Chapter 1. Introduction

This introductory chapter briefly reviews the major experimental motivations for quantum mechanics and then discusses its simplest formalism – Schrödinger's wave mechanics. Much of this material may be found in undergraduate textbooks,[1] *so 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 thermodynamics and statistics, and classical electrodynamics including 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 a 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 thermal equilibrium, the power of electromagnetic radiation by a fully absorbing ("black") surface, per a unit frequency interval, drops exponentially at high frequencies. This is not what could be expected from the combination of classical electrodynamics and statistics, which predicted an infinite growth of the radiation density with frequency.

Indeed, classical electrodynamics shows[3] that electromagnetic field modes evolve in time just as harmonic oscillators, and that the number dN of these modes in a relatively large free-space volume $V >> \lambda^3$, within a small frequency interval $d\omega << \omega$ 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 $c \approx 3\times10^8$ m/s is the free-space speed of light, $k = \omega/c$ is the free-space wave number, and $\lambda = 2\pi/k$ is the radiation wavelength. On the other hand, classical statistics[4] predicts that in thermal equilibrium at temperature T, the average energy E of each 1D harmonic oscillator should be equal to k_BT, 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:

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[1] See, for example, S. Gasiorowicz, *Quantum Physics*, 3rd ed., Wiley, 2003; D. Griffith, *Quantum Mechanics*, 2nd ed., Cambridge U. Press, 2016.

[2] This famous expression was used in a 1900 talk by Lord Kelvin (born William Thomson), in reference to the results of blackbody radiation measurements and the Michelson-Morley experiments, i.e. the precursors of quantum mechanics and relativity theory.

[3] See, e.g., EM Sec. 7.8, in particular Eq. (7.211).

[4] See, e.g., SM Sec. 2.2.

[5] In the SI units, used throughout this series, $k_B \approx 1.38\times10^{-23}$ J/K – see *Appendix UCA: Selected Units and Constants* for the exact value.

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

which diverges at $\omega \to \infty$ (Fig. 1) – the so-called *ultraviolet catastrophe*. On the other hand, the blackbody radiation measurements, improved by O. Lummer and E. Pringsheim, and by H. Rubens and F. Kurlbaum to reach a 1%-scale accuracy, were compatible with the law suggested in 1900 by Max Planck:

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

Planck's radiation law

This law may be reconciled with the fundamental Eq. (1) if the following replacement is made for the average energy of each field oscillator:

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

with the factor

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

Planck's constant

now called *Planck's constant*.[6] At low frequencies ($\hbar\omega << k_B T$), the denominator in Eqs. (3) may be approximated as $\hbar\omega/k_B T$, so the average energy (3b) tends to its classical value $k_B T$, and the Planck law (3a) reduces to the Rayleigh-Jeans formula (2). However, at higher frequencies ($\hbar\omega >> k_B T$), Eq. (3) describes the experimentally observed rapid decrease of the radiation density – see Fig. 1.

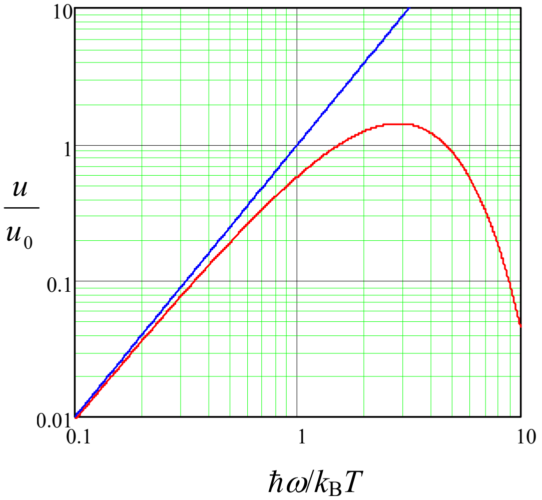

Fig. 1.1. The blackbody radiation density u, in units of $u_0 \equiv (k_B T)^3/\pi^2\hbar^2 c^3$, as a function of frequency, according to the Rayleigh-Jeans formula (blue line) and Planck's law (red line).

M. Plank derived Eq. (3b) from basic statistics, by assuming (just to fit the experimental results for u) that the energy of a field oscillator of frequency ω can only take values that differ by

$$\boxed{E = \hbar\omega .} \tag{1.5}$$

Energy vs frequency

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[6] M. Planck himself wrote $\hbar\omega$ as $h\nu$, where $\nu = \omega/2\pi$ is the "cyclic" frequency, so 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 contemporary terminology and abstain from using the constant h at all, to avoid confusion.

(ii) The photoelectric effect, discovered in 1887 by H. Hertz and studied quantitatively by A. Stoletov in 1888-89, shows a sharp lower boundary ("*red border*") for the frequency of the incident light that may kick electrons out from metallic surfaces, independent of its intensity. Albert Einstein, in one of his three famous 1905 papers, noticed that this threshold $\omega_{\min}$ could be explained by assuming that light consisted of certain particles (later called *photons*) with the same energy (5).[7] Indeed, with this assumption, at the photon absorption by an electron, its energy $E = \hbar\omega$ is divided between a fixed energy U_0 (nowadays called the *workfunction*) of the electron's binding inside the metal, and the excess kinetic energy $m_e v^2/2 > 0$ of the freed electron – see Fig. 2. In this picture, the red border finds a natural explanation as $\omega_{\min} = U_0/\hbar$.[8]

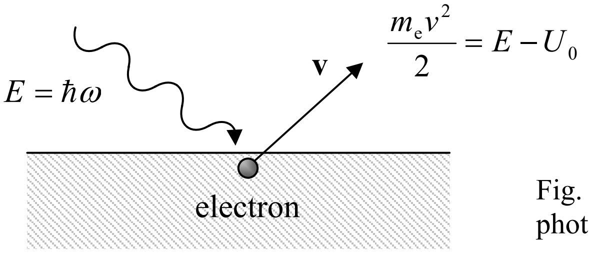

Fig. 1.2. Einstein's explanation of the photoelectric effect's frequency threshold.

(iii) The discrete frequency spectra of the electromagnetic radiation by excited atomic gases could not be explained by classical physics. (Applied to the planetary model of atoms, proposed by Ernst Rutherford, classical electrodynamics predicts the collapse of electrons on nuclei in $\sim 10^{-10}$s, due to the electric-dipole radiation of electromagnetic waves.[9]) Especially challenging was the observation by Johann Jacob Balmer (in 1885) that the radiation frequencies of simple atoms may be well described by simple formulas. For example, for the lightest, hydrogen atom, all radiation frequencies may be numbered with just two positive integers n and $n' > n$:

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

with $\omega_0 \equiv \omega_{1,\infty} \approx 2.07\times10^{16}$ s^{-1}. This observation, and the experimental value of ω_0, have found its first explanation in the famous 1913 theory by Niels Henrik David Bohr, which was a phenomenological precursor of present-day quantum mechanics. In this theory, $\omega_{n,n'}$ was interpreted as the frequency of a photon that obeys Eq. (5), with its energy $E_{n,n'} = \hbar\omega_{n,n'}$ being the difference between two *quantized* (discrete) energy levels of the atom (Fig. 3):

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

Bohr showed that Eq. (6) may be obtained from Eqs. (5) and (7), and classical mechanics, augmented with just one additional postulate[10] equivalent to the assumption that the angular momentum

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[7] As a reminder, A. Einstein received his only Nobel Prize (in 1921) for exactly this work rather than for his relativity theory.

[8] For most metals, U_0 is between 4 and 5 electron-volts (eV), so 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., EM Sec. 8.2.

[10] For more on his actual postulate, see Problem 1.

$L = m_e vr$ of an electron moving with velocity v on a circular orbit of radius r about the hydrogen's nucleus (the proton, assumed to be at rest because of its much higher mass), is quantized as

Angular momentum quantization

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

where $\hbar$ is again the same Planck's constant (4), and n is an integer. (In Bohr's theory, n could not be equal to zero, though in genuine quantum mechanics, it can.)

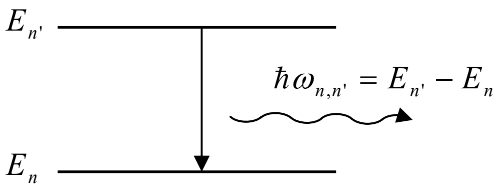

Fig. 1.3. The electromagnetic radiation of a system as a result of the transition between its quantized energy levels.

Indeed, it is sufficient to solve Eq. (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 the 2nd Newton's law for an electron rotating in the Coulomb field of the nucleus. (Here $e \approx 1.6\times10^{-19}$C is the fundamental electric charge, and $m_e \approx 0.91\times10^{-30}$ kg is the electron's rest mass.) The result for r is

Bohr radius

$$\boxed{r = n^2 r_B, \qquad \text{where } r_B \equiv \frac{\hbar^2 / m_e}{e^2 / 4\pi\varepsilon_0} \approx 0.0529\,\text{nm}.} \tag{1.10}$$

The constant r_B, called the *Bohr radius*, is the most important spatial scale of phenomena in atomic, molecular, and condensed-matter physics – and hence in all chemistry and biochemistry.

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

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

we get the following simple expression for the electron's energy levels:

Hydrogen atom's energy levels

$$\boxed{E_n = -\frac{E_H}{2n^2} < 0,} \tag{1.12}$$

which, together with Eqs. (5) and (7), immediately gives Eq. (6) for the radiation frequencies. Here E_H is called the so-called *Hartree energy constant* (or just the "Hartree energy")[11]

Hartree energy constant

$$\boxed{E_H \equiv \frac{\left(e^2 / 4\pi\varepsilon_0\right)^2}{\hbar^2 / m_e} \approx 4.360\times10^{-18}\,\text{J} \approx 27.21\,\text{eV}.} \tag{1.13a}$$

(Please note the useful relations that follow from Eqs. (10) and (13a):

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[11] Unfortunately, another name, the "Rydberg constant", is sometimes used for either this energy unit or its half, $E_H/2 \approx 13.6$ eV. To add to the confusion, the same term "Rydberg constant" is used, in some subfields of physics, for the reciprocal free-space wavelength ($1/\lambda_0 = \omega_0/2\pi c$) corresponding to the frequency $\omega_0 \equiv E_H/2\hbar$.

$$E_H = \frac{e^2}{4\pi\varepsilon_0 r_B} = \frac{\hbar^2}{m_e r_B^2}, \qquad \text{i.e. } r_B = \frac{e^2/4\pi\varepsilon_0}{E_H} = \left(\frac{\hbar^2/m_e}{E_H}\right)^{1/2}; \tag{1.13b}$$

the first of them shows, in particular, that r_B is the distance at which the natural scales of the electron's potential and kinetic energies are equal.)

Note also that Eq. (8), in the form $pr = \hbar n$, where $p = m_e v$ is the electron momentum's magnitude, may be rewritten as the condition that an integer number (n) of wavelengths λ of certain (before the late 1920s, hypothetic) waves[12] fits the circular orbit's perimeter: $2\pi r \equiv 2\pi\hbar n/p = n\lambda$. Dividing both parts of the last equality 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 $p = mv$:

Momentum vs wave number

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

again with the same Planck's constant as in Eq. (5).

(iv) The Compton effect[13] is the reduction of frequency of X-rays at their scattering on free (or nearly free) electrons – see Fig. 4.

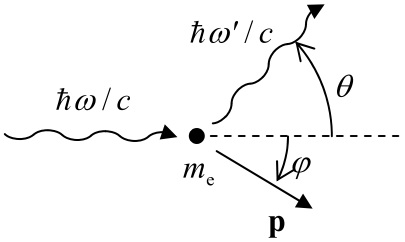

Fig. 1.4. The Compton effect.

The effect may be explained by assuming that the X-ray photon also has a definite momentum that obeys the vector-generalized version of Eq. (14):

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

where **k** is the wavevector (whose magnitude is equal to the wave number k, and whose direction coincides with the unit vector **n** directed along the wave propagation[14]), and that the momenta of both the photon and the electron are related to their energies E by the classical relativistic formula[15]

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

(For a photon, the rest energy m is zero, and this relation is reduced to Eq. (5): $E = cp = c\hbar k = \hbar\omega$.) Indeed, a straightforward solution of the following system of three equations,

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

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[12] This concept was first proposed in 1924 by Louis Victor Pierre Raymond de Broglie (in his PhD thesis!), so instead of speaking of wavefunctions, we are still frequently speaking of the *de Broglie waves*, especially when free particles are discussed. (In some subfields of physics, the term "matter waves" is used for the same notion.)

[13] This effect was observed in 1922, and explained a year later by Arthur Holly Compton, using Eqs. (5) and (15).

[14] See, e.g., EM Sec. 7.1.

[15] See, e.g., EM Sec. 9.3, in particular Eq. (9.78).

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

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

(that express the conservation of, respectively, the full energy of the system and of the two relevant Cartesian components of its full momentum, at the scattering event – see Fig. 4), yields the 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 $\lambda = 2\pi/k = 2\pi/(\omega/c)$:[16]

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

Compton effect

and agrees with experiment.

(v) De Broglie wave diffraction. In 1927, Clinton Joseph Davisson and Lester Germer, and independently George Paget Thomson succeeded in observing the diffraction of electrons on solid crystals (Fig. 5). Specifically, they 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:

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

Bragg condition

where $\lambda = 2\pi/k = 2\pi\hbar/p$ is the de Broglie wavelength of the electrons, and n is an integer. As Fig. 5 shows, this is just the well-known condition[17] that the path 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.[18]

To summarize, all the listed experimental observations could be explained starting from two very simple (and similarly looking) formulas: Eq. (5) (at that stage, for photons only), and Eq. (15) for both photons and electrons – both relations involving the same Planck's constant. This fact might give an impression of experimental evidence sufficient to declare the light consisting of discrete particles (photons), and, on the contrary, electrons being the de Broglie waves rather than particles. However, by

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[16] The constant $\lambda_C \approx 2.426\times10^{-12}$ m that participates in this relation, is called the electron's *Compton wavelength*. This term is somewhat misleading: as the reader can see from Eqs. (17)-(19), no wave in the Compton problem has such a wavelength – either before or after the scattering.

[17] See, e.g., EM Sec. 8.4, in particular Fig. 8.9 and Eq. (8.82). Frequently, Eq. (21) is called the *Bragg condition*, due to the pioneering experiments by W. Bragg on X-ray scattering from crystals, which were started in 1912.

[18] Later, spectacular experiments on diffraction and interference of heavier particles (with the correspondingly smaller de Broglie wavelength), e.g., neutrons, whole atoms, and even large organic molecules, have also been carried out – see, e.g., the review by A. Zeilinger *et al., Rev. Mod. Phys*. **60**, 1067 (1988) and a later publication Y. Fein *et al*., *Nature Physics* **15**, 1242 (2019) and references therein. Nowadays, such interference of heavy particles is used for ultrasensitive measurements of gravity, rotation, and tilt – see, e.g., the reviews by A. Cronin *et al*., *Rev. Mod. Phys*. **81**, 1051 (2009) and M. Arndt, *Phys. Today* **67**, 30 (May 2014).

that time (the mid-1920s), physics has accumulated overwhelming evidence of *wave* properties of light, such as interference and diffraction.[19] In addition, there was also strong evidence for the lumped-particle ("corpuscular") behavior of electrons. It is sufficient to mention the famous oil-drop experiments by Robert Andrew Millikan and Harvey Fletcher (1909-1913), in which only whole electrons could be added to an oil drop, changing its total electric charge by multiples of the electron's charge ($-e$) – and never by its fraction. It was apparently impossible to reconcile these observations with a purely wave picture, in which an electron and hence its charge needed to be spread over the de Broglie wave's extension, so an arbitrary part of it could be cut off using an appropriate experimental setup.

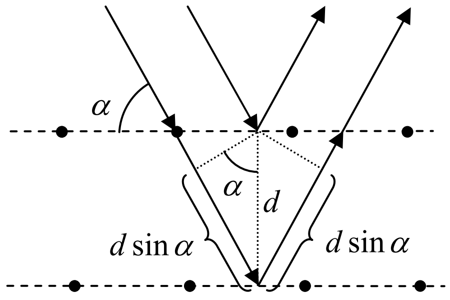

Fig. 1.5. The De Broglie wave interference at electron scattering from a crystal lattice.

Thus the founding fathers of quantum mechanics faced the formidable task of reconciling the wave and corpuscular properties of electrons and photons – and other particles. The decisive breakthrough in that task was 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*[20] *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,[21] non-relativistic point-like particle, whose classical dynamics may be described by a certain Hamiltonian function $H(\mathbf{r}, \mathbf{p}, t)$,[22] where $\mathbf{r}$ is the particle's radius vector and $\mathbf{p}$ is its momentum. (This condition is important because it excludes from our current discussion the systems whose interaction with their environment results in *irreversible* effects, in particular the energy's decay. Such "open" systems need a more general description, which will be discussed in Chapter 7.) Wave mechanics of such *Hamiltonian particles* may be based on the following set of postulates that are comfortingly elegant – though their final justification is given only by the agreement of all their corollaries with experiment.[23]

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[19] See, e.g., EM Sec. 8.4.

[20] *Orbital motion* is the historic (and rather misleading) term used for *any* translational motion of the particle.

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

[22] As a reminder, for many systems (including all 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., CM Sec. 2.3. In what follows, I will assume that $H = E$ until noticed otherwise.

[23] Quantum mechanics, like any theory, may be built on different sets of postulates/axioms leading to the same results. In this text, I will not try to beat down the number of postulates to the absolute possible minimum, not

(i) Wavefunction and probability. Not always such variables as **r** or **p** can be measured exactly, even at "perfect conditions" when all external uncertainties, including measurement instrument imperfection, varieties of the initial state preparation, and unintended particle interactions with its environment, have been removed.[24] Moreover, the **r** and **p** of the same particle can *never* be measured exactly simultaneously. Instead, the *most detailed* description of the particle's state allowed by Nature 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

Probability via wavefunction

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

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

$$\boxed{W = \int_V w\,d^3r = \int_V \Psi^*\Psi\,d^3r.} \qquad (1.22b)$$

In particular, if volume V contains the particle *definitely* (i.e. with the 100% probability, $W = 1$), Eq. (22b) is reduced to the so-called *wavefunction normalization condition*

Normalization condition

$$\boxed{\int_V \Psi^*\Psi\,d^3r = 1.} \qquad (1.22c)$$

(ii) Observables and operators. With each observable A, quantum mechanics associates a certain *linear operator* $\hat{A}$, such that the average measured value of A (usually called the *expectation value*) is expressed as[25]

Observable's expectation value

$$\boxed{\langle A\rangle = \int_V \Psi^*\hat{A}\Psi\,d^3r,} \qquad (1.23)$$

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 that satisfies Eq. (22c). Note immediately that for Eqs. (22) and (23) to be compatible, the *identity* (or "unit") *operator* defined by the relation

Identity operator

$$\boxed{\hat{I}\Psi = \Psi,} \qquad (1.24)$$

has to be associated with a particular type of measurement, namely with the particle's *detection*, i.e. the observation of its presence.

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only because that would require longer argumentation, but chiefly because such attempts typically result in making certain implicit assumptions hidden from the reader – the practice as common as regrettable.

[24] I will imply such perfect conditions in the further narrative, until the discussion of the system's interaction with its environment in Chapter 7.

[25] This key measurement postulate is sometimes called the *Born rule*, though sometimes this term is used for the (less general) Eqs. (22).

(iii) The Hamiltonian operator and the Schrödinger equation. Another particular operator, *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*,

Schrödinger equation

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

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

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

Operators of coordinate and momentum

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

where ∇ is the *del* (or "nabla") vector operator.[26] Thus in the Cartesian coordinates,

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

(v) The correspondence principle. In the limit when quantum effects are insignificant, e.g., when the characteristic scale of action[27] (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 with similar relations between the corresponding operators. For example, the Hamiltonian of a free particle (whose full classical energy consists of its kinetic energy $T = p^2/2m$ alone) has the form

Free particle's Hamiltonian

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

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 a resolution of the apparent contradiction between the wave and corpuscular properties of particles. Indeed, for a free particle, the Schrödinger equation (25), with the substitution of Eq. (27), takes the form

Free particle's Schrödinger equation

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

whose particular but most important solution is a plane, single-frequency ("monochromatic") traveling wave,[28]

Plane wave

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

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[26] If you need, see, e.g., Secs. 8-10 of the *Selected Mathematical Formulas* appendix – below, referred to as MA. Note that according to those formulas, the del operator follows all the rules of the usual (geometric) vectors. This is, by definition, true for other quantum-mechanical vector operators to be discussed below.

[27] See, e.g., CM Sec. 10.3.

[28] See, e.g., CM Sec. 6.4 and/or EM Sec. 7.1.

where a, **k**, and ω are constants. Indeed, plugging Eq. (29) into Eq. (28), we immediately see that such a plane wave, with an arbitrary complex amplitude a, is indeed a solution of this Schrödinger equation, provided a specific *dispersion relation* between the wave number $k \equiv |\mathbf{k}|$ and the frequency ω:

Free particle's dispersion relation

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

The constant a may be calculated, for example, assuming that the wave (29) is extended over a certain volume V, while beyond it, $\Psi = 0$. Then from the normalization condition (22c) and Eq. (29), we get[29]

$$|a|^2 V = 1. \qquad (1.31)$$

Let us use Eqs. (23), (26), and (27) to calculate the expectation values of the particle's momentum **p** and energy $E = H$ in the state (29). The result is

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

according to Eq. (30), the last equality may be rewritten as $\langle E\rangle = \hbar\omega$.

Next, Eq. (23) enables calculation of not only the average (in math speak, the *first moment*) of an observable but also its higher moments, notably the *second moment* – in physics, usually called *variance*:

Observable's variance

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

and hence its *uncertainty* alternatively called the "root-mean-square (r.m.s.) fluctuation",

Observable's uncertainty

$$\boxed{\delta A \equiv \langle \tilde{A}^2 \rangle^{1/2}.} \qquad (1.34)$$

The uncertainty is the scale of deviations $\tilde{A} \equiv A - \langle A \rangle$ of measurement results from their average. In the particular case when the uncertainty δA equals zero, every measurement of the observable A will give the same value $\langle A\rangle$; such a state is said to have a *definite value* of the variable. For example, in application to the state with wavefunction (29), these relations yield $\delta E = 0$, $\delta\mathbf{p} = 0$. This means that in this plane-wave, monochromatic state, the energy and momentum of the particle have definite values, so the statistical average signs in Eqs. (32) might be removed. Thus, these relations are reduced to the experimentally inferred Eqs. (5) and (15).

Hence the wave mechanics postulates indeed may describe the observed wave properties of non-relativistic particles. (For photons, we would need its relativistic generalization – see Chapter 9 below.) On the other hand, due to the linearity of the Schrödinger equation (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 (29) is also a solution to this equation. Such sets, with close values of **k** and hence $\mathbf{p} = \hbar\mathbf{k}$ (and, according to Eq. (30), of ω as well), may be used to describe spatially localized "pulses", called *wave packets* – see Fig. 6. In Sec. 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

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[29] For infinite space ($V \to \infty$), Eq. (31) yields $a \to 0$, i.e. wavefunction (29) vanishes. This formal problem may be readily resolved considering sufficiently long wave packets – see Sec. 2.2 below.

corresponding component of its wave vector as $\delta x \delta k_x \geq ½$, and hence, according to Eq. (15), to the width δp_x of the momentum component distribution as

Heisenberg's uncertainty relation

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

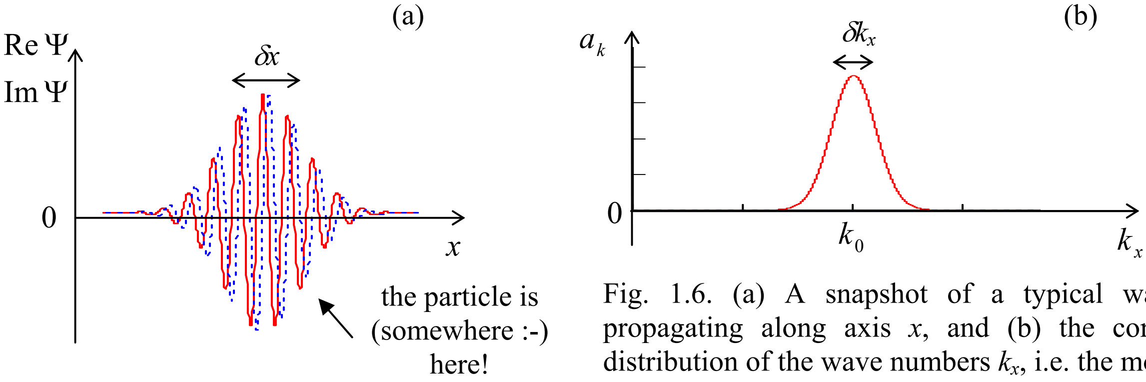

Fig. 1.6. (a) A snapshot of a typical wave packet propagating along axis x, and (b) the corresponding distribution of the wave numbers k_x, i.e. the momenta p_x.

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 particle localization in a very small volume even if the momentum spread in a wave packet is also small on that scale. For example, according to Eq. (35), a 0.1% spread of momentum of a 1 keV electron ($p \sim 1.7\times10^{-24}$ kg·m/s) allows its wave packet to be as small as $\sim 3\times10^{-10}$ 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 wave mechanics, and the first part of this course (Chapters 1-3) will be essentially a discussion of the various effects described by this approach. During this discussion, however, we will not only witness the 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 the reader from their 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 the concluding 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 quantum mechanics so hard to swallow for many star physicists, notably including Albert Einstein – despite his 1905 work, which advanced the field so much. However, this fact has been confirmed by numerous experiments, and (more importantly) there has not been a single confirmed experiment that would contradict this postulate, so 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. (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 classical statistical mechanics, the probability density distribution $w(\mathbf{r}, t)$ may be also calculated from deterministic differential equations, for example, the Liouville equation.[30] The quantum-mechanical description differs from that situation in two important aspects. First, in the perfect conditions outlined above (the best possible initial state preparation and measurements), the Liouville equation is reduced to the 2nd Newton law of classical mechanics, i.e. the statistical uncertainty of its results disappears. In quantum mechanics this is not true: the quantum uncertainly, such as that described by Eq. (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. (22), this complex function also has the *phase* $\varphi \equiv \arg\Psi$, which may affect some observables, describing, in particular, 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*, in this case, a set of many experiments carried out at apparently (*macroscopically*) similar settings including the initial conditions. Indeed, the probability of a certain (n^{th}) result (*outcome*) of an experiment may be only defined for a certain statistical ensemble, as the limit

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

Probability: definition

where M is the total number of experiments, M_n is the number of outcomes of the n^{th} type, and N is the number of different outcomes.

Note that a particular choice of statistical 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 for some reason discarded results of all experiments giving us any rank of hearts. Hence, the ensemble definition (or its *redefinition* in the middle of the game) may change outcome probabilities.

In wave mechanics, with its fundamental relation (22) between w and Ψ, this means that not only the outcome probabilities but the wavefunction itself may also 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. This is why an attribution of the wavefunction to a single experiment, both before and after the measurement, may lead to very unphysical interpretations of the results, including some wavefunction's evolution stages not described by the Schrödinger equation (the so-called *wave packet reduction*), superluminal 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

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[30] See, e.g., SM Sec. 6.1.

wavefunctions on the statistical ensemble's definition (or redefinition), readily resolves most, though not all, paradoxes of quantum measurements.

Note, however, again that the standard quantum mechanics, as discussed in Chapters 1-6 and 9 of this course, is limited to statistical ensembles with *the least possible uncertainty* of the considered systems, i.e. with the best possible knowledge of their state.[31] This condition requires, first, the least uncertain initial preparation of the system, and 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. 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. (23): a better feeling of this expression may be obtained by its comparison with the general definition of the expectation value (i.e. of 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 an observable A; then

Definition of statistical average

$$\boxed{\langle A\rangle \equiv \lim_{M\to\infty}\frac{1}{M}\sum_{n=1}^{N}A_nM_n = \sum_{n=1}^{N}A_nW_n .} \qquad (1.37)$$

Taking into account Eq. (22), which relates W and Ψ, the structures of Eq. (23) and the final form of Eq. (37) are similar. Their exact relation will be further discussed in Sec. 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.[32] Indeed, let us use Eq. (22b) to calculate the rate of change of the probability W to find a particle within a certain volume V:

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

Assuming for simplicity that the boundaries of this 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 (25), together with its complex conjugate,

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

we readily get

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

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[31] 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 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.

[32] Note that this requirement may be violated in the *relativistic* quantum theory – see Chapter 9.

Let the particle move in a field of external forces (not necessarily constant in time), so its classical Hamiltonian function H is the sum of the particle's kinetic energy $T = p^2/2m$ and its potential energy $U(\mathbf{r}, t)$.[33] According to the correspondence principle and Eq. (27), the Hamiltonian operator may be represented as the sum[34]

Potential field: Hamiltonian

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

At this stage, we should notice that this operator, when acting on a real function, gives a real function.[35] 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

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

This means that Eq. (40) may be rewritten as

$$\frac{dW}{dt} = \frac{1}{i\hbar}\left(\Psi^*\hat{H}\Psi - \Psi\hat{H}\Psi^*\right)d^3r = -\frac{\hbar^2}{2m}\frac{1}{i\hbar}\int_V\left(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*\right)d^3r\,. \tag{1.44}$$

Now let us use the general rules of vector calculus[36] to write the following identity:

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

A comparison of Eqs. (44) and (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

Probability current density

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

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,[37] Eq. (46) may be rewritten as the *continuity equation*

Continuity equation: integral form

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

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[33] As a reminder, such a 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., CM Chapters 2 and 10. (A good counter-example when such a description is *impossible* is given by the magnetic component of the Lorentz force – see, e.g., EM Sec. 9.7 and also Sec. 3.1 below.)

[34] 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.

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

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

[37] See, e.g., MA Eq. (12.2).

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

Formulas (47) and (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 intended sanity check. In the general case, Eq. (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 applying Eq. (47) to any wavefunction represented in the polar form $\Psi = ae^{i\varphi}$, with real a and φ:

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

Note that for a real wavefunction, or even for a wavefunction with an arbitrary but space-constant phase φ, the probability current density vanishes. On the contrary, for the traveling wave (29), with a constant probability density (1.22a), $w = a^2$, Eq. (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 the 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 these currents satisfy classical continuity equations similar to Eq. (48).[38]

Finally, let us recast the continuity equation, rewriting Eq. (46) as

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

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

Continuity equation: differential form

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

This differential form of the continuity equation may be more convenient than its integral form (48).

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:[39]

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

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[38] See, e.g., respectively, CM 8.3 and EM Sec. 4.1.

[39] By the way, if any equality involving operators is valid for an arbitrary wavefunction, the latter is frequently dropped from the notation, resulting in *operator equality*. In particular, Eq. (53) may be readily used to prove that the linear operators are *commutative*: $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$, and *associative*: $\left(\hat{A}_1 + \hat{A}_2\right) + \hat{A}_3 = \hat{A}_1 + \left(\hat{A}_2 + \hat{A}_3\right)$.

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

where Ψ_n are arbitrary wavefunctions and 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. (26), and
(ii) the spatial or temporal differentiation, such as in Eqs. (25)-(27).

Next, it is of key importance that the Schrödinger equation (25) is also linear. (This fact was already used in the discussion of wave packets in Sec. 2.) This means that if each of several functions Ψ_n are particular solutions of Eq. (25) with a certain Hamiltonian, then their arbitrary linear combination,

$$\Psi = \sum_n c_n \Psi_n , \quad (1.55)$$

is also a solution of the same equation.[40]

Let us use the linearity to accomplish an apparently impossible feat: immediately find the *general* solution of the Schrödinger equation for the important case when the system's Hamiltonian does not depend on time explicitly – for example, is given by Eq. (41) with time-independent potential energy $U = U(\mathbf{r})$, so the corresponding Schrödinger equation has the form

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

Static field: Schrödinger equation

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

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

Variable separation

qualifies as a particular solution of this equation. Indeed, plugging Eq. (57) into Eq. (25) with *any* time-independent Hamiltonian, using the fact that in this case

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

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

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

The left-hand side of this equation may depend only on time, while the right-hand side, only on coordinates. This may be true for all $\mathbf{r}$ and t only 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.[41] As a result, we are getting two separate equations for the temporal and spatial parts of the wavefunction:

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[40] 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., CM Sec. 5.2. Note, however, that statistical equations of classical dynamics (see, e.g., SM Chapters 5 and 6) also have this property, so it is not specific to quantum mechanics.

[41] This argumentation, leading to *variable separation*, is very common in mathematical physics – see, e.g., its discussion in EM Sec. 2.5.

Stationary Schrödinger equation

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

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

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

Stationary state: time evolution

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

Now plugging Eqs. (57) and (62) into Eq. (22), we see that in the quantum state described by Eqs. (57)-(62), the probability 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. (23) shows that the expectation value of any operator that does not depend on time explicitly is also time-independent:

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

Due to this property, the states described by Eqs. (57)-(62) are called *stationary*; they are fully defined by the possible solutions of the *stationary* (or "time-independent") *Schrödinger equation* (60).[42] Note that for the Hamiltonian (41), the stationary Schrödinger equation (60),

Static field: stationary Schrödinger equation

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

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*,[43] whose *eigenfunctions* ψ_n and *eigenvalues* E_n should be found simultaneously, i.e. self-consistently.[44]

Mathematics[45] tells us that for 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*:

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

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[42] In contrast, the *full* Schrödinger equation (25) is frequently called *time-dependent* or *non-stationary*.

[43] From the German root *eigen*, meaning "particular" or "characteristic".

[44] Eigenvalues of energy are frequently called *eigenenergies*, and it is often said that the eigenfunction ψ_n and the corresponding eigenenergy E_n together determine the n^{th} *stationary eigenstate* of the system.

[45] See, e.g., Sec. 9.3 of the handbook by G. Korn and T. Korn, listed in MA Sec. 16(ii).

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 at the initial moment of its evolution (which I will always, with a few clearly marked exceptions, take for $t = 0$), may be represented as a unique expansion over the eigenfunction set:

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

The expansion coefficients c_n may be readily found by multiplying both sides of Eq. (67) by $\psi^*_{n'}$, integrating the results over the space, and using Eq. (66). The result is

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

Now let us consider the following wavefunction[46]

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

General solution of Eq. (56)

Since each term of the sum has the form (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. (68), then the solution (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 (56), with fixed initial conditions, may have only one (*unique*) solution. This means that in our case of time-independent potential Hamiltonian, Eq. (69) gives the *general* solution of the Schrödinger equation (25).

So, we have succeeded in our apparently over-ambitious goal. Now let us pause 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 (57) of the general solution (69), our procedure gave a very simple and universal result (62), describing a linear change of the phase $\varphi_n \equiv \arg(a_n)$ of this complex function in time, with a constant rate

$$\frac{d\varphi_n}{dt} = -\omega_n = -\frac{E_n}{\hbar} , \qquad (1.70)$$

so the real and imaginary parts of a_n oscillate sinusoidally with this frequency. The relation (70) coincides with the Planck-Einstein conjecture (5), but could these oscillations of the wavefunctions represent a physical reality? Indeed, for photons, described by Eq. (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 up 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. (22)-(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

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[46] Note that according to Eq. (22b), the probability of finding the system in the k^{th} state equals $|c_k|^2$. Because of that, the complex coefficients c_k (or sometimes the products $c_k a_k$) are called *probability amplitudes*.

referred to the same origin as U), in any stationary state. However, let us combine Eq. (5) with Bohr's assumption (7):

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

The *difference* $\omega_{nn'}$ of the eigenfrequencies ω_n and $\omega_{n'}$, participating in this formula, is evidently independent of the energy reference, and as will be proved later in the course, determines the measurable frequency of the electromagnetic radiation (or possibly of a wave of a different physical nature) emitted or absorbed at the quantum transition between the states.

As another but related example, consider two similar particles 1 and 2, each in the same (say, the lowest-energy) eigenstate, but with their potential energies (and hence the ground state energies $E_{1,2}$) different by a constant $\Delta U \equiv U_1 - U_2$. Then, according to Eq. (70), the difference $\varphi \equiv \varphi_1 - \varphi_2$ of their wavefunction phases evolves in time with the reference-independent rate

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

Certain measurement instruments, weakly coupled to the particles, may allow observation of this evolution, while keeping the particle's quantum dynamics virtually unperturbed, i.e. Eq. (70) intact. Perhaps the most spectacular measurement of this type is possible using the *Josephson effect* in weak links between two superconductors – see Fig. 7.[47]

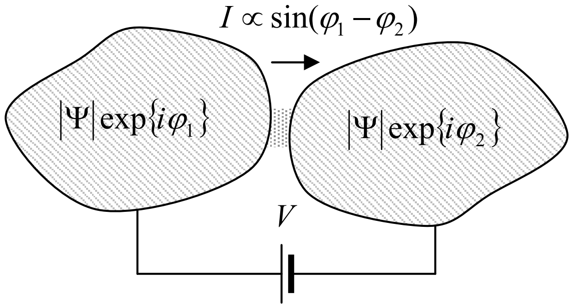

Fig. 1.7. The Josephson effect in a weak link between two bulk superconductor electrodes.

As a brief reminder,[48] 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 behave as Bose particles and form a coherent *Bose-Einstein condensate*.[49] 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,[50] and $q = -2e$ is the electric charge of a Cooper pair. As a result, for the system shown in Fig. 7, in which externally applied voltage V fixes the difference $\phi_1 - \phi_2$ between the electrochemical potentials of the superconductors, Eq. (72) takes the form

Eq. (72) for Josephson effect

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

---

[47] The effect was predicted in 1962 by Brian Josephson (then a graduate student!) and observed soon after that.
[48] For a more detailed discussion, including the derivation of Eq. (75), see e.g. EM Chapter 6.
[49] A detailed discussion of the Bose-Einstein condensation may be found, e.g., in SM Sec. 3.4.
[50] For more on this notion see, e.g. SM Sec. 6.3.

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,

Josephson supercurrent

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

where I_c is some constant, dependent on the weak link's strength.[51] Now combining Eqs. (73) and (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 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)[52] 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 dc 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.[53] 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 (62) of the stationary states, their spatial wavefunctions $\psi_n(\mathbf{r})$ need to be calculated from the problem-specific stationary Schrödinger equation (65). The solution of this equation for various particular cases will be a major focus of the next two chapters. Here I will consider just one simple example, which nevertheless will be the basis for our discussion of more complex problems. Let a particle be confined inside a rectangular hard-wall box. Such confinement may be described by the following potential energy profile:[54]

Hard-wall box: potential

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

---

[51] In some cases, the function $I(\varphi)$ may somewhat deviate from Eq. (74), but these deviations do not affect its fundamental 2π-periodicity, and hence the fundamental relations (75)-(76). (To the best of the author's knowledge, no corrections to them have been found yet.)

[52] For the discussion of this very general effect, see, e.g., CM Sec. 5.4.

[53] The size of these dc current steps (frequently called the *Shapiro steps*) may be readily calculated from Eqs. (73) and (74). Let me leave this task for the reader's exercise.

[54] Another common name for such potential profiles, especially of lower dimensionality, is the *potential well* – in our current case (77), with a flat bottom and vertical, infinitely high walls. Note also that sometimes such potential profiles are called "quantum wells". The last term is very unfortunate because it seems to imply that particle confinement in potential wells is an effect specific to quantum mechanics. However, as we will repeatedly see in this course, the opposite is true: quantum effects do as much as they only can to *overcome* a particle's confinement in a well, sometimes letting it penetrate the "classically forbidden" regions beyond its walls.

The only way to keep the product $U(\mathbf{r})\psi_n$ in Eq. (65) finite outside the box, is to have $\psi = 0$ in these regions. Also, the function has to be continuous everywhere, to avoid the divergence of the kinetic-energy term $(-\hbar^2/2m)\nabla^2\psi_n$. Hence, in this case, we may solve the stationary Schrödinger equation (65) just inside the box, i.e. with $U = 0$, so it takes a simple form

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

with zero boundary conditions on all the walls.[55] 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 our boundary problem becomes:

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

This problem may be readily solved using the same variable separation method as was used in Sec. 5 – now to separate the Cartesian spatial variables from each other, by looking for a partial solution of Eq. (78) in the form

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

(Let us postpone assigning the function indices for a minute.) Plugging this expression into Eq. (78b) 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. (80) turning into the following energy-matching condition:

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

All three ordinary differential equations (81), and hence their solutions, are similar. For example, for $X(x)$, we have the following 1D Helmholtz equation

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

---

[55] Rewritten as $\nabla^2 f + k^2 f = 0$, Eq. (78a) 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., EM Secs. 7.5-7.9 and 8.5.

with simple boundary conditions: $X(0) = X(a_x) = 0$.[56] 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,[57]

Rectangular potential well: 1D eigenfunctions

$$\boxed{X \propto \sin k_x x, \quad \text{with } k_x = \frac{\pi n_x}{a_x}, \quad \text{i.e. } X = \left(\frac{2}{a_x}\right)^{1/2} \sin\frac{\pi n_x x}{a_x}, \quad \text{with } n_x = 1, 2,\ldots,} \qquad (1.84)$$

corresponding to the following eigenenergies:

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

Figure 8 shows these simple results, using a somewhat odd but very graphic and popular representation, in that the eigenenergy values (frequently called the *energy levels*) are used as horizontal axes for plotting the eigenfunctions – despite their different dimensionality.

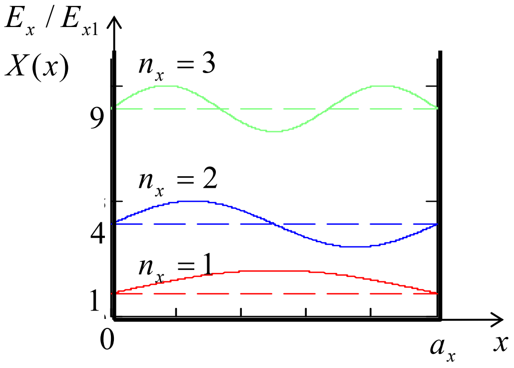

Fig. 1.8. The lowest eigenfunctions (solid lines) and eigenvalues (dashed lines) of Eq. (83) for a 1D potential well of length a_x. Solid black lines show the effective potential energy profile for this 1D eigenproblem.

Due to the similarity of all Eqs. (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 the spectrum of values of the total energy (82) is

Rectangular potential well: energy levels

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

Thus, in this 3D problem, the role of the index n in the general Eq. (69) is played by a set of three independent integers $\{n_x, n_y, n_z\}$. In quantum mechanics, such integers play a key role and thus have a special name, *quantum numbers*. Using them, for our current simple problem that general solution, may be represented as the following sum:

Rectangular potential well: general solution

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

---

[56] Please notice that we would also arrive at this 1D boundary problem if we considered a 1D analog of our 3D problem (77), i.e. a 1D particle placed in a hard-wall, flat-bottom potential well of length a_x. In quantum mechanics, such 1D problems play an important role, and will be the subject of extensive discussions in the next chapter.

[57] The front coefficient in the last expression for X enforces the (ortho)normality condition (66).

with the front coefficients that may be readily calculated from the initial wavefunction $\Psi(\mathbf{r}, 0)$, using Eq. (68) – again with the replacement $n \rightarrow \{n_x, n_y, n_z\}$.

This simple 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 (86), reached in the so-called *ground state* (in our problem, the state with $n_x = n_y = n_z = 1$) is above zero for any finite size of the confining volume.

An example of the opposite case of a *continuous spectrum* for the *unconfined motion* of a free particle is given by the plane waves (29). With the account of relations $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$, such wavefunction may be viewed as the product of the time-dependent factor (62) by the eigenfunction,

Free particle: eigen-functions

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

which is the solution of the stationary Schrödinger equation (78a) if it is valid in the whole space.[58] The reader should not be worried too much by the fact that the fundamental solution (88) in free space is a *traveling* wave (having, in particular, a non-zero 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 $V = a_x \times a_y \times a_z \rightarrow \infty$. Indeed, due to the linearity of wave mechanics, two traveling-wave solutions (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,[59] 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 $\mathbf{j} = 0$. Thus, depending on the convenience for a particular problem, we may represent its 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. (88) can take any real values. (This is why it is more convenient to label these wavefunctions, and the corresponding eigenenergies

Free particle: eigen-energies

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

with their wave vector $\mathbf{k}$ rather than an integer index.)

However, one aspect of continuous-spectrum systems requires a bit more caution with mathematics: the summation (69) should be replaced by the integration over a continuous index or indices – in our current case, the three Cartesian components of the vector $\mathbf{k}$. The main rule of such replacement may be readily extracted from Eq. (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 similar relations for the other two Cartesian components of $\mathbf{k}$. Hence the number of different eigenvalues of the standing-wave vector $\mathbf{k}$ (with $k_x, k_y, k_z \geq 0$), within a volume $d^3k >> 1/V$ of the $\mathbf{k}$ space is $dN = d^3k/(\Delta k_x \Delta k_x \Delta k_x) = (V/\pi^3)d^3k$. Frequently, it is more convenient to work with traveling waves (88); in this case, we should take into account that, as was just discussed, there are two different traveling wave

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

[59] This is, of course, the general property of waves of any physical nature, propagating in a linear medium – see, e.g., CM Sec. 6.5 and/or EM Sec. 7.3.

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 or, equivalently, to an 8-fold smaller number of states per unit volume d^3k:

Number of 3D states

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

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

Summation over 3D states

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

where $f(\mathbf{k})$ is any 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. (91) requires its multiplication by the corresponding *degeneracy factor* of orbital states.[60]

Finally, note that in systems with reduced wavefunction dimensionality, Eq. (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 $A >> 1/k^2$,

Number of 2D states

$$\boxed{dN = \frac{A}{(2\pi)^2} d^2k,} \qquad (1.92)$$

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

Number of 1D states

$$\boxed{dN = \frac{l}{2\pi} dk,} \qquad (1.93)$$

with the corresponding changes in the summation rule (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. (90), (99), and (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.

1.8. Exercise problems

1.1. The actual postulate made by N. Bohr in his original 1913 paper was not directly Eq. (8), but rather the assumption that at quantum leaps between adjacent electron orbits with $n >> 1$, the hydrogen atom either emits or absorbs the energy $\Delta E = \hbar\omega$, where ω is its classical radiation frequency – according to classical electrodynamics, equal to the angular velocity of the electron's rotation.[61] Prove that this postulate, complemented with the natural requirement that $L = 0$ at $n = 0$, is equivalent to Eq. (8).

1.2. Generalize the Bohr theory for a hydrogen-like atom/ion with a nucleus with the electric charge $Q = Ze$, to the relativistic case.

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[60] The front factor 2 in Eq. (1) for the number of electromagnetic wave modes is just one embodiment of the degeneracy factor, in that case describing two different polarizations of the waves with the same wave vector.

[61] See, e.g., EM Sec. 8.2.

1.3. A hydrogen atom, initially in the lowest excited state, returns to its ground state by emitting a photon propagating in a certain direction. Use the same approach as in Sec. 1(iv) to calculate the photon's frequency reduction due to atomic recoil.

1.4. Use Eq. (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: $\left(\hat{A}_1 + \hat{A}_2\right) + \hat{A}_3 = \hat{A}_1 + \left(\hat{A}_2 + \hat{A}_3\right)$.

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

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

1.6. Prove that the Schrödinger equation (25) with the Hamiltonian operator given by Eq. (41) is Galilean form-invariant, provided that the wavefunction is transformed as

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

where the prime sign marks the variables observed in the reference frame 0' that moves, without rotation and with a constant velocity **v**, relative to the "lab" frame 0. Give a physical interpretation of this transformation.

1.7.* Prove the so-called *Hellmann-Feynman theorem*:[62]

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

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

1.8.* Use Eqs. (73) and (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 source applies to the junction a sinusoidal ac voltage with frequency ω and amplitude A.

1.9. 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. (77) and compare the product $\delta x \delta p_x$ with the Heisenberg's uncertainty relation.

1.10. Looking at the lowest (red) line in Fig. 8, it seems plausible that the lowest-energy eigenfunction (84) of the 1D boundary problem (83) may be well approximated with an inverted quadratic parabola: $X(x) \approx Cx(a_x - x)$, where C is a normalization constant. Explore how good this approximation is.

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[62] Despite this common name, H. Hellmann (in 1937) and R. Feynman (in 1939) were not the first ones in the long list of physicists who had (apparently, independently) discovered this equality. Indeed, it has been traced back to a 1922 paper by W. Pauli and was carefully proved by P. Güttinger in 1931.

1.11. A particle placed in a hard-wall rectangular box with sides $\{a_x, a_y, a_z\}$ is in its ground state. Calculate the average force it exerts on each face of the box. Can these forces be characterized by a certain pressure?

1.12. A 1D quantum particle was initially in the ground state of a very deep, flat-bottom 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 is kept constant. Calculate the probability that after the change, the particle is still in the ground state of the system.

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

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

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

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

1.14. Calculate the potential profiles $U(x)$ for which the following wavefunctions,

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

(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 Heisenberg's uncertainty relation.

1.15. The wavefunction of an excited stationary state of a 1D particle moving in a potential profile $U(x)$ is related to that of its ground state as $\psi_e(x) \propto x\psi_g(x)$. Calculate the function $U(x)$.

1.16. A 1D particle of mass m, moving in a potential well $U(x)$, has the following stationary eigenfunction: $\psi(x) = C/\cosh\kappa x$, where C is the normalization constant and κ is a given real constant. Calculate the function $U(x)$ and the state's eigenenergy E.

1.17. Calculate the density dN/dE of traveling-wave quantum states inside large hard-wall rectangular boxes of various dimensions: $d = 1$, 2, and 3.

1.18.* A 1D particle is confined in a potential well of width a, with a flat bottom and hard, infinitely high walls. Use the finite-difference method with steps $a/2$ and $a/3$ to find as many eigenenergies as possible. Compare the results with each other, and with the exact formula.[63]

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[63] You may like to start by reading about the finite-difference method – see, e.g., CM Sec. 8.5 or EM Sec. 2.11.