Quantum Mechanics

Lecture notes

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Konstantin K Likharev

IOP Publishing, Bristol, UK

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Preface to the EAP Series

Essential Advanced Physics

Essential Advanced Physics (EAP) is a series of lecture notes and problems with solutions, consisting of the following four parts[1]:

- *Part CM*: *Classical Mechanics* (a one-semester course),
- *Part EM*: *Classical Electrodynamics* (two semesters),
- *Part QM*: *Quantum Mechanics* (two semesters), and
- *Part SM*: *Statistical Mechanics* (one semester).

Each part includes two volumes: *Lecture Notes* and *Problems with Solutions*, and an additional file *Test Problems with Solutions*.

Distinguishing features of this series—in brief

- condensed lecture notes (~250 pp per semester)—much shorter than most textbooks
- emphasis on simple explanations of the main notions and phenomena of physics
- a focus on problem solution; extensive sets of problems with detailed model solutions
- additional files with test problems, freely available to qualified university instructors
- extensive cross-referencing between all parts of the series, which share style and notation

Level and prerequisites

The goal of this series is to bring the reader to a general physics knowledge level necessary for professional work in the field, regardless on whether the work is theoretical or experimental, fundamental or applied. From the formal point of view, this level (augmented by a few special topic courses in a particular field of concentration, and of course by an extensive thesis research experience) satisfies the typical PhD degree requirements. Selected parts of the series may be also valuable for graduate students and researchers of other disciplines, including astronomy, chemistry, mechanical engineering, electrical, computer and electronic engineering, and material science.

The entry level is a notch lower than that expected from a physics graduate from an average US college. In addition to physics, the series assumes the reader's familiarity with basic calculus and vector algebra, to such an extent that the meaning of the formulas listed in appendix A, 'Selected mathematical formulas' (reproduced at the end of each volume), is absolutely clear.

[1] Note that the (very ambiguous) term *mechanics* is used in these titles in its broadest sense. The acronym *EM* stems from another popular name for classical electrodynamics courses: *Electricity and Magnetism*.

Origins and motivation

The series is a by-product of the so-called 'core physics courses' I taught at Stony Brook University from 1991 to 2013. My main effort was to assist the development of students' problem-solving skills, rather than their idle memorization of formulas. (With a certain exaggeration, my lectures were not much more than introductions to problem solution.) The focus on this main objective, under the rigid time restrictions imposed by the SBU curriculum, had some negatives. First, the list of covered theoretical methods had to be limited to those necessary for the solution of the problems I had time to discuss. Second, I had no time to cover some core fields of physics—most painfully general relativity[2] and quantum field theory, beyond a few quantum electrodynamics elements at the end of *Part QM*.

The main motivation for putting my lecture notes and problems on paper, and their distribution to students, was my desperation to find textbooks and problem collections I could use, with a clear conscience, for my purposes. The available graduate textbooks, including the famous *Theoretical Physics* series by Landau and Lifshitz, did not match the minimalistic goal of my courses, mostly because they are far too long, and using them would mean hopping from one topic to another, picking up a chapter here and a section there, at a high risk of losing the necessary background material and logical connections between the course components—and the students' interest with them. In addition, many textbooks lack even brief discussions of several traditional and modern topics that I believe are necessary parts of every professional physicist's education[3].

On the problem side, most available collections are not based on particular textbooks, and the problem solutions in them either do not refer to any background material at all, or refer to the included short sets of formulas, which can hardly be used for systematic learning. Also, the solutions are frequently too short to be useful, and lack discussions of the results' physics.

Style

In an effort to comply with the Occam's Razor principle[4], and beat Malek's law[5], I have made every effort to make the discussion of each topic as clear as the time/space (and my ability :-) permitted, and as simple as the subject allowed. This effort has resulted in rather succinct lecture notes, which may be thoroughly read by a student during the semester. Despite this briefness, the introduction of every new

[2] For an introduction to this subject, I can recommend either a brief review by S Carroll, *Spacetime and Geometry* (2003, New York: Addison-Wesley) or a longer text by A Zee, *Einstein Gravity in a Nutshell* (2013, Princeton University Press).

[3] To list just a few: the statics and dynamics of elastic and fluid continua, the basics of physical kinetics, turbulence and deterministic chaos, the physics of computation, the energy relaxation and dephasing in open quantum systems, the reduced/RWA equations in classical and quantum mechanics, the physics of electrons and holes in semiconductors, optical fiber electrodynamics, macroscopic quantum effects in Bose–Einstein condensates, Bloch oscillations and Landau–Zener tunneling, cavity quantum electrodynamics, and density functional theory (DFT). All these topics are discussed, if only briefly, in my lecture notes.

[4] *Entia non sunt multiplicanda praeter necessitate*—Latin for 'Do not use more entities than necessary'.

[5] 'Any simple idea will be worded in the most complicated way'.

physical notion/effect and of every novel theoretical approach is always accompanied by an application example or two.

The additional exercises/problems listed at the end of each chapter were carefully selected[6], so that their solutions could better illustrate and enhance the lecture material. In formal classes, these problems may be used for homework, while individual learners are strongly encouraged to solve as many of them as practically possible. The few problems that require either longer calculations, or more creative approaches (or both), are marked by asterisks.

In contrast with the lecture notes, the model solutions of the problems (published in a separate volume for each part of the series) are more detailed than in most collections. In some instances they describe several alternative approaches to the problem, and frequently include discussions of the results' physics, thus augmenting the lecture notes. Additional files with sets of shorter problems (also with model solutions) more suitable for tests/exams, are available for qualified university instructors from the publisher, free of charge.

Disclaimer and encouragement

The prospective reader/instructor has to recognize the limited scope of this series (hence the qualifier *Essential* in its title), and in particular the lack of discussion of several techniques used in current theoretical physics research. On the other hand, I believe that the series gives a reasonable introduction to the *hard core* of physics—which many other sciences lack. With this hard core knowledge, today's student will always feel at home in physics, even in the often-unavoidable situations when research topics have to be changed at a career midpoint (when learning from scratch is terribly difficult—believe me :-). In addition, I have made every attempt to reveal the remarkable logic with which the basic notions and ideas of physics subfields merge into a wonderful single construct.

Most students I taught liked using my materials, so I fancy they may be useful to others as well—hence this publication, for which all texts have been carefully reviewed.

[6] Many of the problems are original, but it would be silly to avoid some old good problem ideas, with long-lost authorship, which wander from one textbook/collection to another one without references. The assignments and model solutions of all such problems have been re-worked carefully to fit my lecture material and style.

Preface to *Quantum Mechanics: Lecture notes*

The structure of this course is more or less traditional, with most attention paid to the non-relativistic quantum mechanics, and only chapter 9 reviewing the relativistic effects–first in electrodynamics, and then for particles with a non-zero rest mass.

One deviation from the tradition is that, due to the counter-intuitive character of quantum mechanics, I have found it necessary to start the course from a short discussion, in the beginning of chapter 1, of the experimental facts that, by the 1920s, has necessitated its development.

However, the feature that distinguishes this course most strongly from many modern textbooks on quantum mechanics is that the discussion of Dirac's bra-ket formalism is postponed until chapter 4, i.e. until after the discussion of numerous wave-mechanical effects in one- and multi-dimensional systems, respectively, in chapters 2 and 3. One reason for that decision was the author's serious adherence (declared in the general *Preface to the EAP Series*) to the Occam Razor principle, in particular to using only the simplest theoretical tools possible for discussions of particular physical phenomena. Another motivation was to discuss the most important quantum effects, including the energy band theory, without the heavy artillery of the bra-ket formalism, to make the discussion more accessible to the potential readership from the electrical engineering and material science communities. Finally, I believe that it is useful for the reader to see how the inconveniences and pitfalls of the wave mechanics approach gradually accumulate, thus justifying the eventual introduction of a more general formalism.

Another distinguishing feature of the course is its large attention to the notions of *dephasing* (alternatively called 'decoherence') and *energy relaxation*–the effects whose description needs to go beyond the usual idealization of a closed (Hamiltonian) quantum system. A clear understanding of these effects is necessary for any educated discussion of the conceptual issues of quantum measurements, and also of the recent numerous experiments with macroscopic-scale quantum systems (such as mechanical and electromagnetic resonators, superconductor qubits, etc), because of a substantial coupling of such systems to their environment. As a result, I felt compelled to give, in chapter 7, a discussion of open quantum systems, which is more typically reserved for statistical mechanics courses.

One more not-very-traditional topic, quantum computation and cryptography, is discussed at the end of chapter 8. Since this is a hot research field, with many aspects still actively debated, the style of its discussion is closer to that of a (brief) research review than to a textbook.

Finally, two related, still-controversial topics, quantum measurements and interpretations of quantum mechanics, are also so special that I have found it natural to place their discussion into a separate, albeit short, chapter 10 at the very end of the course.

Acknowledgments

I am extremely grateful to my faculty colleagues and other readers of the preliminary (circa 2013) version of this series, who provided feedback on certain sections; here they are listed in alphabetical order[7]: A Abanov, P Allen, D Averin, S Berkovich, P-T de Boer, M Fernandez-Serra, R F Hernandez, A Korotkov, V Semenov, F Sheldon, and X Wang. (Obviously, these kind people are not responsible for any remaining deficiencies.)

A large part of my scientific background and experience, reflected in these materials, came from my education, and then research, in the Department of Physics of Moscow State University from 1960 to 1990. The Department of Physics and Astronomy of Stony Brook University provided a comfortable and friendly environment for my work during the following 25+ years.

Last but not least, I would like to thank my wife Lioudmila for all her love, care, and patience—without these, this writing project would have been impossible.

I know very well that my materials are still far from perfection. In particular, my choice of covered topics (always very subjective) may certainly be questioned. Also, it is almost certain that despite all my efforts, not all typos have been weeded out. This is why all remarks (however candid) and suggestions from readers will be greatly appreciated. All significant contributions will be gratefully acknowledged in future editions.

Konstantin K Likharev
Stony Brook, NY

[7] I am very sorry for not keeping proper records from the beginning of my lectures at Stony Brook, so I cannot list all the numerous students and TAs who have kindly attracted my attention to typos in earlier versions of these notes. Needless to say, I am very grateful to all of them as well.

Notation

Abbreviations	Fonts	Symbols
c.c. complex conjugate	F, $\mathscr{F}$ scalar variables[8]	$\dot{}$ time differentiation operator (d/dt)
h.c. Hermitian conjugate	$\mathbf{F}$, $\boldsymbol{\mathscr{F}}$ vector variables	∇ spatial differentiation vector (*del*)
	$\hat{F}$, $\hat{\mathscr{F}}$ scalar operators	$\approx$ approximately equal to
	$\hat{\mathbf{F}}$, $\hat{\boldsymbol{\mathscr{F}}}$ vector operators	$\sim$ of the same order as
	F matrix	$\propto$ proportional to
	$F_{jj'}$ matrix element	$\equiv$ equal to by definition (or evidently)
		$\cdot$ scalar ('dot-') product
		$\times$ vector ('cross-') product
		$\overline{}$ time averaging
		$\langle\ \rangle$ statistical averaging
		[,] commutator
		{ , } anticommutator

Prime signs

The prime signs ($'$, $''$, etc) are used to distinguish similar variables or indices (such as j and j' in the matrix element above), rather than to denote derivatives.

Parts of the series

Part CM: Classical Mechanics
Part EM: Classical Electrodynamics
Part QM: Quantum Mechanics
Part SM: Statistical Mechanics

Appendices

Appendix A: Selected mathematical formulas
Appendix B: Selected physical constants

Formulas

The abbreviation Eq. may mean any displayed formula: either the equality, or inequality, or equation, etc.

[8] The same letter, typeset in different fonts, typically denotes different variables.

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Lecture notes
Konstantin K Likharev

Chapter 1

Introduction

This introductory chapter briefly reviews the major experimental motivations for quantum mechanics, and then discusses its simplest formalism—the Schrödinger's wave mechanics. Much of this material (perhaps besides the last section) may be found in undergraduate textbooks[1]*, so that the discussion is rather brief, and focused on the most important conceptual issues.*

1.1 Experimental motivations

By the beginning of the 1900s, physics (which by that time included what we now call non-relativistic classical mechanics, classical statistics and thermodynamics, and classical electrodynamics including the geometric and wave optics) looked an almost completed discipline, with most human-scale phenomena reasonably explained, and just a couple of mysterious 'dark clouds'[2] on the horizon. However, rapid technological progress and the resulting development of more refined scientific instruments have led to a fast multiplication of observed phenomena that could not be explained on the classical basis. Let me list the most consequential of those experimental findings.

(i) *The blackbody radiation measurements*, pioneered by G Kirchhoff in 1859, have shown that in the thermal equilibrium, the power of electromagnetic radiation by a fully absorbing ('black') surface, per unit frequency interval, drops exponentially at high frequencies. This is not what could be expected from the combination of the classical electrodynamics and statistics, which predicted an infinite growth of the radiation density with frequency. Indeed, the classical electrodynamics shows[3] that

[1] See, for example, [1].
[2] This famous expression was used in a 1900 talk by Lord Kelvin (born W Thomson) in reference to the blackbody radiation measurements and the results of the Michelson-Morley experiments, i.e. the precursors of the quantum mechanics and the relativity theory.
[3] See, e.g. *Part EM* section 7.8, in particular Eq. (7.211).

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electromagnetic field modes evolve in time as harmonic oscillators, and that the number dN of these modes in a large free-space volume $V \gg \lambda^3$, in a small frequency interval $d\omega \ll \omega$ near some frequency ω, is

$$dN = 2V\frac{d^3k}{(2\pi)^3} = 2V\frac{4\pi k^2 dk}{(2\pi)^3} = V\frac{\omega^2}{\pi^2 c^3}d\omega, \tag{1.1}$$

where $c \approx 3 \times 10^8\ \mathrm{m\,s^{-1}}$ is the free-space speed of light, $k = \omega/c$ the free-space wave number, and $\lambda = 2\pi/k$ is the radiation wavelength. On the other hand, the classical statistics[4] predicts that in the thermal equilibrium at temperature T, the average energy E of each 1D harmonic oscillator should be equal to $k_\mathrm{B}T$, where k_B is the Boltzmann constant[5].

Combining these two results, we readily get the so-called *Rayleigh–Jeans formula* for the average electromagnetic wave energy per unit volume:

$$u \equiv \frac{1}{V}\frac{dE}{d\omega} = \frac{k_\mathrm{B}T}{V}\frac{dN}{d\omega} = \frac{\omega^2}{\pi^2 c^3}k_\mathrm{B}T, \tag{1.2}$$

that diverges at $\omega \to \infty$. On the other hand, the blackbody radiation measurements, improved by O Lummer and E Pringsheim, and also by H Rubens and F Kurlbaum to reach a 1% scale accuracy, were compatible with the phenomenological law suggested in 1900 by Max Planck:

$$u = \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{\exp\{\hbar\omega/k_\mathrm{B}T\} - 1}. \tag{1.3a}$$

This law may be reconciled with the fundamental equation (1.1) if the following replacement is made for the average energy of each field oscillator:

$$k_\mathrm{B}T \to \frac{\hbar\omega}{\exp(\hbar\omega/k_\mathrm{B}T) - 1}, \tag{1.3b}$$

with a constant factor

$$\hbar \approx 1.055 \times 10^{-34}\mathrm{J\ s}, \tag{1.4}$$

now called the *Planck's constant*[6]. At low frequencies ($\hbar\omega \ll k_\mathrm{B}T$), the denominator in Eq. (1.3) may be approximated as $\hbar\omega/k_\mathrm{B}T$, so that the average energy (1.3b) tends to its classical value $k_\mathrm{B}T$, and the Planck law (1.3a) reduces to the Rayleigh–Jeans formula (1.2). However, at higher frequencies ($\hbar\omega \gg k_\mathrm{B}T$), Eq. (1.3) describes the experimentally observed rapid decrease of the radiation density—see figure 1.1.

[4] See, e.g. *Part SM* section 2.2.

[5] In the SI units, used through this series, $k_\mathrm{B} \approx 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$—see appendix B for more exact value.

[6] Max Planck himself wrote $\hbar\omega$ as $h\nu$, where $\nu = \omega/2\pi$ is the 'cyclic' frequency (the number of periods per second), so that in early texts on quantum mechanics the term 'Planck's constant' referred to $h \equiv 2\pi\hbar$, while $\hbar$ was called 'the Dirac constant' for a while. I will use the contemporary terminology, and abstain from using the 'old Planck's constant' h at all, in order to avoid confusion.

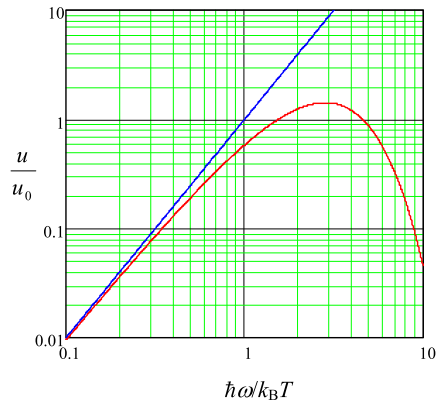

Figure 1.1. The blackbody radiation density u, expressed in units of $u_0 \equiv (k_BT)^3/\pi^2\hbar^2c^3$, as a function of frequency, according to: the Rayleigh–Jeans formula (blue line) and the Planck's law (red line).

(ii) *The photoelectric effect*, discovered in 1887 by H Hertz, shows a sharp lower bound on the frequency of the incident light that may kick electrons out from metallic surfaces, regardless of the light intensity. Albert Einstein, in one of his three famous 1905 papers, noticed that this threshold $\omega_{\min}$ could be readily explained assuming that light consisted of certain particles (now called *photons*) with energy

$$E = \hbar\omega, \tag{1.5}$$

with the same Planck's constant that participates in Eq. (1.3).[7] Indeed, with this assumption, at the photon absorption by the surface, its energy $E = \hbar\omega$ is divided between a fixed energy U_0 (nowadays called the *workfunction*) of electron binding inside the metal, and the excess kinetic energy $m_ev^2/2 > 0$ of the freed electron—see figure 1.2. In this picture, the frequency threshold finds a natural explanation as $\omega_{\min} = U_0/\hbar$.[8] Moreover, as was shown by S Bose in 1924, Eq. (1.5) readily explains[9] the Planck's law (1.3).

(iii) *The discrete frequency spectra* of the electromagnetic radiation by excited atomic gases, known since the 1600s, could not be explained by classical physics. (Applied to the planetary model of atoms, proposed by E Rutherford, classical electrodynamics predicts the collapse of electrons on nuclei in $\sim 10^{-10}$ s, due to electric dipole radiation of electromagnetic waves[10].) Especially challenging was the observation by J Balmer (in 1885) that the radiation frequencies of simple atoms may be well described by simple formulas. For example, for the lightest atom, the

[7] As a reminder, A Einstein received his only Nobel Prize (in 1922) for exactly this work, which essentially jump-started quantum mechanics, rather than for his relativity theory.
[8] For most metals, U_0 is between 4 and 5 electron volts (eV), so that the threshold corresponds to $\lambda_{\max} = 2\pi c/\omega_{\min} = 2\pi c/(U_0/\hbar) \approx 300$ nm—approximately at the border between the visible light and the ultraviolet radiation.
[9] See, e.g. *Part SM* section 2.5.
[10] See, e.g. *Part EM* section 8.2.

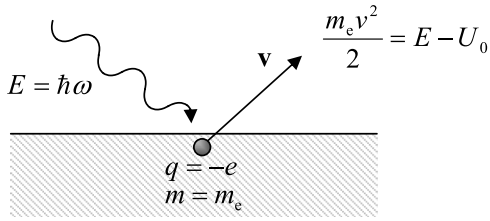

Figure 1.2. The Einstein's explanation of the photoelectric effect's frequency threshold.

hydrogen, all radiation frequencies may be numbered with just two positive integers n and n':

$$\omega_{n,n'} = \omega_0\left(\frac{1}{n^2} - \frac{1}{n'^2}\right), \tag{1.6}$$

with $\omega_0 \equiv \omega_{1,\infty} \approx 2.07 \times 10^{16}\ \mathrm{s}^{-1}$. This observation, and the experimental value of ω_0, have found their first explanation in the famous 1913 theory by Niels Bohr, which was a phenomenological precursor for quantum mechanics. In this theory, $\omega_{n,n'}$ was interpreted as the frequency of a photon that obeys the Einstein's formula (1.5), with its energy $E_{n,n'} = \hbar\omega_{n.n'}$ being the difference between two *quantized* (discrete) energy levels of the atom (figure 1.3):

$$E_{n,n'} = E_{n'} - E_n > 0. \tag{1.7}$$

Bohr showed that Eq. (1.6) may be obtained from Eq. (1.7) and the non-relativistic[11] classical mechanics, augmented with just one additional postulate, equivalent to the assumption that the angular momentum $L = m_e vr$ of the electron moving on a circular trajectory of radius r about the hydrogen's nuclei (i.e. the proton, assumed to stay at rest because of its much higher mass), is *quantized* as

$$L = \hbar n, \tag{1.8}$$

where $\hbar$ is again the same Planck's constant (1.4), and n is an integer. (In Bohr's theory, n could not be equal to zero, though in the genuine quantum mechanics, it can.)

Indeed, it is sufficient to solve Eq. (1.8), $m_e vr = \hbar n$, together with the equation

$$m_e\frac{v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}, \tag{1.9}$$

which expresses Newton's 2nd law for the electron rotating in the Coulomb field of the nucleus, for the electron's velocity v and the radius r. (Here $e \approx 1.6 \times 10^{-19}$ C is the fundamental electric charge, and $m_e \approx 0.91 \times 10^{-30}$ kg is the electron's rest mass.) The result for r is

[11] The non-relativistic approach to the problem is justified *a posteriori* by the fact the resulting energy scale E_H, given by Eq. (1.13), is much smaller than electron's rest energy, $m_e c^2 \approx 0.5$ MeV.

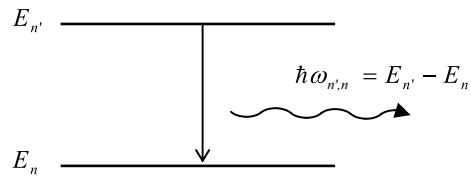

Figure 1.3. The electromagnetic radiation of a system at a result of transition between its quantized energy levels.

$$r = n^2 r_{\mathrm{B}}, \qquad \text{where } r_{\mathrm{B}} \equiv \frac{\hbar^2/m_{\mathrm{e}}}{e^2/4\pi\varepsilon_0} \approx 0.0529 \text{ nm}. \tag{1.10}$$

The constant r_{B}, called the *Bohr radius*, is the most important spatial scale of phenomena in atomic, molecular and condensed matter physics—as well as in all chemistry and biochemistry.

Now plugging these results into the non-relativistic expression for the full electron's energy (with the free electron's rest energy taken for reference),

$$E = \frac{m_{\mathrm{e}} v^2}{2} - \frac{e^2}{4\pi\varepsilon_0 r}, \tag{1.11}$$

we get the following simple expression for the energy levels (which, together with Eqs. (1.5) and (1.7), immediately gives Eq. (1.6) for the radiation frequencies):

$$E_n = -\frac{E_{\mathrm{H}}}{2n^2} < 0, \tag{1.12}$$

where E_{H} is called the so-called *Hartree energy constant* (or just the 'Hartree energy')[12]

$$E_{\mathrm{H}} \equiv \frac{(e^2/4\pi\varepsilon_0)^2}{\hbar^2/m_{\mathrm{e}}} \approx 4.360 \times 10^{-18}\ \mathrm{J} \approx 27.21\mathrm{eV}. \tag{1.13a}$$

(Note the useful relations, which follow from Eqs. (1.10) and (1.13a):

$$E_{\mathrm{H}} = \frac{e^2}{4\pi\varepsilon_0 r_{\mathrm{B}}} = \frac{\hbar^2}{m_{\mathrm{e}} r_{\mathrm{B}}^2}, \qquad \text{i.e. } r_{\mathrm{B}} = \frac{e^2/4\pi\varepsilon_0}{E_{\mathrm{H}}} = \left(\frac{\hbar^2/m_{\mathrm{e}}}{E_{\mathrm{H}}}\right)^{1/2}; \tag{1.13b}$$

the first of them shows, in particular, that r_{B} is the distance at which the coefficient-free scales of the electron's potential and kinetic energies are equal.)

Note also that Eq. (1.8), in the form $pr = \hbar n$, where $p = m_{\mathrm{e}} v$ is the electron momentum's magnitude, may be rewritten as the condition than an integer number (n) of wavelengths λ of certain (then hypothetic) waves[13] fits the circular orbit's

[12] Unfortunately, another name, the 'Rydberg constant', is sometimes used for either this energy unit or its half, $E_{\mathrm{H}}/2 \approx 13.6$ eV. To add to the confusion, the same term 'Rydberg constant' is used in some sub-fields of physics for the reciprocal free-space wavelength ($1/\lambda_0 = \omega_0/2\pi c$) corresponding to the frequency $\omega_0 = E_{\mathrm{H}}/2\hbar$.

[13] This fact was first noticed and discussed in 1924 by L de Broglie (in his PhD thesis!), so that instead of wavefunctions, especially of free particles, we are still frequently speaking of the *de Broglie waves*.

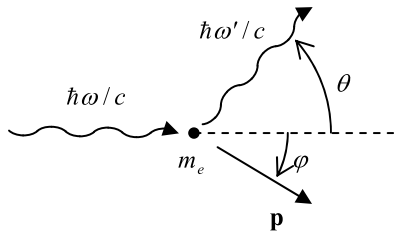

Figure 1.4. The Compton effect.

perimeter: $2\pi r \equiv 2\pi\hbar n/p = n\lambda$. Dividing both parts of the last relation by n, we see that for this statement to be true, the wave number $k \equiv 2\pi/\lambda$ of the de Broglie waves should be proportional to the electron's momentum $p = mv$:

$$p = \hbar k, \tag{1.14}$$

again with the same Planck's constant as in Eq. (1.5).

(iv) *The Compton effect*[14] is the reduction of frequency of x-rays at their scattering on free (or nearly-free) electrons—see figure 1.4. The effect may be explained assuming that the x-ray photon also has a momentum that obeys the vector-generalized version of Eq. (1.14):

$$\mathbf{p}_{\text{photon}} = \hbar\mathbf{k} = \frac{\hbar\omega}{c}\mathbf{n}, \tag{1.15}$$

where $\mathbf{k}$ is the wavevector (whose magnitude is equal to the wave number k, and direction coincides with the unit vector, $\mathbf{n}$, directed along the wave propagation[15]), and that the momenta magnitudes of both the photon and the electron are related to their energies E by the classical relativistic formula[16]

$$E^2 = (cp)^2 + (mc^2)^2. \tag{1.16}$$

(For a photon, the rest energy is zero, and this relation is reduced to Eq. (1.5): $E = cp = \hbar k = \hbar\omega$.) Indeed, a straightforward solution of the following system of three equations,

$$\hbar\omega + m_e c^2 = \hbar\omega' + [(cp)^2 + (m_e c^2)^2]^{1/2}, \tag{1.17}$$

$$\frac{\hbar\omega}{c} = \frac{\hbar\omega'}{c}\cos\theta + p\cos\varphi, \tag{1.18}$$

$$0 = \frac{\hbar\omega'}{c}\sin\theta - p\sin\varphi, \tag{1.19}$$

[14] This effect was observed (in 1922) and explained a year later by A Compton.
[15] See, e.g. *Part EM* section 7.1.
[16] See, e.g. *Part EM* section 9.3, in particular Eq. (9.78).

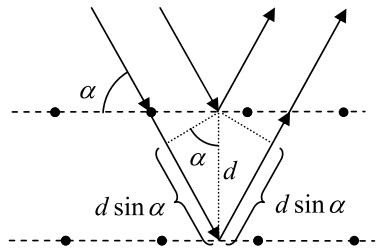

Figure 1.5. The De Broglie wave interference at electron scattering from a crystal lattice.

(which describe, respectively, the conservation of the full energy of the system, and of the two relevant Cartesian components of its full momentum, at the scattering—see figure 1.4), yields the following result,

$$\frac{1}{\hbar\omega'} = \frac{1}{\hbar\omega} + \frac{1}{m_e c^2}(1 - \cos\theta), \tag{1.20a}$$

which is traditionally represented as the relation between the initial and final values of the photon's wavelength $\lambda = 2\pi/k = 2\pi/(\omega/c)$:

$$\lambda' = \lambda + \frac{2\pi\hbar}{m_e c}(1 - \cos\theta) \equiv \lambda + \lambda_C(1 - \cos\theta), \quad \text{with } \lambda_C \equiv \frac{2\pi\hbar}{m_e c}, \tag{1.20b}$$

and is in agreement with experiment[17].

(v) *De Broglie wave diffraction*. In 1927, following the suggestion by W Elassger (who was excited by the de Broglie's conjecture of 'matter waves'), C Davisson and L Germer, and independently G Thomson succeeded in observing the diffraction of electrons on solid crystals (figure 1.5). Specifically, they have found that the intensity of the elastic reflection of electrons from a crystal increases sharply when the angle α between the incident beam of electrons and the crystal's atomic planes, separated by distance d, satisfies the following relation:

$$2d \sin\alpha = n\lambda, \tag{1.21}$$

where $\lambda = 2\pi/k = 2\pi\hbar/p$ is the de Broglie wavelength of the electrons, and n is an integer. As figure 1.5 shows, this is just the well-known condition[18] that the path

[17] The constant λ_C, which participates in this relation, is close to 2.46×10^{-12} m, and is called the *Compton wavelength* of the electron. This term is somewhat misleading: as the reader can see from Eqs. (1.17)–(1.19), no wave in the Compton problem has such a wavelength—either before or after the scattering.

[18] See, e.g. *Part EM* section 8.4, in particular figure 8.9 and Eq. (8.82). Frequently, Eq. (1.21) is called the *Bragg condition*, due to the pioneering experiments by W Bragg with x-ray scattering from crystals (that started in 1912).

difference $\Delta l = 2d \sin \alpha$ between the de Broglie waves reflected from two adjacent crystal planes coincides with an integer number of λ, i.e. of the constructive interference of the waves[19].

To summarize, all the listed effects may be explained starting from two very simple (and similarly looking) formulas: Eq. (1.5) (at that stage, for photons only), and Eq. (1.15) for both photons and electrons—both relations involving the same Planck's constant. This might give an impression of sufficient experimental evidence to declare the light consisting of discrete particles (photons), and, conversely, electrons being some 'matter waves' rather than particles. However, by that time (the mid-1920s), physics had accumulated overwhelming evidence of *wave* properties of light, such as interference and diffraction[20]. In addition, there was also strong evidence for lumped-particle ('corpuscular') behavior of electrons. It is sufficient to mention the famous oil-drop experiments by R Millikan and H Fletcher (1909–13) in which only single (and whole!) electrons could be added to an oil drop, changing its total electric charge by multiples of electron's charge $(-e)$—and never its fraction. It was apparently impossible to reconcile these observations with a purely wave picture, in which an electron and hence its charge need to be spread over the wave's extension, so that its arbitrary part could be cut out using an appropriate experimental setup.

Thus the founding fathers of quantum mechanics faced a formidable task of reconciling the wave and corpuscular properties of electrons and photons—and other particles. The decisive breakthrough in that task has been achieved in 1926 by Ervin Schrödinger and Max Born, who formulated what is now known either formally as the *Schrödinger picture of non-relativistic quantum mechanics of the orbital motion*[21] *in the coordinate representation* (this term will be explained later in the course), or informally just as the *wave mechanics*. I will now formulate the main postulates of this theory.

1.2 Wave mechanics postulates

Let us consider a spinless[22], non-relativistic point-like particle, whose classical dynamics may be described by a certain Hamiltonian function $H(\mathbf{r}, \mathbf{p}, t)$,[23] where $\mathbf{r}$ is the particle's radius-vector and $\mathbf{p}$ is its momentum[24]. Wave mechanics of such

[19] Later, spectacular experiments with diffraction and interference of heavier particles (with much smaller de Broglie wavelength), e.g. neutrons and even C_{60} molecules, have also been performed—see, e.g. a review [2] and a later publication [3]. Nowadays, such interference of heavy particles is used, for example, for ultrasensitive measurements of gravity—see, e.g. a popular review [4], and recent advanced experiments [5].

[20] See, e.g. *Part EM* section 8.4.

[21] The *orbital motion* is the historic (and very unfortunate) term used for *any* motion of the particle as a whole.

[22] Actually, in wave mechanics, the spin of the described particle has not to be equal zero. Rather, it is assumed that the spin's *effects* on the orbital motion of the particle are negligible.

[23] As a reminder, for many systems (including those whose kinetic energy is a quadratic-homogeneous function of generalized velocities, like $mv^2/2$), H coincides with the total energy E—see, e.g. *Part CM* section 2.3.

[24] Note that this restriction is very important. In particular, it excludes from our current discussion the particles whose interaction with their environment is *irreversible*, for example it provides a friction leading to particle energy's decay. Such 'open' systems need a more general description, which will be discussed in chapter 7.

Hamiltonian particles may be based on the following set of postulates[25] that are comfortingly elegant—though their final justification is given only by the agreement of all their corollaries with experiment.

(i) *Wavefunction and probability*. Such variables as **r** or **p** cannot always be measured exactly, even at 'perfect conditions' when all external uncertainties, including measurement instrument imperfection, macroscopic uncertainties of the initial state preparation, and unintended particle interactions with its environment, have been removed[26]. Moreover, **r** and **p** of the same particle can *never* be measured exactly simultaneously. Instead, even the *most detailed* description of the particle's state, allowed by Nature[27], is given by a certain complex function $\Psi(\mathbf{r}, t)$, called the *wavefunction* (or 'wave function'), which generally enables only *probabilistic* predictions of the measured values of **r**, **p**, and other directly measurable variables —in quantum mechanics, usually called *observables*.

Specifically, the probability dW of finding a particle inside an elementary volume $dV \equiv d^3r$ is proportional to this volume, and hence may be characterized by a volume-independent *probability density* $w \equiv dW/d^3r$, which in turn is related to the wavefunction as

$$w = |\Psi(\mathbf{r}, t)|^2 \equiv \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t), \tag{1.22a}$$

where the sign * denotes the usual complex conjugation. As a result, the total probability of finding the particle somewhere inside a volume V may be calculated as

$$W = \int_V w d^3r = \int_V \Psi^*\Psi d^3r. \tag{1.22b}$$

In particular, if the volume V contains the particle *definitely* (i.e. with the 100% probability, $W = 1$), Eq. (1.22*b*) is reduced to the so-called *normalization condition*

$$\int_V \Psi^*\Psi d^3r = 1. \tag{1.22c}$$

(ii) *Observables and operators*. With each observable A, quantum mechanics associates a certain *linear operator* $\hat{A}$, such that, in the perfect conditions mentioned above, the average measured value (also called the *expectation value*) of A is expressed as[28]

[25] Generally, quantum mechanics, as any theory, may be built on different sets of postulates ('axioms') leading to the same conclusions. In this text, I will not try to beat down the number of postulates to the absolute possible minimum, not only because this would require longer argumentation, but chiefly because such attempts typically result in making certain implicit assumptions hidden from the reader—a practice as common as it is regrettable.

[26] I will imply such perfect conditions further on, until the discussion of particle's interaction with environment in chapter 7 and beyond.

[27] This is one more important caveat. As will be discussed in detail in chapter 7, in many cases even Hamiltonian systems cannot be described by certain wavefunctions, and allow only a more general (and less precise) description, e.g. by the *density matrix*.

[28] This key measurement postulate is sometimes called the *Born rule*, though sometimes this term is used for the (less general) Eqs. (1.22).

$$\langle A \rangle = \int_V \Psi^* \hat{A} \Psi d^3 r, \tag{1.23}$$

where $\langle \ldots \rangle$ means the statistical average, i.e. the result of averaging the measurement results over a large *ensemble* (set) of macroscopically similar experiments, and Ψ is the normalized wavefunction, which obeys Eq. (1.22*c*). Note immediately that for Eqs. (1.22) and (1.23) to be compatible, the *identity* ('unit') *operator* defined by the relation

$$\hat{I}\Psi = \Psi, \tag{1.24}$$

has to be associated with a particular type of measurement, namely with the particle's detection.

(iii) *The Hamiltonian and the Schrödinger equation*. Another particular operator, the *Hamiltonian* $\hat{H}$, whose observable is the particle's energy E, also plays in wave mechanics a very special role, because it participates in the *Schrödinger equation*,

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi, \tag{1.25}$$

that determines the wavefunction's dynamics, i.e. its time evolution.

(iv) *The radius-vector and momentum operators*. In the wave mechanics, i.e. in the coordinate representation, the (vector-) operator of particle's radius-vector $\mathbf{r}$ just multiples the wavefunction by this vector, while the operator of particle's momentum[29] is proportional to the spatial derivative:

$$\hat{\mathbf{r}} = \mathbf{r}, \qquad \hat{\mathbf{p}} = -i\hbar\nabla, \tag{1.26a}$$

where ∇ is the *del* (or 'nabla') vector operator[30]. Thus in the Cartesian coordinates,

$$\hat{\mathbf{r}} = \mathbf{r} = \{x,\ y,\ z\}, \qquad \hat{\mathbf{p}} = -i\hbar\left\{\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right\}. \tag{1.26b}$$

(v) *The correspondence principle*. In the limit when quantum effects are insignificant, e.g. when the characteristic scale of action[31] (i.e. the product of the relevant energy and time scales of the problem) is much larger than Planck's constant $\hbar$, all wave mechanics results have to tend to those given by classical mechanics. Mathematically, this correspondence is achieved by duplicating the classical relations between various observables by similar relations between the corresponding operators. For example, for a free particle, the Hamiltonian (which in this particular case corresponds to the kinetic energy $T = p^2/2m$ alone) has the form

[29] For an electrically charged particle in magnetic field, this relation is valid for its *canonical* momentum—see section 3.1 below.

[30] See, e.g. sections 8–10 of the *Selected Mathematical Formulas* appendix (appendix A). Note that according to these formulas, the del operator follows all the geometric rules of the usual vectors. This is, by definition, true for other vector operators of quantum mechanics—to be discussed below.

[31] See, e.g. *Part CM* section 10.3.

$$\hat{H} = \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2. \tag{1.27}$$

Now, even before a deeper discussion of the postulates' physics (offered in the next section), we may immediately see that they indeed provide a formal way toward the resolution of the apparent contradiction between the wave and corpuscular properties of particles. For a free particle, the Schrödinger equation (1.25), with the substitution of Eq. (1.27), takes the form

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi, \tag{1.28}$$

whose particular, but most important solution is a plane, single-frequency ('monochromatic') traveling wave[32],

$$\Psi(\mathbf{r}, t) = ae^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}, \tag{1.29}$$

where a, $\mathbf{k}$ and ω are constants. Indeed, plugging Eq. (1.29) into Eq. (1.28), we immediately see that the plane wave, with an arbitrary amplitude a, is indeed a solution of this Schrödinger equation, provided a specific *dispersion relation* between the wavevector $\mathbf{k}$ and the frequency ω:

$$\hbar\omega = \frac{(\hbar k)^2}{2m}. \tag{1.30}$$

The constant a may be calculated, for example, assuming that the wave (1.29) is extended over a certain volume V, while beyond it, $\Psi = 0$. Then from the normalization condition (1.22*c*) and Eq. (1.29), we get[33]

$$|a|^2 V = 1. \tag{1.31}$$

Now we can use Eqs. (1.23), (1.26) and (1.27) to calculate the expectation values of the particle's momentum $\mathbf{p}$ and energy E (which, for a free particle, coincides with its Hamiltonian function H). The result is

$$\langle\mathbf{p}\rangle = \hbar\mathbf{k}, \quad \langle E\rangle = \langle H\rangle = \frac{(\hbar k)^2}{2m}; \tag{1.32}$$

according to Eq. (1.30), the last equality may be rewritten as $\langle E\rangle = \hbar\omega$.

Next, Eq. (1.23) enables us to calculate not only the average (in the math speak, the *first moment*) of an observable, but also its higher moments, notably the *second moment* (in physics, usually called either the *variance* or *dispersion*):

$$\langle\tilde{A}^2\rangle \equiv \langle(A - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2, \tag{1.33}$$

and hence its root mean square (rms) fluctuation,

[32] See, e.g. *Part CM* section 6.4 and/or *Part EM* section 7.1.

[33] For infinite space ($V \to \infty$), Eq. (1.31) yields $a \to 0$, i.e. wavefunction (1.29) vanishes. This formal problem may be readily resolved considering sufficiently long wave packets—see section 2.2 below.

$$\delta A \equiv \langle \tilde{A}^2 \rangle^{1/2}, \tag{1.34}$$

that characterizes the scale of deviations $\tilde{A} \equiv A - \langle A \rangle$ of measurement results from the average, i.e. the *uncertainty* of the observable A. In the particular case when the uncertainty δA equals zero, every measurement of the observable A will give the value $\langle A \rangle$; such a state is said to have a *definite value* of the variable. For example, in application to the wavefunction (1.29), these relations yield $\delta E = 0$, $\delta \mathbf{p} = 0$. This means that in the plane-wave, monochromatic state (1.29), the energy and momentum of the particle have definite values, so that the statistical average signs in Eqs. (1.32) might be removed. Thus, these relations are reduced to the experimentally-inferred Eqs. (1.5) and (1.15)—though the relation of $\mathbf{k}$ and ω to experimental observations still has to be clarified.

Hence the wave mechanics postulates may indeed explain the observed wave properties of non-relativistic particles. (For photons, we would need a relativistic formalism—see chapter 9 below.) On the other hand, due to the linearity of the Schrödinger equation (1.25), any sum of its solutions is also a solution—the so-called *linear superposition principle*. For a free particle, this means that any set of plane waves (1.29) is also a solution of this equation. Such sets, with close values of $\mathbf{k}$ and hence $\mathbf{p} = \hbar\mathbf{k}$ (and, according to Eq. (1.30), of ω as well), may be used to describe spatially localized 'pulses', called *wave packets*—see figure 1.6. In section 2.1, I will prove (or rather reproduce H Weyl's proof) that the wave packet's extension δx in any direction (say, x) is related to the width δk_x of the distribution of the corresponding component of its wave vector as $\delta x \delta k_x \geqslant ½$, and hence, according to Eq. (1.15), to the width δp_x of the momentum component distribution as

$$\delta x \cdot \delta p_x \geqslant \frac{\hbar}{2}. \tag{1.35}$$

This is the famous *Heisenberg's uncertainty principle*, which quantifies the first postulate's point that the coordinate and the momentum cannot be defined exactly simultaneously. However, since Planck's constant, $\hbar \sim 10^{-34}$ J s, is extremely small on the human scale of things, it still allows for a particle's localization in a very small volume even if the momentum spread in the wave packet is also small on that scale.

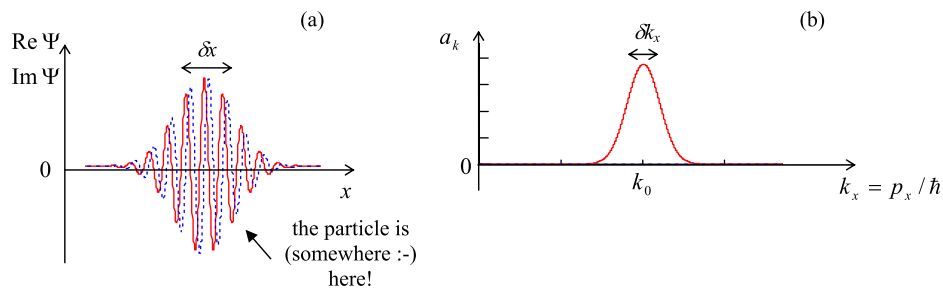

Figure 1.6. (a) A snapshot of a typical wave packet propagating along axis x, and (b) the corresponding distribution of the wave numbers k_x, i.e. the momenta p_x.

For example, according to Eq. (1.35), a 0.1% spread of momentum of a 1 keV electron ($p \sim 1.7 \times 10^{-24}$ kg m s^{-1}) allows its wave packet to be as small as $\sim 3 \times 10^{-10}$ m. (For a heavier particle such as a proton, the packet would be even tighter.) As a result, wave packets may be used to describe the particles that are quite point-like from the macroscopic point of view.

In a nutshell, this is the main idea of the wave mechanics, and the first part of this course (chapters 1–3) will be essentially a discussion of various effects described by this approach. During this discussion, however, we will not only evidence wave mechanics' many triumphs within its applicability domain, but also gradually accumulate evidence for its handicaps, which will force an eventual transfer to a more general formalism—to be discussed in chapter 4 and beyond.

1.3 Postulates' discussion

The wave mechanics' postulates listed in the previous section (hopefully, familiar to reader from his or her undergraduate studies) may look very simple. However, the physics of these axioms is very deep, leading to some counter-intuitive conclusions, and their in-depth discussion requires solutions of several key problems of wave mechanics. This is why in this section I will give only an initial, admittedly superficial discussion of the postulates, and will be repeatedly returning to the conceptual foundations of quantum mechanics throughout the course, especially in chapter 10.

First of all, the fundamental uncertainty of observables, which is in the core of the first postulate, is very foreign to the basic ideas of classical mechanics, and historically has made the quantum mechanics so hard to swallow for many star physicists, notably including A Einstein—despite his 1905 work, which essentially launched the whole field! However, this fact has been confirmed by numerous experiments, and (more importantly) there has not been a single confirmed experiment which would contradict this postulate, so that quantum mechanics was long ago promoted from a theoretical hypothesis to the rank of a reliable scientific theory.

One more remark in this context is that Eq. (1.25) itself is *deterministic*, i.e. conceptually enables an *exact* calculation of the wavefunction's distribution in space at any instant t, provided that its initial distribution, and the particle's Hamiltonian, are known exactly. Note that in the classical statistical mechanics, the probability density distribution $w(\mathbf{r}, t)$ may be also calculated from deterministic differential equations, for example the Liouville equation[34]. The quantum-mechanical description differs from that situation in two important aspects. First, in the perfect conditions outlined above (the exact initial state preparation and the best possible measurements), the Liouville equation reduces to the 2nd Newton law of classical mechanics, i.e. the statistical uncertainty disappears. In quantum mechanics this is not true: the quantum uncertainly, such as described by Eq. (1.35), persists even in this limit. Second, the wavefunction $\Psi(\mathbf{r}, t)$ gives more information than just $w(\mathbf{r}, t)$, because besides the modulus of Ψ, involved in Eq. (1.22), this complex function also

[34] See, e.g. *Part SM* section 6.1.

has the *phase* $\varphi \equiv \arg \Psi$, which may affect some observables, describing, in particular, the interference of the de Broglie waves.

Next, it is very important to understand that the relation between the quantum mechanics and experiment, given by the second postulate, necessarily involves another key notion: that of the corresponding *statistical ensemble*. This ensemble may be defined as a set of many experiments carried out at apparently (*macroscopically*) similar conditions, including the initial conditions, which nevertheless may lead to different measurement results (*outcomes*). Indeed, the probability of a certain (nth) outcome of an experiment may be only defined for a certain ensemble, as the limit

$$W_n \equiv \lim_{M\to\infty} \frac{M_n}{M}, \qquad \text{with } M \equiv \sum_{n=1}^{N} M_n, \tag{1.36}$$

where M is the total number of experiments, M_n is the number of outcomes of the nth type, and N is the number of different outcomes.

Note that a particular choice of an ensemble may affect probabilities W_n very significantly. For example, if we pull out playing cards at random from a standard pack of 52 different cards of 4 suits, the probability W_n of getting a certain card (e.g. the queen of spades) is 1/52. However, if the cards of a certain suit (say, hearts) had been taken out from the pack in advance, the probability of getting the queen of spades is higher, 1/39. It is important that we would also get the last number for the probability even if we had used the full 52 card pack, but by some reason discarded results of all experiments giving us any rank of hearts. Hence, the ensemble definition (or its *re-definition* in the middle of the game) may change outcome probabilities.

In quantum wave mechanics, with its fundamental relation (1.22) between w and Ψ, this means not only the outcome probabilities, but the wavefunction itself also may depend on the statistical ensemble we are using, i.e. not only on the preparation of the system and the experimental setup, but also on the subset of outcomes taken into account. The sometimes accounted attribution of the wavefunction to a single experiment, both before and after the measurement, may lead to very unphysical interpretations of the results, including a wavefunction's evolution not described by the Schrödinger equation (the so-called *wave packet reduct*ion), subluminal action on distance, etc. Later in the course we will see that minding the fundamentally statistical nature of quantum mechanics, and in particular the dependence of wavefunctions on the statistical ensembles' definition (or re-definition), readily resolves some, though not all, paradoxes of quantum measurements.

Note, however, that the standard quantum mechanics, as discussed in chapters 1–6 of this course, is limited to statistical ensembles with *the least uncertainty* of the considered systems, i.e. with best possible knowledge about their state[35]. This condition requires, first, the least uncertain initial preparation of the system, and

[35] The reader should not be surprised by the use of the notion of 'knowledge' (or 'information') in this context. Indeed, due to the statistical character of experiment outcomes, quantum mechanics (or at least its relation to experiment) is intimately related to the information theory. In contrast to much of classical physics, which may be discussed without any reference to information, in quantum mechanics, as in classical statistical physics, such abstraction is possible only in some very special (and not the most interesting) cases.

second, its total isolation from the rest of the world, or at least from its disordered part (the 'environment'), in the course of its evolution in time. Only such ensembles may be described by certain wavefunctions. A detailed discussion of more general ensembles, which are necessary if these conditions are not satisfied, will be given in chapters 7, 8, and 10.

Finally, regarding Eq. (1.23), a better feeling of this definition may be obtained by its comparison with the general definition of the expectation value (i.e. the statistical average) in the probability theory. Namely, let each of N possible outcomes in a set of M experiments give a certain value A_n of observable A; then

$$\langle A \rangle \equiv \lim_{M\to\infty} \frac{1}{M} \sum_{n=1}^{N} A_n M_n = \sum_{n=1}^{N} A_n W_n. \tag{1.37}$$

Taking into account Eq. (1.22), which relates W and Ψ, the structures of Eq. (1.23) and the final form of Eq. (1.37) are similar. Their exact relation will be further discussed in section 4.1.

1.4 Continuity equation

The wave mechanics postulates survive one more sanity check: they satisfy the natural requirement that the particle does not appear or vanish in the course of the quantum evolution[36]. Indeed, let us use Eq. (1.22) to calculate the rate of change of the probability W to find a particle within a certain volume V:

$$\frac{dW}{dt} = \frac{d}{dt} \int_V \Psi\Psi^* d^3r. \tag{1.38}$$

Assuming for simplicity that the boundaries of the volume V do not move, it is sufficient to carry out the partial differentiation of the product $\Psi\Psi^*$ inside the integral. Using the Schrödinger equation (1.25), together with its complex conjugate,

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = (\hat{H}\Psi)^*, \tag{1.39}$$

we readily get

$$\begin{aligned} \frac{dW}{dt} &= \int_V \frac{\partial}{\partial t}(\Psi\Psi^*)\, d^3r \equiv \int_V \left(\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right) d^3r \\ &= \frac{1}{i\hbar} \int_V [\Psi^*(\hat{H}\Psi) - \Psi(\hat{H}\Psi)^*]\, d^3r. \end{aligned} \tag{1.40}$$

Let the particle move in a field of external forces (not necessarily constant in time), so that its classical Hamiltonian function H is the sum of the particle's kinetic

[36] Note that this requirement may be violated in the relativistic quantum theory—see chapter 9.

energy $T = p^2/2m$ and its potential energy $U(\mathbf{r}, t)$.[37] According to the correspondence principle, and Eq. (1.27), the Hamiltonian operator may be represented as the sum[38],

$$\hat{H} = \hat{T} + \hat{U} = \frac{\hat{p}^2}{2m} + U(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}, t). \tag{1.41}$$

At this stage we should notice that this operator, when acting on a real function, returns a real function[39]. Hence, the result of its action on an arbitrary complex function $\Psi = a + ib$ (where a and b are real) is

$$\hat{H}\Psi = \hat{H}(a + ib) = \hat{H}a + i\hat{H}b, \tag{1.42}$$

where $\hat{H}a$ and $\hat{H}b$ are also real, while

$$(\hat{H}\Psi)^* = (\hat{H}a + i\hat{H}b)^* = \hat{H}a - i\hat{H}b = \hat{H}(a - ib) = \hat{H}\Psi^*. \tag{1.43}$$

This means that Eq. (1.40) may be rewritten as

$$\begin{aligned} \frac{dW}{dt} &= \frac{1}{i\hbar}\int_V [\Psi^*\hat{H}\Psi - \Psi\hat{H}\Psi^*]\, d^3r \\ &= -\frac{\hbar^2}{2m}\frac{1}{i\hbar}\int_V [\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*]\, d^3r \end{aligned} \tag{1.44}$$

Now, let us use general rules of vector calculus[40] to write the following identity:

$$\nabla \cdot (\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) = \Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*, \tag{1.45}$$

A comparison of Eqs. (1.44) and (1.45) shows that we may write

$$\frac{dW}{dt} = -\int_V (\nabla \cdot \mathbf{j})\, d^3r, \tag{1.46}$$

where the vector $\mathbf{j}$ is defined as

$$\mathbf{j} \equiv \frac{i\hbar}{2m}(\Psi\nabla\Psi^* - \text{c.c.}) \equiv \frac{\hbar}{m}\text{Im}(\Psi^*\nabla\Psi), \tag{1.47}$$

where c.c. means the complex conjugate of the previous expression—in this case, $(\Psi\nabla\Psi^*)^*$, i.e. $\Psi^*\nabla\Psi$. Now using the well-known divergence theorem[41], Eq. (1.46) may be rewritten as the *continuity equation*

[37] As a reminder, such description is valid not only for conservative forces (in that case U has to be time-independent), but also for any force $\mathbf{F}(\mathbf{r}, t)$ that may be expressed via the gradient of $U(\mathbf{r}, t)$—see, e.g. *Part CM* chapters 2 and 10. (A good example when such a description is *impossible* is given by the magnetic component of the Lorentz force—see, e.g. *Part EM* section 9.7, and also section 3.1 below.)

[38] Historically, this was the main step made (in 1926) by E Schrödinger on the background of L de Broglie's idea. The probabilistic interpretation of the wavefunction was put forward, almost simultaneously, by M Born.

[39] In chapter 4, we will discuss a more general family of *Hermitian operators*, which have this property.

[40] See, e.g. Eq. (A.11.4*a*), combined with the del operator's definition $\nabla^2 \equiv \nabla \cdot \nabla$.

[41] See, e.g. Eq. (A.12.2).

$$\frac{dW}{dt} + I = 0, \quad \text{with } I \equiv \int_S j_n d^2r, \tag{1.48}$$

where j_n is the component of the vector $\mathbf{j}$ along the outwardly directed normal to the closed surface S that limits volume V, i.e. the scalar product $\mathbf{j} \cdot \mathbf{n}$, where $\mathbf{n}$ is the unit vector along this normal.

Eqs (1.47) and (1.48) show that if the wavefunction on the surface vanishes, the total probability W of finding the particle within the volume does not change, providing the required sanity check. In the general case, Eq. (1.48) says that dW/dt equals the flux I of the vector $\mathbf{j}$ through the surface, with the minus sign. It is clear that this vector may be interpreted as the *probability current density*—and I, as the total *probability current* through the surface S. This interpretation may be further supported by rewriting Eq. (1.47) for the wavefunction represented in the polar form $\Psi = ae^{i\varphi}$, with real a and φ:

$$\mathbf{j} = a^2 \frac{\hbar}{m} \nabla \phi. \tag{1.49}$$

Note that for a real wavefunction, or even for a wavefunction with an arbitrary but space-constant phase φ, the probability current density vanishes. In contrast, for the traveling wave (1.29), with a constant probability density $w = a^2$, Eq. (1.49) yields a non-zero (and physically very transparent) result:

$$\mathbf{j} = w\frac{\hbar}{m}\mathbf{k} = w\frac{\mathbf{p}}{m} = w\mathbf{v}, \tag{1.50}$$

where $\mathbf{v} = \mathbf{p}/m$ is particle's velocity. If multiplied by the particle's mass m, the probability density w turns into the (average) mass density ρ, and the probability current density—into the *mass flux density* $\rho\mathbf{v}$. Similarly, if multiplied by the total electric charge q of the particle, with w turning into the *charge density* σ, $\mathbf{j}$ becomes the electric current density. As the reader (hopefully :-) knows, both currents satisfy classical continuity equations similar to Eq. (1.48)[42].

Finally, let us recast the continuity equation, rewriting Eq. (1.46) as

$$\int_V \left(\frac{\partial w}{\partial t} + \nabla \cdot \mathbf{j} \right) d^3r = 0. \tag{1.51}$$

Now we may argue that this equality may be true for any choice of volume V only if the expression under the integral vanishes everywhere, i.e. if

$$\frac{\partial w}{\partial t} + \nabla \cdot \mathbf{j} = 0. \tag{1.52}$$

This differential form of the continuity equation may be more convenient than its integral form (1.48).

[42] See, e.g. respectively, *Part CM* section 8.3 and *Part EM* section 4.1.

1.5 Eigenstates and eigenvalues

Now let us discuss the most important corollaries of wave mechanics' *linearity*. First of all, it uses only *linear operators*. This term means that the operators must obey the following two rules[43]:

$$(\hat{A}_1 + \hat{A}_2)\,\Psi = \hat{A}_1\Psi + \hat{A}_2\Psi, \tag{1.53}$$

$$\hat{A}(c_1\Psi_1 + c_2\Psi_2) = \hat{A}(c_1\Psi_1) + \hat{A}(c_2\Psi_2) = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2, \tag{1.54}$$

where Ψ_n are arbitrary wavefunctions, while c_n are arbitrary constants (in quantum mechanics, frequently called *c-numbers*, to distinguish them from operators and wavefunctions). The most important examples of linear operators are given by:

(i) the multiplication by a function, such as for the operator $\hat{\mathbf{r}}$ given by Eq. (1.26), and

(ii) the spatial or temporal differentiation of the wavefunction, such as in Eqs. (1.25)–(1.27).

Next, it is of key importance that the Schrödinger equation (1.25) is also linear. (We have already used this fact when we discussed wave packets in the last section.) This means that if each of several functions Ψ_n are (particular) solutions of Eq. (1.25) with a certain Hamiltonian, then their arbitrary linear combination

$$\Psi = \sum_n c_n\Psi_n \tag{1.55}$$

is also a solution of the same equation[44].

Let us use this linearity to accomplish an apparently impossible feat: immediately find the *general* solution of the Schrödinger equation for the most important case when system's Hamiltonian does not depend on time explicitly—for example, like in Eq. (1.41) with time-independent potential energy $U = U(\mathbf{r})$, when the Schrödinger equation has the form

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi. \tag{1.56}$$

First of all, let us prove that the following product,

$$\Psi_n = a_n(t)\psi_n(\mathbf{r}), \tag{1.57}$$

[43] By the way, if any equality involving operators is valid for an arbitrary wavefunction, the latter is frequently dropped from notation, resulting in an *operator equality*. In particular, Eq. (1.53) may be readily used to prove that the operators are *commutative*: $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$, and *associative*: $(\hat{A}_1 + \hat{A}_2) + \hat{A}_3 = \hat{A}_1 + (\hat{A}_2 + \hat{A}_3)$.

[44] At first glance, it may seem strange that the *linear* Schrödinger equation correctly describes quantum properties of systems whose classical dynamics is described by *nonlinear* equations of motion (e.g. an anharmonic oscillator —see, e.g. *Part CM* section 5.2). Note, however, that statistical equations of classical dynamics (see, e.g. *Part SM* chapters 5 and 6) also have this property, so it is not specific to quantum mechanics.

qualifies as a (particular) solution of such an equation. Indeed, plugging Eq. (1.56) into Eq. (1.25) with any time-independent Hamiltonian, using the fact that in this case

$$\hat{H}a_n(t)\psi_n(\mathbf{r}) = a_n(t)\hat{H}\psi_n(\mathbf{r}), \tag{1.58}$$

and dividing both parts of the equation by $a_n\psi_n$, we get

$$\frac{i\hbar}{a_n}\frac{da_n}{dt} = \frac{\hat{H}\psi_n}{\psi_n}. \tag{1.59}$$

The left-hand side of this equation may depend only on time, while the right hand one depends only on coordinates. These facts may be only reconciled if we assume that each of these parts is equal to (the same) constant of the dimension of energy, which I will denote as E_n.[45] As a result, we are getting two separate equations for the temporal and spatial parts of the wavefunction:

$$\hat{H}\psi_n = E_n\psi_n, \tag{1.60}$$

$$i\hbar\frac{da_n}{dt} = E_n a_n. \tag{1.61a}$$

The latter of these equations, rewritten in the form

$$\frac{da_n}{a_n} = -i\frac{E_n}{\hbar}dt, \tag{1.61b}$$

is readily integrable, giving

$$\ln a_n = -i\omega_n t + \text{const}, \quad \text{so that } a_n = \text{const} \times \exp\{-i\omega_n t\}, \quad \text{with } \omega_n \equiv \frac{E_n}{\hbar}. \tag{1.62}$$

Now plugging Eqs. (1.57) and (1.62) into Eq. (1.22), we see that in the quantum state described by Eqs. (1.57)–(1.62), the probability w of finding the particle at a certain location does not depend on time:

$$w \equiv \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}) = w(\mathbf{r}). \tag{1.63}$$

With the same substitution, Eq. (1.23) shows that the expectation value of any operator that does not depend on time explicitly is also time-independent:

$$\langle A \rangle \equiv \int \psi_n^*(\mathbf{r})\hat{A}\psi_n(\mathbf{r})d^3r = \text{const}. \tag{1.64}$$

[45] This argumentation, leading to *variable separation*, is very common in mathematical physics—see, e.g. its discussion in *Part CM* section 6.5 and *Part EM* section 2.5 and beyond.

Due to this property, the states described by Eqs. (1.57)–(1.62), are called *stationary*; they are fully defined by the possible solutions (called *eigenfunctions*[46]) of the *stationary* (or 'time-independent') *Schrödinger* equation (1.60).[47]

Note that for the time-independent Hamiltonian (1.41), the stationary Schrödinger equation (1.60),

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + U(\mathbf{r})\psi_n = E_n\psi_n, \tag{1.65}$$

is a linear, homogeneous differential equation for the function ψ_n, with *a priory* unknown parameter E_n. Such equations fall into the mathematical category of *eigenproblems*, in which the eigenfunctions ψ_n and *eigenvalues* E_n should be found simultaneously, i.e. self-consistently[48]. Mathematics tells us that for the such equations with space-confined eigenfunctions ψ_n, tending to zero at $r \to \infty$, the spectrum of eigenvalues is *discrete*. It also proves that the eigenfunctions corresponding to different eigenvalues are *orthogonal,* i.e. that space integrals of the products $\psi_n\psi_{n'}^*$ vanish for all pairs with $n \neq n'$. Due to the Schrödinger equation's linearity, each of these functions may be multiplied by a proper constant coefficient to make their set *orthonormal*:

$$\int \psi_n^*\psi_{n'}d^3r = \delta_{n,n'} \equiv \begin{cases} 1, & \text{if } n = n', \\ 0, & \text{if } n \neq n'. \end{cases} \tag{1.66}$$

Moreover, the eigenfunctions $\psi_n(\mathbf{r})$ form a *full set*, meaning that an arbitrary function $\psi(\mathbf{r})$, in particular the actual wavefunction Ψ of the system in the initial moment of its evolution (which I will take for $t = 0$, with a few exceptions), may be represented as a unique expansion over the eigenfunction set[49]:

$$\Psi(\mathbf{r}, 0) = \sum_n c_n\psi_n(\mathbf{r}). \tag{1.67}$$

The expansion coefficients c_n may be readily found by multiplying both parts of Eq. (1.67) by $\psi_{n'}^*$, integrating the result over the space, and using Eq. (1.66). The result is

$$c_n = \int \psi_n^*(\mathbf{r})\Psi(\mathbf{r}, 0)d^3r. \tag{1.68}$$

Now let us consider the following wavefunction

$$\Psi(\mathbf{r}, t) = \sum_n c_n a_k(t)\psi_k(\mathbf{r}) = \sum_n c_n \exp\left\{-i\frac{E_n}{\hbar}t\right\}\psi_n(\mathbf{r}). \tag{1.69}$$

[46] From the German root *eigen*, meaning 'particular' or 'characteristic'.
[47] For contrast, the full *Schrödinger* equation (1.25) is frequently called *time-dependent* or *non-stationary*.
[48] Eigenvalues of energy are frequently called *eigenenergies*, and it is often said that eigenfunction ψ_n and *eigenenergy* E_n together characterize the *n*th *stationary eigenstate* of the system.
[49] If the reader has any doubt in these properties of linear, homogeneous differential equations, I may recommend reviewing section 9.3 of the wonderful handbook by G Korn and T Korn, listed in section A.16 (ii).

Since each term of the sum has the form (1.57) and satisfies the Schrödinger equation, so does the sum as the whole. Moreover, if the coefficients c_n are derived in accordance with Eq. (1.68), then the solution (1.69) satisfies the initial conditions as well. At this moment we can use one more bit of help from mathematicians, who tell us that the linear, partial differential equation of type (1.65), with fixed initial conditions, may have only one (*unique*) solution. This means that in our case of motion in a time-independent potential Hamiltonian, Eq. (1.69) gives the *general* solution of the Schrödinger equation (1.65).

So, we have succeeded in our apparently over-ambitious goal. Now let us stop this mad mathematical dash for a minute, and discuss this key result.

1.6 Time evolution

For the time-dependent factor, $a_n(t)$, of each component state (1.57) of the general solution (1.69), our procedure gave a very simple and universal result (1.62), describing a linear change of the phase $\varphi_n \equiv \arg(a_n)$ of this complex function in time, with the constant rate

$$\frac{d\varphi_n}{dt} = -\omega_n = -\frac{E_n}{\hbar}, \tag{1.70}$$

so that the real and imaginary parts of a_n oscillate sinusoidally with this frequency. The relation (1.70) coincides with the Einstein's conjecture (1.5) for photons, but could these oscillations of the wavefunctions represent a physical reality? Indeed, for photons, described by Eq. (1.5), E may be (and as we will see in chapter 9, is) the actual, well-defined energy of one photon, and ω is the frequency of the radiation so quantized. However, for non-relativistic particles, described by wave mechanics, the potential energy U, and hence the full energy E, are defined to an arbitrary constant, because we may measure them from an arbitrary reference level. How can such a change of the energy reference level (which may be made just in our mind) alter the frequency of oscillations of a variable?

According to Eqs. (1.22) and (1.23), this time evolution of a wavefunction does not affect the particle's probability distribution, or even any observable (including the energy E, provided that it is always referred to the same origin as U), in any stationary state. However, as will be proved later in the course using the combination of Einstein's formula (1.5) with Bohr's assumption (1.7),

$$\hbar\omega_{nn'} = E_{n'} - E_n, \tag{1.71}$$

the *difference* of the eigenfrequencies ω_n (evidently, independent on the energy reference) of two eigenstates is absolutely physical, because it determines the measurable frequency of the electromagnetic radiation (or possibly a wave of a different physical nature) emitted or absorbed at the quantum transition between the states.

As one more example, consider two similar, independent particles 1 and 2, each in the same (say, the lowest, *ground*) eigenstate, but with the potential energies (and

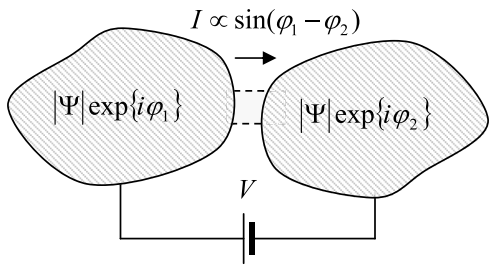

Figure 1.7. The Josephson effect in a weak link between two bulk superconductor electrodes.

hence the ground state energies $E_{1,2}$) different by a constant $\Delta U \equiv U_1 - U_2$. Then, according to Eq. (1.70), the difference $\varphi \equiv \varphi_1 - \varphi_2$ of their wavefunction phases evolves in time with a reference-independent rate

$$\frac{d\varphi}{dt} = -\frac{\Delta U}{\hbar}. \tag{1.72}$$

Certain measurement instruments, weakly coupled to each particle, may allow an observation of this evolution, while keeping the particle's quantum dynamics virtually unperturbed, i.e. Eq. (1.70) intact. Perhaps the most dramatic measurement of this type is possible using the *Josephson effect* in weak links between two superconductors—see figure 1.7.

As a brief reminder[50], superconductivity may be explained by a specific coupling between conduction electrons in solids, that leads, at low temperatures, to the formation of the so-called *Cooper pairs*. Such pairs, each consisting of two electrons with opposite spins and momenta, behave as Bose particles, and form a coherent *Bose–Einstein condensate*[51]. Most properties of such a condensate may be described by a single, common wavefunction Ψ, evolving in time just as that of a free particle, with the effective potential energy $U = q\phi = -2e\phi$, where ϕ is the electrochemical potential[52], and $q = -2e$ is the electric charge of a Cooper pair. As a result, for the system shown in figure 1.7, in which an externally applied voltage V fixes the difference $\phi_1 - \phi_2$ between the electrochemical potentials of two bulk superconductors, Eq. (1.72) takes the form

$$\frac{d\varphi}{dt} = \frac{2e}{\hbar} V, \tag{1.73}$$

where $V = \phi_1 - \phi_2$ is the applied voltage. If the link between the superconductors is weak enough, the electric current I of the Cooper pairs (called the *supercurrent*) through the link may be approximately described by the following simple relation[53],

[50] For a more detailed discussion, including the derivation of Eq. (1.74), see, e.g. *Part EM* section 6.5.
[51] A detailed discussion of the Bose–Einstein condensation may be found, e.g. in *Part SM* section 3.4.
[52] For more on this notion see, e.g. *Part SM* section 6.3.
[53] In some cases, the function $I(\varphi)$ may somewhat deviate from Eq. (1.74), but these deviations do not affect its fundamental 2π-periodicity. As a result, no corrections to the fundamental relations (1.75)–(1.76) have ever been found (yet :-).

$$I = I_c \sin \varphi, \tag{1.74}$$

where I_c is some constant, dependent on the weak link's strength. Now combining Eqs. (1.73) and (1.74), we see that if the applied voltage V is constant in time, the current oscillates sinusoidally, with the so-called *Josephson frequency*

$$\omega_J \equiv \frac{2e}{\hbar} V, \tag{1.75}$$

as high as ~484 MHz per each microvolt of applied dc voltage. This effect may be readily observed experimentally: though its direct detection is a bit tricky, it is easy to observe the *phase locking* (synchronization)[54] of the Josephson oscillations by an external microwave signal of frequency ω. Such phase locking results in the relation $\omega_J = n\omega$ fulfilled within certain current intervals, and hence in the formation, on the weak-link's dc I–V curve, of virtually vertical current steps at dc voltages

$$V_n = n\frac{\hbar\omega}{2e}, \tag{1.76}$$

where n is an integer[55]. Since frequencies may be stabilized and measured with very high precision, this effect is being used in highly accurate standards of dc voltage.

1.7 Spatial dependence

In contrast to the simple and universal time dependence (1.62) of the stationary states, the spatial distributions of their wavefunction $\psi_n(\mathbf{r})$ need to be calculated from the problem-specific stationary Schrödinger equation (1.65). The solution of this equation for various particular cases is a major focus of the next two chapters. For now, let us consider just the simplest example, which nevertheless will be the basis for our discussion of more complex problems, namely a particle confined inside a rectangular hard-wall box. Such confinement may be described by the following potential energy[56]:

$$U(\mathbf{r}) = \begin{cases} 0, & \text{for } 0 < x < a_x,\ 0 < y < a_y,\ \text{and } 0 < z < a_z, \\ +\infty, & \text{otherwise.} \end{cases} \tag{1.77}$$

The only way to keep the product $U(\mathbf{r})\psi_n$ in Eq. (1.65) finite outside the box, is to have $\psi = 0$ in these regions. Also, the function have to be continuous everywhere, to avoid the divergence of its Laplace operator—which would give an unphysical

[54] For the discussion of this general effect, see, e.g. *Part CM* section 5.4.

[55] If ω is not too high, the size of these current steps may be calculated from Eqs. (1.73) and (1.74). Let me leave this task for the reader's exercise.

[56] Another common name for such potentials, especially of lower dimensionality, is the *potential well*, in our current case with a flat 'bottom', and infinitely high 'walls'. Note that sometimes, very unfortunately, such potential profiles are called 'quantum wells'. (This term seems to imply that the particle's confinement in such a well is a phenomenon specific for quantum mechanics. However, as we will repeatedly see in this course, the opposite is true: quantum effects do as much as they can to overcome the particle's confinement in a potential well, letting it partly penetrate the 'classically forbidden' regions beyond the well's walls.)

divergence of its kinetic energy (1.27). Hence, we may solve the stationary Schrödinger equation (1.60) just inside the box, i.e. with $U = 0$, so that it takes a simple form[57]

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n = E_n\psi_n, \tag{1.78a}$$

with zero boundary conditions on all the walls. For our particular geometry, it is natural to express the Laplace operator in the Cartesian coordinates $\{x, y, z\}$ aligned with the box sides, with the origin at one of the corners of its rectangular $a_x \times a_y \times a_z$ volume, so that we get the following boundary problem:

$$\begin{gathered} -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_n = E_n\psi_n, \\ \text{for } 0 < x < a_x,\ 0 < y < a_y, \text{ and } 0 < z < a_z, \\ \text{with } \psi_n = 0 \text{ for: } x = 0 \text{ and } a_x;\ y = 0 \text{ and } a_y;\ z = 0 \text{ and } a_z. \end{gathered} \tag{1.78b}$$

This problem may be readily solved using the same variable separation method as in section 1.5, now to separate the Cartesian spatial variables from each other, by looking for a partial solution of Eq. (1.78) in the form

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z). \tag{1.79}$$

(It is convenient to postpone taking care of the proper indices for a minute.) Plugging this expression into Eq. (1.78*b*) and dividing all terms by the product XYZ, we get

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} - \frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} - \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} = E. \tag{1.80}$$

Now let us repeat the standard argumentation of the variable separation method: since each term on the left-hand side of this equation may be only a function of the corresponding argument, the equality is possible only if each of them is a constant—in our case, with the dimensionality of energy. Calling these constants E_x, etc, we get three similar 1D equations

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} = E_x, \qquad -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} = E_y, \qquad -\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dx^2} = E_z, \tag{1.81}$$

with Eq. (1.80) turning into the following energy-matching condition:

$$E_x + E_y + E_z = E. \tag{1.82}$$

[57] Rewritten as $\nabla^2 f + k^2 f = 0$, this is just the *Helmholtz equation*, which describes waves of any nature (with the wave vector $\mathbf{k}$) in a uniform, isotropic, linear medium—see, e.g. *Part EM* sections 7.5–7.9 and 8.5.

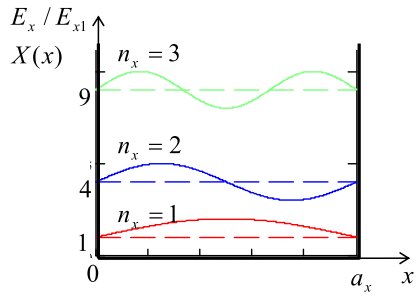

Figure 1.8. The lowest eigenfunctions (solid lines) and eigenvalues (dashed lines) of Eq. (1.83) for a potential well of length a_x. Solid black lines show the effective potential energy profile for the 1D eigenproblem (1.83).

All three ordinary differential equation (1.81), and their solutions, are similar. For example, for $X(x)$, we have a 1D Helmholtz equation

$$\frac{d^2X}{dx^2} + k_x^2 X = 0, \quad \text{with } k_x^2 \equiv \frac{2mE_x}{\hbar^2}, \tag{1.83}$$

and simple boundary conditions: $X(0) = X(a_x) = 0$. Let me hope that the reader knows how to solve this well-known 1D boundary problem—describing, for example, the usual mechanical waves on a guitar string. The problem allows an infinite number of sinusoidal standing-wave eigenfunctions[58],

$$\begin{gathered} X \propto \sin k_x x, \qquad \text{with } k_x = \frac{\pi n_x}{a_x}, \\ \text{so that } X = \left(\frac{2}{a_x}\right)^{1/2} \sin \frac{\pi n_x x}{a_x}, \qquad \text{with } n_x = 1, 2, \ldots, \end{gathered} \tag{1.84}$$

corresponding to the eigenvalues $k_x = \pi n_x / a_x$, and hence the following eigenenergies:

$$E_x = \frac{\hbar^2}{2m} k_x^2 = \frac{\pi^2 \hbar^2}{2ma_x^2} n_x^2 \equiv E_{x1} n_x^2. \tag{1.85}$$

Figure 1.8 shows these simple results, using a somewhat odd but very graphic and hence common way, where the eigenenergy values (frequently called the *energy levels*) are used as horizontal axes for plotting the eigenfunctions, despite their completely different dimensionality.

Due to the similarity of all Eqs. (1.81), $Y(y)$ and $Z(z)$ are absolutely similar functions of their arguments, and may also be numbered by integers (say, n_y and n_z) independent of n_x, so that the spectrum of values of the total energy (1.82) is

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right). \tag{1.86}$$

[58] The front coefficient in the last expression for X ensures the (ortho)normality condition (1.66).

Thus, in this 3D problem, the role of index n in the general Eq. (1.69) is played by a set of 3 independent integers $\{n_x, n_y, n_z\}$. In quantum mechanics, such integers play a key role, and thus have a special name, the *quantum numbers*. Using them, the general solution of our simple problem may be represented as the sum

$$\Psi(\mathbf{r}, t) = \sum_{n_x, n_y, n_z = 1}^{\infty} c_{n_x, n_y, n_z} \sin \frac{\pi n_x x}{a_x} \sin \frac{\pi n_y y}{a_y} \sin \frac{\pi n_z z}{a_z} \exp\left\{-i \frac{E_{n_x, n_y, n_z}}{\hbar} t\right\}, \tag{1.87}$$

with the front coefficients that may be readily calculated from the initial wavefunction $\Psi(\mathbf{r}, 0)$, using Eq. (1.68)—again with the replacement $n \to \{n_x, n_y, n_z\}$. This simplest problem is a good illustration of typical results the wave mechanics gives for spatially-confined motion, including the discrete energy spectrum, and (in this case, evidently) orthogonal eigenfunctions. Perhaps most importantly, its solution shows that the lowest value of the particle's kinetic energy, reached in the so-called *ground state* (in our case, the state with $n_x = n_y = n_z = 1$) is above zero.

An example of the opposite case of a *continuous spectrum* for *unconfined motion* of a free particle is given by the plane waves (1.29). With the account of relations $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$, this wavefunction may be viewed as the product of the time-dependent factor (1.62) by the eigenfunction,

$$\psi_{\mathbf{k}} = a_{\mathbf{k}} \exp\{i\mathbf{k} \cdot \mathbf{r}\}, \tag{1.88}$$

which is the solution of the stationary Schrödinger equation (1.78*a*) if it is valid in the whole space[59]. The reader should not be worried too much by the fact that the fundamental solution (1.86) in free space is a *traveling* wave (having, in particular, a nonvanishing value of the probability current $\mathbf{j}$), while those inside a quantum box are *standing* waves, with $\mathbf{j} = 0$, even though the free space may be legitimately considered as the ultimate limit of a quantum box with volume $V = a_x \times a_y \times a_z \to \infty$. Indeed, due to the linearity of wave mechanics, two traveling-wave solutions (1.88) with equal and opposite values of the momentum (and hence with the same energy) may be readily combined to give a standing-wave solution, for example, $\exp\{i\mathbf{k} \cdot \mathbf{r}\} + \exp\{-i\mathbf{k} \cdot \mathbf{r}\} = 2\cos(\mathbf{k}\cdot\mathbf{r})$, with the net current $\mathbf{j} = 0$.[60] Thus, depending on convenience for solution of a particular problem, we can represent the general solution as a sum of either traveling-wave or standing-wave eigenfunctions.

Since in the unlimited free space there are no boundary conditions to satisfy, the Cartesian components of the wave vector $\mathbf{k}$ in Eq. (1.88) can take any real values. (This is why it is more convenient to label these wavefunctions, and the corresponding eigenenergies,

[59] In some systems (e.g. a particle interacting with a potential well of a finite depth), a discrete energy spectrum within a certain interval of energies may coexist with a continuous spectrum in a complementary interval. However, the conceptual philosophy of eigenfunctions and eigenvalues remains the same in this case as well.

[60] This is, of course, the general property of waves of any physical nature, propagating in a linear medium—see, e.g. *Part CM* section 6.5 and/or *Part EM* section 7.3.

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \geqslant 0, \tag{1.89}$$

with their wave vector **k** rather than an integer index.) However, one aspect of continuous-spectrum systems requires a bit more math caution: the summation (1.69) should be replaced by the integration over a continuous index or indices—in our current case, three Cartesian components of the vector **k**. The main rule of such replacement may be readily extracted from Eq. (1.84): according to this relation, for standing-wave solutions, the eigenvalues of k_x are *equidistant*, i.e. separated by equal intervals $\Delta k_x = \pi/a_x$ (with the similar relations for other two Cartesian components of vector **k**). Hence the number of different eigenvalues of the standing wave vector **k** (with k_x, k_y, $k_z \geqslant 0$), within a volume $d^3k \gg 1/V$ of the **k** space is $dN = d^3k/(\Delta k_x \Delta k_x \Delta k_x) = (V/\pi^3)d^3k$. Since in the continuum it is more convenient to work with traveling waves (1.88), we should take into account that, as was just discussed, there are two different traveling wave numbers (say, $+k_x$ and $-k_x$) corresponding to each standing wave vector's $k_x > 0$. Hence the same number of physically different states corresponds to a $2^3 = 8$ fold larger **k** space (which now is infinite in all directions) or, equivalently, to an 8-fold smaller number of states per unit volume d^3k:

$$dN = \frac{V}{(2\pi)^3} d^3k. \tag{1.90}$$

For $dN \gg 1$, this expression is independent on the boundary conditions, and is frequently represented as the following *summation rule*

$$\lim_{k^3 V \to \infty} \sum_{\mathbf{k}} f(\mathbf{k}) = \int f(\mathbf{k}) dN = \frac{V}{(2\pi)^3} \int f(\mathbf{k}) d^3k, \tag{1.91}$$

where $f(\mathbf{k})$ is an arbitrary function of **k**. Note that if the same wave vector **k** corresponds to several internal quantum states (such as spin—see chapter 4), the right-hand side of Eq. (1.91) requires its multiplication by the corresponding *degeneracy factor*.

1.8 Dimensionality reduction

To conclude this introductory chapter, let me discuss the conditions when the spatial dimensionality of a wave mechanics problem may be reduced[61]. Naively, one may think that if the particle's potential energy depends on just one spatial coordinate, say $U = U(x, t)$, then its wavefunction has to be one-dimensional as well: $\psi = \psi(x, t)$. Our discussion of the particular case $U = \text{const}$ in the previous section shows that this assumption is wrong. Indeed, though this potential is just a special case of the potential $U(x, t)$, most of its eigenfunctions, given by Eqs. (1.87) or (1.88), do depend on other two coordinates. This is why the solutions $\psi(x, t)$ of the 1D Schrödinger equation

[61] Many textbooks on quantum mechanics jump to the formal solution of 1D problems without such discussion, and most of my beginning graduate students did not understand that in realistic physical systems, such dimensionality restriction is adequate only under very specific conditions.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + U(x,\,t)\Psi, \tag{1.92}$$

which follows from Eq. (1.65) by assuming $\partial\Psi/\partial y = \partial\Psi/\partial z = 0$, are insufficient to form the general solution of Eq. (1.65) for this case.

This fact is easy to understand physically for the simplest case of a stationary 1D potential: $U = U(x)$. The absence of the y- and z-dependence of the potential energy U may be interpreted as a potential well which is flat in two directions, y and z. Replicating the arguments of the previous section for this case, we see that the eigenfunctions of a particle in such a well have the form

$$\psi(\mathbf{r}) = X(x)\exp\left\{i\left(k_y y + k_z z\right)\right\}, \tag{1.93}$$

where $X(x)$ are the eigenfunction of the following stationary 1D Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} + U_{\text{ef}}(x)X = EX, \tag{1.94}$$

where $U_{\text{ef}}(x)$ is not the full potential energy of the particle, as would follow from Eq. (1.92), but rather its effective value including the kinetic energy of lateral motion:

$$U_{\text{ef}} \equiv U + \left(E_y + E_z\right) = U + \frac{\hbar^2}{2m}\left(k_y^2 + k_z^2\right). \tag{1.95}$$

In plain English, the particle's partial wavefunction $X(x)$, and its full energy, depends of its transverse momenta, which have continuous spectrum—see the discussion of Eq. (1.89). This means that Eq. (1.92) is adequate only if the condition $k_y = k_z = 0$ is somehow enforced, and in most physical problems, it is not. For example, if a de Broglie (or any other) plane wave $\Psi(x,\,t)$ is incident on a potential step, it would be reflected exactly back, i.e. with $k_y = k_z = 0$, only if the wall's surface is a perfect plane and exactly normal to the axis x. Any imperfection (and there are so many of them in real physical systems -:) may cause excitation of waves with nonvanishing values of k_y and k_z, due the continuous character of the functions $E_y(k_y)$ and $E_z(k_z)$.[62]

There is essentially one, perhaps counter-intuitive way to make the 1D solutions 'robust' to small perturbations: that is to provide a *rigid lateral confinement*[63] in two other directions. As the simplest example, consider a narrow *quantum wire* (figure 1.9a), provided by the potential

[62] This problem is not specific for quantum mechanics. The classical motion of a particle in a 1D potential may be also unstable with respect to lateral perturbations, especially is the potential is time-dependent, i.e. capable of exciting low-energy lateral modes.

[63] The term 'quantum confinement', sometimes used to describe this phenomenon, is as unfortunate as the 'quantum well', because of the same reason: the confinement is a purely classical effect, and as we will repeatedly see in this course, the quantum mechanical effects reduce, rather than enable it.

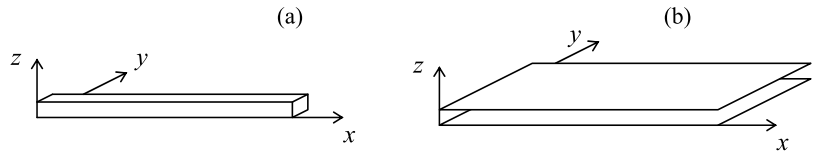

Figure 1.9. Partial confinement in: (a) two dimensions, and (b) one dimensions.

$$U(\mathbf{r}) = \begin{cases} U(x), & \text{for } 0 < y < a_y, \text{ and } 0 < z < a_z, \\ +\infty, & \text{otherwize.} \end{cases} \tag{1.96}$$

Performing the standard variable separation (1.79), we see that the corresponding stationary Schrödinger equation is satisfied if the partial wavefunction $X(x)$ obeys Eqs. (1.94)–(1.95), but now with a discrete energy spectrum in the transverse directions:

$$U_{\text{ef}} = U + \frac{\pi^2\hbar^2}{2m}\left(\frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2}\right). \tag{1.97}$$

If the lateral confinement is tight, a_y, $a_z \to 0$, then there is a large energy gap,

$$\Delta U \sim \frac{\pi^2\hbar^2}{2ma_{y,\,z}^2}, \tag{1.98}$$

between the ground-state energy of the lateral motion (with $n_y = n_z = 1$) and that for all its excited states. As a result, if the particle is initially placed into the lateral ground state, and its energy E is much smaller than ΔU, it would stay in this state, i.e. it may be described by a 1D Schrödinger equation similar to Eq. (1.92)—even in the time-dependent case, if the characteristic frequency of energy variations is much smaller than $\Delta U/\hbar$. Absolutely similarly, the strong lateral confinement in just one dimension (say, z, see figure 1.9b) enables systems with a robust 2D evolution of the particle's wavefunction.

The tight lateral confinement may ensure the dimensionality reduction even if the potential well is not exactly rectangular in the lateral direction(s), as described by Eq. (1.96), but is described by some x- and t-independent profile, if it still provides a sufficiently large energy gap ΔU. For example, many 2D quantum phenomena, such as the quantum Hall effect[64], have been studied experimentally using electrons confined at semiconductor heterojunctions (e.g. epitaxial interfaces GaAs/$Al_xGa_{1-x}As$), where the potential well in the direction perpendicular to the interface has a nearly triangular shape, and provides the energy gap ΔU of the order of 10^{-2} eV.[65] This splitting energy corresponds to k_BT with $T \sim 100$ K, so that careful experimentation at liquid helium temperatures (4 K and below) may keep the electrons performing purely 2D motion in the 'lowest subband' ($n_z = 1$).

[64] To be discussed in section 3.2.
[65] See, e.g. [6].

Finally, note that in systems with a reduced dimensionality, Eq. (1.90) for the number of states at large **k** (i.e. for an essentially free particle motion) should be replaced accordingly: in a 2D system of area $A \gg 1/k^2$,

$$dN = \frac{A}{(2\pi)^2} d^2k, \tag{1.99}$$

while in a 1D system of length $l \gg 1/k$,

$$dN = \frac{l}{2\pi} dk, \tag{1.100}$$

with the corresponding changes of the summation rule (1.91). This change has important implications for the density of states on the energy scale, dN/dE: it is straightforward (and hence left for the reader) to use Eqs. (1.90), (1.99), and (1.100) to show that for free 3D particles the density increases with E (proportionally to $E^{1/2}$), for free 2D particles it does not depend on energy at all, while for free 1D particles it scales as $E^{-1/2}$, i.e. decreases with energy.

1.9 Problems

Problem 1.1. The actual postulate made by N Bohr in his original 1913 paper was not directly Eq. (1.8), but an assumption that at quantum leaps between adjacent large (quasiclassical) orbits with $n \gg 1$, the hydrogen atom either emits or absorbs energy $\Delta E = \hbar\omega$, where ω is its classical radiation frequency—according to classical electrodynamics, equal to the angular velocity of electron's rotation[66]. Prove that this postulate is indeed compatible with Eqs. (1.7) and (1.8).

Problem 1.2. Use Eq. (1.53) to prove that the linear operators of quantum mechanics are commutative: $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$, and associative: $(\hat{A}_1 + \hat{A}_2) + \hat{A}_3 = \hat{A}_1 + (\hat{A}_2 + \hat{A}_3)$.

Problem 1.3. Prove that for any time-independent Hamiltonian operator $\hat{H}$ and two arbitrary complex functions $f(\mathbf{r})$ and $g(\mathbf{r})$,

$$\int f(\mathbf{r})\hat{H}g(\mathbf{r})\, d^3r = \int \hat{H}f(\mathbf{r})g(\mathbf{r})\, d^3r.$$

Problem 1.4. Prove that the Schrödinger equation (1.25) with the Hamiltonian operator given by Eq. (1.41), is Galilean form-invariant, provided that the wave-function is transformed as

$$\Psi'(\mathbf{r}', t') = \Psi(\mathbf{r}, t) \exp\left\{-i\frac{m\mathbf{v}\cdot\mathbf{r}}{\hbar} + i\frac{mv^2 t}{2\hbar}\right\},$$

where the prime sign denotes the variables measured in the reference frame 0′ that moves, without rotation, with a constant velocity **v** relatively to the 'lab' frame 0. Give a physical interpretation of this transformation.

[66] See, e.g. *Part EM* section 8.2.

Problem 1.5.* Prove the so-called *Hellmann–Feynman theorem*[67]:

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_n ,$$

where λ is some c-number parameter, on which the time-independent Hamiltonian $\hat{H}$, and hence its eigenenergies E_n, depend.

Problem 1.6.* Use Eqs. (1.73) and (1.74) to analyze the effect of phase locking of Josephson oscillations on the dc current flowing through a weak link between two superconductors (frequently called the *Josephson junction*), assuming that an external microwave source applies to the junction a sinusoidal ac voltage with frequency ω and amplitude A.

Problem 1.7. Calculate $\langle x \rangle$, $\langle p_x \rangle$, δx, and δp_x for the eigenstate $\{n_x, n_y, n_z\}$ of a particle in a rectangular, hard-wall box, described by Eq. (1.77), and compare the product $\delta x \delta p_x$ with the Heisenberg's uncertainty relation.

Problem 1.8. Looking at the lower (red) line in figure 1.8, it seems plausible that the 1D ground-state function (1.84) of the simple potential well (1.77) may be well approximated with an inverted quadratic parabola:

$$X_{\text{trial}}(x) = C\, x\, (a_x - x),$$

where C is a normalization constant. Explore how good this approximation is.

Problem 1.9. A particle, placed in a hard-wall, rectangular box with sides a_x, a_y, and a_z, is in its ground state. Calculate the average force acting on each face of the box. Can the forces be characterized by a certain pressure?

Problem 1.10. A 1D quantum particle was initially in the ground state of a very deep, rectangular potential well of width a:

$$U(x) = \begin{cases} 0, & \text{for } -a/2 < x < +a/2, \\ +\infty, & \text{otherwise.} \end{cases}$$

At some instant, the well's width is abruptly increased to a new value $a' > a$, leaving the potential symmetric with respect to the point $x = 0$, and then left constant. Calculate the probability that after the change, the particle is still in the ground state of the system.

Problem 1.11. At $t = 0$, a 1D particle of mass m is placed into a hard-wall, flat-bottom potential well

$$U(x) = \begin{cases} 0, & \text{for } 0 < x < a, \\ +\infty, & \text{otherwise,} \end{cases}$$

[67] Despite the theorem's common name, H Hellmann (in 1937) and R Feynman (in 1939) were not the first ones in the long list of physicists who have (apparently, independently) discovered this fact. Indeed, it may be traced back at least to a 1922 paper by W Pauli, and was carefully proved by P Güttinger in 1931.

in a 50/50 linear superposition of the lowest (ground) state and the first excited state. Calculate:

(i) the normalized wavefunction $\Psi(x, t)$ for arbitrary time $t \geqslant 0$, and
(ii) the time evolution of the expectation value $\langle x \rangle$ of the particle's coordinate.

Problem 1.12. Calculate the potential profiles $U(x)$ for that the following wavefunctions,

(i) $\Psi = c \exp\{-ax^2 - ibt\}$, and
(ii) $\Psi = c \exp\{-a \mid x \mid - ibt\}$,

(with real coefficients $a > 0$ and b), satisfy the 1D Schrödinger equation for a particle with mass m. For each case, calculate $\langle x \rangle$, $\langle p_x \rangle$, δx, and δp_x, and compare the product $\delta x \delta p_x$ with the Heisenberg's uncertainty relation.

Problem 1.13. A 1D particle of mass m, moving in the field of a stationary potential $U(x)$, has the following eigenfunction

$$\psi(x) = \frac{C}{\cosh \kappa x},$$

where C is the normalization constant, and κ is a real constant. Calculate the function $U(x)$ and the state's eigenenergy E.

Problem 1.14. Calculate the density dN/dE of traveling-wave states in large rectangular potential wells of various dimensions: $d = 1$, 2, and 3.

Problem 1.15.* Use the finite-difference method with steps $a/2$ and $a/3$ to find as many eigenenergies as possible for a 1D particle in the infinitely deep, hard-wall 1D potential well of width a. Compare the results with each other, and with the exact formula[68].

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[68] You may like to start from reading about the finite-difference method—see, e.g. *Part CM* section 8.5 or *Part EM* section 2.11.

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