{2.57}$$

2. Determine the energy levels in a wedge quantum well, limited from the left by infinite barrier at $x = 0$, and by linear potential on the right $V = \alpha x$.

Hint

The stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi''(x) + \alpha x\psi(x) = E\psi(x) \tag{2.58}$$

by the change of variable to

$$Z = \left(x - \frac{E}{\alpha}\right)\left(\frac{2m\alpha}{\hbar^2}\right)^{\frac{1}{3}} \tag{2.59}$$

is transformed into the Airy equation

$$\psi''(Z) - Z\psi(Z) = 0. \tag{2.60}$$

The Airy equation has two linearly independent solutions $Ai(Z)$ and $Bi(Z)$. The full wave function thus can be written in the form

$$\psi(Z) = C_1 Ai(Z) + C_2 Bi(Z).$$

In view of the boundary conditions – $\psi(x)$ should vanish at both $x = 0$ and $x = \infty$ only the first kind Airy function will contribute:

$$Ai(x) = \frac{1}{\pi}\int_0^{\infty} \cos\left(\frac{t^3}{3} + xt\right) dt.$$

The energy spectrum is determined by the set of roots $\{\sigma_n\}_n$ of the $Ai(x)$ function [DNG00]:

$$E_n = \sigma_n \left(\frac{\hbar^2\alpha^2}{2m}\right)^{\frac{1}{3}} \tag{2.61}$$

2.3.1 The probability current

To impose correct boundary conditions on the Schrödinger equation we first need a concept of the probability current density. To write these condition, we need to represent the time derivative of the probability of quantum state in the form of a *conservation law*, using the fact that the time derivative of the wave function is determined by the Schrödinger equation (2.51). Doing so, we get

$$\begin{aligned}\frac{d}{dt}\int|\Psi|^2dq &= \int\left[\frac{d\overline{\Psi}}{dt}\Psi+\overline{\Psi}\frac{d\Psi}{dt}\right]dq = \int\left[\Psi\left(\frac{\imath}{\hbar}\overline{\hat{H}}\right)\overline{\Psi}-\frac{\imath}{\hbar}\overline{\Psi}\hat{H}\psi\right]dq = \\ &= \frac{\imath}{\hbar}\int(\Psi\hat{H}\overline{\Psi}-\overline{\Psi}\hat{H}\psi)dq. \end{aligned} \tag{2.62}$$

For instance, using a particular form of the Hamiltonian of a particle in a potential field

$$\hat{H}=\overline{\hat{H}}=-\frac{\hbar^2}{2m}\Delta+U(x),$$

we get

$$\begin{aligned}\frac{d}{dt}\int|\Psi|^2dV &= -\frac{\imath\hbar}{2m}\left(\Psi\Delta\overline{\Psi}-\overline{\Psi}\Delta\Psi\right)\\ &= -\frac{\imath\hbar}{2m}\int\nabla\left(\Psi\nabla\overline{\Psi}-\overline{\Psi}\nabla\Psi\right)dV.\end{aligned}$$

Therefore, the vector of the probability current density, which is conserved, has the form

$$\boldsymbol{j}=\frac{\imath\hbar}{2m}\left(\Psi\nabla\overline{\Psi}-\overline{\Psi}\nabla\Psi\right), \tag{2.63}$$

and the conservation law for the probability of finding a particle in a given volume can be written as

$$\frac{d}{dt}\int|\Psi|^2dV=-\int\mathrm{div}\boldsymbol{j}\ dV. \tag{2.64}$$

The conservation law (2.64) can be written in a "hydrodynamic" form

$$\frac{d}{dt}\int_V\rho dV+\oint_{\partial V}\boldsymbol{j}\cdot d\boldsymbol{S}=0, \tag{2.65}$$

i.e., the change of probability of finding a particle in a given volume V is equal to the integral of the probability density current over the surface ∂V, which is the boundary of V.

2.3.2 Free particle

The stationary Schrödinger equation for a free particle

$$\left(\frac{\hbar^2}{2m}\Delta+E\right)\psi(x)=0 \tag{2.66}$$

allows for the solutions finite over all space. Particular form of these solutions depends on the boundary conditions.

For the quantum states localised nowhere in space, but having a definite momentum (i.e., moving in a definite direction), the solution, first suggested by Louis de Broglie, is the plane wave

$$\psi(\boldsymbol{x})=A\exp\left(\frac{\imath}{\hbar}(\boldsymbol{px}-Et)\right). \tag{2.67}$$

The probability density current of the de Broglie wave is

$$\boldsymbol{j}=|A|^2\frac{\boldsymbol{p}}{m}=|A|^2\boldsymbol{v}. \tag{2.68}$$

For this reason the plane waves (de Broglie waves) are often normalised by $A=\sqrt{\frac{m}{p}}$, i.e., one particle per second through the unit area normal to vector $\boldsymbol{p}$.

2.3.3 Particle in a box

Let us consider a quantum particle, the motion of which is bounded within a rectangular box (L_x, L_y, L_z) with unpassable walls. The Schrödinger equation, which determines the stationary states of the particle inside the box, has the form

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z). \tag{2.69}$$

Due to the independence of motion in x, y and z directions, the solution of the equation (2.69) can be found by representing wave function in a form of a product

$$\psi(x,y,z) = X(x)Y(y)Z(z). \tag{2.70}$$

Substituting this factorisation into (2.69), we get

$$E + \frac{\hbar^2}{2m}\left(\frac{X''}{X}+\frac{Y''}{Y}+\frac{Z''}{Z}\right) = 0$$
$$\frac{X''}{X} = -a^2, \quad \frac{Y''}{Y} = -b^2, \quad \frac{Z''}{Z} = -c^2,$$

where a, b, c are some constants. The solutions in all three directions are the linear combinations of the sine and the cosine functions. For instance, the solution along the x direction can be written as

$$X(x) = A\sin ax + B\cos ax,$$

with the coefficients A and B to be determined from the boundary conditions.

For the unpassable walls, it should be a zero probability of finding a particle on the the wall, and hence the following boundary conditions should hold:

$$X(0) = X(L_x) = Y(0) = Y(L_y) = Z(0) = Z(L_z) = 0. \tag{2.71}$$

This means only the sine waves survive in the solution, with their frequencies being an integer multiples of π, to ensure zeros on the right boundaries:

$$a = \frac{\pi n}{L_x}, \quad b = \frac{\pi m}{L_y}, \quad c = \frac{\pi k}{L_z}.$$

Therefore, the energy spectrum of a massive particle bounded within a rectangular box with unpassable walls is determined by the sum of squares of three quantum numbers, defining the motion in x, y and z directions, respectively:

$$E_{mnk} = \frac{\hbar^2\pi^2}{2m}\left[\left(\frac{n}{L_x}\right)^2+\left(\frac{m}{L_y}\right)^2+\left(\frac{k}{L_z}\right)^2\right]. \tag{2.72}$$

The amplitude of the wave function is determined from the normalisation condition

$$1 = \int |X(x)|^2 dx = A^2\int_0^{L_x}\sin^2\left(\frac{\pi n}{L_x}x\right)dx = A^2\frac{L_x}{2}.$$

The full time-dependent solution of the Schrödinger equation describing the motion of a particle with mass m in a rectangular box (L_x, L_y, L_z) with unpassable walls has the form

$$\Psi(t,x,y,z) = \sqrt{\frac{8}{L_xL_yL_z}}\frac{\sin n\pi x}{L_x}\frac{\sin m\pi y}{L_y}\frac{\sin k\pi z}{L_z}\exp\left(-\frac{\imath}{\hbar}E_{mnk}t\right). \tag{2.73}$$

Exercise

Find matrix elements $\langle m|\hat{x}|n\rangle$ of the position operator $\hat{x}$ between the m-th and the n-th energy levels for a massive particle in an infinitely deep potential well of width L.

Solution

Matrix elements of the coordinate x in one spatial dimension have the form

$$x_{mn} = \int \overline{\psi_m(x)} x \psi_n(x) dx. \tag{2.74}$$

For a free non-relativistic particle of mass m the eigenvalues of free Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

can be represented as a linear combinations of a sine and cosine functions. Since the particle cannot pass the infinite walls of the potential well, we have the boundary conditions

$$\psi(0) = \psi(L) = 0.$$

Taking into account the unit normalisation of wave functions, the eigenfunction corresponding to the n-th energy level is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi n x}{L}, \tag{2.75}$$

see the solution (2.73).

The wanted matrix elements can be obtained by substitution of eigenfunctions (2.75) into equation (2.74).

Making use of the identity

$$2\sin\alpha\sin\beta = \cos(\alpha-\beta) - \cos(\alpha+\beta),$$

we get

$$x_{mn} = \frac{1}{L}\int_0^L x\cos\left(\frac{\pi}{L}x(m-n)\right)dx - \frac{1}{L}\int_0^L x\cos\left(\frac{\pi}{L}x(m+n)\right)dx. \tag{2.76}$$

Integration by parts in equation (2.76) gives

$$\int x\cos(\alpha x)dx = \frac{1}{\alpha}\int x d\sin(\alpha x) = \frac{1}{\alpha}x\sin(\alpha x) - \frac{1}{\alpha}\int \sin(\alpha x)dx.$$

Substituting the value $\alpha = \frac{\pi}{L}$ and using the limits of integration $\int_0^L$, we obtain the value of the first integral in (2.76):

$$\frac{1}{L}\cdot\frac{L}{\pi(m-n)}\cdot x\sin\frac{\pi}{L}x(m-n) + \frac{1}{L}\cdot\frac{L^2}{\pi^2(m-n)^2}\cos\frac{\pi}{L}x(m-n)\Bigg|_0^L. \tag{2.77}$$

Similarly, for the second integral in (2.76), we get

$$\frac{1}{L}\cdot\frac{L}{\pi(m+n)}\cdot x\sin\frac{\pi}{L}x(m+n) + \frac{1}{L}\cdot\frac{L^2}{\pi^2(m+n)^2}\cos\frac{\pi}{L}x(m+n)\Bigg|_0^L. \tag{2.78}$$

Both integrals are different from zero only if $(m-n)$ is odd.

Taking the difference of the two integrals (2.77)-(2.78), we get the final result:

$$\begin{aligned} x_{mn} &= \frac{L}{\pi^2(m-n)^2}\left[\cos(\pi(m-n)) - 1\right] - \frac{L}{\pi^2(m+n)^2}\left[\cos(\pi(m+n)) - 1\right] \\ &= -\frac{8Lmn}{(m+n)^2(m-n)^2}. \end{aligned} \tag{2.79}$$

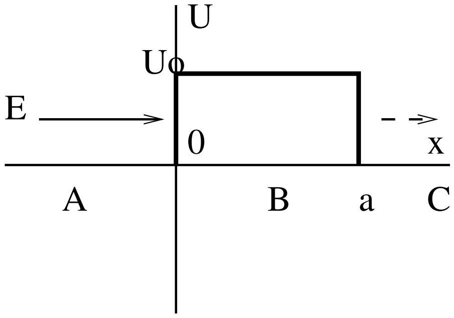

Figure 2.3: Tunnelling of a particle through a potential barrier of rectangular shape

2.3.4 Quantum tunnelling through a potential barrier

In classical mechanics the motion of a particle in a region where $E - U(x) < 0$ is strictly forbidden, see Fig. 2.3. In quantum mechanics the solution of the Schrödinger equation (2.53) in a classically forbidden domain

$$\left(\frac{\hbar^2}{2m}\Delta + [E - U(x)]\right)\psi(x) = 0$$

leads to *imaginary* values of the momentum. Nevertheless, there is nonzero probability of *tunnelling* between two classically allowed regions 'beneath' the barrier.

Let us consider a one-dimensional problem. A particle of mass m and momentum $p_x > 0$ is incident to the wall of a rectangular potential barrier of height U_0 located on the interval $x \in [0, a]$, as shown in Fig. 2.3. In the region (A), to the left from the barrier, we will look for the solution of the stationary Schrödinger equation in a form of a linear superposition of an incident and a reflected waves:

$$\psi_1(x) = A_1 e^{\imath kx} + A_2 e^{-\imath kx}; \tag{2.80}$$

in the region (B), the barrier domain, we will look for a solution in the form

$$\psi_2(x) = B_1 e^{\imath \kappa x} + B_2 e^{-\imath \kappa x}. \tag{2.81}$$

In the domain (C), to the right from the barrier, we will look for a solution in the form of a single plane wave passed through the barrier and moving rightwards:

$$\psi_3(x) = C e^{\imath kx}. \tag{2.82}$$

To solve the Schrödinger equation we need to glue the solutions (2.80,2.81,2.82) on the left and the right boundaries of the barrier, taking into account the continuity of both the wave function and its first derivative. The latter requirement stands for the continuity of the probability current: there should be neither particle creation nor particle annihilation on the boundaries of the barrier.

Gluing the solutions on two edges of the barrier, at $x=0$ and $x=a$, we get the system of equations

$$\begin{aligned}
A_1 + A_2 &= B_1 + B_2, \qquad (2.83)\\
A_1 - A_2 &= \frac{\kappa}{k}(B_1 - B_2),\\
B_1 e^{\imath \kappa a} + B_2 e^{-\imath \kappa a} &= C e^{\imath ka},\\
B_1 e^{\imath \kappa a} - B_2 e^{-\imath \kappa a} &= C\frac{k}{\kappa} e^{\imath ka},
\end{aligned}$$

where we have denoted

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \kappa = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}. \tag{2.84}$$

To calculate the probability of tunnelling through barrier we need the ratio of squared modulus of the outgoing wave amplitude to that of the incident wave – the *transition coefficient*

$$D = |C/A_1|^2. \tag{2.85}$$

Solving the system of equations (2.83) we get

$$\begin{aligned}
A_1 &= \frac{1}{2}\left[\left(1+\frac{\kappa}{k}\right)B_1 + \left(1-\frac{\kappa}{k}\right)B_2\right], \\
A_2 &= \frac{1}{2}\left[\left(1-\frac{\kappa}{k}\right)B_1 + \left(1+\frac{\kappa}{k}\right)B_2\right], \\
B_1 &= \frac{1}{2}Ce^{-\imath\kappa a+\imath ka}\left(1+\frac{k}{\kappa}\right), \\
B_2 &= \frac{1}{2}Ce^{\imath\kappa a+\imath ka}\left(1-\frac{k}{\kappa}\right),
\end{aligned}$$

from where we get

$$\begin{aligned}
A_1 &= \frac{1}{2}\left[\left(1+\frac{\kappa}{k}\right)\frac{1}{2}Ce^{-\imath\kappa a+\imath ka}\left(1+\frac{k}{\kappa}\right) + \left(1-\frac{\kappa}{k}\right)\frac{1}{2}Ce^{\imath\kappa a+\imath ka}\left(1-\frac{k}{\kappa}\right)\right], \\
A_2 &= \frac{1}{2}\left[\left(1-\frac{\kappa}{k}\right)\frac{1}{2}Ce^{-\imath\kappa a+\imath ka}\left(1+\frac{k}{\kappa}\right) + \left(1+\frac{\kappa}{k}\right)\frac{1}{2}Ce^{\imath\kappa a+\imath ka}\left(1-\frac{k}{\kappa}\right)\right],
\end{aligned}$$

or

$$\frac{A_1}{C} = \frac{1}{4}\left[\left(1+\frac{k}{\kappa}\right)\left(1+\frac{\kappa}{k}\right)e^{\imath(k-\kappa)a} + \left(1-\frac{k}{\kappa}\right)\left(1-\frac{\kappa}{k}\right)e^{\imath(k+\kappa)a}\right].$$

Hence, the transition coefficient for the rectangular potential barrier is equal to

$$\left|\frac{C}{A_1}\right|^2 = \frac{16k^2\kappa^2}{|(k+\kappa)^2e^{-\imath\kappa a} + (k-\kappa)^2e^{\imath\kappa a}|^2}.$$

Finally, after straightforward algebra, we get:

1. For the particles with the energy values above the barrier $E \geq U_0$:

   $$D = \frac{1}{1+\left(\frac{k^2-\kappa^2}{2k\kappa}\right)^2\sin^2\kappa a}. \tag{2.86}$$

   It is clear from this equation that the *transition probability may be less than unity even for the particles with energy exceeding the barrier height.* This implies the possibility of the reflection for the over-barrier particles, with the reflection coefficient equal to $R = 1 - D$.

2. For the particles with the energy values below the barrier $E < U_0$,

   $$\kappa = \imath\kappa' = \imath\sqrt{\frac{2m(U_0-E)}{\hbar^2}},$$

   the transition coefficient is equal to

   $$D = \frac{1}{1+\left(\frac{k^2+\kappa'^2}{2k\kappa'}\right)^2\sinh^2\kappa' a}. \tag{2.87}$$

Therefore, in either of these two cases, the behaviour of quantum particles is essentially different from that of their classical counterparts. This behaviour is determined by both the parameters of the de Broglie wave of the incident particle and the parameters of the potential barrier.

In real situations the barriers hampering the particles to pass through certain regions of space are of more complex shapes than that of the rectangular barrier. These barriers are usually approximated by polynomial, rational or other functions, for which the solution of the Schrödinger equation is known. For realistic potentials, as a rule, two problems are to be solved: (i) calculation of the energy spectra of (quasi) stationary states, (ii) calculation of the transition coefficients from those states, which determines the life-time of these states. Interestingly, tuning the shape of the potential – e.g., by doping the complexes of nanoparticles – the pre-designed energy spectra may be obtained [CZ99]. The technique of the solution of the Schrödinger equation for practically important potential is usually relied on the quasi-classical Wentzel-Kramers-Brillouin approximation which can be found e.g., in [LL65]. Alternatively, numerical methods can be used.

Exercise

Find a reflection coefficient for a projectile with the energy E passing over a potential barrier $U_0 < E$.

Solution

Let the barrier lie in the domain $x \geq 0$. To the left from the barrier we have a free particle motion, described by the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_I(x) = E\psi_I(x).$$

To the right from the barrier, we have a motion in the potential U_0, described by the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U_0\right]\psi_{II}(x) = E\psi_{II}(x).$$

The solution to the left from the barrier, in the domain I, can be written in the form

$$\psi_I(x) = A_1 e^{\imath kx} + A_2 e^{-\imath kx}.$$

The solution in the barrier domain, domain II, can be written in the form

$$\psi_{II}(x) = B_1 e^{\imath \kappa x}.$$

(There is no reflected wave over the barrier).

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \kappa = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}.$$

At the boundary between the domains I and II, i.e. at $x = 0$, both the solutions and their derivatives should coincide. This gives the equations

$$\begin{aligned} A_1 + A_2 &= B_1, \\ A_1 - A_2 &= \frac{\kappa}{k}B_1, \end{aligned}$$

where from we get

$$r = \frac{A_2}{A_1} = \frac{1-\frac{\kappa}{k}}{1+\frac{\kappa}{k}}.$$

The reflection coefficient is equal to the squared modulus of the ratio of the reflected wave to the incident one:

$$R = |r|^2.$$