ELEMENTS
OF
MODERN PHYSICS

Dr. Ing. Valerică D. Ninulescu

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Preface

This text has grown out of an introductory course in modern physics taught to second year undergraduates at the Faculty of Engineering in Foreign Languages, *Politehnica* University of Bucharest. It was intended from the beginning that the book would include all the essentials of an introductory course in quantum physics and it would be illustrated whenever appropriate with thechnical applications.

A set of solved problems is included at the end of each chapter.

V. Ninulescu
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Glossary of notations

e	exponential function, $\mathrm{e}^z = \exp(z)$
i	complex unity, $\mathrm{i}^2 = -1$
$\mathrm{Im}(.)$	imaginary part of a complex number
$\mathbb{R}$	the set of real numbers
c.c.	complex conjugate of the expression written in front of c.c.
z^*	complex conjugated of z
$\boldsymbol{v}$	vector
$\langle . \rangle$	average
$\int_{\boldsymbol{r}}$	integral over the whole three-dimensional space
$\hat{A}$	operator A
$\hat{A}^\dagger$	adjoint of $\hat{A}$
$\sim$	roughly similar; poorly approximates
k_B	Boltzmann constant
CM	centre of mass
lhs	left hand side
rhs	right hand side
1-D	one-dimensional
TDSE	time-dependent Schrödinger equation
TISE	time-independent Schrödinger equation

Chapter 1

The experimental foundations of quantum mechanics

At the end of the 19th century, it seemed that physics was able to explain all physical processes. According to the ideas of that time, the Universe was composed of matter and radiation; the matter motion could be studied by Newton's laws and the radiation was described by Maxwell's equations. Physics of that time is now called *classical physics.* The theory of special relativity (Albert Einstein, 1905) generalized classical physics to include phenomena at high velocities.

This confidence began to disintegrate due to the inability of the classical theories of mechanics and electromagnetism to provide a satisfactory explanation of some phenomena related to the electromagnetic radiation and the atomic structure. This chapter presents some physical phenomena that led to new ideas such us *the quantization of the physical quantities*, *the particle properties of radiation*, and *the wave properties of matter.* Certain physical quantities, such as energy and angular momentum, were found to take on a discrete, or *quantized*, set of values in some conditions, contrary to the predictions of classical physics. This discreteness property gave rise to the name of *quantum mechanics* for the new theory in physics.

Quantum mechanics reveals the existence of a universal physical constant, *Planck's constant*, whose present day accepted value in SI units is

$$h = 6.626\,068\,96(33) \times 10^{-34}\,\mathrm{J\,s}\,.$$

Its small value when measured in the macroscopic units of the SI shows that quantum physics is basically used at much smaller levels, such as the atomic and subatomic levels.

1.1 Thermal radiation

It is well known that every body with non-zero absolute temperature emits electromagnetic radiation with a continuous spectrum that contains all wavelengths. Let us explain this phenomenon in the frame of classical physics. Atoms and molecules are composed of charged particles. The irregular thermal motion produces irregular oscillatory motion of the electrons inside atoms, characterized by a continuous spectrum of frequencies. Since an oscillation is accelerated motion, each oscillation at a particular frequency leads to the emission of electromagnetic radiation of the same frequency.

Examples of thermal radiation include the solar radiation, the visible radiation emitted by a light bulb, or the infrared radiation of a household radiator.

The radiation incident on the surface of a body is partially reflected and the other part is absorbed. Dark bodies absorb most of the incident radiation and light bodies reflect most of the radiation. For example, a surface covered with lampblack absorbs about 97 % of the incident light and polished metal surfaces, on the other hand, absorb only about 6 % of the incident radiation, reflecting the rest. The *absorptance* (*absorption factor*) α of a surface is defined as the ratio of the radiant energy absorbed to that incident upon it; this quantity is dependent on wavelength, temperature, and the nature of the surface.

Suppose a body at thermal equilibrium with its surroundings. Such a body emits and absorbs the same energy in unit time, otherwise its temperature can not remain constant. The radiation emitted by a body at thermal equilibrium is termed *thermal radiation.*

A *blackbody* is an object that absorbs all electromagnetic radiation falling on it.[1] This property refers to radiation of all wawelengths and all angles of incidence. However, a blackbody is an abstraction that does not exist in the real world. The best practical blackbody is the surface of a small hole in a container maintained at a constant temperature and having blackened interior, because any radiation entering through the hole suffers multiple reflections, a lot getting absorbed on each reflection, and ultimately is completely absorbed inside (Fig. 1.1). Consider now the reverse process in which radiation emitted by the interior cavity walls escapes through the hole. The interior walls are constantly radiating and reabsorbing their own radiation and after a while the state of thermal equilibrium is attained.[2] A small frac-

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[1] The term arises because such bodies do not reflect incident visible radiation, and therefore appear black.

[2] The small size of the hole ensures that neither the radiation which enters the cavity

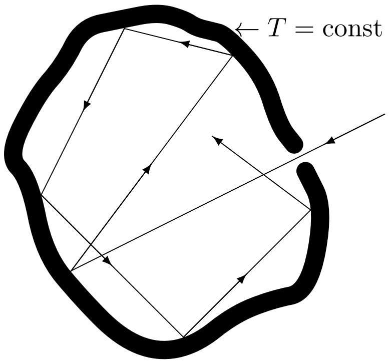

Fig. 1.1 A cavity with a small hole behaves as a perfect absorber. The inner walls are blackened and maintained at temperature $T = \text{const}$.

tion of this radiation is incident upon the hole and pass through it. Since the surface behaves as a blackbody, the radiation that escapes the cavity has the properties of a blackbody radiator. The study of the cavity radiation led Gustav Robert Kirchhoff to the conclusion that blackbody radiation is homogeneous, isotropic, nonpolarized, independent of the nature of the walls or the form of the cavity.

The ability of a surface to emit thermal radiation is characterized by its *emittance* ε, defined as the ratio of the radiant energy emitted by a surface to that emitted by a blackbody at the same temperature. As the absorptance, the emittance depends on wavelength, temperature, and the nature of the surface.

The emittance of a surface can be related to its absorptance as follows. Suppose the surface of the interior cavity in Fig. 1.1. Let us denote by L_λ the spectral radiance inside the cavity (power per unit surface per unit solid angle per unit frequency interval). Taking into account that at equilibrium the walls emit as much as they absorb, we have $\varepsilon_\lambda L_\lambda = \alpha_\lambda L_\lambda$, so that

$$\varepsilon_\lambda = \alpha_\lambda \, . \tag{1.1}$$

This result is known as *Kirchhoff's radiation law* (1859). According to Eq. (1.1), objects that are good emitters are also good absorbers. For example, a blackened surface is an intense emitter surface as well as an intense absorber one.

A *grey body* is defined as a body with constant emittance/absorptance over all wavelengths and temperatures. Such an ideal body does not exist in practice but this assumption is a good approximation for many objects.

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from outside, nor that which escapes outside, can alter the thermal equilibrium in the cavity.

The laws governing the emission or absorption of thermal radiation by blackbodies have a universal character and is therefore of special interest.

1.1.1 Quantitative laws for blackbody radiation

Stefan–Boltzmann law

The *radiant exitance* (energy radiated from a body per unit area per unit time), M, of a blackbody at temperature T grows as T^4:

$$M(T) = \sigma T^4 \,, \tag{1.2}$$

where $\sigma \approx 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$ is Stefan–Boltzmann constant. The law was first formulated in 1879 by Josef Stefan as a result of his experimental measurements; the same law was derived in 1884 by Ludwig Boltzmann from thermodynamic considerations.

Stephan–Boltzmann law can be extended to a grey body of emittance ε as

$$M(T) = \varepsilon\sigma T^4 \,. \tag{1.3}$$

Wien's displacement law

Wilhelm Wien experimental studies on the spectral distribution of blackbody radiation revealed:

- the radiative power per wavelength interval has a maximum at a certain wavelength λ_{max};
- the maximum shifts to shorter wavelengths as the temperature T is increased.

Wien's displacement law (1893) states that the wavelength for maximum emissive power from a blackbody is inversely proportional to its absolute temperature,

$$\lambda_{\mathrm{max}} T = b \,. \tag{1.4}$$

The constant b is called *Wien's displacement constant* and its value is $b \approx 2.898 \times 10^{-3}\,\mathrm{m\,K}$.

For example, when iron is heated up in a fire, the first visible radiation is red. Further increase in temperature causes the colour to change to orange, then yellow, and white at very high temperatures, signifying that all the visible frequencies are being emitted equally.

Wien's displacement law can be used to determine the temperature of a blackbody spectroscopically by measuring the wavelength at which the intensity of the radiation is maximum. This method has been used extensively in determining stellar temperatures.

Rayleigh–Jeans law. Ultraviolet catastrofe

The spectral distribution of blackbody radiation is specified by the *spectral radiant exitance* M_λ—that is, emitted power per unit of area and unit of wavelength. In an attempt to furnish a formula for M_λ, it proves convenient to focus our attention on the radiation inside a cavity. Let ρ_λ denote the *spectral radiant energy density*, which is defined as the energy per unit of volume and unit of wavelength. It can be shown that (see Problem 1.6)

$$M_\lambda = (1/4)c\rho_\lambda\,, \tag{1.5}$$

where c is the speed of light in vacuum.

It is also useful to consider the spectral quantities as functions of frequency instead of wavelength. Based on the relationship $\nu = c/\lambda$, the radiation with the wavelength inside the interval $(\lambda, \lambda + \mathrm{d}\lambda)$ has the frequency between $\nu - \mathrm{d}\nu$ and ν, where $\mathrm{d}\nu = |\mathrm{d}\nu/\mathrm{d}\lambda|\,\mathrm{d}\lambda = (c/\lambda)^2\mathrm{d}\lambda$. Now, the spectral radiant exitance in terms of frequency M_ν and the spectral radiant exitance in terms of wavelength M_λ are related by

$$M_\nu(\nu)\,\mathrm{d}\nu = M_\lambda(\lambda)\,\mathrm{d}\lambda\,. \tag{1.6}$$

Similarly,

$$\rho_\nu(\nu)\,\mathrm{d}\nu = \rho_\lambda(\lambda)\,\mathrm{d}\lambda\,. \tag{1.7}$$

The classical physics result for ρ_ν is

$$\rho_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3}\,k_\mathrm{B}T\,, \tag{1.8}$$

known as *Rayleigh–Jeans formula.* The comparison with the experimental results shows a good agreement for small frequencies. However, ρ_ν do not exhibite a maximum, being an increasing function of frequency. More than that, the radiant energy density is

$$\rho(T) = \int_0^\infty \rho_\nu(\nu, T)\,\mathrm{d}\nu = \frac{8\pi k_\mathrm{B}T}{c^3}\int_0^\infty \nu^2\mathrm{d}\nu = \infty\,,$$

an unacceptable result, known as *the ultraviolet catastrophe.*

Planck's radiation law

In 1900 Max Planck determined a formula which agrees with the experiment at whatever frequency based on a new and revolutionary idea: the exchange of energy between a body and its surroundings can be performed only in discrete portions, the minimum energy implied in the exchange being proportional to the frequency, $h\nu$. *Planck radiation law* reads

$$\rho_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp(h\nu/k_\mathrm{B}T) - 1} . \tag{1.9}$$

The constant h is called *Planck's constant* and has the value $h \approx 6.626 \times 10^{-34}\,\mathrm{J\,s}$.

By use of Eq. (1.7), we get

$$\rho_\lambda(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(hc/\lambda k_\mathrm{B}T) - 1} . \tag{1.10}$$

To express the radiant exitance E_λ, Eq. (1.5) is used:

$$E_\lambda(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{\exp(hc/\lambda k_\mathrm{B}T) - 1} . \tag{1.11}$$

Planck's radiation formula contains all the information previously obtained. Figure 1.2 presents the graph of the spectral energy density $\rho_\lambda(\lambda, T)$ given by Eq. (1.10).

Applications

- Pyrometer: device for measuring relatively high temperatures by measuring radiation from the body whose temperature is to be measured.
- Infrared thermography: a fast non-distructive inspection method that maps the temperature differences of any object in a range from −50 °C to 1500 °C.

1.2 Photoelectric effect

The photoelectric effect consists in the ejection of electrons from a solid by an incident electromagnetic radiation of sufficiently high frequency. This frequency is in the visible range for alkali metals, near ultraviolet for other metals, and far ultraviolet for non-metals. The ejected electrons are called *photoelectrons.*

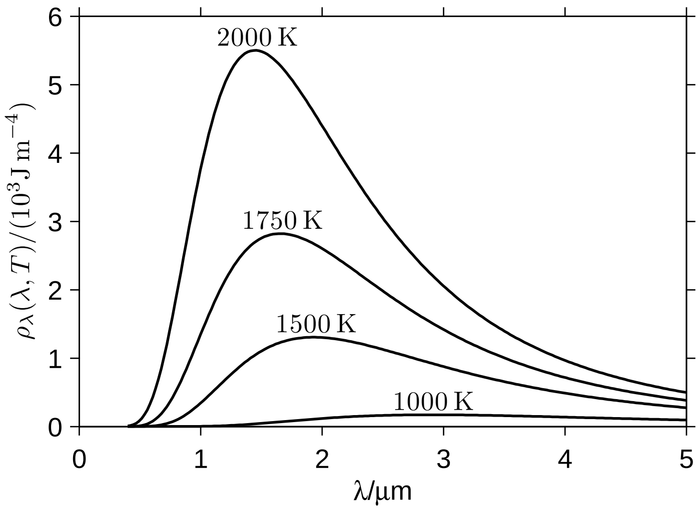

Fig. 1.2 Spectral energy density $\rho_\lambda(\lambda, T)$ of a blackbody at a few temperatures.

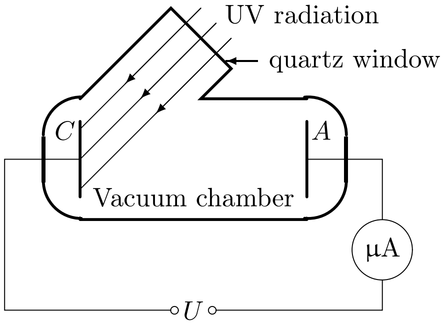

Fig. 1.3 Experimental arrangement for the study of the photoelectric effect.

The phenomenon was first observed by Heinrich Hertz in 1887; he noticed that the minimum voltage required to draw sparks from a pair of metallic electrodes was reduced when they were illuminated by ultraviolet radiation. Wilhelm Hallwachs (1888) found that when ultraviolet radiation was incident on a negatively charged zinc surface, the charge leaked away quickly; if the surface was positively charged, there was no loss of charge due to the incident radiation. More than that, a neutral surface became positively charged when illuminated by ultraviolet radiation. It is evident that only negative charges are emitted by the surface under its exposing to ultraviolet radiation. Joseph John Thomson (1899) established that the ultraviolet radiation caused electrons to be emitted, the same particles found in cathode rays.

A typical arrangement for the study of the photoelectric effect is depicted

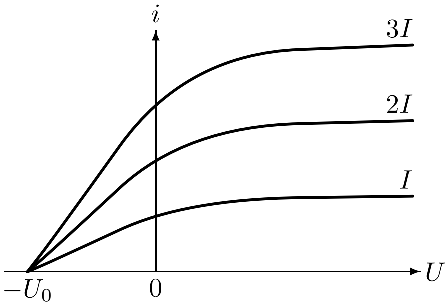

Fig. 1.4 Photocurrent (i) versus potential difference (U) between cathode and anode for different values of the intensity (I, $2I$, and $3I$) of the monochromatic beam of light.

in Fig. 1.3. A vacuumed glass tube contains two electrodes (A = anode = collecting plate, C = cathode) and a quartz window allowing light to shine on the cathode surface. The electrons are emitted at the cathode, fall on the anode, and complete a circuit. The resulting current is measured by a sensitive ammeter. It is very important that the surface of the cathode is as clean as possible. An adjustable potential difference U of a few volts is applied across the gap between the cathode and the anode to allow the photocurrent control.

- If A is made positive with respect to C, the electrons are accelerated toward A. When all electrons are collected, the current saturates.
- If A is made negative with respect to C, the electric field tends to repel the electrons back towards the cathode. For an electron to reach the collecting plate, it must have a kinetic energy of at least eU, where e is the magnitude of the electron charge and U is the retarding voltage. As the repelling voltage is increased, fewer electrons have sufficient energy to reach the plate, and the current measured by the ammeter decreases. Let U_0 denote the voltage where the current just vanishes; the maximum kinetic energy of the emitted electrons is

  $$(1/2)mv_{\max}^2 = eU_0\,, \tag{1.12}$$

  where m denotes the mass of the electron. U_0 is called *stopping potential* (*voltage*).

The experimental results for a given emitting cathode are sketched in Figs. 1.4 and 1.5. From Fig. 1.4 it is clear that for a given metal and frequency of incident radiation, the rate at which photoelectrons are ejected is proportional to the intensity of the radiation. Figure 1.5 reveals other two results. First, a given surface only emits electrons when the frequency of the radiation with which it is illuminated exceeds a certain value; this frequency, ν_0 in Fig. 1.5, is called *threshold frequency*. It is experimentally proven that

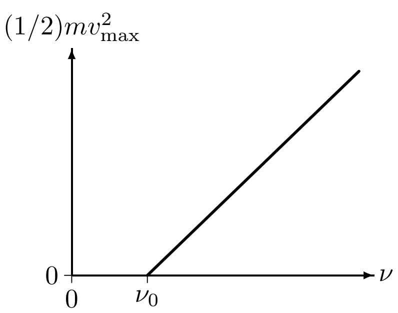

Fig. 1.5 Dependence of the maximum kinetic energy of photoelectrons on the frequency of the incident radiation.

ν_0 depends on the cathode material. Secondly, the energy of the photoelectrons is independent of the radiation intensity, but varies linearly with the radiation frequency. The experiment also shows that there is no significant delay between irradiation and electron emission (less than 10^{-9} s).

The minimum energy Φ needed to extract the electron from the material is called *work function*. If the electron absorb a larger energy then Φ, the energy in excess is kinetic energy of the photoelectron.

The experimental results disagree with the Maxwell wave theory of light:

- According to this theory, as the electromagnetic wave reaches the surface, the electron start to absorb energy from the wave. The more intense the incident wave, the greater the kinetic energy with which the electrons should be ejected from the surface. In contrast, the experiment shows that the increase of the wave intensity produces an increase in the number of photoelectrons, but not their energy.
- The wave picture predicts the occurence of the photoelectric effect for any radiation, regardless of frequency.
- There should be a significant delay between the surface irradiation and the release of photoelectrons (see Problem 1.8).

In order to account for the photoelectric effect experimental results, Albert Einstein (1905) proposed a new theory of light. According to this theory, light of fixed frequency ν consists of a collection of indivisible discrete packages, called *quanta*, whose energy is

$$E = h\nu\,. \tag{1.13}$$

The word *photon* for these quantized packets of light energy came later, given by Gilbert Newton Lewis (1926).

Einstein assumed that when light strikes a metal, a single photon interacts with an electron and the photon energy is transferred to the electron. If

$h\nu > \Phi$, then the electron is emitted from the surface with residual kinetic energy

$$(1/2)mv_{\mathrm{max}}^2 = h\nu - \Phi \,. \tag{1.14}$$

Otherwise, the electron remains trapped in the metal, regardless of the intensity of the radiation; the threshold frequency of the photoelectric effect is

$$\nu_0 = \Phi/h \,. \tag{1.15}$$

Einstein equation of the photoelectric effect [Eq. (1.14)] exactly explains the observed dependence of the maximum kinetic energy on the frequency of the radiation (Fig. 1.5).

Let us continue the explanation of the experimental photoelectric effect findings. Increasing the intensity of the radiation n times means an n times increase of the number of photons, while the energy of each individual photon remains the same. For sufficiently low radiation intensities, it can be assumed that the probability of an electron to absorb two or more photons is negligibly small compared to the probability of absorbing a single photon. It follows that the number of electrons emitted increases also by the factor n . Finally, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electrons is nearly instantaneous upon absorption of the light.

Combining Eqs. (1.12) and (1.14) we get

$$U_0 = (h/e)\nu - \Phi/e \,. \tag{1.16}$$

The stopping voltage as a function of the radiation frequency is a straight line whose slope is h/e and whose intercept with the frequency axis is $\nu_0 = \Phi/h$. This experimental dependence can be used to calculate Planck's constant and the work function of the metal. (The value of e is considered as known.) The result for the Planck's constant is the same as that found for blackbody radiation; this agreement can be considered as a further justification of the portion of energy $h\nu$ introduced by Planck. From the observed value of ν_0, the workfunction is calculated as $\Phi = h\nu_0$. Table 1.1 furnishes the work function of some chemical elements.

The photoelectric effect is perhaps the most direct and convincing evidence of the corpuscular nature of light. That is, it provides undeniable evidence of the quantization of the electromagnetic field and the limitations of the classical field equations of Maxwell. Another evidence in support of the existence of photons is provided by the Compton effect.

Applications: photocells, photomultiplier

Table 1.1 Electron work function Φ of some elements [10]. In general, Φ differs for each face of a monocrystalline sample. Inside the table, 'polycr' is an abbreviation for 'polycrystalline sample'.

Element	Plane	Φ/eV	Element	Plane	Φ/eV
Ag (silver)	100	4.64	Cu (copper)	100	5.10
	110	4.52		110	4.48
	111	4.74		111	4.94
Al (aluminum)	100	4.20	Fe (iron)	100	4.67
	110	4.06		111	4.81
	111	4.26	K (potassium)	polycr	2.29
Au (gold)	100	5.47	Li (lithium)	polycr	2.93
	110	5.37	Mg (magnesium)	polycr	3.66
	111	5.31	Na (sodium)	polycr	2.36
Ca (calcium)	polycr	2.87	Rb (rubidium)	polycr	2.261
Cr (chromium)	polycr	4.5	Ti (titanium)	polycr	4.33
Cs (cesium)	polycr	1.95	Zn (zinc)	polycr	3.63

1.3 Wave–particle duality of radiation

The phenomena of the interference and diffraction can be explained only on the hypothesis that radiant energy is propagated as a wave. The results of the experiments on the photoelectric effect leave no doubt that in its interaction with matter, radiant energy behaves as though it were composed of particles; it will be shown later that similar behaviour is observed in the Compton effect and the processes of emission and absorption of radiation. The two pictures should be understood as complementary views of the same physical entity. This is called the *wave–particle duality of radiation*.

A particle is characterized by its energy and momentum; a wave is characterized by its wave vector and angular frequency. We perform here the link between the two pictures.

The energy of a photon is given by Eq. (1.13). We complete the characterization of the photon with a formula for its momentum.

Classical electromagnetic theory shows that a wave carries momentum in addition to energy; the relation between the energy E contained in a region and the corresponding momentum p is

$$E = cp\,. \tag{1.17}$$

It is natural to extend this formula for the quantum of radiation, i.e., the photon. For a plane wave of wave vector $\boldsymbol{k}$, the angular frequency of the wave is $\omega = k/c$ and the photon momentum can be written

$$p = \frac{E}{c} = \frac{\hbar\omega}{c} = \hbar k\,. \tag{1.18}$$

This formula can be written with vectors,

$$\boldsymbol{p} = \hbar\boldsymbol{k}\,. \tag{1.19}$$

To sum up, the two behaviours of radiation are linked by *Planck–Einstein relations*

$$\boxed{E = h\nu = \hbar\omega \quad \text{and} \quad \boldsymbol{p} = \hbar\boldsymbol{k}\,.} \tag{1.20}$$

1.4 Compton effect

The existence of photons is also demonstrated by experiments in which x-rays or γ-rays are scattered by a target. The experiments performed in 1922 by Arthur Holly Compton with x-rays and a graphite target show that, in addition to the incident radiation, there is another radiation present, of higher wavelenth. The radiation scattering with change in wawelength is called *Compton effect.* Given that λ is the wavelength of the incident radiation and λ' that of the scattered radiation, Compton found that $\lambda' - \lambda$ does not depend upon the wavelength of the incident rays or upon the target material; it depends only on the direction θ of scattering (angle between the incident wave and direction in which scattered waves are detected) according to the experimental relation

$$\lambda' - \lambda = \lambda_{\mathrm{C}}(1 - \cos\theta)\,. \tag{1.21}$$

The constant $\lambda_{\mathrm{C}} \approx 2.426 \times 10^{-12}$ m is nowadays called *Compton wavelength of the electron.*

The scattered radiation is interpreted as radiation scattered by free or loosely bound electrons in the atoms of matter.

The classical treatment of the x-rays or γ-rays as waves implies that an electron is forced to oscillate at a frequency equal to that of the wave. The oscillating electron now acts as a source of new electromagnetic waves having the same frequency. Therefore, the wavelengths of the incident and scattered x-rays should be identical. We must therefore conclude that the classical theory fails in explaining the Compton effect.

Treating the radiation as a beam of photons, a photon can transfer part of its energy and linear momentum to a loosely bound electron in a collision

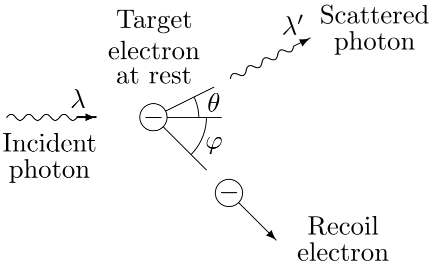

Fig. 1.6 In Compton scattering an x-ray photon of wavelength λ collides with an electron initially at rest. The photon scattered in the direction θ has the wavelength $\lambda' > \lambda$.

(Fig. 1.6). Since the energy of a photon is proportional to its frequency, after the collision the photon has a lower frequency and thus a longer wavelength. To be more specific, let $p = h\nu/c = h/\lambda$ and $p' = h\nu'/c = h/\lambda'$ be the momenta of the photon before and after the collision. The electron can be considered initially at rest. After the collision it acquires a kinetic energy

$$T = h\nu - h\nu' = hc/\lambda - hc/\lambda' \tag{1.22}$$

and a momentum

$$\boldsymbol{p}_\mathrm{e} = \boldsymbol{p} - \boldsymbol{p}', \quad p_\mathrm{e}^2 = (\boldsymbol{p} - \boldsymbol{p}')^2 = \frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - 2\,\frac{h}{\lambda}\,\frac{h}{\lambda'}\cos\theta\,, \tag{1.23}$$

as required by the conservation of energy of momentum. Here, T and $\boldsymbol{p}_\mathrm{e}$ are related by the relativistic equation

$$T = c\sqrt{p_\mathrm{e}^2 + m^2c^2} - mc^2\,. \tag{1.24}$$

Inserting Eqs. (1.22) and (1.23) into Eq. (1.24), rearranging and squaring, we get

$$\left(\frac{hc}{\lambda} - \frac{hc}{\lambda'} + mc^2\right)^2 = \frac{h^2c^2}{\lambda^2} + \frac{h^2c^2}{\lambda'^2} - 2\,\frac{hc}{\lambda}\,\frac{hc}{\lambda'}\cos\theta + m^2c^4\,.$$

After performing the elementary calculations it is obtained Eq. (1.21), where

$$\lambda_\mathrm{C} = h/mc\,. \tag{1.25}$$

The presence of the radiation with the same wavelength as the incident radiation is not predicted by Eq. (1.21). This radiation is explained by the scattering of the incident radiation by tightly bound electrons. In this case, the photon collides with the entire atom, whose mass is considerably greater than the mass of a single electron. The photon and atom exchange momentum, but the amount of exchanged energy is much less than in case of the photon–electron collision; the wavelength shift is not significant.

Compton scattering is of prime importance to radiobiology, as it happens to be the most probable interaction of high energy x-rays with atomic nuclei in living beings and is applied in radiation therapy.

1.5 Atomic spectra

By the early 1900s, the following observations concerning the atomic emission spectra had been done:

- When a gas of an element at low pressure is subjected to an input of energy, such as from an electric discharge, the gas emits electromagnetic radiation.
- On passing through a very thin slit and then through a prism the electromagnetic radiation can be separated into its component frequencies. It was found that a gas at low pressure emits only discrete lines on the frequency scale.
- The *emission spectrum* is made up of *spectral series* in the different regions (infrared, visible, and ultraviolet) of the spectrum of electromagnetic radiation; the spectral lines in a series get closer together with increasing frequency.
- Each element has its own unique emission spectrum.

The simpliest line spectrum is that of the hydrogen atom. Its four spectral lines in the visible have wavelengths that can be represented accurately by the Johann Balmer formula (1885)

$$\lambda_n = C\frac{n^2}{n^2-4} \qquad n = 3, 4, \dots\ , \tag{1.26}$$

where $C \approx 364.6\,\mathrm{nm}$. This formula was written by Johannes Rydberg (1888) for wavenumbers,

$$\tilde{\nu}_n = \frac{1}{\lambda_n} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, \dots\ ,$$

where the new constant R is nowadays called *Rydberg constant*, and generalized in the form

$$\tilde{\nu}_{n_1n_2} = \frac{1}{\lambda_{n_1n_2}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{R}{n_1^2} - \frac{R}{n_2^2}\,, \ n_1 = 2, 3, \dots, \ n_2 = 3, 4, \dots, \tag{1.27}$$

and $n_1 < n_2$. Here, n_1 defines the spectral series. For a given series, with increasing values of n_2 , the wavenumber approaches the limit R/n_1^2 . The separation of consecutive wavenumbers of a given series decreases so that the wavenumber can not exceed the *series limit.* In principle, an infinite number of lines lie at the series limit.

According to Eq. (1.27) the wavenumber of any line of the hydrogen spectrum is the difference of two *spectral terms*:

$$\tilde{\nu}_{n_1 n_2} = \mathcal{T}_{n_1} - \mathcal{T}_{n_2}, \tag{1.28}$$

with

$$\mathcal{T}_n = R/n^2. \tag{1.29}$$

It proves empirically that the lines of other chemical elements can also be expressed as the difference of two terms; however, a spectral term has a more complicated form.

None of the above quantitative result could be explained satisfactorily in the frame of clasical physics.

1.6 Bohr model of the hydrogen atom

Atoms have radii on the order of 10^{-10} m. To study the internal structure of atoms, Ernest Rutherford, Hans Geiger and Ernest Marsden (1909) directed α-particles from radioactive radium at thin gold foil. Based on the results of the α-particles scattering by the gold atoms, Rutherford (1911) furnished the *nuclear atom model* (*planetary model of the atom*): the atom consists of a positively charged heavy core (nucleus) of radius on the order of 10^{-15} m and a cloud of negatively charged electrons. Atomic structure was pictured as analogous to the solar system, with the nucleus playing the role of the Sun and the electrons that of the planets bound in their orbits by Coulomb attraction to the nucleus.

About as soon as the model was published it was realized that the atom model suffers from two serious deficiencies:

1. Orbital motion is an accellerated motion and electrons are charged particles. According to the electromagnetic theory, the electrons should radiate energy in the form of electromagnetic waves. Electrons lose energy and they should spiral into the nucleus in a time of the order of 10^{-8} s. This conclusion completely disagrees with experiment, since the atoms are stable.

2. The frequency of the radiated energy is the same as the orbiting one. As the orbiting frequency can take a continuous range of values, the discrete emission spectrum of atoms can not be explained.

To overcome these deficiencies, Niels Bohr (1913) improved the Rutherford model of the atom by introducing the following postulates:

- For every atom there is an infinite number of stationary states in which the atom can exist without emitting radiation. The energies of the stationary states,
$$E_1,\ E_2,\ E_3, \ldots ,$$
form a discrete set of values.

- Emission and absorption of radiation are always associated to a transition of the atom from one stationary state to another. The frequency ν of the radiation emitted or absorbed respectively during such a transition is given by the equation
$$h\nu = |E_2 - E_1| \, , \tag{1.30}$$
where E_1 and E_2 denote the energy of the atom in the two stationary states.

Bohr applied these postulates for the hydrogen atom. The electron of mass m and electric charge $-e$ is assumed to move around the nucleus of electric charge e in a circular orbit. The selection of the allowed stationary states is performed by the following *quantization rule* for the angular momentum: the angular momentum of the electron in a stationary state is an integer multiple of $\hbar$:

$$mvr = n\hbar \, , \quad \text{where} \quad n = 1, 2, 3, \ldots \, . \tag{1.31}$$

We are now in a position to solve the problem. Newton's second law applied for the electron motion on a circular orbit of radius r with the velocity v under the attractive Coulomb force exerted by the nucleus yields

$$m\frac{v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \, . \tag{1.32}$$

Combining Eqs. (1.31) and (1.32), we find

$$r_n = \frac{4\pi\epsilon_0 \hbar^2}{me^2} n^2 = a_0 n^2 \tag{1.33}$$

and

$$v_n = \frac{e^2}{4\pi\epsilon_0 \hbar} \frac{1}{n} \, . \tag{1.34}$$

The radius

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \approx 5.29 \times 10^{-11}\,\mathrm{m} \tag{1.35}$$

is called the *Bohr radius*. This value sets the scale for atomic dimension.

The potential energy of the electron in the hydrogen atom is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \,. \tag{1.36}$$

The energy of the atom in state n is

$$E_n = T_n + V_n = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\epsilon_0 r_n}$$

that gives

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}\,, \quad n = 1, 2, 3, \dots \,. \tag{1.37}$$

The integer n determines the energy of the bound state of the atom and it is called *principal quantum number.* Figure 1.7 presents the *diagram of energy levels* for the hydrogen atom. The state of minimum energy, called *ground-state*, has the energy

$$E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx 13.6\,\mathrm{eV}\,. \tag{1.38}$$

This value sets the scale for atomic energy. The states of higher energy are called *excited states.* All energies of the bound atom are negative; states of positive energies refers to the ionized atom.

The *ionization energy* of the hydrogen atom, defined as the amount of energy required to force the electron from its lowest energy level entirely out of the atom is

$$E_{\mathrm{I}} = -E_1 \approx 13.6\,\mathrm{eV}\,. \tag{1.39}$$

Let us now calculate the frequencies of the hydrogen spectrum. In the transition between the states n_1 and $n_2 > n_1$, the frequency of the radiation emitted or absorbed is

$$\nu_{n_1 n_2} = (E_{n_2} - E_{n_1})/h$$

and the calculus yields

$$\nu_{n_1 n_2} = \frac{m}{4\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) . \tag{1.40}$$

The wavelength $\lambda_{n_1 n_2} = c/\nu_{n_1 n_2}$ of the radiation is given by

$$\frac{1}{\lambda_{n_1 n_2}} = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) , \tag{1.41}$$

where

$$R_\infty = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx 1.097\times 10^7\,\mathrm{m}^{-1} \tag{1.42}$$

is the *Rydberg constant* for hydrogen; the subscript reminds us the premise that the nucleus is exceedingly massive compared with the electron.

The great success of the Bohr model had been in explaining the spectra of hydrogen-like (single electron around a positive nucleus) atoms. Even though the Bohr theory is now extended and altered in some essential respects by quantum mechanics, its knowledge considerably helps the understanding of new theories. In fact, a number of phenomena in spectroscopy can be dealt with by making use of Bohr theory alone.

1.7 Correspondence principle

One of the guiding principles used in the development of quantum theory was Bohr's correspondence principle (1920) which indicates that *quantum theory should give results that approach the classical physics results for large quantum numbers.*

To illustrate this principle let us discuss the hydrogen atom spectrum. The quantum description of the atom is performed in the Bohr theory framework. By use of Eq. (1.40) the frequency of the radiation in the transition between states $n-1$ and n is

$$\nu_{n-1,n} = \frac{m}{4\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left[\frac{1}{(n-1)^2}-\frac{1}{n^2}\right] = \frac{m}{4\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{2n-1}{n^2(n-1)^2}\,.$$

We consider now large quantum numbers, i.e., $n \gg 1$. The frequency of the quantum transition becomes

$$\nu_{n-1,n} \approx \frac{m}{4\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{2n}{n^4} = \frac{m}{2\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^3}\,.$$

On the other hand the motion of the electron on the nth orbit has the frequency

$$\nu_n = \frac{v_n}{2\pi r_n} = \frac{m}{2\pi\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^3}\,,$$

where Eqs. (1.33) and (1.34) were used. According to classical theory the atom emits radiation at the frequency ν_n; the comparison of the frequency expressions gives $\nu_{n-1,n} \approx \nu_n$ in agreement to the correspondence principle.

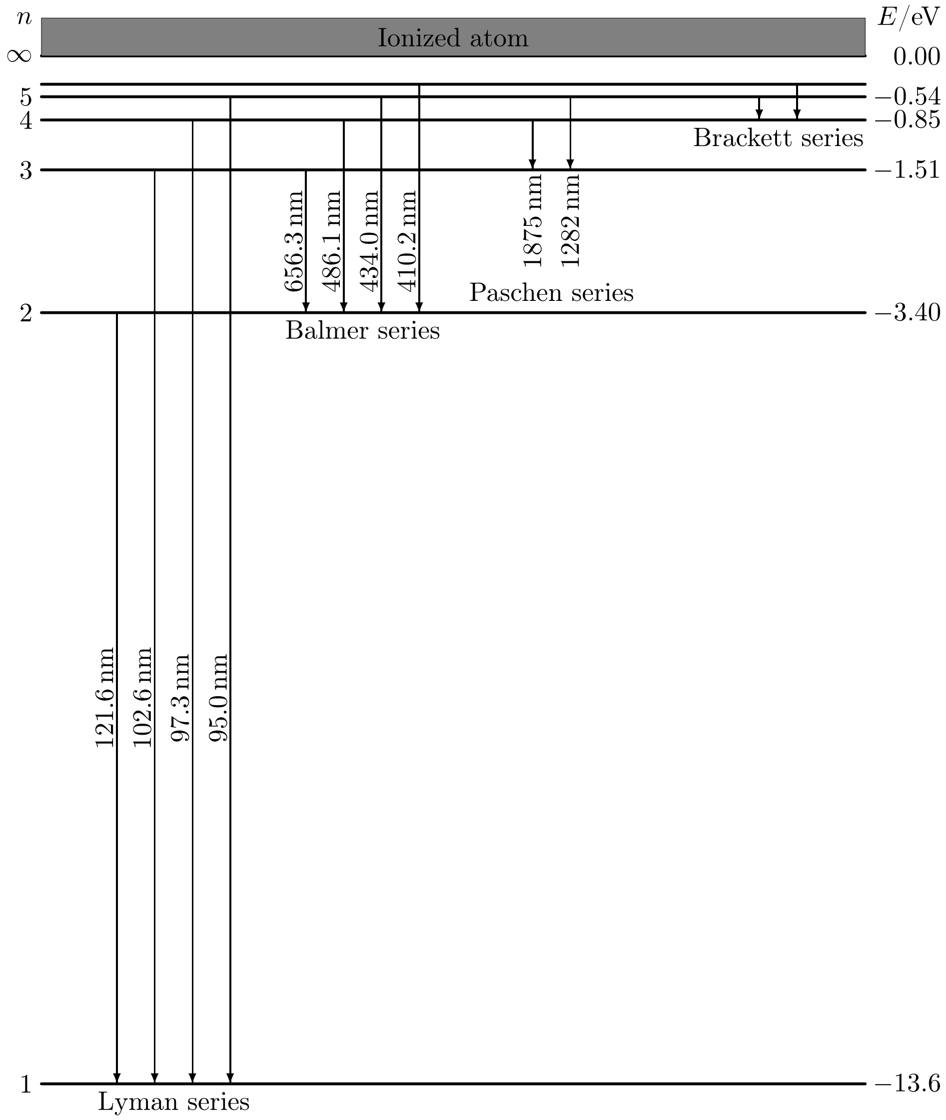

Fig. 1.7 Energy level diagram for hydrogen and a few spectral lines of the Lyman, Balmer, and Paschen series.

More that that, for large values of the quantum number n the hydrogen energy levels lie so close together that they form almost a continuum; it follows that the classical continuum description of the spectrum should correspond to transitions between two such states.

1.8 Einstein's phenomenological theory of radiation processes

In 1917 Einstein explained phenomenologically the radiation-matter interaction based on the quantum ideas of that time: Planck's quantum hypothesis and Bohr's planetary model of the hydrogen atom. Einstein's postulates could all be justified by the later developed quantum mechanical treatments of the interaction processes.

Suppose N identical atoms in unit volume, each atom having a pair of bound-state energy levels E_1 and E_2, $E_2 > E_1$ (Fig. 1.8). The two atomic levels are allowed to be multiplets with degeneracies g_1 and g_2. The mean numbers of atoms per unit volume in the two multiplet states are denoted by N_1 and N_2. Assuming that all the atoms are in these states,

$$N_1 + N_2 = N\,. \tag{1.43}$$

The atomic medium is considered in a radiation field whose spectral radiant energy density at frequency ν given by

$$h\nu = E_2 - E_1 \tag{1.44}$$

is $\rho_\nu(\nu)$.

Einstein considers three basic interaction processes between radiation and atoms (Fig. 1.8).

1. Spontaneous emission

An atom in state 2 spontaneously performes a transition to state 1 and a photon of frequency ν is emitted. The photon is emitted in a random direction with arbitrary polarization. The probability per unit time for occurence of this process is denoted by A_{21} and is called *Einstein coefficient for spontaneous emission.*

The total rate of spontaneous emissions is

$$-\dot{N}_2(t) = A_{21}N_2(t)$$

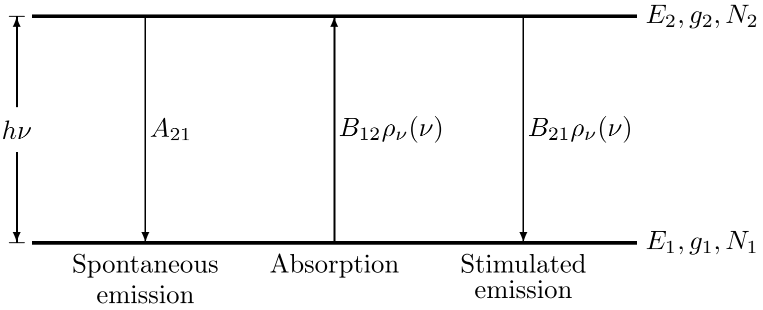

Fig. 1.8 Radiative transitions between to energy levels.

Table 1.2 Transition probability A for hydrogen lines in the visible range [10]. Each transition is identified by the wavelength λ and the statistical weights g_i and g_k, of the lower (i) and upper (k) states.

λ/nm	g_i	g_k	A/s^{-1}
410.173	8	72	9.732×10^5
434.046	8	50	2.530×10^6
486.132	8	32	8.419×10^6
656.280	8	18	4.410×10^7

and the integration with the initial condition at $t = 0$ gives

$$N_2(t) = N_2(0)\exp(-A_{21}t)\,.$$

The time in which the population falls to 1/e of its initial value is

$$\tau_{21} = 1/A_{21} \tag{1.45}$$

and is called *lifetime* of level 2 with respect to the spontaneous transition to level 1 (see Problem 1.16).

A few values of the transition probability rate are provided by Table 1.2.

In the absence of a radiation field the transition 1 → 2 is impossible due to violation of the energy conservation law.

2. Absorption

In the presence of a radiation field an atom initially in state 1 can jump to state 2 by absorption of a photon of frequency ν. The probability per unit time for this process is assumed to be proportional to the spectral energy density at frequency ν; the total rate of absorptions is

$$-\dot{N}_1 = B_{12}\rho_\nu(\nu)N_1\,, \tag{1.46}$$

where B_{12} is called *Einstein coefficient for absorption.*

3. Stimulated emission

Einstein postulates that the presence of a radiation field can also stimulate the transition 2 → 1 of the atom; energy conservation law asks for the emission of a photon of frequency ν. The probability per unit time for this process is assumed to be proportional to the spectral energy density at frequency ν; the total rate of stimulated emissions is

$$-\dot{N}_2 = B_{21}\rho_\nu(\nu)N_2\,, \tag{1.47}$$

where B_{21} is called *Einstein coefficient for stimulated emission.* The radiation produced during the stimulated emission process adds coherently to the existing one; this means that radiation created through stimulated emission has the same frequency, direction of propagation, polarization and phase as the radiation that forces the emission process.

The stimulated emission process was unknown before 1917. The reason for its introduction by Einstein will be made clear during next section.

Einstein coefficients defined above are independent of the radiation field properties and are treated here as phenomenological parameters. They depend only on the properties of the two atomic states.

Due to all radiative transitions presented above, the populations $N_{1,2}$ of the two energy levels change in time according to the equations

$$\dot{N}_1 = -\dot{N}_2 = -B_{12}\rho_\nu(\nu)\,N_1 + [A_{21} + B_{21}\rho_\nu(\nu)]N_2\,, \quad N_1 + N_2 = N\,. \tag{1.48}$$

1.8.1 Relations between Einstein coefficients

Let us consider the atomic system defined above in equilibrium with thermal radiation; the spectral radiant energy density $\rho_\nu(\nu)$ is given now by Planck's formula [Eq. (1.9)]. This special case will lead us to establish relations between Einstein coefficients.

The equilibrium condition for the radiation-matter interaction expresses as follows. For the radiation field the equilibrium condition means equality of emitted quanta and absorbed quanta. For the atomic system, the equilibrium condition writes $\dot{N}_1 = \dot{N}_2 = 0$. These conditions are equivalent. From Eq. (1.48) at equilibrium,

$$-B_{12}\rho_\nu(\nu,T)N_1 + [A_{21} + B_{21}\rho_\nu(\nu,T)]N_2 = 0\,,$$

the spectral energy density of the thermal field can be expressed as

$$\rho_\nu(\nu, T) = \frac{A_{21}/B_{21}}{(B_{12}/B_{21})(N_1/N_2) - 1}\,.$$

In thermal equilibrium, atomic energy levels are occupied according to the Maxwell–Boltzmann statistics. In exact terms the ratio of the population densities of the two levels is

$$N_1/N_2 = (g_1/g_2)\exp[-(E_1 - E_2)/k_\mathrm{B}T] = (g_1/g_2)\exp(h\nu/k_\mathrm{B}T)\,.$$

The use of this ratio into the expression of $\rho_\nu(\nu, T)$ gives

$$\rho_\nu(\nu, T) = \frac{A_{21}/B_{21}}{(g_1 B_{12}/g_2 B_{21})\exp(h\nu/k_\mathrm{B}T) - 1}\,. \tag{1.49}$$

This formula should be Planck's radiation formula (1.9), so

$$g_1 B_{12} = g_2 B_{21} \tag{1.50a}$$

and

$$\frac{A_{21}}{B_{21}} = \frac{8\pi\nu^2}{c^3}\,h\nu\,. \tag{1.50b}$$

Relations (1.50) are known as *Einstein's relations.* These relations permit to express the transition rates between a pair of levels in terms of a single Einstein coefficient.

1.8.2 Spontaneous emission and stimulated emission as competing processes

An atom in an excited state can jump to a lower energy state through a spontaneous emission or a stimulated one. Which process is most likely?

To ask this question, we consider the ratio R of the stimulated emission rate and spontaneous emission one. This ratio is

$$R = \frac{B_{21}\rho_\nu(\nu)}{A_{21}}$$

and is dependent on the radiation field and frequency.

To be more specific, let us consider the thermal radiation field. The use of Planck's radiation formula and the second Einstein equation gives

$$R = \frac{1}{\exp(h\nu/k_\mathrm{B}T) - 1}\,.$$

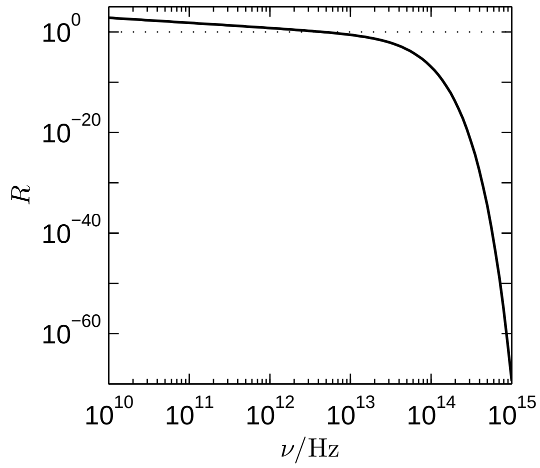

Fig. 1.9 Ratio of stimulated emission probability and spontaneous emission probability for a two-level atom in a thermal radiation field of temperature $T = 300\,\mathrm{K}$.

For numerical evaluations we choose a typical temperature $T = 300\,\mathrm{K}$. The ratio is $R = 1$ for $\nu = (k_\mathrm{B}T/h)\ln 2 \approx 4.33\times 10^{12}\,\mathrm{Hz}$ ($\lambda \approx 69.2\,\mu\mathrm{m}$) in infrared region. The dependence R versus frequency is presented in Fig. 1.9.

- In the microwave region, for example at $\nu = 10^{10}\,\mathrm{Hz}$, $R \approx 624$, so the stimulated emission in more likely than the spontaneous emission. For smaller frequencies spontaneous emission becomes negligible with respect to stimulated emission.
- In the near-infrared and visible region the ratio R takes on very small values, so the spontaneous emission is the dominant process.

Can stimulated emission dominate over spontaneous emission for a conventional source of visible radiation? It can be proven that the spectral energy density of a spectroscopic lamp is not sufficient to ensure a ratio $R > 1$. The stimulated emission dominates over spontaneous for a laser.

1.9 Experimental confirmation of stationary states

The idea of stationary states had been introduced to explain the discrete spectrum of atomic systems. The first experimental confirmation of this hypothesis was provided by James Franck and Gustav Hertz (1914). Their experimental set-up is presented schematically in Fig. 1.10. Electrons emitted from a hot cathode C are accelerated toward the mesh grid G through a low pressure gas of Hg vapour by means of an adjustable voltage U. Between the grid and the anode A a small retarding voltage $U' \sim 0.5\,\mathrm{V}$ is applied

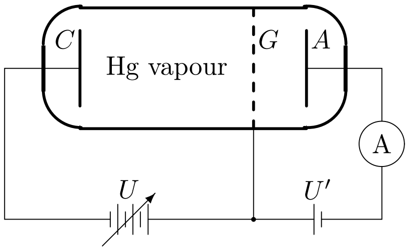

Fig. 1.10 Franck-Hertz set-up.

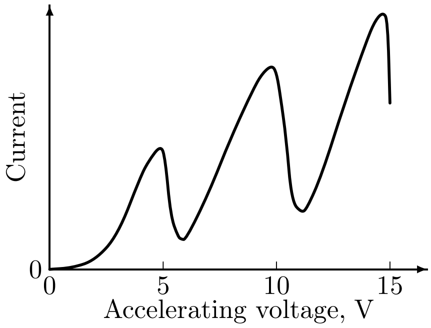

Fig. 1.11 Current through a tube of Hg vapor versus accelerating voltage in the Franck–Hertz experiment.

so that only those electrons above an energy threshold (eU') will reach it. The anodic current as a function of voltage (Fig. 1.11) does not increase monotonically, as would be the case for a vacuum tube, but rather displays a series of peaks at multiples of 4.9 V.

The experimental result is explained in terms of electron–mercury atom collisions. Due to the interaction between electron and atom, there is an exchange of energy. Let us denote E_1 and E_2 the energy of the atom in its ground state and first excited state, respectively. The minimum kinetic energy of the electron for the atom excitation is practically $E_2 - E_1$ (see Problem 1.14).

- If $U < 4.9\,\mathrm{V}$, an electron has not sufficient kinetic energy to excite a mercury atom in a collision. The collision is elastic (i.e., the kinetic energy is conserved) and the electron moves through the vapor losing energy very slowly (see Problem 1.15). The current through the tube increases with rising the accelerating voltage.
- For $4.9\,\mathrm{V} < U < 4.9\,\mathrm{V} + U'$, in an electron–mercury atom collision the electron can transfer the energy $E_2 - E_1 = 4.9\,\mathrm{eV}$ to the mercury atom; such an electron can not reach the anode, therefore the anodic current shows a decrease.[3]

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[3] If there was no countervoltage applied, all electrons would reach the anode and the

- Further increase in the accelerating voltage gives rise to an increase in current. If the voltage is more than twice 4.9 V, the electron is able to regain 4.9 eV of kinetic energy and cause a second excitation event before reaching the anode. This explains the sequence of peaks.

From spectroscopy, mercury vapor, when excited, emits radiation whose wavelength is $\lambda = 253.7\,\mathrm{nm}$; the energy of the corresponding photons is $hc/\lambda \approx 4.9\,\mathrm{eV}$. Radiation of this wavelength is observed in Franck and Hertz experiment. Thus this experiment is one of the most striking proofs of the existence of stationary states.

1.10 Wave–particle duality of matter

The dual nature of radiation, wave and particle, was treated in Sect. 1.3.

In 1924 Louis de Broglie put forward the following hypothesis: *material particles, just like photons, can have a wavelike behaviour.* One therefore associates with a material particle of energy E and momentum $\boldsymbol{p}$, a wave characterized by the angular frequency ω and the wavevector $\boldsymbol{k}$; the wave characteristics are related to the particle ones by the same relations as for photons [see Eq. (1.20)],

$$\omega = E/\hbar \quad \text{and} \quad \boldsymbol{k} = \boldsymbol{p}/\hbar\,. \tag{1.51}$$

The corresponding wavelength,

$$\lambda = 2\pi/k = h/p\,, \tag{1.52}$$

is called *de Broglie wavelength.*

He argued that the stationary states of the electrons in the atom should be such that there is an integral number of wavelengths around the orbit.

There was no experimental evidence for the matter waves in 1924. In support of his hypothesis, de Broglie showed how Bohr's quantization rule [Eq. (1.31)] could be derived from this hypothesis. Let us suppose that the electron moves in a circular orbit of radius r with velocity v. De Broglie argued that, if this is to be a stable stationary state, the wave associated with the electron must be a standing wave (see Fig. 1.12). This requirement is fulfilled if the circumference $2\pi r$ contains an integral number n ($n = 1, 2, \ldots$) of electron wavelengths:

$$2\pi r = n\lambda = nh/p = nh/mv\,.$$

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current would increase monotonically.

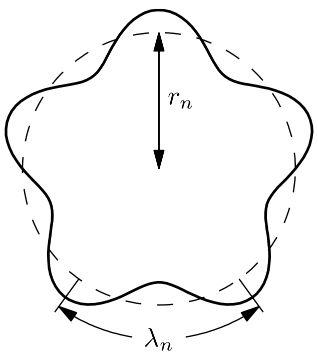

Fig. 1.12 Standing-wave pattern for an electron wave in the $n = 5$ stationary state of hydrogen.

The equation can be rearranged to give $mvr = n\hbar$, i.e., the Bohr quantization condition.

Let us discuss on the experimental confirmation of the matter waves. We expect interference and diffraction effects with matter waves when these waves pass through apertures or slits with dimensions comparable with the de Broglie wavelength. For a macroscopic particle of say, $m = 1\,\mathrm{kg}$ and speed $v = 1\,\mathrm{m/s}$, the de Broglie wavelength is $\lambda \approx 6.6 \times 10^{-34}\,\mathrm{m}$, which is many orders of magnitude smaller than any imaginable aperture. To reach much larger de Broglie wavelengths, waves associated to microparticles will be investigated. If electrons are considered, the de Broglie wavelength of a non-relativistic electron of energy $E = p^2/2m$ is

$$\lambda = \frac{h}{\sqrt{2mE}} \approx \frac{1.23}{\sqrt{E/\mathrm{eV}}}\,\mathrm{nm}\,. \tag{1.53}$$

From this equation we immediately see that the de Broglie wavelength associated with electrons of energy $1\,\mathrm{eV}$, $100\,\mathrm{eV}$, and $10\,\mathrm{keV}$ are $1.23\,\mathrm{nm}$, $0.123\,\mathrm{nm}$, and $0.0123\,\mathrm{nm}$, respectively.[4] As these wavelengths are comparable with the spacing of atoms in a crystal lattice, electrons with energies in the eV to keV range are expected to be diffracted by crystal lattices. This idea was confirmed experimentally in 1927 by Clinton Davisson and Lester Germer, and independently by George Paget Thomson.

1.10.1 Davisson–Germer experiment

The experimental arrangement used by Davisson and Germer is schematically shown in Fig. 1.13. The tungsten filament F is heated by a low voltage

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[4] Electrons with these energies are obtained by accelerating them through a potential difference of 1 V, 100 V, and 10 kV, respectively.

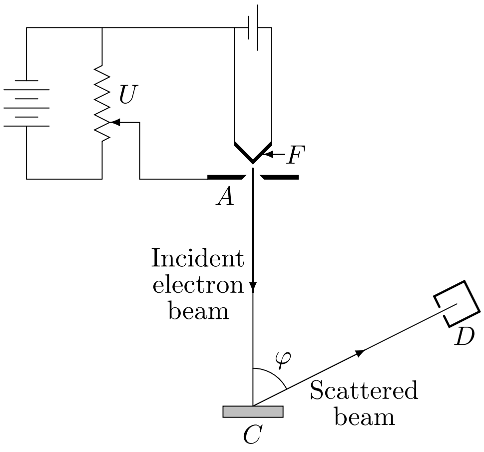


Fig. 1.13 Outline of the experimental arrangement in the electron diffraction experiments of Davisson and Germer.

power supply and emits electrons. These electrons are then accelerated in the adjustable potential difference U towards the anode A; at the exit of the electron gun, the electrons possess the kinetic energy $E = eU$. The collimated electron beam is directed normally against a target C cut from a single crystal of nickel. The electrons are scattered in all directions by the atoms of the crystal; the intensity of the beam in the direction φ is measured by the electron detector D which is connected to a sensitive galvanometer. By rotating the detector D, the dependence of the intensity of the scattered beam on the scattering angle φ can be investigated. The apparatus is enclosed in a vacuum chamber.

For a given voltage U, the intensity versus scattering angle plot shows a peak. The experimental result is similar to that in case of x-rays scattered by a crystal surface. Hence, the existence of the maximum proves qualitatively the de Broglie hypothesis. To derive the condition for constructive interference, the crystal is regarded as being composed of a set of parallel planes which contain all of the atoms in the crystal (see Fig. 1.14). A part of the incident electron wave is reflected by each of the planes. The reflected waves interfere and a maximum is obtained when the scattered waves from adjacent planes are in phase, i.e., the path difference is an integral number of wavelengths.

Figure 1.15 shows the scattering of the rays I and II by two adjacent planes. The rays are incident at the angle θ to the planes of the crystal and then reflected at this same angle; the angle θ is related by the angle φ by $\theta = \pi/2 - \varphi/2$. Ray II travels a longer path than ray I; this difference in path is $MN + NP = 2d \sin\theta$. The condition for constructive interference is

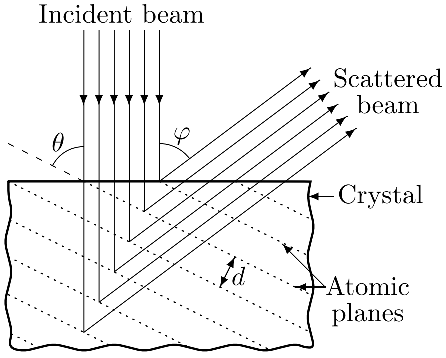


Fig. 1.14 The scattering of electron wave by a crystal is interpreted as reflection on a series of parallel atomic planes followed by the interference of the reflected waves. θ is the angle between the incident wave and an atomic plane and d is the the distance between two adjacent atomic planes.

thus

$$2d \sin\theta = n\lambda\,, \quad n = \text{integer}, \tag{1.54}$$

which is known as the *Bragg equation.* By use of the distance D between atoms, the distance between the atomic planes can be expressed in the form

$$d = D\cos\theta\,.$$

The Bragg condition becomes now

$$D\sin 2\theta = n\lambda\,, \quad n = \text{integer},$$

or, in terms of the scattering angle φ,

$$D\sin\varphi = n\lambda\,, \quad n = \text{integer}. \tag{1.55}$$

Davisson and Germer verified the validity of this condition for the scattering of an electron beam on a nickel crystal; the atomic spacing $D = 2.15 \times 10^{-10}\,\mathrm{m}$ was known from x-rays diffraction experiments. Davisson and Germer found that for the accelarating voltage $U = 54\,\mathrm{V}$ the maximum intensity is observed in the direction $\varphi = 50°$. Assuming a first-order diffraction maximum ($n = 1$), Eq. (1.55) gives the wavelength

$$\lambda = 2.15 \times 10^{-10}\,\mathrm{m} \times \sin 50° \approx 1.65 \times 10^{-10}\,\mathrm{m}\,.$$

On the other hand, the de Broglie wavelength of a 54 eV electron calculated from Eq. (1.53) gives $\lambda \approx 1.67 \times 10^{-10}\,\mathrm{m}$, which agrees with the value of $1.65 \times 10^{-10}\,\mathrm{m}$, within the limits of experimental error. Similar measurements were performed at other accelerating voltages and the agreement between the wavelength calculated based on the Bragg condition and that calculated based on the de Broglie relation is maintained.

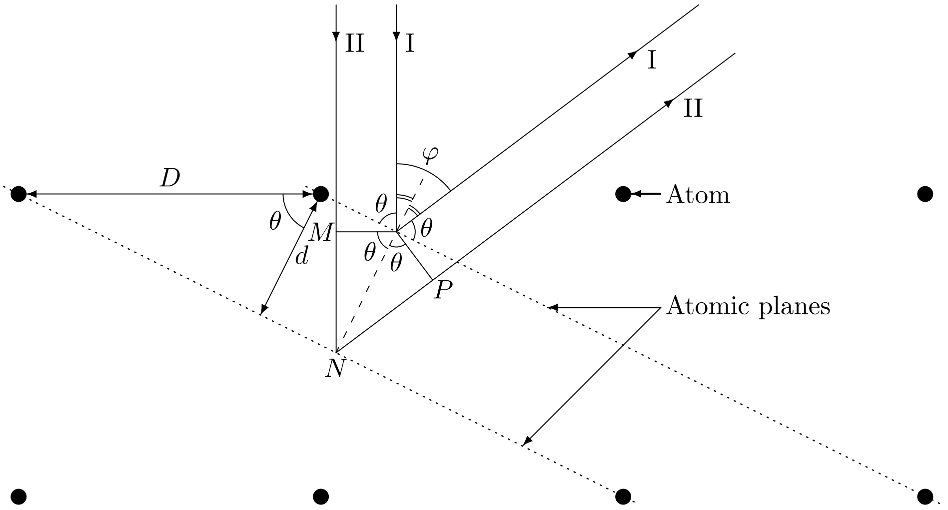


Fig. 1.15 Derivation of the Bragg equation.

1.11 Heisenberg uncertainty principle

An interesting interpretation of the wave-particle duality of all physical entities has been given by Werner Heisenberg (1927). The uncertainty principle, or indeterminacy principle, refers to the simultaneous measurement of the position and the momentum of a particle and states that the uncertainty Δx involved in the measurement of a coordonate of the particle and the uncertainty Δp_x involved in the measurement of the momentum in the same direction are related by the relationship

$$\boxed{\Delta x \, \Delta p_x \geq \hbar/2 \, .} \tag{1.56}$$

To illustrate the uncertainty principle, we consider a thought experiment. Suppose a parallel beam of monoenergetic electrons that passes through a narrow slit and is then recorded on a photographic plate (Fig. 1.16). The precision with which we know the y-position of an electron is determined by the size of the slit; if d is the width of the slit, the uncertainty of the y-position is $\Delta y \sim d$. Reducing the width of the slit, a diffraction pattern is observed on the photographic plate. The wavelength of the wave associated to the electrons is given by Eq. (1.52), where p designates the momentum of the electrons. The uncertainty in the knowledge of the y-component of electron momentum after passing through the slit is determined by the angle θ corresponding to the central maximum of the diffraction pattern; according

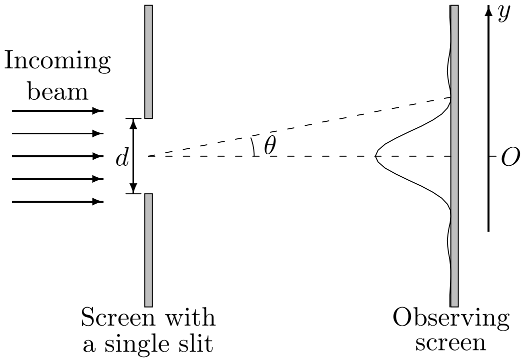


Fig. 1.16 Diffraction through a single slit.

to the theory of the diffraction produced by a rectangular slit, the angle θ is given by $d \sin\theta = \lambda$. We have

$$\Delta p_y \sim p \sin\theta = p\,\frac{\lambda}{d} = \frac{h}{d}$$

and

$$\Delta y\, \Delta p_y \sim d\,\frac{h}{d} = h\,,$$

in agreement with Eq. (1.56). Note that:

- To reduce the uncertainty in the determination of the coordinate y of the particle, a narrower slit is required. This slit produces a wider central maximum in the diffraction pattern, i.e., a larger uncertainty in the determination of the y-component of the momentum of the particle.

- To improve the precision in the determination of the y-component of the momentum of the particle, the width of the central maximum in the diffraction pattern must be reduced. This requires a larger slit, which means a larger uncertainty in the y-coordinate of the particle.

It is common to consider in everyday life that a measurement can be performed without changing the state of the physical system. The above example clearly shows that in contrast to the classical situation, *at the atomic level, measurement inevitably introduces a significant perturbation in the system.*

The uncertainty principle implies that *the concept of trajectory for particles of atomic dimensions is meaningless.* It follows that for such particles the description of the motion needs a different picture.

For everyday macroscopic objects the uncertainty principle plays a negligible role in limiting the accuracy of measurements, because the uncertainties implied by this principle are too small to be observed.

1.11.1 Uncertainty relation and the Bohr orbits

In Sect. 1.6 the electron of the hydrogen atom is supposed in a circular motion around the nucleus. Let us investigate the compatibility of this picture with the uncertainty relation [Eq. (1.56)].

The classical treatment of the electron motion is justified for small uncertainties in the position and momentum,

$$\Delta x \ll r \quad \text{and} \quad \Delta p_x \ll p\,, \tag{1.57}$$

from which we infer

$$\frac{\Delta x}{r}\,\frac{\Delta p_x}{p} \ll 1\,. \tag{1.58}$$

For the motion on the Bohr orbit n, the quantization rule gives $pr = n\hbar$. The use of Heisenberg uncertainty relation yields

$$\frac{\Delta x}{r}\,\frac{\Delta p_x}{p} \geq \frac{1}{2n}\,.$$

It is clear now that this result is in contradiction with Eq. (1.58) for small values of the quantum number n. It follows that the classical motion picture of the electron on circular orbits must be rejected.

1.12 Questions and problems

1.1 Does a blackbody always appear black?

1.2 Explain the cooling of Earth surface at night. When is the Earth surface coldest?

1.3 Determine the number of photons emitted per second by a $P = 2\,\text{mW}$ He-Ne laser operating on the wavelength $\lambda = 632.8\,\text{nm}$.

Solution. The energy of a photon is hc/λ. The number of photons emitted per second is

$$\frac{P}{hc/\lambda} \approx 6.37 \times 10^{15}\,\text{photons/s}\,.$$

1.4 In a television tube, electrons are accelerated by a potential difference of 25 kV. Determine the minimum wavelength of the x-rays produced when the electrons are stopped at the screen.

Solution. The energy acquired by an electron accelerated by the potential difference $U = 25\,\mathrm{kV}$ is $E = eU$. This energy may be radiated as a result of electron stopping; the minimum wavelength radiated is obtained when all energy is radiated as a single photon:

$$\lambda_{\min} = hc/E = hc/eU \approx 5.0 \times 10^{-11}\,\mathrm{m} = 50\,\mathrm{pm}\,.$$

Almost all of this radiation is blocked by the thick leaded glass in the screen.

1.5 The temperature of a person skin is $\theta_{\mathrm{skin}} = 35\,^{\circ}\mathrm{C}$.

(a) Determine the wavelength at which the radiation emitted from the skin reaches its peak.

(b) Estimate the net loss of power by the body in an environment of temperature $\theta_{\mathrm{environment}} = 20\,^{\circ}\mathrm{C}$. The human skin has the emittance $\varepsilon = 0.98$ in infrared and the surface area of a typical person can be estimated as $A = 2\,\mathrm{m}^2$.

(c) Estimate the net loss of energy during one day. Express the result in calories by use of the conversion relation $1\,\mathrm{cal} = 4.184\,\mathrm{J}$.

Solution. (a) By use of Eq. (1.4),

$$\lambda_{\max} = \frac{b}{T_{\mathrm{skin}}} \approx 9.5\,\mu\mathrm{m}\,.$$

This wavelength is in the infrared region of the spectrum.

(b) The power emitted by the body is [see Eq. (1.3)]

$$P_{\mathrm{emitted}} = \varepsilon\sigma T_{\mathrm{skin}}^4 A \approx 974\,\mathrm{W}\,,$$

while the power absorbed from the environment is

$$P_{\mathrm{absorbed}} = \varepsilon\sigma T_{\mathrm{environment}}^4 A \approx 819\,\mathrm{W}\,.$$

The net outward flow of energy is

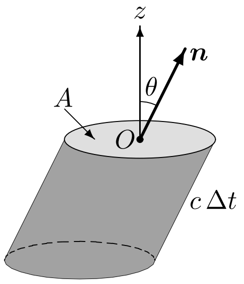
$$P = P_{\mathrm{emitted}} - P_{\mathrm{absorbed}} \approx 155\,\mathrm{W}\,.$$

(c) The net loss of energy in a time $t = 24 \times 3\,600\,\mathrm{s}$ is $E = Pt \approx 3\,207\,\mathrm{kcal}$. The result is an overestimation of the real net loss of energy, because the clothes we wear contribute to a significant reduction of the skin emittance.

1.6 Prove that the relation between radiant exitance M of a blackbody and the energy density ρ of the blackbody cavity is

$$M = (1/4)c\rho\,. \tag{1.59}$$

Solution. Let us consider a small surface of the body; this can be considered as plane. Let us denote by A the area. We choose a 3-D Cartesian coordinate system with the origin O on the emitting surface and the Oz-axis perpendicular to the surface and directed outward (see figure below).



We first write the flux of energy through the surface of area A inside the solid angle $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$ around the direction $\boldsymbol{n}$ determined by polar angles θ and φ. During the time interval Δt, the energy emitted inside the solid angle $\mathrm{d}\Omega$ is located inside the cylinder of generatrix paralell to $\boldsymbol{n}$ and length $c\,\Delta t$. The energy inside this volume is $\rho A c\,\Delta t\cos\theta$ and only the fraction $\mathrm{d}\Omega/4\pi$ propagates in the considered solid angle.

The total energy emitted through the surface of area A in the time interval Δt is

$$\int_{\theta=0}^{\theta=\pi/2}\int_{\varphi=0}^{\varphi=2\pi}\rho A c\,\Delta t\cos\theta\,\frac{\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi}{4\pi} = \frac{1}{4}c\rho A\,\Delta t.$$

It follows that the energy emitted in unit time by unit area is given by Eq. (1.59).

Remark. In case we are interested in the relation between the spectral quantities M_λ and ρ_λ, we restrict ourselves to the radiation in the wavelength interval $(\lambda, \lambda + \mathrm{d}\lambda)$. The energy emitted with the wavelength in the specified interval in Δt is

$$\int_{\theta=0}^{\theta=\pi/2}\int_{\varphi=0}^{\varphi=2\pi}\rho_\lambda \mathrm{d}\lambda\, A c\,\Delta t\cos\theta\,\frac{\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi}{4\pi} = \frac{1}{4}c\rho_\lambda\,\mathrm{d}\lambda\,A\,\Delta t.$$

The energy emitted in unit time through the unit area of surface is

$$E_\lambda \mathrm{d}\lambda = (1/4)c\rho_\lambda\,\mathrm{d}\lambda$$

from which Eq. (1.5) is inferred.

1.7 Derive Wien's displacement law from Eq. (1.10).

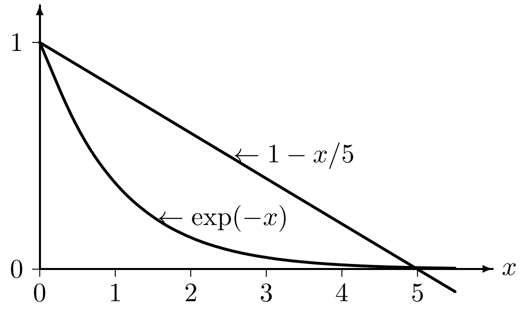
Solution.

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\rho_\lambda(\lambda) = \frac{40\pi hc}{\lambda^6}\,\frac{\exp(hc/\lambda k_\mathrm{B}T)}{[\exp(hc/\lambda k_\mathrm{B}T) - 1]^2}\left[-1 + \frac{1}{5}\,\frac{hc}{\lambda k_\mathrm{B}T} + \exp\!\left(-\frac{hc}{\lambda k_\mathrm{B}T}\right)\right].$$

The condition $\mathrm{d}\rho_\lambda(\lambda)/\mathrm{d}\lambda = 0$ yields the transcendental equation

$$1 - x/5 = \exp(-x)\,,$$

where the shorthand notation $x = hc/\lambda k_\mathrm{B}T$ have been used. Besides the trivial solution $x = 0$, a positive solution exists, $x \approx 4.965$ (see figure below).



Graphical solution of the equation $1 - x/5 = \exp(-x)$.

The spectral energy density is maximum for the wavelength λ_{max} given by

$$\lambda_{\text{max}} T \approx \frac{hc}{4.965\, k_{\text{B}}} \approx 2.898 \times 10^{-3}\,\text{m K}.$$

1.8 A zinc plate is irradiated at a distance $R = 1\,\text{m}$ from a mercury lamp that emits through a spectral filter $P = 1\,\text{W}$ radiation power at $\lambda = 250\,\text{nm}$. The penetration depth of the radiation is approximately equal to the radiation wavelength. In the classical model of radiation-matter interaction, the radiation energy is equally shared by all free electrons. Calculate the minimum irradiation time for an electron to accumulate sufficient energy to escape from the metal. Free electron density in zinc is $n = 10^{29}\,\text{m}^{-3}$ and the work function is $\Phi = 4\,\text{eV}$.

Solution. In a time interval t the plate of area A receives the energy

$$\frac{A}{4\pi R^2} Pt$$

and this is accumulated by the free electrons in the volume $A\lambda$. On the condition that an electron acquires the energy Φ ,

$$\frac{A}{4\pi R^2} Pt = nA\lambda\Phi \,.$$

The minimum irradiation time is

$$t = \frac{4\pi R^2 n\lambda\Phi}{P} \approx 2.0 \times 10^5\,\text{s}$$

in strong contradiction to the experimental results.

1.9 Blue light of wavelength $\lambda = 456\,\text{nm}$ and power $P = 1\,\text{mW}$ is incident on a photosensitive surface of cesium. The electron work function of cesium is $\Phi = 1.95\,\text{eV}$.

(a) Determine the maximum velocity of the emitted electrons and the stopping voltage.

(b) If the quantum efficiency of the surface is $\eta = 0.5\,\%$, determine the magnitude of the photocurrent. The quantum efficiency is defined as the ratio of the number of photoelectrons to that of incident photons.

Solution. (a) The threshold wavelength of the photoelectric effect for cesium is

$$\lambda_0 = hc/\Phi \approx 636\,\mathrm{nm} < \lambda\,,$$

so electrons are extracted from cesium.

To calculate the maximum velocity of the photoelectrons, we make use of Eq. (1.14), where $\nu = c/\lambda$. We get $v_{\max} \approx 5.2 \times 10^5\,\mathrm{m\,s^{-1}}$. As $v_{\max}/c \ll 1$, the nonrelativistic expression of the kinetic energy proves to be justified.

The stopping voltage is given by Eq. (1.16), where $\nu = c/\lambda$. We get $U_0 \approx 0.77\,\mathrm{V}$.

(b) The number of electrons extracted in unit time is

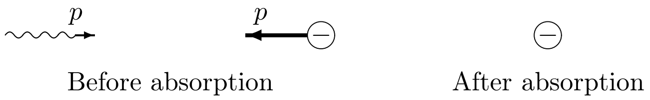
$$n = \eta \frac{P}{hc/\lambda}$$

forming a current of magnitude

$$I = ne = \eta \frac{\lambda e P}{hc} \approx 1.8\,\mu\mathrm{A}\,.$$

1.10 Prove that a free electron cannot absorb a photon.

Solution. The collision between the photon and the electron is investigated in their centre of mass reference frame, i.e., the frame of reference in which the total momentum is zero. The hypothetical process is presented below. Here, p denote the magnitude of the momentum of the electron and photon.



Let us denote by m_e the electron mass. The initial energy of the system is $pc + \sqrt{m_\mathrm{e}^2c^4 + p^2c^2}$, while the energy of the final state is $m_\mathrm{e}c^2$. It is clear that conservation of energy is violated, so the process cannot occur.

Remark. An electron participating in the photoelectric effect is not free, but bound to either an atom, molecule, or a solid. The electron and the heavy matter to which the electron is coupled share the energy and momentum absorbed and it is always possible to satisfy both momentum and energy conservation. However, this heavy matter carries only a very small fraction of the photon energy, so that it is usually not considered at all.

1.11 X-rays of wavelength 70.7 pm are scattered from a graphite block.

(a) Determine the energy of a photon.

(b) Determine the shift in the wavelength for radiation leaving the block at an angle of 90° from the direction of the incident beam.

(c) Determine the direction of maximum shift in wavelength and the magnitude of this shift.

(d) Determine the maximum shift in the wavelength for radiation scattered by an electron tightly bound to its carbon atom.

Solution. (a) $E = hc/\lambda \approx 2.81 \times 10^{-15}\,\mathrm{J} \approx 1.75 \times 10^{4}\,\mathrm{eV}$.

Remark. This energy is several orders of magnitude larger than the binding energy of the outer carbon electrons, so treating these electrons as free particles in the Compton effect is a good approximation.

(b) By making use of Eq. (1.21), we get $\Delta\lambda = \lambda' - \lambda \approx 2.43\,\mathrm{pm}$.

(c) The direction of maximum shift in wavelength is $\theta = \pi$, i.e., the photon is scattered backwards; $(\Delta\lambda)_{\max} = 2\lambda_{\mathrm{C}} \approx 4.85\,\mathrm{pm}$.

(d) The photon collides with the entire atom whose mass is $12\,\mathrm{u}$. Compton wavelength of the carbon atom is $1.11\times10^{-16}\,\mathrm{m}$. The maximum change of the wavelength due to scattering is $2.22\times10^{-16}\,\mathrm{m}$, too small to be measured.

1.12 In a Compton scattering experiment (see Fig. 1.6) a photon of energy E is scattered by a stationary electron through an angle θ.

(a) Determine the angle φ between the direction of the recoiling electron and that of the incident photon.

(b) Determine the kinetic energy of the recoiling electron.

Solution. (a) Given that $\boldsymbol{p}$ is the momentum of the incident photon and $\boldsymbol{p}'$ and $\boldsymbol{p}_{\mathrm{e}}$ the momenta of scattered photon and electron after the collision, the conservation of momentum requires that

$$\boldsymbol{p}_{\mathrm{e}} = \boldsymbol{p} - \boldsymbol{p}'\,.$$

This relation is projected on two perpendicular axes shown in the figure:

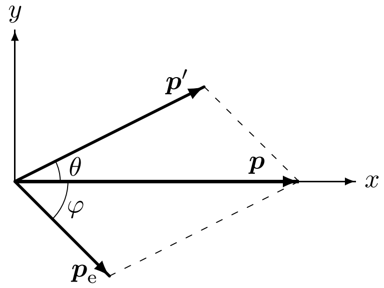
$$\begin{aligned} p_{\mathrm{e}} \cos\varphi &= \frac{h}{\lambda} - \frac{h}{\lambda'} \cos\theta\,, \\ p_{\mathrm{e}} \sin\varphi &= \frac{h}{\lambda'} \sin\theta\,. \end{aligned}$$

Dividing side by side the two equations we get

$$\cot\varphi = \frac{\lambda'}{\lambda \sin\theta} - \cot\theta\,.$$

By use of Eq. (1.21), the angle φ is given by

$$\cot\varphi = \left(1 + \frac{\lambda_{\mathrm{C}}}{\lambda}\right) \tan\frac{\theta}{2} = \left(1 + \frac{E}{mc^2}\right) \tan\frac{\theta}{2}\,.$$



Momentum conservation in the Compton effect and the choice of a xOy coordinate system.

(b) The kinetic energy of the recoiling electron is equal to the energy loss of the photon:

$$T = \frac{hc}{\lambda} - \frac{hc}{\lambda'} = \frac{hc}{\lambda}\,\frac{\lambda_C(1-\cos\theta)}{\lambda + \lambda_C(1-\cos\theta)} = \frac{(E/mc^2)(1-\cos\theta)}{1+(E/mc^2)(1-\cos\theta)}E\,.$$

1.13 Use position-momentum uncertainty relation to estimate the dimensions and the energy of the hydrogen atom in its ground state.

Solution. Let the electron be confined to a region of linear dimension r. We estimate the energy of the atom.

The potential energy of the electron is of the order of

$$\langle V\rangle = -\frac{e^2}{4\pi\epsilon_0 r}\,.$$

According to the uncertainty principle, the uncertainty Δp in its momentum is $\Delta p \geq \hbar/r$. The average kinetic energy of the electron is $\langle T\rangle = (1/2m)\langle p^2\rangle$ and assuming a zero average momentum we get

$$\langle T\rangle = \frac{1}{2m}(\Delta p)^2 \geq \frac{\hbar^2}{2mr^2}\,.$$

The total energy of the atom is

$$E = \langle T\rangle + \langle V\rangle \geq \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\,.$$

Let us denote

$$E_{\text{min}}(r) = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\,.$$

The atom settles to a state of lowest energy. Notice that for large r values, the potential energy dominates; it follows that expanding the atom increases the total energy. However, for small enough r, the kinetic energy is the dominant contribution and the total energy lowers as the atom expands.

It follows that there must exists a value of r for which the total energy is a minimum. We have

$$\frac{\mathrm{d}E_{\mathrm{min}}}{\mathrm{d}r} = -\frac{\hbar^2}{mr^3} + \frac{e^2}{4\pi\epsilon_0 r^3} = \frac{e^2}{4\pi\epsilon_0 r^3}\left(r - \frac{4\pi\epsilon_0\hbar^2}{me^2}\right).$$

The energy attains indeed a minimum for $r = 4\pi\epsilon_0\hbar^2/me^2 = a_0$. The total energy for this radius is exactly the energy of the ground state of the hydrogen atom [see Eq. (1.38)].

It should be pointed out that the Heisenberg uncertainty relation can be used to give only an order of magnitude of the hydrogen atom size or its ground state energy. The exact quantitative agreement is accidental. In fact, we had intentionally chosen the lower bound value in the Heisenberg uncertainty relation in such a way (i.e., $\hbar$) that the resulting ground state energy is exact.

1.14 An electron is bombarding an atom at rest in its ground state of energy E_1. Prove that the threshold kinetic energy of the electron, required for the atom excitation to the first excited state of energy E_2, is approximately equal to $E_2 - E_1$.

Solution. Let us denote m and M the mass of the electron and the atom, respectively. We have

$$\frac{m}{M} \le \frac{m}{M_{\mathrm{H}}} \approx \frac{1}{1836}.$$

The threshold condition for the excitation of the atom as a result of the collision will be expressed in the centre of mass (CM) frame of reference: all kinetic energy of the system is used for the atom excitation. In other words, in the CM frame of reference, the electron and the atom are both at rest after the collision.

We denote $\boldsymbol{p}$ and $\boldsymbol{P}$ the initial momentum of the electron and the atom in the CM frame of reference, respectively. The conservation of momentum and energy in the CM frame of reference gives

$$\boldsymbol{p} + \boldsymbol{P} = 0 \quad \text{and} \quad \frac{1}{2m}p^2 + \frac{1}{2M}P^2 + E_1 = E_2.$$

Combining these equations we get

$$p^2 = \frac{2Mm}{M+m}(E_2 - E_1).$$

The initial velocities of the particles with respect to the CM frame of reference are

$$\boldsymbol{v} = \frac{\boldsymbol{p}}{m} \quad \text{and} \quad \boldsymbol{V} = \frac{\boldsymbol{P}}{M} = -\frac{\boldsymbol{p}}{M}.$$

The initial velocity of the electron with respect to the atom is

$$\boldsymbol{v} - \boldsymbol{V} = \left(\frac{1}{m} + \frac{1}{M}\right)\boldsymbol{p}\,.$$

The sought kinetic energy is

$$T = \frac{1}{2}\,m(\boldsymbol{v} - \boldsymbol{V})^2 = \frac{(M+m)^2}{2M^2 m}p^2 = \left(1 + \frac{m}{M}\right)(E_2 - E_1) \approx E_2 - E_1\,.$$

1.15 Show that the change in kinetic energy of a particle of mass m, with initial kinetic energy T, when it collides with a particle of mass M initially at rest in the laboratory frame of reference is

$$\Delta T = -\frac{4M/m}{(1 + M/m)^2}T\,.$$

Discuss the case $M \gg m\,.$

Solution. Let us designate the velocity of the projectile in the laboratory frame of reference by $\boldsymbol{v}$. We choose an axis with the orientation of $\boldsymbol{v}$. The conservation of momentum and energy gives

$$mv = mv' + MV \quad \text{and} \quad \frac{1}{2}mv^2 = \frac{1}{2}mv'^2 + \frac{1}{2}MV^2,$$

where v' and V denote the final velocity of particle m and M, respectively. Arranging the two equations in the form

$$m(v - v') = MV \quad \text{and} \quad m(v - v')(v + v') = MV^2,$$

first degree equations are obtained:

$$v - v' = (M/m)V \quad \text{and} \quad v + v' = V\,.$$

The velocity of particle M after the collision is

$$V = \frac{2}{1 + M/m}v\,.$$

The change in the kinetic energy of the projectile m is

$$\Delta T = -\frac{1}{2}MV^2 = -\frac{4M/m}{(1 + M/m)^2}T$$

For $M \gg m$ we have

$$\frac{|\Delta T|}{T} \approx \frac{4M/m}{(M/m)^2} = 4\frac{m}{M} \ll 1\,.$$

1.16 Justify the name of lifetime for the time interval defined by $\tau = 1/A$ [see Eq. (1.45)].

Solution. We calculate the average time spent by the atom before de-excitation. Suppose at $t = 0$ there are $N(0)$ atoms in the upper energy level. During the time interval $(t - \mathrm{d}t/2, t + \mathrm{d}t/2)$, a number

$$AN(t)\,\mathrm{d}t = AN(0)\exp(-At)\,\mathrm{d}t$$

of atoms de-excite. These atoms have spent a time t in the upper energy level. Thus, the probability that an atom remains in the upper energy level a time t is

$$\frac{AN(t)\,\mathrm{d}t}{N(0)} = A\exp(-At)\,\mathrm{d}t\,.$$

The average time spent by an atom in the upper energy level is

$$\int_0^\infty tA\exp(-At)\,\mathrm{d}t = -t\exp(-At)\Big|_0^\infty + \int_0^\infty \exp(-At)\,\mathrm{d}t = \frac{1}{A} = \tau\,.$$

1.17 The wavepacket for a particle of mass m has the uncertainty Δx. After what time the wavepacket will spread appreciably?

Solution. The uncertainty in the particle momentum is $\Delta p \sim \hbar/2\Delta x$. The uncertainty in the particle velocity is then $\Delta v = \Delta p/m \sim \hbar/2m\Delta x$. After a time t the spreading of the wavepacket due to the uncertainty of its velocity is $(\Delta v)t$. This spreading becomes important when it is of the same order of magnitude as the initial spreading, Δx. We define the spreading time t_s by $(\Delta v)t_\mathrm{s} = \Delta x$. It results

$$t_\mathrm{s} = \frac{\Delta x}{\Delta v} \sim \frac{2m(\Delta x)^2}{\hbar}\,.$$

1.18 The wavelength λ associated to a particle is known up to $\Delta\lambda$, where $\Delta\lambda \ll \lambda$. Derive a formula for the uncertainty Δx in the particle position.

Solution. The uncertainty in the wavelength implies an uncertainty in the momentum

$$\Delta p = \Delta\left(\frac{h}{\lambda}\right) \approx \frac{h}{\lambda^2}\,\Delta\lambda\,.$$

The uncertainty in the particle position is

$$\Delta x \sim \frac{\hbar/2}{\Delta p} = \frac{\lambda^2}{4\pi\Delta\lambda}\,.$$

Chapter 2

Postulates of quantum mechanics and applications

2.1 First postulate

Postulate 1 For a particle moving under the influence of an external potential, there is an associated wavefunction. That wavefunction determines everything that can be known about the particle and is a single-valued function of the space coordinates and the time. In general, it is a complex function whose squared modulus, evaluated at a particular point and time, is proportional to the probability density of the particle at that point and time.

2.2 Schrödinger equation

In case of light, the interference pattern or diffraction one is explained using waves of form

$$\psi(\boldsymbol{r},t) = A\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]\,. \tag{2.1}$$

We extend the treatment for the case of microparticles. For simplicity, we consider the one-dimensional case. The expression of a wave of constant k_x and angular frequency ω is

$$\psi(x,t) = A\exp[\mathrm{i}(k_x x - \omega t)]\,. \tag{2.2}$$

In case of microparticles,

$$k_x = \frac{p_x}{\hbar} \quad \text{and} \quad \omega = \frac{E}{\hbar} = \frac{p_x^2}{2m\hbar}\,, \tag{2.3}$$

$$\psi(x,t) = A \exp\left[\frac{\mathrm{i}}{\hbar}(p_x x - Et)\right] = A \exp\left[\frac{\mathrm{i}}{\hbar}(p_x x - \frac{p_x^2}{2m}t)\right] . \tag{2.4}$$

We have

$$\frac{\partial}{\partial t}\psi = -\frac{\mathrm{i}}{\hbar}E\psi , \quad \mathrm{i}\hbar\frac{\partial}{\partial t}\psi = E\psi = \frac{p_x^2}{2m}\psi , \tag{2.5}$$

$$\frac{\partial}{\partial x}\psi = \frac{\mathrm{i}}{\hbar}p_x\psi , \quad \frac{\partial^2}{\partial x^2}\psi = -\frac{1}{\hbar^2}p_x^2\psi . \tag{2.6}$$

Combining these equations,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi . \tag{2.7}$$

As the differential equation is linear and homogeneous, the general solution is

$$\psi(x,t) = \int_{-\infty}^{\infty} A(p_x) \exp\left[\frac{\mathrm{i}}{\hbar}(p_x x - E(p_x)t)\right] \mathrm{d}p_x . \tag{2.8}$$

Equation (2.7) is called the Schrödinger equation for the free particle, in the one-dimensional case. Let us extend the equation for the non-free particle. We do this for the case of a force F_x deriving from a potential energy $V(x,t)$:

$$F_x = -\frac{\partial}{\partial x}V(x,t) . \tag{2.9}$$

The energy of the particle is now given by

$$E = p_x^2/2m + V(x,t) . \tag{2.10}$$

How the extend Eq. (2.7)? We associate operators to the dynamical variables E and p_x of the particle:

$$\hat{E} = \mathrm{i}\hbar\frac{\partial}{\partial t} \quad \text{and} \quad \hat{p}_x = -\mathrm{i}\hbar\frac{\partial}{\partial x} . \tag{2.11}$$

By writing Eq. (2.7) in the form

$$\hat{E}\psi = \hat{T}\psi$$

where

$$\hat{T} = \hat{p}_x^2/2m \tag{2.12}$$

is the kinetic energy operator, the natural extension of the equation is

$$\hat{E}\psi = (\hat{T} + \hat{V})\psi .$$

We take $\hat{V} = V$. The 1D-Schrödinger equation for a particle in a potential field is now

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V(x,t)\,. \tag{2.13}$$

The extension to the three-dimensional case is

$$\boxed{\mathrm{i}\hbar\,\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\,\psi(\boldsymbol{r},t)\,.} \tag{2.14}$$

Postulate 2 The time evolution of the wavefunction is given by the *time-dependent Schrödinger equation* (TDSE).

2.3 Probability conservation

Consider the wavefunction $\psi(\boldsymbol{r},t)$ is normalized at some time t_0. The wavefunction evolves in time according to the time-dependent Schrödinger equation. The probability interpretation of the wavefunction only makes sense if the normalization condition remains satisfied at all subsequent times; it is proven below that this is the case.

The probability of locating the particle within a volume $\mathcal{V}$ at time t is proportional to $\int_{\mathcal{V}} |\psi(\boldsymbol{r},t)|^2\,\mathrm{d}^3r$. The rate of change of this quantity can be calculated from the rate of change of ψ as given by TDSE (2.14),

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}} |\psi(\boldsymbol{r},t)|^2\,\mathrm{d}^3r &= \int_{\mathcal{V}}\left[\psi^*(\boldsymbol{r},t)\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) + \psi(\boldsymbol{r},t)\frac{\partial}{\partial t}\psi^*(\boldsymbol{r},t)\right]\mathrm{d}^3r\\
&= \frac{\mathrm{i}\hbar}{2m}\int_{\mathcal{V}}\left[\psi^*(\boldsymbol{r},t)\nabla^2\psi(\boldsymbol{r},t) - \psi(\boldsymbol{r},t)\nabla^2\psi^*(\boldsymbol{r},t)\right]\mathrm{d}^3r\\
&= \frac{\mathrm{i}\hbar}{2m}\int_{\mathcal{V}}\nabla\cdot\left[\psi^*(\boldsymbol{r},t)\nabla\psi(\boldsymbol{r},t) - \psi(\boldsymbol{r},t)\nabla\psi^*(\boldsymbol{r},t)\right]\mathrm{d}^3r\\
&= -\int_{\mathcal{V}}\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t)\,\mathrm{d}^3r\,,
\end{aligned} \tag{2.15}$$

where

$$\boldsymbol{j}(\boldsymbol{r},t) = -\mathrm{i}\frac{\hbar}{2m}\left[\psi^*(\boldsymbol{r},t)\nabla\psi(\boldsymbol{r},t) - \psi(\boldsymbol{r},t)\nabla\psi^*(\boldsymbol{r},t)\right]. \tag{2.16}$$

Applying the divergence theorem, which relates the volume integral of the divergence of a vector to the surface integral of the vector,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}} |\psi(\boldsymbol{r},t)|^2\,\mathrm{d}^3r = -\oint_{\Sigma}\boldsymbol{j}(\boldsymbol{r},t)\cdot\boldsymbol{n}\,\mathrm{d}S\,, \tag{2.17}$$

where Σ is the bounding surface of $\mathcal{V}$ and $\boldsymbol{n}$ is the surface's outward unit normal.

If we extend the surface Σ to infinity, the wavefunction must approach zero to ensure the posibility of normalization; the surface integral must vanish,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\boldsymbol{r}} |\psi(\boldsymbol{r},t)|^2 \,\mathrm{d}^3r = 0\,, \tag{2.18}$$

so the norm of the wavefunction does not change in time.

Let us analyze the physical content of Eq. (2.17). On the left side we have the rate of change of the probability that the particle is located within $\mathcal{V}$. It follows that rhs can be interpreted as a current of probability and $\boldsymbol{j}$ is the *probability current density*; this quantity is the analog of the current density encountered in electricity. Now, Eq. (2.17) is the integral form of the law of probability conservation.

Let us come back to Eq. (2.15) and arrange it as

$$\int_{\mathcal{V}} \left[\frac{\partial}{\partial t}|\psi(\boldsymbol{r},t)|^2 + \nabla\cdot\boldsymbol{j}(\boldsymbol{r},t)\right] \mathrm{d}^3r = 0\,.$$

Since the volume $\mathcal{V}$ is arbitrary, the integrand must vanish everywhere:

$$\frac{\partial}{\partial t}P(\boldsymbol{r},t) + \nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0\,. \tag{2.19}$$

This is the *continuity equation* or the local law of probability conservation.

In one dimension, the probability current density (2.16) acquires the form

$$j(x,t) = \mathrm{i}\frac{\hbar}{2m}\left[\psi(x,t)\frac{\partial}{\partial x}\psi^*(x,t) - \psi^*(x,t)\frac{\partial}{\partial x}\psi(x,t)\right]. \tag{2.20}$$

Let us calculate the probability current density for the free-particle wavefunction

$$\psi(x,t) = A\exp[\mathrm{i}(px-Et)/\hbar]\,.$$

We have

$$j(x,t) = \mathrm{i}\frac{\hbar}{2m}\left(-\mathrm{i}\frac{p|A|^2}{\hbar} - \mathrm{i}\frac{p|A|^2}{\hbar}\right) = \frac{p}{m}\,|A|^2\,. \tag{2.21}$$

Thus, the probability current density is equal to the probability density $|A|^2$ multiplied by the particle velocity p/m. This is analogous to electricity, in which the current density is the charge density multiplied by the velocity of charge carriers.

2.4 Constraints on the wavefunction

The probability amplitude interpretation of the wavefunction and its time evolution equation imply some constraints on the wavefunction:

1. To guarantee a unambiguous value of probability of finding the particle at a particular position and time, the quantity $|\psi|^2$ must be single valued. The wavefunction may be a complex valued function, since it is only $|\psi|^2$ that has physical significance.

2. To ensure that the probability for finding the particle in any region of space do not exceed unity, the wavefunction must be square integrable, i.e.,

$$\int_{\boldsymbol{r}} |\psi|^2(\boldsymbol{r}, t)\, \mathrm{d}^3 r < \infty\,.$$

This implies that the wavefunction approaches zero at infinity. Sometimes functions that violate this condition are used and Eq. gives one such function.

3. The wavefunction must be continuous everywhere.

4. For the existence of second spatial derivative, first derivative has to be continuous (the wavefunction is smooth). This requirement can not be fulfilled

Having set up these constraints on the wavefunction we are now ready to consider the solutions to the Schrödinger equation in some specific cases.

2.5 Time-independent Schrödinger equation

Suppose the potential V does not have explicit time dependence. For example, an electron in an atom experiences an electrostatic force directed towards the nucleus; this force derive from a potential dependent only on the distance between electron and nucleus. It is shown below that TDSE can be simplified to a form not containing the time variable. the method of separation of variables.

We look for a solution in the form of a product of spatial and temporal terms,

$$\psi(\boldsymbol{r}, t) = u(\boldsymbol{r})\, T(t)\,. \tag{2.22}$$

This is substituted into the TDSE (2.14). After dividing both sides by $u(\boldsymbol{r})\, T(t)$ we get

$$\mathrm{i}\hbar \frac{1}{T(t)} \frac{\mathrm{d}}{\mathrm{d}t} T(t) = \frac{1}{u(\boldsymbol{r})} \left[-\frac{\hbar^2}{2m} \nabla^2 u(\boldsymbol{r}) + V(\boldsymbol{r})\, u(\boldsymbol{r}) \right].$$

Since the lhs depends only on t, and the rhs only on $\boldsymbol{r}$, the only way this equation can be true is if both sides equal a constant; as the dimension of the constant is that of energy, the constant is denoted by E:

$$\mathrm{i}\hbar \frac{1}{T(t)} \frac{\mathrm{d}}{\mathrm{d}t} T(t) = E \quad \text{and} \quad \frac{1}{u(\boldsymbol{r})} \left[-\frac{\hbar^2}{2m} \nabla^2 u(\boldsymbol{r}) + V(\boldsymbol{r})\, u(\boldsymbol{r}) \right] = E\,.$$

The first of these differential equations can be solved immediately,

$$T(t) = \exp(-\mathrm{i}Et/\hbar)\,. \tag{2.23}$$

The second equation, arranged as

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 u(\boldsymbol{r}) + V(\boldsymbol{r})\, u(\boldsymbol{r}) = E\, u(\boldsymbol{r})\,,} \tag{2.24}$$

is the *time-independent Schrödinger equation* (TISE). Based on our previous discussion on the individual terms of the TDSE, E is identified as the energy of the system.

TISE is a linear second-order differential equation in which one has to solve simultaneously for a set of energy values, E, and a set of corresponding functions $u(\boldsymbol{r})$. This equation is an eigenvalue one for the operator

$$\hat{\mathscr{H}} = -\frac{\hbar^2}{2m} \nabla^2 + V(\boldsymbol{r}) \tag{2.25}$$

called *energy operator*; E is called energy eigenvalue, while $u(\boldsymbol{r})$ is referred to as energy eigenfunction (eigenstate). To each eigenvalue E it corresponds one ore more eigenfunctions; in the latter case we say that the eigenvalue is degenerate.

Let E be an energy eigenvalue and $u(\boldsymbol{r})$ an energy eigenfunction for E; the corresponding solution of TDSE is

$$\psi(\boldsymbol{r}, t) = u(\boldsymbol{r}) \exp(-\mathrm{i}Et/\hbar)\,. \tag{2.26}$$

The time-dependence of this solution is contained entirely in an overall phase with no physical implications; this property justifies the name of *stationary state* for the state given by Eq. (2.26).

The general solution of TDSE is a linear combination of functions given by Eq. (2.26).

For the one-dimensional problems, TISE (2.24) becomes

$$\boxed{-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} u(x) + V(x)\, u(x) = E\, u(x)\,.} \tag{2.27}$$

Most of the effort in quantum mechanics goes into solving the TISE for various systems; a few simple examples follow.

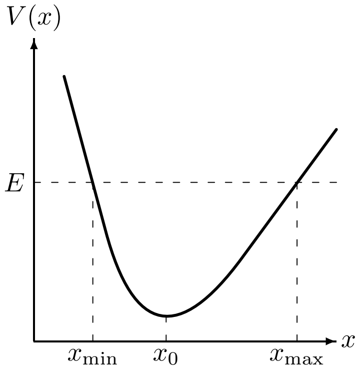


Fig. 2.1 A one-dimensional potential well. The classical motion of a particle of energy E takes place in the coordinate interval $[x_{\text{min}}, x_{\text{max}}]$.

2.6 Potential wells

There are many examples of particles whose motion is confined to a limited region of space: electrons in metals, electrons in atoms, nucleons in nuclei, and so on. The interaction between particles in such cases is represented through a potential energy that possesses a local minimum. The region surrounding the local minimum of potential energy is called *potential well.*

Consider for simplicity the one-dimensional case (Fig. 2.1). Classically, a particle having the potential energy $V(x)$ is subjected to the force

$$F_x(x) = -\frac{\mathrm{d}}{\mathrm{d}x}V(x)\,. \tag{2.28}$$

The force is zero for the local minimum position, x_0, i.e., this position is an equilibrium one; if the particle is displaced from x_0, the force tends to bring the particle back toward this position. The energy of the particle is $E \geq V_{\text{min}}$ and the motion takes place between the abscissas x_{min} and x_{max} determined as solutions of the equation $V(x) = E$. It is said that the particle is in a *bound state.*

Suppose now a potential which is bounded above and a particle of energy E such that $V(x) \leq E$ for all x-values. The classical mechanics treatment of the motion allows the particle to be found in whatever position on the axis; the state of the particle is called *unbound state.*

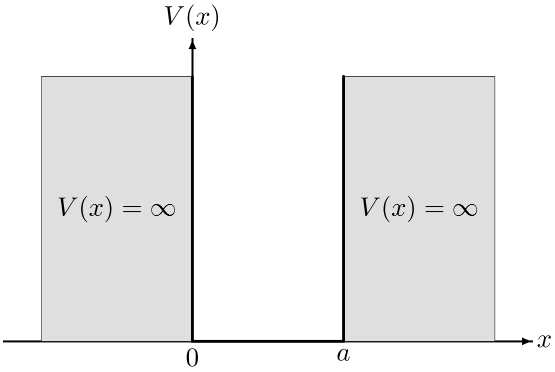


Fig. 2.2 The infinitely deep one-dimensional square potential well of width a.

2.7 The one-dimensional infinite well

2.7.1 Introduction

Let us imagine a particle of mass m is moving freely inside a closed tube of length a; collisions between the particle and the ends of the tube are assumed to be elastic. Since the particle can not leave the tube, the potential experienced by the particle can be approximated as

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & \text{otherwise,} \end{cases} \tag{2.29}$$

where the axis Ox is chosen with the origin at one end of the tube and the other end is positioned at $x = a$ (Fig. 2.2); the constant value of the potential inside the tube is chosen $V(x) = 0$. It is clear that real potentials can not be infinite, nor can they change infinitely fast; the approximation is justified for reasons of mathematical simplicity.

Classically, the particle inside such a well can be at rest or it bounces back and forth due to ellastic collisions with the walls. The energy of the particle is $E = 0$ in the first case and $E > 0$ in the latter. Whatever value $E > 0$ is possible; we say that the particle has a continuous spectrum of energy. For the moving particle, the probability per unit length of finding the particle is constant inside the well and the normalization condition gives

$$P_{\mathrm{cl}}(x) = 1/a\,. \tag{2.30}$$

2.7.2 Energy eigenvalues and eigenfunctions

In the quantum mechanical framework, we need to solve the one dimensional time-independent Schrödinger equation (2.27) with the potential given by Eq. (2.29).

In the regions $x < 0$ and $x > a$ we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u(x) + \infty\, u(x) = E\, u(x)$$

and the only possible solution is $u(x) = 0$ which means that the probability of finding the particle outside the well is zero.

In the interval $[0, a]$ the time-independent equation is that of a free particle of zero potential energy,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u(x) = E\, u(x)\,,$$

that can be expressed as

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}u(x) + \frac{2m}{\hbar^2}E\, u(x) = 0\,. \tag{2.31}$$

The form of the solution depends on the sign of the energy.

Let us first look for negative energies. Defining $\kappa = \sqrt{-2mE}/\hbar$ the solution is

$$u(x) = A\exp(\kappa x) + B\exp(-\kappa x)\,, \quad 0 \le x \le a\,,$$

where A and B are constants that are to be determined. The solution

$$u(x) = \begin{cases} A\exp(\kappa x) + B\exp(-\kappa x) & 0 \le x \le a \\ 0 & \text{otherwise,} \end{cases}$$

must be a continuous function. Continuity of the wavefunction at the points $x = 0$ and $x = a$ gives

$$A + B = 0 \quad \text{and} \quad A\exp(\kappa a) + B\exp(-\kappa a) = 0\,.$$

The result is $A = B = 0$, so $u(x) = 0$ everywhere. This is not an acceptable wavefunction. We conclude that the particle can not have a negative energy. The result is that expected as the energy is the sum of the kinetic energy, a positive defined quantity, and the potential one which is also positive here.

Next we look for an energy $E = 0$. The equation (2.31) has the solution

$$u(x) = Ax + B\,, \quad 0 \le x \le a$$

and the continuity condition of the wavefunction

$$u(x) = \begin{cases} Ax + B & 0 \le x \le a \\ 0 & \text{otherwise,} \end{cases}$$

gives $B = 0$ and $Aa + B = 0$ with the solution $A = B = 0$. Again $u(x) = 0$ everywhere, i.e., a unacceptable solution. The result is that expected, as a state of zero energy would imply an exact position determination and also an exact value (zero) of the momentum in contradiction with the Heisenberg uncertainty principle.

We turn now to searching for positive energies. Defining

$$k = \sqrt{2mE}/\hbar > 0\,, \tag{2.32}$$

Eq. (2.31) has the general solution

$$u(x) = A \sin kx + B \cos kx\,, \quad 0 \le x \le a$$

and the wavefunction is

$$u(x) = \begin{cases} A \sin kx + B \cos kx & 0 \le x \le a \\ 0 & \text{otherwise.} \end{cases} \tag{2.33}$$

The continuity condition at $x = 0$ gives $B = 0$. The same condition at $x = 0$ reads $A \sin ka = 0$. Not to get $u(x) = 0$ everywhere, the condition $\sin ka = 0$ must be satisfied; this equation can be recognized as the condition for a standing wave in the interval $[0, a]$. Since $k > 0$ the solution is

$$ka = n\pi\,, \quad n = 1, 2, \dots\,. \tag{2.34}$$

This means that the wavenumber k is quantized (takes on discrete values) and can have only the particular values

$$k_n = n\pi/a\,, \quad n = 1, 2, \dots\,. \tag{2.35}$$

Now, from Eq. (2.32) the energy of the particle is also quantized:

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2, \quad n = 1, 2, \dots\,. \tag{2.36}$$

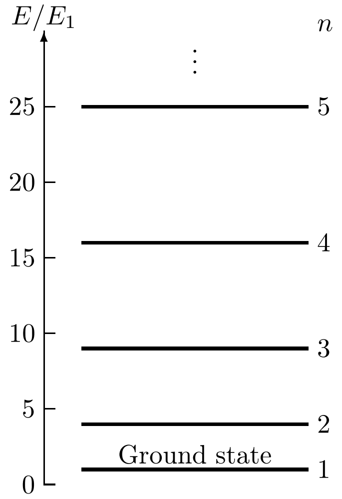


Fig. 2.3 Energy level diagram for the particle in the one-dimensional infinite well. In the ground state ($n = 1$) the energy is positive.

The energy level diagram of the particle is shown in Fig. 2.3. Quantification of the energy arises naturally by imposing boundary conditions on solutions of Schrödinger equation as opposed to its ad-hoc introduction in its model of the hydrogen atom.

Normalization condition determines the value of the constant A:

$$\int_{-\infty}^{\infty} |u(x)|^2 \, \mathrm{d}x = \int_0^a |A_n|^2 \sin^2 \frac{n\pi}{a} x \, \mathrm{d}x = \frac{a}{2} |A_n|^2 = 1$$

hence $|A_n| = \sqrt{2/a}$. Since the phase of the constant remains arbitrary, we take the simpliest choice, i.e., $\arg A_n = 0$. The wavefunctions can now be written in the final form

$$u_n(x) = \begin{cases} \sqrt{2/a} \, \sin n\pi x/a & 0 \le x \le a \\ 0 & \text{otherwise,} \end{cases} \qquad n = 1, 2, \dots \, . \tag{2.37}$$

The probability per unit length of finding the particle at x in a state n is

$$P_n(x) = |u_n(x)|^2 = \begin{cases} (2/a) \sin^2 n\pi x/a & 0 \le x \le a \\ 0 & \text{otherwise,} \end{cases} \qquad n = 1, 2, \dots \, . \tag{2.38}$$

Figure 2.4 shows the plot of first few wavefunctions and probability densities. In a plot of the probability density, the peaks correspond to positions of high probability of finding the particle; the valleys correspond to positions of low probability.

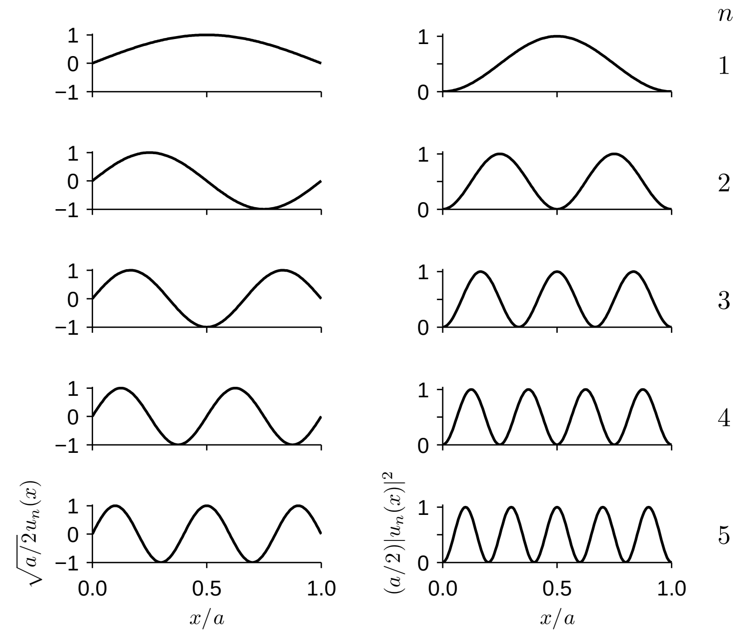


Fig. 2.4 The lowest five energy eigenfunctions for the infinite potential well (*left*) and the corresponding probability densities (*right*). With increasing n, each successive eigenfunction has one more node.

2.7.3 Discussion

1. Let us consider an example of system we are dealing with. Suppose an electron trapped in an atomic-scale potential well of width $a = 0.5\,\mathrm{nm}$. The energy of the ground state is $E_1 = \pi^2\hbar^2/2ma^2 \approx 1.51\,\mathrm{eV}$, the next energy levels being positioned at 5.02 eV, 13.55 eV, and so on.

2. Classically a particle in an infinite potential well can have zero velocity, so zero energy. The quantum description shows that the minimum energy is strictly positive. This is a manifestation of the uncertainty principle since the particle is localized within $\Delta x = a/2$ so $\Delta p_x \geq \hbar/2\Delta x = \hbar/a$ and

$$E = \frac{1}{2m}\langle p_x^2\rangle = \frac{1}{2m}\left(\langle p_x^2\rangle - \langle p_x\rangle^2\right) = \frac{1}{2m}(\Delta p_x)^2 \geq \frac{\hbar^2}{2ma^2}\,.$$

The actual ground state energy E_1 is π^2 larger than the lower bound; note that the dependence on $\hbar$, m and a is the same as that of E_1.

The uncertainty principle is often used to provide a quick order of magnitude estimate for the ground state energy.

3. Equation (2.30) gives the probability per unit length of finding the particle inside the well in the classical description. Let us derive this result as a limit case of the quantum description. According to the correspondence principle, classical behaviour is expected for large values of the quantum number n. We consider an interval of length Δx inside the well; for large values of n, the probability density (2.38) has many oscillations on the interval and its average value is

$$\frac{2}{a}\left\langle \sin^2\frac{n\pi x}{a}\right\rangle = \frac{2}{a}\frac{1}{2} = \frac{1}{a}\,,$$

i.e., the classical result.

4. To make clear why we do not detect the quantum nature of matter at a macroscopic scale let us consider a mass of 1 kg of energy 1 J trapped in a potential well of width 1 m. Supposing the system in an energy eigenstate, Eq. (2.36) gives $n \approx 4.3 \times 10^{33}$. The energy spacing to adjacent levels $n \pm 1$ is

$$|E_{n\pm1} - E_n| \approx \frac{\pi^2\hbar^2}{2ma^2}\,2n = \frac{2}{n}E_n \approx 4.7 \times 10^{-34}\,\mathrm{J}\,,$$

much less than the energy of the system and impossibly small to detect; energy appears to take on a continuous range of values. Further, the probability per unit length has a number of peaks of the order of 10^{33}. The peak spacing is $\sim 10^{-33}$ m, and hence unresolvable from each other; the significant probability density is the averaged one and this coincides with the classical one.

5. Let us choose the axis origin in the middle of the well. Now, the potential is an even-parity function [$V(-x) = V(x)$ for all x]. The energy eigenfunctions for $x \in [-a/2, a/2]$ reads

$$u_n(x) = \sqrt{\frac{2}{a}}\,\sin\frac{n\pi(x+a/2)}{a} = \sqrt{\frac{2}{a}}\,\sin\Big(\frac{n\pi x}{a} + \frac{n}{2}\pi\Big)$$

and by a phase change of π in case of need

$$u_n(x) = \begin{cases} \sqrt{2/a}\,\cos n\pi x/a & n \text{ odd} \\ \sqrt{2/a}\,\sin n\pi x/a & n \text{ even.} \end{cases} \tag{2.39}$$

These wavefunctions are alternatively even and odd, so $|u_n(-x)|^2 = |u_n(x)|^2$ for all n and x, that is, the probability density is the same at x and $-x$. The physical background of this is that there is no reason for the particle to distinguish between the two sides of a symmetrical well.

The property of energy eigenfunctions to have a definite parity is a general one in case of a symmetric well and useful to simplify the determination of the TISE solution.

2.8 The rectangular potential barrier. Potential barrier penetration

We now consider the scattering of a particle by a potential barrier such as the one shown in Fig. 2.5. This potential barrier can be written mathematically

$$V(x) = \begin{cases} 0 & x < 0,\ x > a \\ V_0 & 0 \le x \ge a\,. \end{cases} \tag{2.40}$$

The energy of a particle in this potential is $E > 0$. We shall consider the cases $0 < E < V_0$ and $E > V_0$ separately.

2.8.1 Case $0 < E < V_0$

Classical mechanics predicts that a particle coming from the left with an energy $0 < E < V_0$ is reflected back at $x = 0$.

Let us now consider the quantum mechanical treatment. We can immediately write the general solution of the TISE:

$$u(x) = \begin{cases} C_1 \exp(\mathrm{i}kx) + C_2 \exp(-\mathrm{i}kx) & x < 0 \\ C_3 \exp(\kappa x) + C_4 \exp(-\kappa x) & 0 \le x \ge a \\ \exp[\mathrm{i}k(x-a)] & x > a\,, \end{cases} \tag{2.41}$$

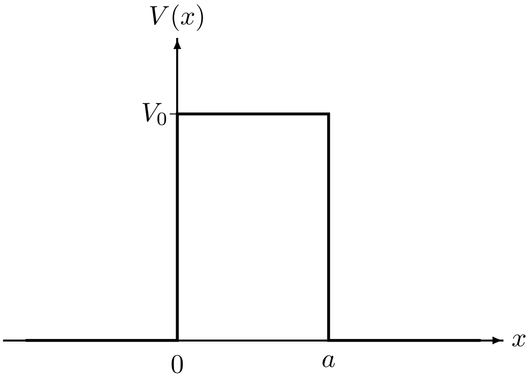


Fig. 2.5 A 1-D rectangular potential barrier of width a and height V_0. A particle is incident from the left.

where

$$k = (2mE)^{1/2}/\hbar \tag{2.42}$$

and

$$\kappa = [2m(V_0 - E))]^{1/2}/\hbar \,. \tag{2.43}$$

For a particle incident from the left we anticipate that in the region $x > a$ there is no wave propagating to the left. For simplicity, the amplitude of the wave in the region $x > a$ has modulus 1.

By applying the boundary conditions at $x = 0$ and $x = a$, we get the set of algebraic equations

$$C_1 + C_2 = C_3 + C_4 \,, \tag{2.44a}$$

$$\mathrm{i}k(C_1 - C_2) = \kappa(C_3 - C_4) \,, \tag{2.44b}$$

$$C_3 \exp(\kappa a) + C_4 \exp(-\kappa a) = 1 \,, \tag{2.44c}$$

$$\kappa[C_3 \exp(\kappa a) - C_4 \exp(-\kappa a)] = \mathrm{i}k \,. \tag{2.44d}$$

The solution for C_1 is

$$C_1 = \cosh \kappa a + (\mathrm{i}/2)(\kappa/k - k/\kappa) \sinh \kappa a \,. \tag{2.45}$$

There is solution whatever the value of E. It means that the energy has a continuous spectrum. In other words, the energy of the particle is not quantized.

Let us consider now the probability flux density. In region $x < a$ there are two counterpropagating waves: the incident wave and the reflected wave. The probability current density in this region is (see Problem 2.1)

$$j(x) = \frac{\hbar k}{m} \left(|C_1|^2 - |C_2|^2\right) \,, \quad x < 0 \tag{2.46}$$

while the probability current density in the region $x > a$ is

$$j(x) = \frac{\hbar k}{m}\,. \tag{2.47}$$

We define the *transmission coefficient* of the barrier as

$$T = \frac{|j_{\text{transmitted}}|}{|j_{\text{incident}}|}\,. \tag{2.48}$$

Here,

$$T = \frac{1}{|C_1|^2}\,.$$

The expression of C_1 is introduced here and it yields

$$T^{-1} = 1 + \frac{1}{4}\left(\frac{\kappa}{k} + \frac{k}{\kappa}\right)^2 \sinh^2 \kappa a = 1 + \frac{1}{4}\,\frac{V_0^2}{E(V_0 - E)} \sinh^2\left(\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}\,a\right). \tag{2.49}$$

In order to write the transmission coefficient in a simpler form, we introduce the dimensionless parameters

$$\alpha = \sqrt{\frac{2mV_0}{\hbar^2}}\,a \quad \text{and} \quad \varepsilon = E/V_0\,. \tag{2.50}$$

The parameter α characterizes the potential barrier and it will be called *strength parameter*. The parameter ε expresses the energy in units of the barrier height. The use of these parameters in the expression of the transmission coefficient gives

$$T^{-1} = 1 + \frac{\sinh^2 \alpha\sqrt{1-\varepsilon}}{4\varepsilon(1-\varepsilon)}\,. \tag{2.51}$$

The transmission coefficient T is the probability that the particle reaches the point $x = a$, thus passing the potential barrier and penetrating into the region on the right. The phenomenon is called *barrier penetration* or the *tunnel effect*.

Special case: For $\alpha\sqrt{1-\varepsilon} \gg 1$ the transmission coefficient is small and Eq. (2.51) can be approximated:

$$T^{-1} \approx \frac{[(1/2)\exp(\alpha\sqrt{1-\varepsilon})]^2}{4\varepsilon(1-\varepsilon)} = \frac{\exp(2\kappa a)}{16\varepsilon(1-\varepsilon)}$$

so

$$T \approx 16\varepsilon(1-\varepsilon)\exp(-2\kappa a)\,. \tag{2.52}$$

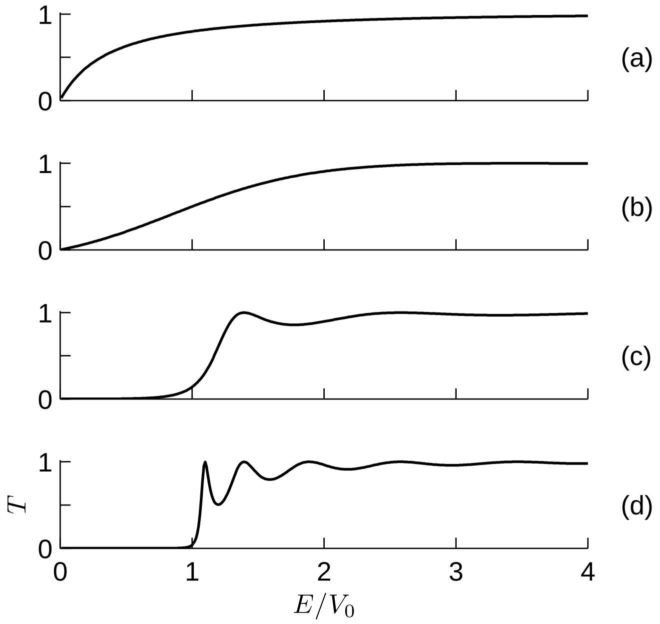


Fig. 2.6 Transmission coefficient of a rectangular potential barrier versus normalized energy of the incident particle for some values of the barrier parameter α: (a) $\alpha = 1$, (b) $\alpha = 2$, (c) $\alpha = 5$, and (d) $\alpha = 10$.

2.8.2 Case $E > V_0$

In this case there is no classical forbidden region. The calculations are performed similarly. Formally, the results can be obtained from the above analysis by the simple replacement

$$\kappa \to \mathrm{i}k' = \mathrm{i}\sqrt{2m(E - V_0)/\hbar^2}$$

This turns $\sinh \kappa x$ into $\sin k'x$ and k2 into k'2. Exercise:

$$T^{-1} = 1 + \frac{\sin^2 \alpha\sqrt{\varepsilon - 1}}{4\varepsilon(\varepsilon - 1)} \,. \tag{2.53}$$

Figure 2.6 shows the transmission coefficient of a barrier as a function of the normalized energy for various values of the barrier strength parameter.

2.8.3 Discussion

- $0 < \varepsilon < 1$. The transmission coefficient is an increasing function of energy and it can take significant values for sufficiently small values of the strength parameter α.

Examples:

1. Electron ($m_\mathrm{e} \approx 9.1 \times 10^{-31}\,\mathrm{kg}$), $V_0 = 2\,\mathrm{eV}$, $a = 0.1\,\mathrm{nm}$, $E = 1\,\mathrm{eV}$. We get $\alpha \approx 0.72$, $\varepsilon = 0.5$ and $T \approx 0.78$; there is a significant probability of barrier penetration.

2. Proton ($m_\mathrm{p} \approx 1\,836\, m_\mathrm{e}$), $V_0 = 2\,\mathrm{eV}$, $a = 0.1\,\mathrm{nm}$, $E = 1\,\mathrm{eV}$.

We get $\alpha \approx 31$, $\varepsilon = 0.5$ and $T \approx 3.5 \times 10^{-19}$. The probability of barrier penetration is not significant.

Barrier penetration can also be explained in terms of energy–time uncertainty relation. The energy of the particle fluctuates; the magnitude of the fluctuation is ΔE on a timescale $\Delta t \sim \hbar/\Delta E$. A fluctuation giving the energy $E + \Delta E > V_0$ can enable the particle to pass over the barrier.

- $\varepsilon > 1$. The graphs exhibit oscillations and the transmission is unity for

$$\alpha\sqrt{\varepsilon - 1} = n\pi\,, \quad n = 1, 2, 3, \ldots\,. \tag{2.54}$$

By introducing the constant of the wave inside the barrier

$$k' = [(2m(E - V_0)^{1/2}/\hbar \tag{2.55}$$

the condition for maxima becomes

$$k'a = n\pi\,. \tag{2.56}$$

In other words, the width of the barrier is an integral number of half wavelengths. This condition was encountered in optics, in the study of the Fabry–Perot interferometer. The maxima are explained as a constructive interference of waves.

2.9 Non-rectangular potential barriers

The expressions (2.51) of the transmission probability is restricted to rectangular barriers only. In reality, we are not likely to encounter such a simple-shaped barrier. We give below an approximate formula for the transmission coefficient of an arbitrary slowly-varying barrier.

Figure 2.7 shows a barrier towards which a particle of mass m and energy E is directed from the left. We divide the barrier into a large number of back-to-back rectangular barriers; however, the thickness should not be too small for the condition $\alpha\sqrt{1 - \varepsilon} \gg 1$ to hold for each barrier. We start

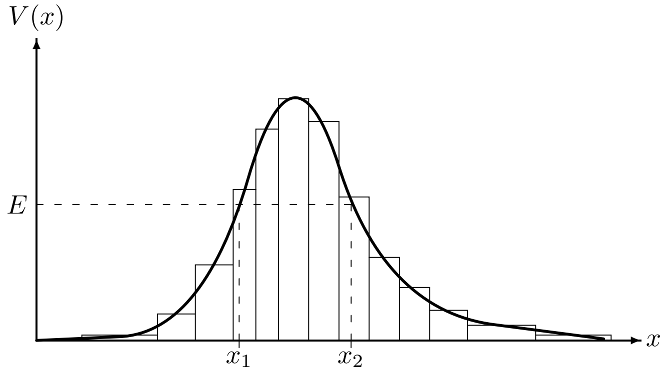


Fig. 2.7 A potential barrier of arbitrary shape. The barrier is decomposed into a sequence of rectangular barriers. For the energy E of the incident particle, the coordinates x_1 and $x_2 > x_1$ are defined by $V(x_1) = V(x_2) = E$.

from Eq. (2.52). The factor $16\varepsilon(1-\varepsilon)$ is due to reflection losses at the two boundaries $x = 0$ and $x = a$, while the decreasing exponential describes the wavefunction amplitude decay within the barrier. Retaining only the attenuation of the wave on traversing the barrier,

$$T \approx \exp(-2\kappa a)\,.$$

For the barrier in Fig. 2.7 we replace κa by $\sum_i \kappa(x_i)\Delta x_i$ and taking the limit of small Δx_i, the summation approaches the integral $\int_{x_1}^{x_2} \kappa(x)\,\mathrm{d}x$. The use of the definition of κ [see Eq. (2.43)] yields

$$T = \exp\left\{-2\int_{x_1}^{x_2} \frac{\sqrt{2m[V(x)-E]}}{\hbar}\,\mathrm{d}x\right\}. \tag{2.57}$$

2.9.1 Applications of tunneling

Field emission of electrons

Electrons in a metal are bound by a potential that may be approximated by a finite potential well. Electrons fill up these energy levels up to an energy E_F called *Fermi energy.* The energy difference $V_0 - E_\mathrm{F}$ (V_0 is the height of the well) is the electron work function Φ of the metal. Electrons can be extracted from the metal in the photoelectric effect (see Sect. 1.2); another method that gives rise to the emission of electrons from a metal is the application of an intense electric field, a process referred to as *field emission.*

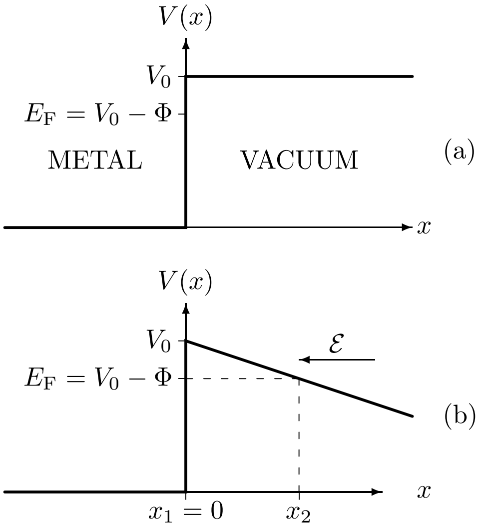


Fig. 2.8 Field emission of electrons: (a) The electrons in a conductor placed in the region $x < 0$ are restrained by a potential step of minimal height equal to the work function Φ; (b) In the presence of an electric field $\mathcal{E}$ the potential step is changed into a triangular potential barrier that can be penetrated by electrons.

We consider the metal situated in the region $x < 0$. The potential experienced by metal electrons is shown in Fig. 2.8(a). The application of a uniform electric field $\mathcal{E}$ directed towards the metal surface $x = 0$ produces a change in the potential field obeying $\mathrm{d}V = -e\mathcal{E}\mathrm{d}x$, where e denotes the magnitude of the electron charge. By integration with the condition $V(0) = V_0$ we find the modified potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 - e\mathcal{E}x & x \geq 0\,. \end{cases} \tag{2.58}$$

shown in Fig. 2.8(b). The electrons faces now a potential barrier and its penetration is expected. By approximating the linear part $V(x) = V_0 - e\mathcal{E}x$ by a series of square barriers the transmission coefficient for electrons is calculated by help of Eq. (2.57). We apply this formula for electrons at energy $E = E_F$; the integration ends in Eq. (2.57) are $x_1 = 0$ and x_2 given by $V_0 - e\mathcal{E}x_2 = E_F$, i.e., $x_2 = \Phi/e\mathcal{E}$. A straightforward calculation gives

$$T = \exp\left(-\frac{4\sqrt{2m}\,\Phi^{3/2}}{3\hbar e\mathcal{E}}\right). \tag{2.59}$$

It can be seen that the probability of emission increases strongly as the electric field strength near the surface of the metal increases. The tunneling is also advantaged by a small work function (see Table 1.1). To obtain a high probability of tunneling, electric field strengths as high as 10^{10} V/m are required.

The field emission of electrons from a metal surface is used for imaging surfaces at the atomic level in the scanning tunneling microscope (STM). A very sharp conducting probe is brought close to the surface of a solid conducting medium and a large voltage difference is applied between the probe and the surface. Electrons tunneling between the surface and the probe tip give rise to a weak electric current whose magnitude is proportional to the tunneling probability given by Eq. (2.59). Assuming that the potential difference is held constant, the current is an extremely sensitive function of the spacing between the tip and the surface; an STM can thus be used to construct a very accurate contour map of the surface under investigation.

Alpha-particle emission

An α-particle is a synonymous term for a helium nucleus. α-emission is the process wherein a nucleus spontaneously decays by emitting an α-particle. A good example is provided by the decay of the isotope uranium-238 (parent nucleus) into thorium-234 (daughter nucleus). The half-life of this process is about 4.47 billion years and the kinetic energy of the ejected α-particle is about 4.2 MeV.

The explanation of this process is based on the assumption that an α particle has a separate existence inside the nucleus. Here it experiences strong attractive nuclear forces; the resulting potential can be modeled as a deep rectangular well of radius r_1 that is interpreted as the nucleus radius (see Fig. 2.9). For $r > r_1$ the α-particle is repelled by the Coulomb force between it and the daughter nucleus; the electrostatic potential energy is

$$V(r) = \frac{2(Z-2)e^2}{4\pi\epsilon_0 r}\,,$$

where Z denotes the atomic number of the parent nucleus. For a particle of energy E_α smaller than $V(r_1)$ the barrier extends to the radius r_2 given by

$$\frac{2(Z-2)e^2}{4\pi\epsilon_0 r_2} = E_\alpha\,.$$

The α-decay can be modeled as a penetration through this nuclear-plus-Coulomb barrier.

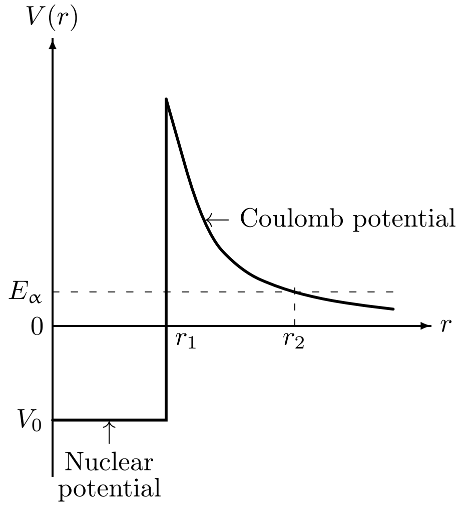


Fig. 2.9 The potential energy experienced by an α-particle inside the atomic nucleus ($0 \leq r < r_1$) and its vicinity.

2.10 The quantum harmonic oscillator

In classical mechanics, a harmonic oscillator (also known as linear oscillator or simple oscillator) is a physical system that is bound to a position of stable equilibrium by a restoring force proportional to the displacement from this position. A typical example of a harmonic oscillator is that of a mass attached to a spring. The restoring force is the elastic force F given by Hooke's law

$$F = -kx \,, \tag{2.60}$$

where x is the displacement and k is the spring constant. The motion of a body of mass m attached to the spring is governed by Newton's second law

$$m\frac{\mathrm{d}^2}{\mathrm{d}t^2}x(t) = -kx \tag{2.61}$$

whose general solution is

$$x(t) = A\cos(\omega t + \phi) \,. \tag{2.62}$$

Here,

$$\omega = \sqrt{k/m} \tag{2.63}$$

is the natural oscillating frequency, A is the amplitude of the oscillation, and ϕ is the phase constant; both A and ϕ are constants determined by the initial condition (initial displacement and velocity).

The work of force F between two positions x_1 and x_2 is

$$W = \int_{x_1}^{x_2} F(x)\,\mathrm{d}x = \frac{1}{2}kx_1^2 - \frac{1}{2}kx_2^2 \tag{2.64}$$

and this do not depend on the path between them, so a potential energy $V(x)$ can be defined. As a general rule,

$$W = -\Delta V = V(x_1) - V(x_2)\,, \tag{2.65}$$

so $V(x) = (1/2)kx^2 + \text{const}$; the simple choice $V(0) = 0$ gives

$$V(x) = (1/2)kx^2 = (1/2)m\omega^2x^2. \tag{2.66}$$

The harmonic oscillator is one of the most important models in mechanics because any potential $V(x)$ can be approximated as a harmonic potential in the vicinity of a stable equilibrium point.

We now turn our attention to the quantum description of the harmonic oscillator. The 1-D TISE with the potential given by Eq. (2.66) is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u(x) + \frac{1}{2}m\omega^2x^2u(x) = E\,u(x)\,. \tag{2.67}$$

As first step in this equation solving, dimensionless coordinate and energy are introduced; the substitutions

$$\xi = (m\omega/\hbar)^{1/2}x = \alpha x \quad \text{and} \quad \varepsilon = E/(\hbar\omega/2) \tag{2.68}$$

give the equation

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}u(\xi) + (\varepsilon - \xi^2)u(\xi) = 0\,. \tag{2.69}$$

There is not a straightforward method to solve this equation. We first investigate the asymptotic behavior of $u(y)$. For large values of $|\xi|$, the parameter ε is negligible compared to ξ^2 and the above equation becomes

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}u(\xi) - \xi^2u(\xi) = 0\,.$$

The approximate solutions of this equation are

$$u(\xi) = C\exp(\pm\xi^2/2)\,, \quad C = \text{const}\,.$$

Indeed,

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}u(\xi) = (\xi^2 \pm 1)u(\xi) \approx \xi^2u(\xi) \quad \text{for large } |\xi|\,.$$

The function defined by $u(\xi) = \exp(\xi^2/2)$ is not satisfactory because it becomes infinite as $|\xi| \to \infty$ and the function defined by $u(\xi) = \exp(-\xi^2/2)$ approaches 0 at infinity, so it is well-behaved. Retaining the asymptotic behavior given by $\exp(-\xi^2/2)$, we are led for searching solutions of the form

$$u(\xi) = H(\xi)\,\exp(-\xi^2/2)\,, \tag{2.70}$$

where $H(\xi)$ is a function to be determined.

Substitution of Eq. (2.70) into Eq. (2.69) gives

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}H(\xi) - 2\xi\frac{\mathrm{d}}{\mathrm{d}\xi}H(\xi) + (\varepsilon - 1)H(\xi) = 0\,. \tag{2.71}$$

The solution of this differential equation is searched in the form of a series

$$H(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots\,. \tag{2.72}$$

This form of H is inserted into Eq. (2.71); the coefficient of ξ^s $(s \in \mathbb{N})$ in left-hand side of the equation is

$$(s+1)(s+2)a_{s+2} - 2sa_s + (\varepsilon - 1)a_s$$

and it must be zero, so

$$a_{s+2} = \frac{2s+1-\varepsilon}{(s+1)(s+2)}\,a_s\,, \quad s \in \mathbb{N}\,. \tag{2.73}$$

In the limit of large s , $a_{s+2}/a_s = 2/s$, and this ratio can also be encountered in the Taylor expansion of $\exp(\xi^2)$:

$$\mathrm{e}^{\xi^2} = c_0 + c_1\xi + c_2\xi^2 + c_3\xi^3 + \cdots = 1 + \xi^2 + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + \cdots\,.$$

Indeed, the ratio of adjacent coefficients for large s is

$$\frac{c_{2s+2}}{c_{2s}} = \frac{1}{s+1} \approx \frac{1}{s} = \frac{2}{2s}\,.$$

It follows that $H(\xi)$ and $\exp(\xi^2)$ have the same asymptotic behaviour. Coming back to the solution (2.70) of Schrödinger equation, this behaves like $\exp(\xi^2/2)$ for large ξ. This function diverges and is not an acceptable solution. The only way to avoid the divergence of the wave function is to terminate the series (2.72) after a finite number of terms. Examining Eq. (2.73)

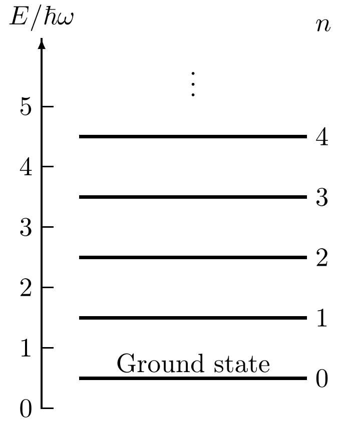


Fig. 2.10 Energy level diagram for the quantum harmonic oscillator.

we find that a_n ($n \in \mathbb{N}$) is the last term in the series if $2n+1-\varepsilon=0$, which means

$$\varepsilon = 2n+1 \equiv \varepsilon_n, \quad n \in \mathbb{N}.$$

By use of Eq. (2.68), the possible values of the energy are given by

$$E_n = (\hbar\omega/2)\varepsilon_n = \hbar\omega(n+1/2), \quad n \in \mathbb{N}. \tag{2.74}$$

The energy of the quantum oscillator is thus quantified. The energy levels are equally spaced and the minimum energy is $\hbar\omega/2 > 0$ (see Fig 2.10). The positive value of the ground state energy is consistent with the uncertainty principle, since zero energy would require $x = 0$ and $p_x = 0$, simultaneously.

We now focus on the energy eigenfunctions determination. The use of ε_n into Eq. (2.71) gives

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}H(\xi) - 2\xi\frac{\mathrm{d}}{\mathrm{d}\xi}H(\xi) + 2nH(\xi) = 0. \tag{2.75}$$

The solution of this equation is known as *Hermite polynomial* of order n and is usually expressed in the form

$$H_n(\xi) = (-1)^n \mathrm{e}^{\xi^2}\frac{\mathrm{d}^n}{\mathrm{d}\xi^n}\mathrm{e}^{-\xi^2}. \tag{2.76}$$

Table 2.1 lists first few Hermite polynomials.

The solution of Schrödinger equation for the energy E_n reads now

$$u_n(x) = N_n \exp(-\alpha^2x^2/2)\, H_n(\alpha x), \tag{2.77}$$

Table 2.1 First six Hermite polynomials.

n	$H_n(x)$
0	1
1	$2x$
2	$4x^2$
3	$8x^3 - 12x$
4	$16x^4 - 48x^2 + 12$
5	$32x^5 - 160x^3 + 120x$

Table 2.2 Vibrational frequency of some diatomic molecules.

Molecule	$\nu/(10^{13}\mathrm{Hz})$
C_2	4.921
N_2	7.074
O_2	4.374
NO	5.708
CO	6.508

where N_n is the normalization constant. By imposing

$$\int_{-\infty}^{\infty} |u_n(x)|^2 \mathrm{d}x = 1\,, \tag{2.78}$$

it is found

$$N_n = \sqrt{\frac{\alpha}{2^n n! \sqrt{\pi}}}\,. \tag{2.79}$$

Figure 2.11 shows first few energy eigenfunctions and corresponding probability per unit length.

Applications of the quantum oscillator

- Study of the oscillations of the atoms of a molecule about their equilibrium position

- Study of the oscillations of atoms of a crystalline lattice

- Study of a the electromagnetic field of radiation

  One mode of the radiation field is treated as a quantum oscillator. For a radiation field of angular frequency ω, the energy level separation is $\hbar\omega$. Suppose the radiation field in the energy eigenstate n; the energy of the field is $n\hbar\omega$ above the ground state. One can associate a set of n

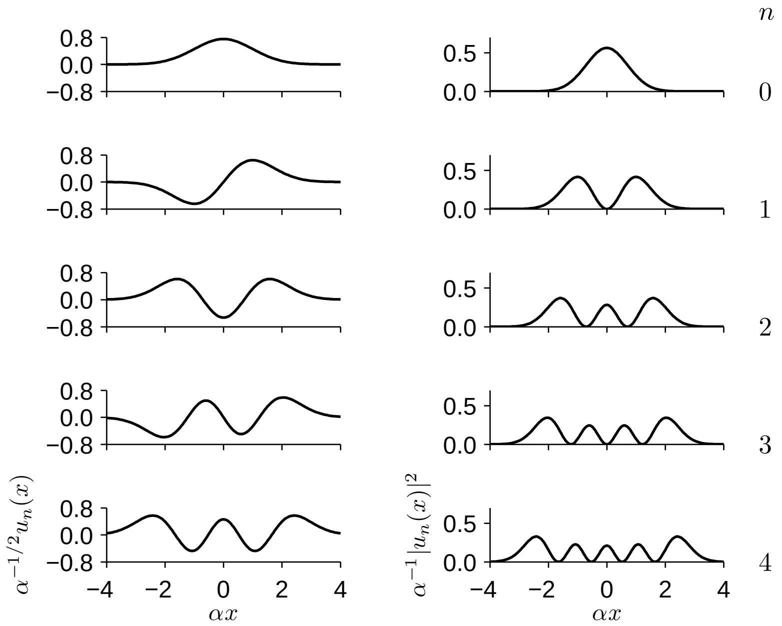


Fig. 2.11 The lowest five energy eigenfunctions for the quantum harmonic oscillator (*left*) and the corresponding probability densities (*right*).

identical particles to the radiation field, each one carrying the energy $\hbar\omega$; these particles are called *photons.* The transition of the radiation field from one energy eigenstate to another corresponds to the creation (emission) or destruction (absorption) of a number of photons.

The interaction between the radiation field and an atom can produce jumps of the atom from one state to another. This subject was treated phenomenologically in Sect. 1.8. The quantum theory confirms Einstein's theory. If the field is in an excited state ($n \geq 1$), the interaction processes are the stimulated (induced) emission and absorption. If the radiation field is in its ground state[1] and the atom in an excited state, the fluctuations of the field *induce* the dezexcitation of the atom; the phenomenon is the spontaneous emission.

2.11 Three-dimensional Schrödinger equation

Unlike the 1-D case, 3-D TISE [Eq. (2.24)] is a partial differential equation which gives rise to considerable mathematical complications in general; solving of the 3-D TISE will be limited below to those cases where the separation of variables technique can be used.

Let us consider the case where the potential energy $V(\boldsymbol{r})$ can be written as a sum of three terms, each of which is a function of only one of the three Cartesian coordinates:

$$V(\boldsymbol{r}) = V_x(x) + V_y(y) + V_z(z)\,. \tag{2.80}$$

We look for wavefunctions that express as a product of three one-dimensional functions,

$$u(\boldsymbol{r}) = X(x)\,Y(y)\,Z(z)\,. \tag{2.81}$$

Substituting Eqs. (2.80) and (2.81) into Eq. (2.24), dividing by $X(x)Y(y)Z(z)$ and rearranging, we get

$$\begin{aligned}\left[-\frac{\hbar^2}{2m}\,\frac{1}{X(x)}\,\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} + V_x(x)\right] + \left[-\frac{\hbar^2}{2m}\,\frac{1}{Y(y)}\,\frac{\mathrm{d}^2Y(y)}{\mathrm{d}y^2} + V_y(y)\right]&\\ + \left[-\frac{\hbar^2}{2m}\,\frac{1}{Z(z)}\,\frac{\mathrm{d}^2Z(z)}{\mathrm{d}z^2} + V_z(z)\right] = E\,.&\end{aligned} \tag{2.82}$$

This equation says that a function of x alone (the term inside the first square bracket), plus one of y alone, plus one of z alone, equals a constant E. The

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[1] Classically, there is no radiation field.

equation can only be true if each square bracket is independently constant. Denoting E_x, E_y, and E_z the constants, Eq. (2.82) split into three one-dimensional TISEs:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2}+V_x(x)X(x)=E_xX(x)\,, \tag{2.83a}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y(y)}{\mathrm{d}y^2}+V_y(y)Y(y)=E_yY(y)\,, \tag{2.83b}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Z(z)}{\mathrm{d}z^2}+V_z(z)Z(z)=E_zZ(z)\,. \tag{2.83c}$$

After solving these three problems, the energy eigenfunctions of the 3-D TISE [Eq. (2.24)] are given by Eq. (2.81) and the energy eigenvalues are given by

$$E=E_x+E_y+E_z\,. \tag{2.84}$$

2.11.1 Example: The three-dimensional infinite well

As an example of a 3-D TISE solving we consider a particle of mass m trapped in a 3-D infinitely deep potential well of sides a_x, a_y and a_z:

$$V(x)=\begin{cases}0 & 0\le x\le a_x\,,\ 0\le y\le a_y\,,\ 0\le z\le a_z\\ \infty & \text{otherwise.}\end{cases} \tag{2.85}$$

This potential approximates, for example, that of the electrons in a metal.

Based on the results of Sect. 2.7, an energy eigenstate is specified by three quantum numbers, $n_x, n_y, n_z = 1, 2, \ldots$. The state specified by (n_x, n_y, n_z) has the energy eigenfunction inside the well given by

$$u_{n_xn_yn_z}(x,y,z)=\sqrt{\frac{8}{a_xa_ya_z}}\,\sin\frac{n\pi x}{a_x}\,\sin\frac{n\pi y}{a_y}\,\sin\frac{n\pi z}{a_z} \tag{2.86}$$

and the energy of the state is

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

Degeneracy

It is possible that distinct quantum states have the same energy value:

$$E_{n_xn_yn_z}=E_{n'_xn'_yn'_z}\quad\text{for}\quad(n_x,n_y,n_z)\neq(n'_x,n'_y,n'_z)\,.$$

Table 2.3 First few energy eigenvalues and corresponding degeneracies of the particle of mass m in the 3-D infinite potential well with all side lengths equal to a.

n_x, n_y, n_z	$E_{n_x n_y n_z}/(\pi^2\hbar^2/2ma^2)$	Degeneracy
1, 1, 1	3	single
1, 1, 2	6	three-fold
1, 2, 2	9	three-fold
1, 1, 3	11	three-fold
2, 2, 2	12	single
1, 2, 3	14	six-fold

Such an energy level is said to be *degenerate*; the degeneracy of that level is equal to the number of distinct quantum states that have the same energy eigenvalue.

To exemplify, let us assume that the potential well considered above has all side lengths equal, $a_x = a_y = a_z = a$. The expression of the energy levels becomes

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right). \tag{2.87}$$

The distinct states (n_x, n_y, n_z) and (n'_x, n'_y, n'_z) that satisfy the condition

$$n_x^2 + n_y^2 + n_z^2 = n_x'^2 + n_y'^2 + n_z'^2$$

are degenerate.

The minimum energy is obtained for $(n_x, n_y, n_z) = (1, 1, 1)$ and there is not another way to get the same energy; the ground level is therefore not degenerate. The first excited level is obtained for $(n_x, n_y, n_z) = (1, 1, 2)$, $(1, 2, 1)$, or $(2, 1, 1)$; the energy level is three-fold degenerate. Table 2.3 describes the lowest few energy levels. The degeneracy in all the cases included in the table are related to a symmetry in the physical system; such degeneracies are called *systematic degeneracies.* Degeneracies may also occur not related to a symmetry; for example, $(n_x, n_y, n_z) = (3, 3, 3)$ and $(n_x, n_y, n_z) = (1, 1, 5)$ give the same energy $(3^2 + 3^2 + 3^2 = 1^2 + 1^2 + 5^2)$. Such a degeneracy is referred to as *accidental degeneracy.*

2.12 Problems

2.1 A particle of mass m and energy E is placed in a region of the Ox axis where $V(x) = V_0 = \text{const}$. Calculate the probability current density of the particle for

(a) $E > V_0$.
(b) $E < V_0$.
Interpret the results.

Solution. The solution of the 1-D TDSE in the region $V(x) = V_0 = \text{const}$ is

$$\psi(x,t) = u(x)\ \exp[-\mathrm{i}(E/\hbar)t]\,,$$

where

(a) $u(x) = A\exp(\mathrm{i}kx) + B\exp(-\mathrm{i}kx)$; A and B are complex constants and $k = \sqrt{2m(E - V_0)}/\hbar$.

(b) $u(x) = A\exp(\kappa x) + B\exp(-\kappa x)$; A and B are complex constants and $\kappa = \sqrt{2m(V_0 - E)}/\hbar$.

We make use of Eq. (2.20); for the stationary state here, the probability current density acquires the form

$$j(x) = \mathrm{i}\frac{\hbar}{2m}\left[u(x)\frac{\mathrm{d}}{\mathrm{d}x}u^*(x) - u^*(x)\frac{\mathrm{d}}{\mathrm{d}x}u(x)\right].$$

(a) We get

$$j(x) = \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right).$$

The (total) probability current density expresses as a difference of two currents:

$$j(x) = j_+(x) - j_-(x)\,,$$

where $j_+(x) = (\hbar k/m)|A|^2$ is a probability current density in the positive Ox direction and $j_-(x) = (\hbar k/m)|B|^2$ is a probability current density in the negative Ox direction.

(b) We get

$$j(x) = \mathrm{i}\frac{\hbar\kappa}{m}(-AB^* + A^*B) = \mathrm{i}\frac{\hbar\kappa}{m}(-2\mathrm{i})\mathrm{Im}(AB^*) = \frac{2\hbar\kappa}{m}\mathrm{Im}(AB^*)\,.$$

A necessary condition for a non-zero probability current is that both A and B are non-zero.

2.2 Consider a particle of mass m in a 1-D potential well $V(x)$.

(a) Prove that there is no degeneracy in a bound state.

(b) Prove that the energy eigenfunction of a bound state can always be chosen real in the coordinate basis.

(c) Prove that for every normalizable solution of the `TISE`, the energy must exceed the minimum value of the potential.

(d) If the potential satisfies $V(-x) = V(x)$ for all x, then any energy eigenfunction u is an even- or odd-parity function.

Solution. (a) Let u_1 and u_2 be two solutions of Eq. (2.27) for the same energy E:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,u_1(x)+V(x)\,u_1(x)=E\,u_1(x)$$

and

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,u_2(x)+V(x)\,u_2(x)=E\,u_2(x).$$

We multiply the first equation by u_2 and the second equation by u_1, then substract the equations. We get

$$u_1\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,u_2(x)-u_2\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,u_1(x)=0,$$

or

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(u_1\frac{\mathrm{d}u_2(x)}{\mathrm{d}x}-u_2\frac{\mathrm{d}u_1(x)}{\mathrm{d}x}\right)=0$$

so that

$$u_1\frac{\mathrm{d}u_2(x)}{\mathrm{d}x}-u_2\frac{\mathrm{d}u_1(x)}{\mathrm{d}x}=\text{const}.$$

To determine the constant, we consider $x\to\infty$ or $x\to-\infty$ where u_1 and u_2 vanish. It follows that

$$u_1\frac{\mathrm{d}u_2(x)}{\mathrm{d}x}-u_2\frac{\mathrm{d}u_1(x)}{\mathrm{d}x}=0,$$

or

$$\frac{\mathrm{d}u_2}{u_2}=\frac{\mathrm{d}u_1}{u_1}.$$

The integration gives $u_2=\text{const}\,u_1$, i.e., the two energy eigenfunctions are linearly dependent.

(b) Let u be solution of Eq. (2.27) for the energy E:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,u(x)+V(x)\,u(x)=E\,u(x).$$

We write the energy eigenfunction in the form

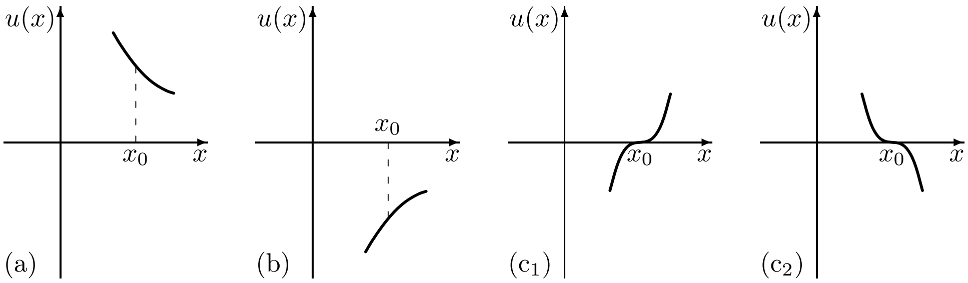
$$u(x)=\mathrm{Re}\,u(x)+\mathrm{i}\,\mathrm{Im}\,u(x).$$

The use of this form into the above equation reveals that both the real and the imaginary parts of u satisfy `TISE` with eigenvalue E. As there is just one independent solution, the energy eigenfunction can be chosen $\mathrm{Re}\,u(x)$ [or $\mathrm{Im}\,u(x)$].

(c) Let us denote by $V_{\min}$ the minimum value of the potential. We first rewrite `TISE` as

$$\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2}=\frac{2m}{\hbar^2}[V(x)-E]u(x).$$

If $E<V_{\min}$, from the above equation it is clear that $\mathrm{d}^2u(x)/\mathrm{d}x^2$ and $u(x)$ always have the same sign. The shape of the function u in the neighbourhood of an arbitrary point x_0 is shown in the figure. $|u(x)|\to\infty$ when $x\to\pm\infty$, so the function is not normalizable. The arguments remain valid for the case $E=V_{\min}$.



Local behaviour of a `TISE` real solution $u(x)$ near a point x_0, when $E < V_{\min}$: (a) $u(x_0) > 0$, (b) $u(x_0) < 0$, and (c$_{1,2}$) $u(x_0) = 0$.

(d) Let u be solution of Eq. (2.27) for the energy E. On replacing x with $-x$ into Eq. (2.27) we get

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}(-x)^2}\,u(-x) + V(-x)\,u(-x) = E\,u(-x).$$

As $\mathrm{d}^2/\mathrm{d}(-x)^2 = \mathrm{d}^2/\mathrm{d}x^2$ and $V(-x) = V(x)$, it follows that $u(-x)$ is also an energy eigenfunction with the energy eigenvalue E. As the energy eigenfunctions are not degenerate,

$$u(-x) = c\,u(x), \quad c \in \mathbb{R},$$

for all x-values. Changing x to $-x$ we obtain

$$u(x) = c\,u(-x)$$

for all x-values. From the last two equations, we get $c^2 = 1$, so $c = \pm 1$ which proves the sought result.

2.3 The electrons in the conduction band of a semiconductor are usually free to move in all directions; their energy is of thermal type. When one dimension of the crystal becomes comparable to, or smaller than, the de Broglie wavelength of a thermalized electron, the electron motion in that direction will be quantized. The phenomenon is called *quantum confinement.* Estimate the length scales to observe quantum confinement effects at room temperature in GaAs. The electron effective mass in GaAs is $m^* = 0.067m$, where m denotes the free electron mass.

Solution. The thermal kinetic energy of an electron at temperature T due to its motion in one direction, say x-direction, is

$$\frac{1}{2}k_{\mathrm{B}}T = \frac{\langle p_x^2\rangle}{2m^*}.$$

The de Broglie wavelength of the electron is of the order of

$$\lambda = \frac{h}{\sqrt{\langle p_x^2\rangle}} = \frac{h}{\sqrt{m^* k_{\mathrm{B}} T}}.$$

For the an electron in GaAs at $T = 300\,\mathrm{K}$, we get $\lambda \approx 42\,\mathrm{nm}$. Consequently, we require length scales of about 40 nm or less to observe quantum confinement effects at room temperature in GaAs.

2.4 Determine the ground state energy of an electron confined to an infinite square well of width equal to the diameter of a hydrogen atom, $a = 0.11\,\mathrm{nm}$.

Solution. Equation (2.36) is used. Taking the constants $\hbar$, m_e and e from Appendix B, we get $E_1 \approx 33.6\,\mathrm{eV}$.

2.5 The nuclear potential energy that binds protons and neutrons in a nucleus is often approximated by a square well potential. Imagine a proton confined in an infinitely high square well of width 10 fm, a typical nuclear diameter. Assuming the proton makes a transition from the first excited state to the ground state, calculate the wavelength of the emitted photon. Identify the region of the electromagnetic spectrum to which this wavelength belongs.

Solution. The energy of the proton ($m \approx 1.67 \times 10^{-27}\,\mathrm{kg}$) in the nth energy eigenstate is given by Eq. (2.36), where $a = 10\,\mathrm{fm}$. The wavelength λ of the emitted photon at the transition from the $n = 2$ state to the $n = 1$ state is given by

$$\frac{hc}{\lambda} = E_2 - E_1 = \frac{\pi^2\hbar^2}{2ma^2}(2^2 - 1^2).$$

One gets

$$\lambda = \frac{8}{3}\frac{mca^2}{h} \approx 2.02 \times 10^{-13}\,\mathrm{m}.$$

The wavelength is in the gamma ray region of the spectrum.

2.6 An electron is trapped in an infinite potential well of 1 cm width. Is quantum theory required for system description?

2.7 The surface of an electrode lies in the plane $x = 0$ and the potential energy outside it is approximated in the form

$$V(x) = \begin{cases} V_0(1 - x^2/a^2) & 0 \le x \le a \\ 0 & \text{otherwise.} \end{cases}$$

Calculate the probability of penetration of this barrier for an electron of energy $0 < E < V_0$.

Solution. The transmission coefficient of the barrier is calculated by help of Eq. (2.57). The integration ends are $x_1 = 0$ and $x_2 > 0$ given by $V_0(1-x^2/a^2) = E$, so $x_2 = a\sqrt{1-\varepsilon}$ with $\varepsilon = E/V_0$.

$$
\begin{aligned}
T &= \exp\left(-\frac{2\sqrt{2mV_0}}{\hbar}\int_0^{a\sqrt{1-\varepsilon}}\sqrt{1-\varepsilon-\frac{x^2}{a^2}}\,\mathrm{d}x\right)\\
&= \exp\left[-\frac{2\sqrt{2mV_0}}{\hbar}a(1-\varepsilon)\int_0^{\pi/2}\cos^2\theta\,\mathrm{d}\theta\right] = \exp\left[-\frac{\pi\sqrt{2mV_0}}{2\hbar}\,a(1-\varepsilon)\right]\\
&\qquad\qquad = \exp\left[-\frac{\pi\sqrt{2mV_0}}{2\hbar}\,a\left(1-\frac{E}{V_0}\right)\right].
\end{aligned}
$$

2.8 Consider the 1-D harmonic oscillator of mass m and angular frequency ω and assume a ground state energy eigenfunction $u(x) \propto \exp(-ax^2)$.

(a) Determine the constant a and the ground state energy.

(b) Determine the normalized energy eigenfunction.

Solution. (a) We write $u(x) = N\exp(-ax^2)$. The use of this function in Eq. (2.67) gives

$$-\frac{\hbar^2}{2m}(-2a+4a^2x^2)+\frac{1}{2}m\omega^2x^2 = E\,.$$

This equation must be true for all x, so

$$\frac{\hbar^2}{m}a = E \quad\text{and}\quad -\frac{4a^2\hbar^2}{2m}+\frac{1}{2}m\omega^2 = 0\,.$$

There is a unique solution for a and E, namely $a = m\omega/2\hbar$ and $E = \hbar\omega/2$. To sum up, $E = \hbar\omega/2$ is an allowed energy and the corresponding eigenfunction is

$$u(x) = N\exp(-ax^2) = N\exp(-\alpha^2x^2/2)\,,$$

where $\alpha = (m\omega/\hbar)^{1/2}$.

(b)

$$1 = \int_{-\infty}^{\infty}|u(x)|^2\mathrm{d}x = |N|^2\,\frac{\pi^{1/2}}{\alpha} \quad\Rightarrow\quad |N| = \frac{\alpha^{1/2}}{\pi^{1/4}}\,.$$

As $\arg N$ has no physical meaning, we take the simpliest choice $\arg N = 0$. The normalized energy eigenfunction of the ground state is

$$u(x) = \frac{\alpha^{1/2}}{\pi^{1/4}}\,\mathrm{e}^{-\alpha^2x^2/2}\,.$$

2.9 Determine the probability of finding a particle in the ground state of a harmonic oscillator, outside of the classically allowed region.

Solution. The amplitude A of the classical oscillator of energy $E_0 = \hbar\omega/2$ is given by

$$\frac{1}{2}\hbar\omega = \frac{1}{2}m\omega^2 A^2, \quad \text{so} \quad A = \sqrt{\frac{\hbar}{m\omega}} = \frac{1}{\alpha}\,.$$

The nonclassical region is $(-\infty, -A) \cup (A, \infty)$. The sought probability is therefore

$$\begin{aligned}\int_{-\infty}^{-A} |u_0(x)|^2 \,\mathrm{d}x + \int_{A}^{\infty} |u_0(x)|^2 \,\mathrm{d}x &= 2\int_{A}^{\infty} \frac{\alpha}{\pi^{1/2}} \exp(-\alpha^2 x^2)\,\mathrm{d}x \\ &= \frac{2}{\pi^{1/2}} \int_{1}^{\infty} \exp(-\xi^2)\,\mathrm{d}\xi = \operatorname{erfc}(1) \approx 0.157\,.\end{aligned}$$

In the above, erfc denotes the complementary error function.

Chapter 3

Formal development of quantum mechanics

3.1 State vectors

First postulate of quantum mechanics asserts that all information about a quantum system is contained in the wavefunction $\psi(\boldsymbol{r}, t)$. A more general way to specify the state of a system is through the *state function* $|\psi(t)\rangle$. This is a vector in an abstract linear (vector) space over the complex numbers. It will be called a *ket*; $|\psi\rangle$ is pronounced "ket ψ." The null vector is usually represented as 0 without a ket symbol.

It is natural to choose a set of basis vectors $\{|\phi_i\rangle\}_i$ such that any given ket $|\psi\rangle$ can be written as a linear combination of the basis vectors,

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle, \tag{3.1}$$

where the expansion coefficients c_i are complex numbers. The dimension of the vector space is the number of vectors required to make up a basis for the space. It is assumed in Eq. (3.1) that the index i takes on discrete values.

In the abstract linear space we introduce an inner (scalar) product. If $|\psi_1\rangle$ and $|\psi_2\rangle$ are two kets, their inner product is denoted $\langle\psi_1|\psi_2\rangle$. In contrast to many mathematics textbooks, quantum mechanics takes the inner product as linear in the second factor:

$$\langle\psi|(c_1|\psi_1\rangle + c_2|\psi_2\rangle) = c_1\langle\psi|\psi_1\rangle + c_2\langle\psi|\psi_2\rangle. \tag{3.2}$$

If $\langle\psi_1|\psi_2\rangle = 0$, the kets $|\psi_1\rangle$ and $|\psi_2\rangle$ are called orthogonal.

The norm of a ket $|\psi\rangle$, denoted as $\|\psi\|$, is defined as the square root of the inner product of the ket and itself:

$$\|\psi\| = \sqrt{\langle\psi|\psi\rangle}. \tag{3.3}$$

If $\|\psi\| = 1$, the ket is called normalized.

It is always possible to construct a basis $\{|\phi_i\rangle\}_i$ formed of kets of norm one and additionally each ket is orthogonal to every other:

$$\langle\phi_i|\phi_{i'}\rangle = \delta_{ii'}, \tag{3.4}$$

where $\delta_{ii'}$ is the *Kronecker delta* defined by

$$\delta_{ii'} = \begin{cases} 1, & i = i' \\ 0, & i \neq i'. \end{cases} \tag{3.5}$$

Such a basis is called *orthonormal.*

It may be verified that the functions u_n which we have found during `TISE` solving for the particle in an infinitely deep potential well are orthonormal (see Problem 3.1), where the scalar product is defined by

$$\langle u_n|u_{n'}\rangle = \int_{-\infty}^{\infty} u_n^*(x)\, u_{n'}(x)\, \mathrm{d}x. \tag{3.6}$$

For an orthonormal basis $\{|\phi_i\rangle\}_i$, we have:

- The coefficients in Eq. (3.1) are given by

$$c_i = \langle\phi_i|\psi\rangle. \tag{3.7}$$

- The inner product of the kets

$$|\psi_1\rangle = \sum_i a_i|\phi_i\rangle \quad \text{and} \quad |\psi_2\rangle = \sum_{i'} b_{i'}|\phi_{i'}\rangle \tag{3.8}$$

  is

$$\langle\psi_1|\psi_2\rangle = \sum_{i,i'} a_i^* b_{i'}\langle\phi_i|\phi_{i'}\rangle = \sum_i a_i^* b_i. \tag{3.9}$$

- The norm of ket $|\psi\rangle$ given by Eq. (3.1) is

$$\|\psi\| = \sqrt{\sum_i |c_i|^2}. \tag{3.10}$$

3.2 Operators

A linear operator on the vector space is a mathematical object that transforms kets into kets in a linear way. In quantum mechanics, operators are marked with a "hat," for example $\hat{A}$. The operator $\hat{A}$ is said to be linear if for any two kets $|\psi_1\rangle$ and $|\psi_2\rangle$ and any complex number c, the following two conditions are satisfied:

$$\hat{A}(|\psi_1\rangle + |\psi_2\rangle) = \hat{A}|\psi_1\rangle + \hat{A}|\psi_2\rangle, \tag{3.11a}$$

$$\hat{A}(c|\psi\rangle) = c\hat{A}|\psi\rangle. \tag{3.11b}$$

Linearity is of special importance in quantum mechanics because of its connection to the principle of superposition.

Two examples are immediate:

1. The identity operator $\hat{1}$, defined by $\hat{1}|\psi\rangle = |\psi\rangle$ for any ket $|\psi\rangle$.
2. The null operator $\hat{0}$, defined by $\hat{0}|\psi\rangle = 0$ for any ket $|\psi\rangle$.

These operators are often written 1 and 0, respectively.

The sum of the operators $\hat{A}$ and $\hat{B}$, denoted $\hat{A} + \hat{B}$, is defined by

$$(\hat{A} + \hat{B})|\psi\rangle = \hat{A}|\psi\rangle + \hat{B}|\psi\rangle \tag{3.12}$$

for any ket $|\psi\rangle$.

The product of operators $\hat{A}$ and $\hat{B}$, denoted $\hat{A}\hat{B}$, is defined by

$$(\hat{A}\hat{B})|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) \tag{3.13}$$

for any ket $|\psi\rangle$.

3.2.1 The commutator

In general, the order of operators in the product $\hat{A}\hat{B}$ cannot be interchanged, i.e., $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. One defines the *commutator* of operators $\hat{A}$ and $\hat{B}$ by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{3.14}$$

If $[\hat{A}, \hat{B}] = 0$, one says that operators $\hat{A}$ and $\hat{B}$ *commute*. The main algebraic properties of the commutator are antisymmetry, linearity and the product rule:

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}], \tag{3.15a}$$

$$[\hat{A}, b\hat{B} + c\hat{C}] = b[\hat{A}, \hat{B}] + c[\hat{A}, \hat{C}] \quad \forall b, c \in \mathbb{C}, \tag{3.15b}$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]. \tag{3.15c}$$

See Problem 3.2 for the proofs.

3.2.2 Hermitian conjugate operator

We define the Hermitian conjugate of the operator $\hat{A}$, denoted by $\hat{A}^\dagger$ and read as "A dagger," by the relation

$$\langle\psi_1|\hat{A}^\dagger|\psi_2\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle^* \quad \text{for all} \quad |\psi_{1,2}\rangle. \tag{3.16}$$

This relation may be written

$$\langle\hat{A}^\dagger\psi_2|\psi_1\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle$$

and, after a change of notations,

$$\langle\hat{A}^\dagger\psi_1|\psi_2\rangle = \langle\psi_1|\hat{A}|\psi_2\rangle. \tag{3.16$'$}$$

The Hermitian conjugate operator is also linear.

The following calculational properties of Hermitian conjugation are easily proved (see Problem 3.3):

$$\hat{A}^{\dagger\dagger} = \hat{A}, \tag{3.17a}$$

$$(a\hat{A} + b\hat{B})^\dagger = a^*\hat{A}^\dagger + b^*\hat{B}^\dagger, \quad a, b \in \mathbb{C}, \tag{3.17b}$$

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger. \tag{3.17c}$$

An operator $\hat{A}$ is said to be *Hermitian* or *self-adjoint* if

$$\hat{A}^\dagger = \hat{A} \quad \Leftrightarrow \quad \langle\psi_1|\hat{A}|\psi_2\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle^* \quad \text{for all} \quad |\psi_{1,2}\rangle. \tag{3.18}$$

3.2.3 Eigenvalue problem

In general, $\hat{A}|\psi\rangle$ is not a constant times $|\psi\rangle$. An *eigenket* of the operator $\hat{A}$ is a non-zero ket $|a\rangle$ such that the applying of $\hat{A}$ to it reproduces the ket apart from a multiplicative complex number:

$$\hat{A}|a\rangle = a|a\rangle. \tag{3.19}$$

The complex number a is called *eigenvalue* of operator $\hat{A}$. The set of all eigenvalues is called the *spectrum* of $\hat{A}$. It is possible that two or more linearly independent eigenvectors correspond to the same eigenvalue; if there are at most n linearly independent eigenkets having the same eigenvalue, then we say that the eigenvalue is n-fold degenerate. A non-degenerate eigenvalue is called *simple.*

The quantum state corresponding to an eigenket is called *eigenstate.*

The crucial significance of Hermitian operators for quantum mechanics is contained in the following two properties:

- The eigenvalues of a Hermitian operator are real.

- The eigenvectors of a Hermitian operator belonging to different eigenvalues are orthogonal.

To prove these properties, let $|a_n\rangle$ and $|a_{n'}\rangle$ be two eigenvectors of the Hermitian operator $\hat{A}$ and a_n and $a_{n'}$ be the associated eigenvalues:

$$\hat{A}|a_n\rangle = a_n|a_n\rangle \quad \text{and} \quad \hat{A}|a_{n'}\rangle = a_{n'}|a_{n'}\rangle.$$

We consider the matrix element $\langle a_n|\hat{A}|a_{n'}\rangle$. Since $|a_{n'}\rangle$ is eigenvector and $a_{n'}$ is the corresponding eigenvalue, we yield

$$\langle a_n|\hat{A}|a_{n'}\rangle = a_{n'}\langle a_n|a_{n'}\rangle.$$

On the other hand, by use of the Hermiticity property of operator $\hat{A}$ the matrix element can be expressed as

$$\langle a_n|\hat{A}|a_{n'}\rangle = \langle a_{n'}|\hat{A}|a_n\rangle^* = a_n^*\langle a_{n'}|a_n\rangle^* = a_n^*\langle a_n|a_{n'}\rangle.$$

Equating the two expressions for $\langle a_n|\hat{A}|a_{n'}\rangle$, we find

$$(a_{n'} - a_n^*)\langle a_n|a_{n'}\rangle = 0. \tag{3.20}$$

- For $|a_{n'}\rangle = |a_n\rangle$ and $a_{n'} = a_n$ the above equation inplies $a_n^* = a_n$, that is, the eigenvalue a_n is real. The use of this property in Eq. (3.20) gives

$$(a_{n'} - a_n)\langle a_n|a_{n'}\rangle = 0. \tag{3.21}$$

- For $a_{n'} \neq a_n$ we get $\langle a_n|a_{n'}\rangle = 0$, which proves the orthogonality property.

3.3 Postulate 3

Every dynamical variable may be represented by a Hermitian operator. The eigenvalues of the operator are the possible results in a measurement of the value of the variable. Immediately after such a measurement the state ket of the system is the eigenket of the relevant operator which corresponds to the eigenvalue obtained as a result of the measurement.

Remarks:

- The need for a Hermitian operator is a consequence of the condition that the possible results in a measurement are real values.

- Note that the measurement induces a change in the state vector. The measurement forces the state vector to become an eigenvector of the relevant operator. After the measurement, the state vector evolves according to `TDSE`.

3.4 Postulate 4

The choice of the Hermitian operators representing the physical observables is furnished by postulate 4:

The operators representing the position $\boldsymbol{r}$ *and momentum* $\boldsymbol{p}$ *of a particle are*

$$\hat{\boldsymbol{r}} = \boldsymbol{r} \tag{3.22}$$

and

$$\hat{\boldsymbol{p}} = -\mathrm{i}\hbar\boldsymbol{\nabla}, \tag{3.23}$$

respectively. Operators representing other physical observables are related to these operators in the same way that the classical quantities are related to the classical position and momentum variables.

Remarks:

1. Position and momentum operators must be Hermitian. Their choice obeys this condition. To prove this, let us consider for simplicity the 1-D case. Let us consider the arbitrary state vectors $|\psi_1(x,t)\rangle$ and $|\psi_2(x,t)\rangle$. Then

$$\langle\psi_1|\hat{x}|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^* x \psi_2 \,\mathrm{d}x = \left(\int_{-\infty}^{\infty} \psi_2^* x \psi_1 \,\mathrm{d}x\right)^* = \langle\psi_2|\hat{x}|\psi_1\rangle^*,$$

which proves that $\hat{x}$ is Hermitian [see Eq. (3.18)]. To prove that $\hat{p}_x$ is Hermitian, we proceed similarly:

$$\langle\psi_1|\hat{p}_x|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^* \hat{p}_x \psi_2 \,\mathrm{d}x = \int_{-\infty}^{\infty} \psi_1^* (-\mathrm{i}\hbar) \frac{\mathrm{d}}{\mathrm{d}x} \psi_2 \,\mathrm{d}x.$$

Integrating by parts we find

$$\langle\psi_1|\hat{p}_x|\psi_2\rangle = -\mathrm{i}\hbar\psi_1^*\psi_2\big|_{-\infty}^{\infty} + \mathrm{i}\hbar\int_{-\infty}^{\infty} \psi_2 \frac{\mathrm{d}}{\mathrm{d}x}\psi_1^* \,\mathrm{d}x.$$

The first term on the right-hand side vanishes because the wavefunctions are approaching zero at infinity. By rearranging the second term we have

$$\begin{aligned}\langle\psi_1|\hat{p}_x|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_2 \left(-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\psi_1\right)^* \mathrm{d}x = \left[\int_{-\infty}^{\infty} \psi_2^* \left(-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\psi_1\right) \mathrm{d}x\right]^* \\ = \langle\psi_2|\hat{p}_x|\psi_1\rangle^*,\end{aligned}$$

which proves that $\hat{p}_x$ is Hermitian.

2. Let us calculate the commutators implying the position and momentum operators. To calculate $[\hat{x}, \hat{p}_x]$, we consider the action of the commutator operator upon an arbitrary wavefunction $\psi(x,t)$:

$$[\hat{x}, \hat{p}_x]\psi(x,t) = x(-\mathrm{i}\hbar)\frac{\partial}{\partial x}\psi(x,t) - (-\mathrm{i}\hbar)\frac{\partial}{\partial x}\big(x\psi(x,t)\big) = \mathrm{i}\hbar\psi(x,t).$$

As the wavefunction $\psi(x,t)$ is arbitrary, it is inferred

$$[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar. \tag{3.24a}$$

Similarly,

$$[\hat{y}, \hat{p}_y] = \mathrm{i}\hbar \tag{3.24b}$$

and

$$[\hat{z}, \hat{p}_z] = \mathrm{i}\hbar. \tag{3.24c}$$

If the position and momentum operators correspond to different axes, the commutator is zero:

$$[\hat{x}, \hat{p}_y] = 0, \quad [\hat{x}, \hat{p}_z] = 0, \ldots. \tag{3.25}$$

The commutators of two coordinate operators, or two momentum projections are also zero:

$$[\hat{x}, \hat{y}] = [\hat{y}, \hat{z}] = [\hat{z}, \hat{x}] = 0 \tag{3.26}$$

and

$$[\hat{p}_x, \hat{p}_y] = [\hat{p}_y, \hat{p}_z] = [\hat{p}_z, \hat{p}_x] = 0. \tag{3.27}$$

3. Let us use the fourth postulate to construct the energy operator. In classical mechanics, the energy of a particle of mass m having the potential energy $V(\boldsymbol{r})$ is

$$E = \frac{1}{2m}\boldsymbol{p}^2 + V.$$

The quantum energy operator, denoted by $\hat{H}$ and called *Hamiltonian* is

$$\hat{H} = \frac{1}{2m}(-\mathrm{i}\hbar\boldsymbol{\nabla})^2 + V = -\frac{\hbar^2}{2m}\nabla^2 + V. \tag{3.28}$$

The Hermiticity of $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ ensures the Hermiticity of $\hat{H}$.

By use of the Hamiltonian operator, `TISE` [see Eq. (2.24)] is expressed in the general form

$$\hat{H}|u\rangle = E|u\rangle, \tag{3.29}$$

i.e., the eigenvalue problem of the energy operator.

It should be pointed out that the definition of the Hamiltonian extends to the case of a time-dependent potential. The use of the Hamiltonian operator in `TDSE` [see Eq. (2.14)] gives the general form of this equation

$$\mathrm{i}\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H}|\psi\rangle. \tag{3.30}$$

3.5 Postulate 5

The eigenkets of an observable form a complete (generally infinite) set of linearly independent kets such that any state ket can be expressed as a linear superposition of them. If a measurement of the observable represented by the operator $\hat{A}$ is performed on the system with the normalized state ket

$$|\psi\rangle = \sum_i c_i |a_i\rangle, \tag{3.31}$$

where $|a_i\rangle$ is the normalized eigenket of $\hat{A}$ with eigenvalue a_i, then the probability of obtaining the result a_i is $|c_i|^2$.

According to this postulate, a measurement forces the system to jump from its state $|\psi\rangle$ into an eigenstate of the observable that is being measured. In other words, *the measurement usually changes the state of the system.* We do not know in advance into which of the a_i's the system will jump; the probability of the value a_i is $|c_i|^2 = |\langle a_i|\psi\rangle|^2$.

Let us clarify the statistical meaning of this postulate. Suppose that we prepare N identical copies of the system all in exactly the same fashion so that each copy is presumably in the same quantum state $|\psi\rangle$; the set of identical copies is called an *ensemble.* If we then perform a measurement of the observable A for each member of the ensemble, we find the randomly varying results a_1, a_2, ...; the outcomes are all eigenvalues of the operator $\hat{A}$ associated to the observable. We count up the number of times N_i we get the result a_i; then the fraction of times the result a_i is obtained is N_i/N. The Postulate 5 asserts that in the limit of a large number of identical copies, the fraction N_i/N approaches the value $|c_i|^2 = |\langle a_i|\psi\rangle|^2$, i.e.

$$\lim_{N\to\infty} \frac{N_i}{N} = |c_i|^2 = |\langle a_i|\psi\rangle|^2.$$

The use of this postulate is exemplified in Problem 3.5.

3.6 The eigenvalues and eigenfunctions of the momentum operator

The eigenvalue equation of the momentum operator is

$$\hat{p}_x\phi(x) = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\phi(x) = p_x\phi(x). \tag{3.32}$$

This is a first-order differential equation; the general solution is

$$\phi_{p_x}(x) = c\exp(\mathrm{i}p_x x/\hbar), \tag{3.33}$$

where c is a constant. Equation (3.32) has solution for any value of p_x; it follows that the momentum eigenvalue spectrum is continuous. For one value p_x, there is just one eigenfunction; the momentum eigenvalues are thus not degenerate.

We next study the normalization of momentum eigenfunctions. Since $|\phi_{p_x}(x)|^2 = |c|^2$,

$$\int_{-\infty}^{\infty} |\phi_{p_x}(x)|^2\mathrm{d}x = \infty$$

and the momentum eigenfunctions can not be normalized in the strict sense. It means that such a state, in which the momentum p_x is precisely known, can not be practically reached.

By use of the $\hat{p}_x$ eigenfunctions, the wavefunction of a system at time t can be expressed as

$$\psi(x,t) = \int_{-\infty}^{\infty} c(p_x,t)\ \exp(\mathrm{i}p_x x/\hbar)\,\mathrm{d}p_x. \tag{3.34}$$

3.7 Expectation values

By use of Postulate 5, the expectation value of the observable A in the state $|\psi\rangle$ is

$$\langle A\rangle = \sum_i |c_i|^2 a_i. \tag{3.35}$$

Although this expression is simple enough, it is not very useful, since in order to evaluate it we would need to compute al the c_i. Fortunately there is a much more convenient method. Consider first of all what we would expect for the mean value of the position x. Since $|\psi(x)|^2$ is the probability density at x we can immediately write

$$\langle x\rangle = \int_{-\infty}^{\infty} |\psi(x)|^2 x\,\mathrm{d}x = \int_{-\infty}^{\infty} \psi^*(x)\,x\,\psi(x)\,\mathrm{d}x = \langle\psi|\hat{x}|\psi\rangle. \tag{3.36}$$

For an arbitrary observable A the above formula can be generalized under the form

$$\boxed{\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle.} \tag{3.37}$$

Indeed, let us expand $|\psi\rangle$ in terms of $|a_i\rangle$'s, the eigenkets of $\hat{A}$. Then

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_{i,i'} c_i^* c_{i'} a_{i'} \langle a_i|a_{i'}\rangle = \sum_i |c_i|^2 a_i.$$

The average value of the observable A, $\langle A\rangle$, is an ensemble average. Let us imagine that for the given system in the quantum state $|\psi\rangle$ we have created a large number of identical copies, all prepared in the state $|\psi\rangle$. The observable A is measured for each system; the average of the outcomes, in the limit of a large number of copies, is $\langle A\rangle$.

3.8 Time dependence of expectation values

The expectation value $\langle A\rangle$ of the observable A [see Eq. (3.37)] is, in general, a function of time. Its rate of change is

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\langle\psi|\hat{A}|\psi\rangle = \left\langle\frac{\partial\psi}{\partial t}\middle|\hat{A}\middle|\psi\right\rangle + \left\langle\psi\middle|\hat{A}\middle|\frac{\partial\psi}{\partial t}\right\rangle + \left\langle\psi\middle|\frac{\partial\hat{A}}{\partial t}\middle|\psi\right\rangle.$$

The derivatives with respect to time of the state vector $|\psi\rangle$ are now expressed by use of Eq. (3.30):

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle\hat{H}\psi|\hat{A}|\psi\rangle - \frac{\mathrm{i}}{\hbar}\langle\psi|\hat{A}\hat{H}|\psi\rangle + \left\langle\psi\middle|\frac{\partial\hat{A}}{\partial t}\middle|\psi\right\rangle.$$

Since $\hat{H}$ is a Hermitian operator we can write $\langle\hat{H}\psi|\hat{A}|\psi\rangle = \langle\psi|\hat{H}\hat{A}|\psi\rangle$. Next, in summing the first two terms

$$\langle\psi|\hat{H}\hat{A}|\psi\rangle - \langle\psi|\hat{A}\hat{H}|\psi\rangle = \langle\psi|[\hat{H},\hat{A}]|\psi\rangle = \langle[\hat{H},\hat{A}]\rangle,$$

where Eq. (3.37) for the commutator operator $[\hat{H},\hat{A}]$ has been used in the last step. Applying again Eq. (3.37) for the last term on the rhs, we finally get

$$\boxed{\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle[\hat{H},\hat{A}]\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle,} \tag{3.38}$$

which is *Ehrenfest's theorem.* Thus the rate of change of the expectation value of the observable A is the sum of two terms: one is proportional to the expectation value of the commutator of $\hat{A}$ and the Hamiltonian of the system, and the other is the expectation value of the operator $\partial\hat{A}/\partial t$.

Most operators used in quantum mechanics do not depend explicitly on time, so $\partial\hat{A}/\partial t = 0$. In such a case, the rate of change of the expectation value of the observable A is

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle[\hat{H},\hat{A}]\rangle. \tag{3.39}$$

Moreover, if $\hat{A}$ commutes with the Hamiltonian operator, then the expectation value of A in any quantum state is a constant. Such an observable is called a *constant of the motion.* This implies that the classical observable A is conserved.

Let us consider a 1-D motion of a particle of mass m in the potential $V(x)$. The Hamiltonian of the particle is

$$\hat{H} = \frac{1}{2m}\hat{p}_x^2 + V(x). \tag{3.40}$$

We shall apply Ehrenfest theorem for the case of the observables x and p_x. In the first case we have

$$\begin{aligned}\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle[\hat{H},\hat{x}]\rangle = \frac{\mathrm{i}}{\hbar}\left\langle\left[\frac{1}{2m}\hat{p}_x^2,\hat{x}\right]\right\rangle &= \frac{\mathrm{i}}{2m\hbar}\langle\hat{p}_x[\hat{p}_x,\hat{x}] + [\hat{p}_x,\hat{x}]\hat{p}_x\rangle\\ &= \frac{\mathrm{i}}{2m\hbar}(\langle -\mathrm{i}\hbar\hat{p}_x\rangle + \langle -\mathrm{i}\hbar\hat{p}_x\rangle) = \frac{1}{m}\langle\hat{p}_x\rangle\end{aligned}$$

or, equivalently,

$$m\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \langle\hat{p}_x\rangle. \tag{3.41}$$

This result corresponds to the classical definition of momentum.

In a similar way,

$$\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle[\hat{H},\hat{p}_x]\rangle = \frac{\mathrm{i}}{\hbar}\langle[V(x),\hat{p}_x]\rangle.$$

To evaluate the commutator $[V(x),\hat{p}_x]$, we consider its action upon an arbitrary wavefunction $\psi(x,t)$:

$$[V(x),\hat{p}_x]\psi(x,t) = -\mathrm{i}\hbar V(x)\frac{\partial}{\partial x}\psi(x,t) + \mathrm{i}\hbar\frac{\partial}{\partial x}\big(V(x)\,\psi(x,t)\big) = \mathrm{i}\hbar\frac{\mathrm{d}V(x)}{\mathrm{d}x}\psi(x,t).$$

As the wavefunction $\psi(x,t)$ is arbitrary, it is inferred

$$[V(x), \hat{p}_x] = \mathrm{i}\hbar \frac{\mathrm{d}V(x)}{\mathrm{d}x}.$$

Ehrenfest's theorem for p_x thus becomes

$$\frac{\mathrm{d}\langle p_x \rangle}{\mathrm{d}t} = \left\langle -\frac{\mathrm{d}V}{\mathrm{d}x} \right\rangle = \langle F_x(x) \rangle, \tag{3.42}$$

where F_x is the classical force. This equation is the quantum version of Newton's second law: in any quantum state $|\psi(x,t)\rangle$, the time derivative of the expectation value of the x component of momentum is equal to the expectation value of the x component of the applied force.

3.9 Compatibility of observables

The uncertainty principle (see Sect. 1.11) states the impossibility of complete knowledge of two observables—position and momentum—of a particle. We are now in position to discuss this subject in the frame of quantum mechanics.

Suppose that we wish to simultaneously measure two observables of a system. It can be assumed that these measurements are made so quickly that the time evolution of the state ket can be neglected. Let us denote by A and B the two observables and $\hat{A}$ and $\hat{B}$ the corresponding Hermitian operators. The measurement of observable A forces the system in a state which is eigenket of $\hat{A}$. Generally, this ket is not an eigenket of operator $\hat{B}$, but a superposition of $\hat{B}$ eigenkets. The subsequent measurement of the observable B will give an uncertain result, unless $\hat{A}$ and $\hat{B}$ have common eigenkets. We describe the situation by saying that the observables are *compatible* if their operators have common eigenkets, and *incompatible* otherwise.

Let us find a formal condition for the compatibility of the two observables. Consider an eigenket of $\hat{A}$, $|\phi\rangle$, with eigenvalue a, also be an eigenstate of $\hat{B}$, with eigenvalue b:

$$\hat{A}|\phi\rangle = a|\phi\rangle \quad \text{and} \quad \hat{B}|\phi\rangle = b|\phi\rangle. \tag{3.43}$$

We left-multiply the first equation by $\hat{B}$, and the second equation by $\hat{A}$, and then substract the first equation from the second. The result is

$$(\hat{A}\hat{B} - \hat{B}\hat{A})|\phi\rangle = 0. \tag{3.44}$$

The expression within parantheses is the commutator of operators $\hat{A}$ and $\hat{B}$. Since the eigenstates of an observable must form a complete set, any state ket $|\psi\rangle$ can be expanded in terms of $|\phi\rangle$'s. It follows that Eq. (3.44) can be generalized to

$$[\hat{A}, \hat{B}]|\psi\rangle = 0. \tag{3.45}$$

Now, since $|\psi\rangle$ is arbitrary, we have

$$[\hat{A}, \hat{B}] = 0. \tag{3.46}$$

Thus, the condition for two observables to be compatible is that their operators commute. The converse is also true: if the operators representing two observables commute then they have common eigenkets, i.e., they are compatible. We prove below this theorem only in case of non-degenerate eigenvalues; the proof for the general case can be found in literature. Let a be an eigenvalue of the operator $\hat{A}$ and $|a\rangle$ the corresponding eigenket:

$$\hat{A}|a\rangle = a|a\rangle. \tag{3.47}$$

We apply the operator $\hat{B}$ to both sides of this equation. By use of $\hat{B}\hat{A} = \hat{A}\hat{B}$, we get

$$\hat{A}(\hat{B}|a\rangle) = a(\hat{B}|a\rangle). \tag{3.48}$$

- If $\hat{B}|a\rangle = 0$, then $|a\rangle$ is an eigenket of $\hat{B}$ with the eigenvalue $b = 0$;
- If $\hat{B}|a\rangle \neq 0$, since a is a simple eigenvalue of $\hat{A}$, the ket $\hat{B}|a\rangle$ is proportional to $|a\rangle$:

  $$\hat{B}|a\rangle = b|a\rangle, \tag{3.49}$$

  where b is a non-zero scalar. This relation shows that $|a\rangle$ is an eigenket of operator $\hat{B}$ with eigenvalue $b \neq 0$.

It is now clear that, given two compatible observables, there exists a basis in the state space made up of common eigenkets.

3.10 Complete set of commuting observables

Consider an observable A whose eigenvalues are all non-degenerate. If $\{a_n\}_n$ is the set of eigenvalues, each eigenvalue identifies uniquely one eigenket. Hence we can label the eigenkets by their eigenvalue. For example, the eigenket of $\hat{A}$ corresponding to the eigenvalue a_n is written $|a_n\rangle$; the set $\{|a_n\rangle\}_n$ constitutes a basis in the state space. In this case, the eigenvalues of $\hat{A}$ completely specify the quantum state of the system. We say that the observable A forms by itself a *complete set of commuting observables* (`CSCO`).

In case of some degenerate eigenvalues of $\hat{A}$, the eigenvalues are no longer sufficient to identify the eigenkets. We look for another observable B whose attached operator $\hat{B}$ commutes with $\hat{A}$ and a basis of common eigenkets is chosen. If each pair of eigenvalues (a, b), where a is eigenvalue of $\hat{A}$ and b is eigenvalue of $\hat{B}$, identifies uniquely one ket of the basis, then the set $\{A, B\}$ is a `CSCO`.

The process of adding new observables that commute with each other continues until there is no more degeneracy.

A remarkable example of `CSCO` is offered by the solutioning of `TISE` for the hydrogen atom. There one finds that the Hamiltonian, the square of the orbital angular momentum operator, and the projection on the z-axis of the orbital angular momentum operator form a `CSCO`. As a consequence, an energy eigenfunction is labelled by three quantum numbers, indicating the eigenvalues of the three operators.

3.11 Heisenberg uncertainty principle

3.11.1 Generalized Heisenberg uncertainty principle

We are now in position to prove the Heisenberg uncertainty formula $\Delta x\, \Delta p_x \geq \hbar/2$; moreover, an uncertainty formula for a pair of arbitrary observables is obtained.

Let us consider two observables A and B represented by the Hermitian operators $\hat{A}$ and $\hat{B}$, respectively. In the normalized state $|\psi\rangle$, the expectation value of the two observables are $\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle$ and $\langle B\rangle = \langle\psi|\hat{B}|\psi\rangle$.

In classical statistics, an appropriate measure of the uncertainty of a variable is the mean square root deviation. Accordingly, we define in quantum mechanics the uncertainty of the observable A in state $|\psi\rangle$, ΔA, by

$$(\Delta A)^2 = \langle(\hat{A} - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2 = \langle\psi|\hat{A}^2|\psi\rangle - \langle\psi|\hat{A}|\psi\rangle^2. \tag{3.50}$$

Similarly, the uncertainty ΔB of the observable B is given by

$$(\Delta B)^2 = \langle B^2\rangle - \langle B\rangle^2 = \langle\psi|\hat{B}^2|\psi\rangle - \langle\psi|\hat{B}|\psi\rangle^2. \tag{3.51}$$

We shall show that the uncertainties ΔA and ΔB associated with the simultaneous measurement of the two observables are linked by the *generalized uncertainty principle*

$$\boxed{\Delta A\, \Delta B \geq \frac{1}{2}|\langle\psi|\mathrm{i}[\hat{A}, \hat{B}]|\psi\rangle|.} \tag{3.52}$$

To prove Eq. (3.52), let us define the deviations from the expectation values, δ_A and δ_B, by

$$\delta_A = A - \langle A \rangle \quad \text{and} \quad \delta_B = B - \langle B \rangle, \tag{3.53}$$

and the corresponding Hermitian operators

$$\hat{\delta}_A = \hat{A} - \langle A \rangle \quad \text{and} \quad \hat{\delta}_B = \hat{B} - \langle B \rangle. \tag{3.54}$$

The expectation values of δ_A and δ_B are zero, $\langle \delta_A \rangle = 0$ and $\langle \delta_B \rangle = 0$, and their uncertainties are given by

$$(\Delta\delta_A)^2 = \langle \delta_A^2 \rangle = (\Delta A)^2 \quad \text{and} \quad (\Delta\delta_B)^2 = \langle \delta_B^2 \rangle = (\Delta B)^2. \tag{3.55}$$

Let us consider the ket

$$|\phi\rangle = (\hat{\delta}_A + \mathrm{i}\lambda\hat{\delta}_B)|\psi\rangle, \tag{3.56}$$

where λ is an arbitrary real parameter to be determined below. Since the inner product of a ket with itself is positive, we have

$$\begin{aligned} 0 \leq \langle \phi|\phi \rangle &= \langle \psi|(\hat{\delta}_A - \mathrm{i}\lambda\hat{\delta}_B)(\hat{\delta}_A + \mathrm{i}\lambda\hat{\delta}_B)|\psi\rangle \\ &= \langle \psi|\hat{\delta}_A^2|\psi\rangle + \lambda\langle\psi|\mathrm{i}(\hat{\delta}_A\hat{\delta}_B - \hat{\delta}_B\hat{\delta}_A)|\psi\rangle + \lambda^2\langle\psi|\hat{\delta}_B^2|\psi\rangle \\ &= (\Delta A)^2 + \lambda\langle \mathrm{i}[\hat{\delta}_A, \hat{\delta}_B]\rangle + \lambda^2(\Delta B)^2. \end{aligned}$$

Here, the commutator $[\hat{\delta}_A, \hat{\delta}_B]$ is equal to $[\hat{A}, \hat{B}]$. Accordingly, we may write

$$(\Delta B)^2\lambda^2 + \langle \mathrm{i}[\hat{A}, \hat{B}]\rangle\lambda + (\Delta A)^2 \geq 0 \quad \forall\lambda \in \mathbb{R}. \tag{3.57}$$

Since the operator $\mathrm{i}[\hat{A}, \hat{B}]$ is Hermitian (see Problem 3.4), its expectation value is real. The above equation requires that the discriminant of the second-order polynomial in λ is negative or zero:

$$\langle \mathrm{i}[\hat{A}, \hat{B}]\rangle^2 - 4(\Delta A)^2(\Delta B)^2 \leq 0,$$

from which Eq. (3.52) is obtained.

The content of Heisenberg uncertainty principle is interpreted as follows. Consider a large number N of identical systems all in the same quantum state $|\psi\rangle$. We measure A on $N_A \gg 1$ systems and B on $N_B = N - N_A \gg 1$ systems. Then the experimental results are used to calculate the uncertainties ΔA and ΔB; equation (3.52) must be satisfied.

When the generalized uncertainty principle is applied to the pair of observables x and p_x, since $[x, \hat{p}_x] = \mathrm{i}\hbar$ [see Eq. (3.24a)], the result is

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2}. \tag{3.58a}$$

Similar applications of Eq. (3.52) for the other two Cartesian position-momentum pairs yield

$$\Delta y \, \Delta p_y \geq \frac{\hbar}{2} \tag{3.58b}$$

and

$$\Delta z \, \Delta p_z \geq \frac{\hbar}{2}. \tag{3.58c}$$

If the position and momentum observables correspond to different axes, the commutators are zero and Eq. (3.52) give

$$\Delta x \, \Delta p_y \geq 0, \quad \Delta y \, \Delta p_z \geq 0, \ldots . \tag{3.59}$$

Thus, a Cartesian coordinate and a momentum component along a different Cartesian direction may be precisely determined simultaneously.

It's vital that you distinguish quantum mechanical uncertainty, which is a well-defined quantity we calculate from wavefunctions, from experimental uncertainty. The latter arises from limitations inherent in the apparatus we use to perform measurements and has nothing to do with the quantum mechanical uncertainty.

3.11.2 The minimum uncertainty wave packet

The minimum value of the product $\Delta A \, \Delta B$ is

$$\Delta A \, \Delta B = \frac{1}{2} |\langle \psi | \mathrm{i}[\hat{A}, \hat{B}] | \psi \rangle|. \tag{3.60}$$

This occurs when the discriminant in Eq. (3.57) is zero, which implies the value of λ

$$\lambda_0 = -\frac{\langle \mathrm{i}[\hat{A}, \hat{B}] \rangle}{2(\Delta B)^2}. \tag{3.61}$$

For $\lambda = \lambda_0$, the ket $|\phi\rangle$ is zero. By use of Eq. (3.56), the corresponding quantum state $|\psi\rangle$ satisfies

$$[(\hat{A} - \langle A \rangle) + \mathrm{i}\lambda_0(\hat{B} - \langle B \rangle)]|\psi\rangle = 0 \tag{3.62}$$

and is termed *minimum uncertainty state.*

Let us determine the minimum uncertainty states for the pair of observables $A = x$ and $B = p_x$. The use of the operators $\hat{x} = x$ and $\hat{p}_x = -\mathrm{i}\hbar\,\mathrm{d}/\mathrm{d}x$ in the above equations gives

$$\Delta x\,\Delta p_x = \frac{\hbar}{2}, \tag{3.63}$$

$$\lambda_0 = \frac{\hbar}{2(\Delta p_x)^2} = \frac{2(\Delta x)^2}{\hbar}, \tag{3.64}$$

and

$$\left[x - \langle x\rangle + \mathrm{i}\frac{2(\Delta x)^2}{\hbar}\left(-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} - \langle p_x\rangle\right)\right]\psi(x) = 0. \tag{3.65}$$

The last equation is a first-order ordinary differential equation for the minimum uncertainty wavefunction ψ. Integrating by separation of variables yields

$$\psi(x) = C\exp\left(\mathrm{i}\frac{\langle p_x\rangle}{\hbar}x\right)\exp\left[-\frac{(x-\langle x\rangle)^2}{4(\Delta x)^2}\right],$$

where $C \in \mathbb{C}$ is the constant of integration. Imposing the normalization condition

$$\int_{-\infty}^{\infty}|\psi(x)|^2\mathrm{d}x = 1,$$

the minimum uncertainty wavefunction acquires the form

$$\psi(x) = \frac{1}{(\Delta x)^{1/2}(2\pi)^{1/4}}\exp\left(\mathrm{i}\frac{\langle p_x\rangle}{\hbar}x\right)\exp\left[-\frac{(x-\langle x\rangle)^2}{4(\Delta x)^2}\right]. \tag{3.66}$$

Thus, the wavefunction ψ for a particle with minimum position–momentum uncertainty [see Eq. (3.63)] is a Gaussian wave packet centered at $\langle x\rangle$. An example of such function is the ground state energy eigenfunction of the harmonic oscillator (see Problem 3.9).

3.11.3 Energy–time uncertainty principle

In quantum mechanics the time is not an observable, but an independent variable, of which the observables are functions. Hence there is no operator which corresponds to the measurement of time. In spite of the absence of the time operator, an energy–time uncertainty relation

$$\Delta E\,\Delta t \geq \hbar/2 \tag{3.67}$$

can be established. We now proceed to the derivation of this relation.

Consider a quantum system of Hamiltonian $\hat{H}$ in the initial state $|\psi\rangle$. Let us use an observable A, represented by the Hermitian operator $\hat{A}$ that does not depend explicitly on time, to characterize the temporal change in the system. The rate of change of $\langle A\rangle$ is given by Eq. (3.39). On the other hand, the Heisenberg uncertainty principle [see Eq. (3.52)] for the operators $\hat{H}$ and $\hat{A}$ gives

$$\Delta E\,\Delta A \geq \frac{1}{2}|\langle\psi|\mathrm{i}[\hat{H},\hat{A}]|\psi\rangle|. \tag{3.68}$$

Combining Eqs. (3.39) and (3.68) we get

$$\Delta E\,\Delta A \geq \frac{\hbar}{2}\left|\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t}\right|. \tag{3.69}$$

We define the evolution time Δt associated to the observable A by

$$\Delta t = \frac{\Delta A}{|\mathrm{d}\langle A\rangle/\mathrm{d}t|}. \tag{3.70}$$

So, Δt is the time required for the expectation value of A, $\langle A\rangle$, to change by the uncertainty of A, ΔA. Now, the use of Δt into Eq. (3.69) leads to energy–time uncertainty relation (3.67).

The meaning of the energy–time uncertainty relation is clear from its derivation. Namely, let ΔE be the uncertainty in the energy of the system in the initial state. Time evolution of the system is investigated by monitoring the observable A. The shortest time Δt it takes the system to change significantly is given by

$$\Delta E\,\Delta t \sim \hbar/2. \tag{3.71}$$

In the limit case of an initial state $|\psi\rangle$ which is an energy eigenvector, then $\Delta E = 0$ and the above equation gives $\Delta t \to \infty$, which makes sense since the state is stationary.

Let us consider an example. Suppose a quantum system with a Hamiltonian which has no explicit time dependence. We start the system in the initial state

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}|E_1\rangle + \frac{1}{\sqrt{2}}|E_2\rangle,$$

which is a linear combination of the energy eigenstates $|E_1\rangle$ and $|E_2\rangle$, where $E_2 > E_1$. We have

$$\langle E\rangle = \frac{1}{2}E_1 + \frac{1}{2}E_2, \quad \langle E^2\rangle = \frac{1}{2}E_1^2 + \frac{1}{2}E_2^2$$

and

$$\Delta E = \sqrt{\langle E^2\rangle - \langle E\rangle^2} = \frac{E_2 - E_1}{2}.$$

The change in time of the state vector obeys `TDSE` and at time $\Delta t > 0$ the state vector becomes

$$|\psi(\Delta t)\rangle = \frac{1}{\sqrt{2}}\mathrm{e}^{-\mathrm{i}E_1\Delta t/\hbar}|E_1\rangle + \frac{1}{\sqrt{2}}\mathrm{e}^{-\mathrm{i}E_2\Delta t/\hbar}|E_2\rangle.$$

The quantum states $|\psi(0)\rangle$ and $|\psi(\Delta t)\rangle$ are clearly distinguishable if they are orthogonal. The condition $\langle\psi(\Delta t)|\psi(0)\rangle = 0$ leads to

$$\frac{1}{2}\mathrm{e}^{\mathrm{i}E_1\Delta t/\hbar} + \frac{1}{2}\mathrm{e}^{\mathrm{i}E_2\Delta t/\hbar} = 0, \quad \Delta t = \frac{\pi\hbar}{E_2 - E_1}.$$

We have

$$\Delta E\,\Delta t = \pi(\hbar/2) > \hbar/2$$

as expected.

3.12 Questions and problems

3.1 Verify that the energy eigenvectors for the particle in an infinitely deep potential well [see Eq. (2.37)] are orthonormal.

Solution. The energy eigenvectors are already normalized. For $n, n' \in \mathbb{N}^*$ and $n \neq n'$, we have

$$\begin{aligned}\langle u_n|u_{n'}\rangle &= \int_{-\infty}^{\infty} u_n^*(x)\,u_{n'}(x)\,\mathrm{d}x = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}\,\sin\frac{n'\pi x}{a}\,\mathrm{d}x \\ &= \frac{1}{a}\int_0^a \left[\cos\frac{(n'-n)\pi x}{a} - \cos\frac{(n+n')\pi x}{a}\right]\mathrm{d}x \\ &= \int_0^1 [\cos(n'-n)\pi\xi - \cos(n+n')\pi\xi]\,\mathrm{d}\xi = 0.\end{aligned}$$

3.2 Prove the commutator properties [Eqs. (3.15)].

Solution. $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = -\hat{B}\hat{A} + \hat{A}\hat{B} = -(\hat{B}\hat{A} - \hat{A}\hat{B}) = -[\hat{B},\hat{A}]$,

$$\begin{aligned}[\hat{A}, b\hat{B} + c\hat{C}] &= \hat{A}(b\hat{B} + c\hat{C}) - (b\hat{B} + c\hat{C})\hat{A} = b(\hat{A}\hat{B} - \hat{B}\hat{A}) + c(\hat{A}\hat{C} - \hat{C}\hat{A}) \\ &= b[\hat{A},\hat{B}] + c[\hat{A},\hat{C}],\end{aligned}$$

$$[\hat{A},\hat{B}\hat{C}] = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} = (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{C} + \hat{B}(\hat{A}\hat{C} - \hat{C}\hat{A}) = [\hat{A},\hat{B}]\hat{C} + \hat{B}[\hat{A},\hat{C}].$$

3.3 Prove the properties of Hermitian conjugation [Eqs. (3.17)].

Solution. To prove the properties of Hermitian conjugation, let us consider two arbitrary kets $|\psi_1\rangle$ and $|\psi_2\rangle$. Then

$$\langle\psi_1|\hat{A}^{\dagger\dagger}|\psi_2\rangle = \langle\psi_2|\hat{A}^\dagger|\psi_1\rangle^* = ((\langle\psi_1|\hat{A}|\psi_2\rangle^*))^* = \langle\psi_1|\hat{A}|\psi_2\rangle,$$

$$\begin{aligned}\langle\psi_1|(a\hat{A}+b\hat{B})^\dagger|\psi_2\rangle &= \langle\psi_2|(a\hat{A}+b\hat{B})|\psi_1\rangle^* = (a\langle\psi_2|\hat{A}|\psi_1\rangle + b\langle\psi_2|\hat{B}|\psi_1\rangle)^* \\ &= a^*\langle\psi_2|\hat{A}|\psi_1\rangle^* + b^*\langle\psi_2|\hat{B}|\psi_1\rangle^* = a^*\langle\psi_1|\hat{A}^\dagger|\psi_2\rangle + b^*\langle\psi_1|\hat{B}^\dagger|\psi_2\rangle \\ &= \langle\psi_1|a^*\hat{A}^\dagger + b^*\hat{B}^\dagger|\psi_2\rangle\end{aligned}$$

and

$$\langle\psi_1|(\hat{A}\hat{B})^\dagger|\psi_2\rangle = \langle\psi_2|\hat{A}\hat{B}|\psi_1\rangle^* = \langle\hat{A}^\dagger\psi_2|\hat{B}\psi_1\rangle^* = \langle\hat{B}^\dagger\hat{A}^\dagger\psi_2|\psi_1\rangle^* = \langle\psi_1|\hat{B}^\dagger\hat{A}^\dagger|\psi_2\rangle.$$

The asked operatorial relations are obtained due to the arbitrary choice of the kets.

3.4 Prove that if $\hat{A}$ and $\hat{B}$ are Hermitian operators, then $\mathrm{i}[\hat{A},\hat{B}]$ is Hermitian.

Solution.

$$\begin{aligned}(\mathrm{i}[\hat{A},\hat{B}])^\dagger &= -\mathrm{i}(\hat{A}\hat{B}-\hat{B}\hat{A})^\dagger = -\mathrm{i}(\hat{B}^\dagger\hat{A}^\dagger - \hat{A}^\dagger\hat{B}^\dagger) = -\mathrm{i}(\hat{B}\hat{A}-\hat{A}\hat{B}) = \mathrm{i}(\hat{A}\hat{B}-\hat{B}\hat{A}) \\ &= \mathrm{i}[\hat{A},\hat{B}].\end{aligned}$$

3.5 A particle in an infinite square well is described by the initial wavefunction

$$\psi(x) = \begin{cases} Nx(a-x), & 0 \le x \le a \\ 0, & \text{otherwise,}\end{cases}$$

where N is a complex constant.

(a) Normalize the wavefunction.

(b) Determine the probabilities of the energy eigenstates.

Solution. (a)

$$\begin{aligned}1 &= \int_{-\infty}^{\infty}|\psi(x)|^2\mathrm{d}x = |N|^2\int_0^a x^2(a-x)^2\mathrm{d}x = |N|^2\int_0^a (a^2x^2 - 2ax^3 + x^4)\,\mathrm{d}x \\ &= |N|^2\left(\frac{1}{3}a^5 - \frac{1}{2}a^5 + \frac{1}{5}a^5\right) = \frac{1}{30}a^5|N|^2 \quad\Rightarrow\quad |N| = \sqrt{\frac{30}{a^5}}.\end{aligned}$$

As the value of $\arg N$ has no physical implications, we choose $\arg N = 0$, so $N = |N| = \sqrt{30/a^5}$.

(b) We write ψ as a linear combination of the energy eigenfunctions given by Eq. (2.37):

$$\psi(x) = \sum_{n=1}^{\infty} c_n u_n(x).$$

The coefficient c_n is

$$c_n = \int_{-\infty}^{\infty} u_n^*(x)\,\psi(x)\,\mathrm{d}x = \sqrt{\frac{2}{a}}\sqrt{\frac{30}{a^5}}\int_0^a x(a-x)\sin\frac{n\pi x}{a}\,\mathrm{d}x = \begin{cases} \dfrac{8\sqrt{15}}{\pi^3 n^3}, & n \text{ odd} \\ 0, & n \text{ even.} \end{cases}$$

The probability p_n of the energy eigenstate u_n is

$$p_n = |c_n|^2 = \begin{cases} \dfrac{960}{\pi^6 n^6}, & n \text{ odd} \\ 0, & n \text{ even.} \end{cases}$$

The probability of the state u_1 is $p_1 = 960/\pi^6 \approx 0.9986$ very close to one indicating that the first state dominates.

3.6 Suppose A and B are two observables represented by Hermitian operators with non-degenerate eigenvalues. There are performed three successive measurements in the order A, B, A. Is the outcome of the second measurement of A the same as in the first measurement?

Solution. First measurement of A, with the result a, throws the state of the system into the eigenstate $|a\rangle$ of the operator $\hat{A}$. The prediction on the result of the second measurement is dependent on whether A are B compatible or not:

- If A and B are compatible observables, the state ket $|a\rangle$ is also eigenket of $\hat{B}$. The measurement of B do not change the state ket and the subsequent measurement of A will give again the outcome a.
- If A and B are incompatible observables, the state ket $|a\rangle$ is not eigenket of $\hat{B}$. The measurement of B with the result b changes the state ket $|a\rangle$ into $|b\rangle$ which is generally a superposition of operator $\hat{A}$ eigenkets $|a_1\rangle, |a_2\rangle, \ldots$. The subsequent measurement of A will give as outcome one of the eigenvalues $a_1, a_2, \ldots$. Thus, the outcome of the second measurement of A is not necessarily the same as in the first measurement.

3.7 The Hamiltonian operator of a system has the basis $\{|u_1\rangle, |u_2\rangle, |u_3\rangle\}$ such that

$$\hat{H}|u_1\rangle = E|u_1\rangle,\ \hat{H}|u_2\rangle = 2E|u_2\rangle,\ \text{and } \hat{H}|u_3\rangle = 2E|u_3\rangle.$$

Suppose the system is prepared in the state

$$|\psi\rangle = \sqrt{\frac{1}{2}}\,|u_1\rangle + \sqrt{\frac{1}{3}}\,|u_2\rangle + \sqrt{\frac{1}{6}}\,|u_3\rangle.$$

(a) What values of the energy can be found and with what probabilities? Determine the expectation value of the energy.

(b) Suppose the energy is measured and found to be $2E$. What is the state of the system after measurement?

Solution. (a) The state vector $|\psi\rangle$ is normalized:

$$\langle\psi|\psi\rangle = \frac{1}{2} + \frac{1}{3} + \frac{1}{6} = 1.$$

The possible results of energy measurement are:

- E; the probability of this is $(\sqrt{1/2}\,)^2 = 1/2$.
- $2E$; the probability of this is $(\sqrt{1/3}\,)^2 + (\sqrt{1/6}\,)^2 = 1/2$.

The expectation value of the energy is

$$(1/2)E + (1/2)2E = (3/2)E.$$

(b) Assuming the result $2E$ of the energy measurement, after the measurement the state of the system is

$$|\psi'_{\text{after}}\rangle = \sqrt{\frac{1}{3}}\,|u_2\rangle + \sqrt{\frac{1}{6}}\,|u_3\rangle$$

whose square norm is

$$\|\psi'_{\text{after}}\|^2 = \langle\psi'_{\text{after}}|\psi'_{\text{after}}\rangle = \frac{1}{3} + \frac{1}{6} = \frac{1}{2}.$$

The normalized state vector is

$$|\psi_{\text{after}}\rangle = \frac{1}{\|\psi'_{\text{after}}\|}|\psi'_{\text{after}}\rangle = \sqrt{\frac{2}{3}}\,|u_2\rangle + \sqrt{\frac{1}{3}}\,|u_3\rangle.$$

3.8 Calculate the expectation values of x, x^2, p_x, and p_x^2 for the particle in the nth stationary state of the infinite square well (see Sect. 2.7) and verify the validity of the uncertainty relation $\Delta x\,\Delta p_x \geq \hbar/2$ in these states.

Solution. The energy eigenfunctions are given by Eq. (2.37). In the nth stationary state we have

$$\langle x\rangle_n = \langle u_n|\hat{x}|u_n\rangle = \int_{-\infty}^{\infty} u_n^*(x)\,x\,u_n(x)\,\mathrm{d}x = \frac{2}{a}\int_0^a x\sin^2\frac{n\pi x}{a}\,\mathrm{d}x.$$

The change of variable $\xi = (n\pi/a)x$ leads to

$$\langle x\rangle_n = \frac{2a}{n^2\pi^2}\int_0^{n\pi}\xi\sin^2\xi\,\mathrm{d}\xi.$$

The value of the integral is $n^2\pi^2/4$, so $\langle x\rangle_n = a/2$ for all n values.

$$\langle x^2\rangle_n = \langle u_n|\hat{x}^2|u_n\rangle = \int_{-\infty}^{\infty} u_n^*(x)\, x^2 u_n(x)\,\mathrm{d}x = \frac{2}{a}\int_0^a x^2 \sin^2\frac{n\pi x}{a}\,\mathrm{d}x$$
$$= \frac{2a^2}{n^3\pi^3}\int_0^{n\pi} \xi^2 \sin^2\xi\,\mathrm{d}\xi.$$

The value of the integral is $(1/6)n^3\pi^3 - (1/4)n\pi$, so

$$\langle x^2\rangle_n = \left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)a^2.$$

The statistics of the momentum is carried out similarly:

$$\langle p_x\rangle_n = \langle u_n|\hat{p}_x|u_n\rangle = \int_{-\infty}^{\infty} u_n^*(x)(-\mathrm{i}\hbar)\frac{\mathrm{d}}{\mathrm{d}x}u_n(x)\,\mathrm{d}x$$
$$= -\mathrm{i}\hbar\,\frac{2}{a}\,\frac{n\pi}{a}\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}\,\mathrm{d}x.$$

The value of the integral is 0, so $\langle p_x\rangle_n = 0$.

$$\langle p_x^2\rangle_n = \langle u_n|\hat{p}_x^2|u_n\rangle = \int_{-\infty}^{\infty} u_n^*(x)(-\mathrm{i}\hbar)^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}u_n(x)\,\mathrm{d}x$$
$$= -\hbar^2\left(-\frac{n^2\pi^2}{a^2}\right)\|u_n\|^2 = \frac{n^2\pi^2\hbar^2}{a^2}.$$

The standard deviation of position and momentum are

$$(\Delta x)_n = \sqrt{\langle x^2\rangle_n - \langle x\rangle_n^2} = \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}\,a$$

and

$$(\Delta p_x)_n = \sqrt{\langle p_x^2\rangle_n - \langle p_x\rangle_n^2} = \frac{n\pi\hbar}{a},$$

respectively. The product of these uncertainties is

$$(\Delta x)_n(\Delta p_x)_n = \sqrt{\frac{n^2\pi^2}{3} - 2}\,\frac{\hbar}{2} \geq \sqrt{\frac{\pi^2}{3} - 2}\,\frac{\hbar}{2} > \sqrt{\frac{3^2}{3} - 2}\,\frac{\hbar}{2} = \frac{\hbar}{2}.$$

3.9 Calculate the expectation values of x, x^2, p_x, and p_x^2 for the harmonic oscillator in the ground state (see Sect. 2.10) and verify the validity of the uncertainty relation $\Delta x\,\Delta p_x \geq \hbar/2$ in this state.

Solution. The ground state energy eigenfunction is

$$u_0(x) = \frac{\alpha^{1/2}}{\pi^{1/4}} \exp(-\alpha^2 x^2/2), \quad \text{where} \quad \alpha = (m\omega/\hbar)^{1/2}.$$

We have

$$\langle x \rangle = \langle u_0|\hat{x}|u_0\rangle = \int_{-\infty}^{\infty} u_0^*(x)\, x\, u_0(x)\, \mathrm{d}x = \frac{\alpha}{\pi^{1/2}} \int_{-\infty}^{\infty} x \exp(-\alpha^2 x^2)\, \mathrm{d}x.$$

The integrand is odd and so the integral is zero. Hence $\langle x \rangle = 0$.

$$\langle x^2 \rangle = \langle u_0|\hat{x}^2|u_0\rangle = \int_{-\infty}^{\infty} u_0^*(x)\, x^2 u_0(x)\, \mathrm{d}x = \frac{\alpha}{\pi^{1/2}} \int_{-\infty}^{\infty} x^2 \exp(-\alpha^2 x^2)\, \mathrm{d}x.$$

The integrand now is even, so the integral is twice the integral from 0 to ∞. Then, we perform the change of variable $\alpha x = t^{1/2}$:

$$\begin{aligned} \int_{-\infty}^{\infty} x^2 \exp(-\alpha^2 x^2)\, \mathrm{d}x &= 2\int_{0}^{\infty} x^2 \exp(-\alpha^2 x^2)\, \mathrm{d}x = \frac{1}{\alpha^3} \int_{0}^{\infty} t^{1/2} \exp(-t)\, \mathrm{d}t \\ &= \frac{1}{\alpha^3}\Gamma\left(\frac{3}{2}\right) = \frac{1}{\alpha^3}\frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{\pi^{1/2}}{2\alpha^3}. \end{aligned}$$

$$\langle x^2 \rangle = \frac{\alpha}{\pi^{1/2}} \frac{\pi^{1/2}}{2\alpha^3} = \frac{1}{2\alpha^2} = \frac{\hbar}{2m\omega}.$$

The statistics of the momentum is carried out similarly:

$$\begin{aligned} \langle p_x \rangle = \langle u_0|\hat{p}_x|u_0\rangle &= \int_{-\infty}^{\infty} u_0^*(x)(-\mathrm{i}\hbar)\frac{\mathrm{d}}{\mathrm{d}x} u_0(x)\, \mathrm{d}x \\ &= -\mathrm{i}\hbar \frac{\alpha}{\pi^{1/2}}(-\alpha^2)\int_{-\infty}^{\infty} x \exp(-\alpha^2 x^2)\, \mathrm{d}x = 0. \end{aligned}$$

$$\begin{aligned} \langle p_x^2 \rangle = \langle u_0|\hat{p}_x^2|u_0\rangle &= \int_{-\infty}^{\infty} u_0^*(x)(-\mathrm{i}\hbar)^2 \frac{\mathrm{d}^2}{\mathrm{d}x^2} u_0(x)\, \mathrm{d}x \\ &= \frac{\alpha^3\hbar^2}{\pi^{1/2}}\int_{-\infty}^{\infty} (1-\alpha^2 x^2)\exp(-\alpha^2 x^2)\, \mathrm{d}x = \frac{\alpha^3\hbar^2}{\pi^{1/2}}\left(\frac{\pi^{1/2}}{\alpha} - \alpha^2\frac{\pi^{1/2}}{2\alpha^3}\right) = \frac{1}{2}\alpha^2\hbar^2 \\ &= \frac{1}{2} m\hbar\omega. \end{aligned}$$

The standard deviation of position and momentum are

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \sqrt{\frac{\hbar}{2m\omega}} \quad \text{and} \quad \Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2} = \sqrt{\frac{1}{2}m\hbar\omega}\,,$$

respectively. The product of these uncertainties is

$$\Delta x\, \Delta p_x = \hbar/2.$$

The ground state of the harmonic oscillator is an example of minimum uncertainty state (see Sect. 3.11.2).

3.10 Use position-momentum uncertainty relation to estimate the ground state energy of the quantum oscillator of frequency ω.

Solution. The energy of the quantum oscillator of mass m and frequency ω in a stationary state is

$$\begin{aligned} E &= \langle T+V\rangle = \langle T\rangle + \langle V\rangle = \frac{1}{2m}\langle p^2\rangle + \frac{1}{2}m\omega^2\langle x^2\rangle \\ &= \frac{1}{2m}\left[(\Delta p)^2 + \langle p\rangle^2\right] + \frac{1}{2}m\omega^2\left[(\Delta x)^2 + \langle x\rangle^2\right] = \frac{1}{2m}(\Delta p)^2 + \frac{1}{2}m\omega^2(\Delta x)^2. \end{aligned}$$

Now we use the uncertainty relation $\Delta x\,\Delta p \geq \hbar/2$:

$$E \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m\omega^2(\Delta x)^2.$$

Right-hand side of this inequality is interpreted as a function of Δx. The kinetic energy term is a decreasing function of Δx, while the potential energy term is an increasing function of Δx. Let us notice that the product of the two terms is constant. It follows that the sum attains a minimum and this happens when the two terms are equal. The use of the inequality of arithmetic and geometric means leads to

$$E \geq 2\sqrt{\frac{\hbar^2}{8m(\Delta x)^2}\frac{1}{2}m\omega^2(\Delta x)^2} = \frac{\hbar\omega}{2}.$$

The estimated ground state energy $\hbar\omega/2$ turns out to be the exact value.

Chapter 4

Angular momentum

Max Planck provided us with the electron's angular momentum constant, commonly denoted h.

In quantum systems the angular momentum is important in studies of atomic, molecular, and nuclear structure and spectra.

4.1 Introduction

Consider a particle of mass m, moving with the momentum $\boldsymbol{p}$ relative to an inertial frame of reference. We define the angular momentum $\boldsymbol{L}$ of the particle with respect to the origin O (see Fig. 4.1) as

$$\boldsymbol{L} = r \times \boldsymbol{p}\,. \tag{4.1}$$

In Cartesian coordinates $\boldsymbol{L}$ expresses as

$$\boldsymbol{L} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}. \tag{4.2}$$

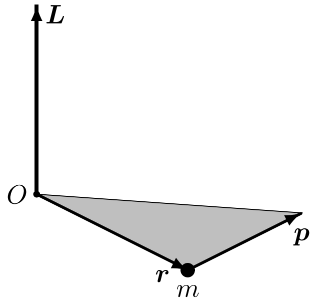


Fig. 4.1 The definition of the angular momentum of a particle. $\boldsymbol{L}$ is perpendicular to the plane determined by $\boldsymbol{r}$ and $\boldsymbol{p}$.

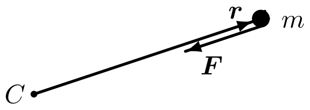


Fig. 4.2 The force $\boldsymbol{F}$ has no torque around the force centre C.

The Cartesian components of the vector $\boldsymbol{L}$ are

$$L_x = yp_z - zp_y\,, \quad L_y = zp_x - xp_z\,, \quad \text{and} \quad L_z = xp_y - yp_x\,. \tag{4.3}$$

The square of the magnitude of the vector $\boldsymbol{L}$ is given in terms of these components by

$$L^2 = \boldsymbol{L} \cdot \boldsymbol{L} = L_x^2 + L_y^2 + L_z^2\,. \tag{4.4}$$

The time evolution of the angular momentum is governed by the equation

$$\frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t} = \boldsymbol{M}\,, \tag{4.5}$$

where M is the moment of force, or torque, acting on the particle.

In many cases of interest $\boldsymbol{M} = 0$, the most important example being that of a particle moving under the action of a central force field (see Fig. 4.2); an electron motion in the Coulumb field of a nucleus is one example. It follows that the angular momentum is a constant of the motion.

4.2 Angular momentum operators

The angular momentum operator is obtained by replacing $\boldsymbol{r}$ and $\boldsymbol{p}$ in the classical definition, Eq. (4.2), by their corresponding quantum operators:

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -\mathrm{i}\hbar \boldsymbol{r} \times \nabla\,. \tag{4.6}$$

Considering a Cartesian coordinate system, we have

$$\hat{\boldsymbol{L}} = \hat{L}_x \boldsymbol{i} + \hat{L}_y \boldsymbol{j} + \hat{L}_z \boldsymbol{k}\,, \tag{4.7}$$

where

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -\mathrm{i}\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{4.8a}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -\mathrm{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \tag{4.8b}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{4.8c}$$

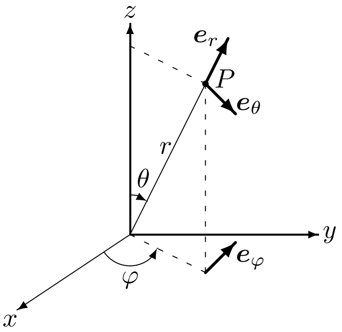


Fig. 4.3 Definition of the spherical polar coordinates r, θ, and φ of an arbitrary point P in space. $\boldsymbol{e}_r$, $\boldsymbol{e}_\theta$, and $\boldsymbol{e}_\varphi$ are the basic unit vectors of the spherical polar system.

Since $[y, \hat{p}_z] = [z, \hat{p}_y] = 0$, Eq. (4.8a) is unambiguous with respect to the order of operators in multiplications; similar remarks apply to $\hat{L}_y$ and $\hat{L}_z$.

Note in addition that

$$\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \,. \tag{4.9}$$

To represent a physical variable, the above operators must be Hermitian. For the operator L_x we have

$$\begin{aligned}\hat{L}_x^\dagger &= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)^\dagger = (\hat{y}\hat{p}_z)^\dagger - (\hat{z}\hat{p}_y)^\dagger = \hat{p}_z^\dagger \hat{y}^\dagger - \hat{p}_y^\dagger \hat{z}^\dagger = \hat{p}_z\hat{y} - \hat{p}_y\hat{z} = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ &= \hat{L}_x \,.\end{aligned}$$

Similarly, $\hat{L}_y$ and $\hat{L}_z$ are Hermitian.

When considering the motion of a particle in a central force field, it is advantageous to use a spherical polar coordinate system (see Fig. 4.3). The spherical polar coordinates r, θ, and φ of a point are related to the Cartesian coordinates of the same point by

$$x = r\sin\theta\cos\varphi \,, \tag{4.10a}$$
$$y = r\sin\theta\sin\varphi \,, \tag{4.10b}$$
$$z = r\cos\theta \,. \tag{4.10c}$$

We can apply these equations to relate the polar spherical basis to its Cartesian counterpart:

$$\boldsymbol{e}_r = \boldsymbol{i}\sin\theta\cos\varphi + \boldsymbol{j}\sin\theta\sin\varphi + \boldsymbol{k}\cos\theta \,, \tag{4.11a}$$

$$\begin{aligned}\boldsymbol{e}_\theta &= \boldsymbol{i}\sin(\theta + \pi/2)\cos\varphi + \boldsymbol{j}\sin(\theta + \pi/2)\sin\varphi + \boldsymbol{k}\cos(\theta + \pi/2) \\ &= \boldsymbol{i}\cos\theta\cos\varphi + \boldsymbol{j}\cos\theta\sin\varphi - \boldsymbol{k}\sin\theta \,,\end{aligned} \tag{4.11b}$$

$$\begin{aligned}\boldsymbol{e}_\varphi &= \boldsymbol{i}\sin(\pi/2)\cos(\varphi + \pi/2) + \boldsymbol{j}\sin(\pi/2)\sin(\varphi + \pi/2) + \boldsymbol{k}\cos(\pi/2) \\ &= -\boldsymbol{i}\sin\varphi + \boldsymbol{j}\cos\varphi \,.\end{aligned} \tag{4.11c}$$

The inverse relations are

$$\begin{aligned}
\boldsymbol{i} &= (\boldsymbol{i}\cdot\boldsymbol{e}_r)\boldsymbol{e}_r + (\boldsymbol{i}\cdot\boldsymbol{e}_\theta)\boldsymbol{e}_\theta + (\boldsymbol{i}\cdot\boldsymbol{e}_\varphi)\boldsymbol{e}_\varphi \\
&= \boldsymbol{e}_r \sin\theta\cos\varphi + \boldsymbol{e}_\theta \cos\theta\cos\varphi - \boldsymbol{e}_\varphi \sin\varphi\,, \qquad (4.12a)\\
\boldsymbol{j} &= (\boldsymbol{j}\cdot\boldsymbol{e}_r)\boldsymbol{e}_r + (\boldsymbol{j}\cdot\boldsymbol{e}_\theta)\boldsymbol{e}_\theta + (\boldsymbol{j}\cdot\boldsymbol{e}_\varphi)\boldsymbol{e}_\varphi \\
&= \boldsymbol{e}_r \sin\theta\sin\varphi + \boldsymbol{e}_\theta \cos\theta\sin\varphi + \boldsymbol{e}_\varphi \cos\varphi\,, \qquad (4.12b)\\
\boldsymbol{k} &= (\boldsymbol{k}\cdot\boldsymbol{e}_r)\boldsymbol{e}_r + (\boldsymbol{k}\cdot\boldsymbol{e}_\theta)\boldsymbol{e}_\theta + (\boldsymbol{k}\cdot\boldsymbol{e}_\varphi)\boldsymbol{e}_\varphi \\
&= \boldsymbol{e}_r \cos\theta - \boldsymbol{e}_\theta \sin\theta\,. \qquad (4.12c)
\end{aligned}$$

In terms of the spherical polar coordinates the angular momentum operators become[1] (see Appendix A)

$$\hat{L}_x = \mathrm{i}\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\,\frac{\partial}{\partial\varphi}\right), \qquad (4.13a)$$

$$\hat{L}_y = -\mathrm{i}\hbar\left(\cos\varphi\,\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\,\frac{\partial}{\partial\varphi}\right), \qquad (4.13b)$$

$$\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}\,, \qquad (4.13c)$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]. \qquad (4.14)$$

Notice that all of angular momentum operators can be represented as differential operators involving the angular spherical coordinates (θ and φ), but not involving the radial coordinate (r). Furthermore, the comparison of $\hat{L}^2$ expression in polar spherical coordinates and the Laplacian in the same coordinate system,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\,, \qquad (4.15)$$

it follows that $\hat{L}^2$ has the same angular dependence as ∇^2. The two operators are related by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\,\frac{\hat{L}^2}{\hbar^2}\,. \qquad (4.16)$$

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[1] Appendix not asked for the exam.

4.3 Angular momentum commutators

We now investigate whether the angular momentum operators represent quantities that are compatible. The commutator of $\hat{L}_x$ and $\hat{L}_y$ is

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z].$$

Here, the second commutator vanishes because all the implied operators commute. Similarly, the third commutator is zero. For the remaining commutators we have

$$[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] = \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] = -\mathrm{i}\hbar\hat{y}\hat{p}_x$$

and

$$[\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z] = \mathrm{i}\hbar\hat{x}\hat{p}_y\,.$$

Collecting all these intermediate results, we find

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = \mathrm{i}\hbar\hat{L}_z\,.$$

The commutators $[\hat{L}_y, \hat{L}_z]$ $[\hat{L}_z, \hat{L}_x]$ are be calculated similarly and one gets

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z\,, \tag{4.17a}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x\,, \tag{4.17b}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y\,. \tag{4.17c}$$

We now calculate the commutator $[\hat{L}^2, \hat{L}_x]$:

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]\,.$$

Taking separately the commutators,

$$[\hat{L}_y^2, \hat{L}_x] = \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x]\hat{L}_y = \hat{L}_y(-\mathrm{i}\hbar\hat{L}_z) - \mathrm{i}\hbar\hat{L}_z\hat{L}_y = -\mathrm{i}\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$$

and

$$[\hat{L}_z^2, \hat{L}_x] = \hat{L}_z[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z = \hat{L}_z\mathrm{i}\hbar\hat{L}_y + \mathrm{i}\hbar\hat{L}_y\hat{L}_z = \mathrm{i}\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)\,.$$

Combining these results we yield $[\hat{L}^2, \hat{L}_x] = 0$. Likewise, it can be demonstrated that $\hat{L}^2$ commutes with the other two Cartesian components of the angular momentum operator. Thus,

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0\,. \tag{4.18}$$

The commutation relations (4.17) and (4.18) imply that we can only simultaneously measure the magnitude of the angular momentum together with, at most, one of its Cartesian components. The simpleness of Eq. (4.13c) makes it convenient the choice of $\hat{L}_z$. In an experiment we usually have one or more privileged directions (e.g., the direction of an external electric or magnetic field) which gives a natural z axis. If not, this direction is purely arbitrary.

4.4 Eigenvalues and eigenfunctions

We shall seek simultaneous eigenfunctions of the angular momentum operators $\hat{L}_z$ and $\hat{L}^2$. Since both of these operators can be represented as purely angular differential operators, the problem will be solved in a polar spherical coordinate system. Thus, we can write

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar\, Y_l^m(\theta,\varphi)\,, \tag{4.19a}$$

$$\hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)\lambda\hbar^2\, Y_l^m(\theta,\varphi)\,. \tag{4.19b}$$

Here, $Y_l^m(\theta,\varphi)$ are the eigenstates, whereas $m\hbar$ and $l(l+1)\hbar^2$ are the eigenvalues of $\hat{L}_z$ and $\hat{L}^2$, respectively.

We expect that the eigenfunctions Y_l^m are mutually orthogonal. The orthonormalization condition is

$$\int_0^{\pi}\int_0^{2\pi} Y_l^{m*}(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi = \delta_{ll'}\delta_{mm'}\,. \tag{4.20}$$

In the above, $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$ is the element of solid angle lying in the direction (θ,φ).

4.4.1 The eigenvalue problem of $\hat{L}_z$

The eigenvalue equation for $\hat{L}_z$ is

$$-\mathrm{i}\hbar\frac{\partial}{\partial\varphi}Y_l^m(\theta,\varphi) = m\hbar\, Y_l^m(\theta,\varphi)\,. \tag{4.21}$$

We look for solutions $Y_l^m(\theta,\varphi)$ by separation of variables method:

$$Y_l^m(\theta,\varphi) = \Theta_l^m(\theta)\,\Phi_m(\varphi)\,, \tag{4.22}$$

where the φ-dependent function involves only the parameter m and not the parameter l. Introducing Eq. (4.22) into Eq. (4.21), we get

$$\frac{\mathrm{d}}{\mathrm{d}\varphi}\Phi_m(\varphi) = \mathrm{i}m\Phi_m(\varphi)$$

whose solution is

$$\Phi_m(\varphi) = C_m \exp(\mathrm{i}m\varphi)\,, \tag{4.23}$$

where C_m is a complex-valued constant.

An acceptable eigenfunction must be single-valued and continuous. Accordingly, we require that

$$\Phi_m(\varphi + 2\pi) = \Phi_m(\varphi) \quad \text{for all } \varphi\,,$$

so that

$$\exp(\mathrm{i}2m\pi) = 1\,.$$

This equation implies that m is an integer, positive or negative. Thus, the eigenvalues of $\hat{L}_z$ are quantized and take the values $m\hbar$, where m is an integer; m is called *magnetic cuantum number.*

Finally, we verify that $\hat{L}_z$ eigenfunctions are orthogonal and we normalize them. From Eq. (4.20), the orthonormalization condition for the $\hat{L}_z$ eigenfunctions is

$$\int_0^{2\pi} \Phi_m^*(\varphi)\,\Phi_{m'}(\varphi)\,\mathrm{d}\varphi = \delta_{mm'}\,. \tag{4.24}$$

By use of Eq. (4.23), we get

$$\int_0^{2\pi} \Phi_m^*(\varphi)\,\Phi_{m'}(\varphi)\,\mathrm{d}\varphi = C_m^* C_{m'} \int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m'-m)\varphi}\mathrm{d}\varphi = \begin{cases} 0\,, & m \neq m' \\ 2\pi|C_m|^2\,, & m = m'\,. \end{cases}$$

It can be seen that $\hat{L}_z$ eigenfunctions are orthogonal; the normalization condition gives $C_m = 1/\sqrt{2\pi}$. Thus, the normalized $\hat{L}_z$ eigenfunctions are

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}m\varphi}\,. \tag{4.25}$$

4.4.2 The eigenvalue problem of $\hat{L}^2$

We solve Eq. (4.19b), where $\hat{L}^2$ is supplied by Eq. (4.14) and the eigenfunctions are sought of form given by Eq. (4.22). Combining these equations, the function Θ_l^m satisfies the second-order differential equation

$$\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\,\frac{\mathrm{d}}{\mathrm{d}\theta}\right) - \frac{m^2}{\sin^2\theta} + l(l+1)\right]\Theta_l^m(\theta) = 0\,. \tag{4.26}$$

From Eqs. (4.20) and (4.24), the normalization condition of the Θ_l^m functions is

$$\int_0^{\pi} \Theta_l^{m*}(\theta,\varphi)\,\Theta_{l'}^m(\theta,\varphi)\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi = \delta_{ll'}\,. \tag{4.27}$$

Equation (4.27) is simplified by the change of variable

$$u = \cos\theta\,. \tag{4.28}$$

The resulting equation for

$$\Theta_l^m(\theta) = P_l^m(\cos\theta) = P_l^m(u) \tag{4.29}$$

is

$$\frac{\mathrm{d}}{\mathrm{d}u}\left[(1-u^2)\,\frac{\mathrm{d}P_l^m(u)}{\mathrm{d}u}\right] + \left[l(l+1) - \frac{m^2}{1-u^2}\right] P_l^m(u) = 0\,. \tag{4.30}$$

This equation is known as *associated Legendre equation.* The equation exhibits singularities at the points $u = 1$ ($\theta = 0$) and $u = -1$ ($\theta = \pi$). The study of the solution behaviour near these points, gives that acceptable solutions are found only for

$$l = \text{nonnegative integer} \quad \text{and} \quad |m| \leq l\,. \tag{4.31}$$

The number l is called *orbital quantum number.*

The normalized function Θ_l^m is given by

$$\Theta_l^m(\theta) = \frac{(-1)^{l+m}}{2^l l!}\sqrt{\frac{2l+1}{2}\,\frac{(l-m)!}{(l+m)!}}\,\sin^m\theta\,\frac{\mathrm{d}^{l+m}}{\mathrm{d}(\cos\theta)^{l+m}}\sin^{2l}\theta\,. \tag{4.32}$$

4.4.3 $\hat{L}_z$ and $\hat{L}^2$ common eigenfunctions

The expression for Y_l^m is obtained by substituting Eqs. (4.25) and (4.32) into Eq. (4.22):

$$Y_l^m(\theta,\varphi) = \frac{(-1)^{l+m}}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\,\mathrm{e}^{\mathrm{i}m\varphi}\sin^m\theta\,\frac{\mathrm{d}^{l+m}}{\mathrm{d}(\cos\theta)^{l+m}}\sin^{2l}\theta \tag{4.33}$$

These functions are known as *spherical harmonics.* The spherical harmonics for $l = 0$, 1, and 2 are listed in Table 4.1.

The spherical harmonics form a complete set. In other words, any continuous and uniforn function $f(\theta,\varphi)$ can be represented as a superposition of spherical harmonics:

$$f(\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} c_{lm} Y_l^m(\theta,\varphi)\,. \tag{4.34}$$

Table 4.1 Normalized spherical harmonics for $l = 0, 1, 2$.

$$
\begin{aligned}
Y_0^0(\theta,\varphi) &= \left(\frac{1}{4\pi}\right)^{1/2} \\
Y_1^0(\theta,\varphi) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\
Y_1^{\pm1}(\theta,\varphi) &= \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\varphi} \\
Y_2^0(\theta,\varphi) &= \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\
Y_2^{\pm1}(\theta,\varphi) &= \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, \mathrm{e}^{\pm \mathrm{i}\varphi} \\
Y_2^{\pm2}(\theta,\varphi) &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, \mathrm{e}^{\pm 2\mathrm{i}\varphi}
\end{aligned}
$$

4.5 Problems

4.1 The wavefunction of a system has the form

$$\psi(r,\theta,\varphi) = f(r,\theta)\cos^2\varphi\,.$$

Determine the possible outcomes of a measurement of the z component of the orbital angular momentum, their probabilities and the average value.

Solution.

$$
\begin{aligned}
\psi(r,\theta,\varphi) = f(r,\theta)\cos^2\varphi = \frac{1}{2}\,(1{+}\cos 2\varphi) f(r,\theta) &= \frac{1}{2}\left(1 + \frac{1}{2}\,\mathrm{e}^{\mathrm{i}2\varphi} + \frac{1}{2}\,\mathrm{e}^{-\mathrm{i}2\varphi}\right) f(r,\theta) \\
&= \frac{1}{4}\left(\mathrm{e}^{-\mathrm{i}2\varphi} + 2\mathrm{e}^{\mathrm{i}0\varphi} + \mathrm{e}^{\mathrm{i}2\varphi}\right) f(r,\theta)\,.
\end{aligned}
$$

The possible values of the azimuthal cuantum number are $m = -2$, 0, and 2. Their probabilities are

$$
\begin{aligned}
p_{-2} &= \frac{1^2}{1^2+2^2+1^2} = \frac{1}{6}\,, \\
p_0 &= \frac{2^2}{1^2+2^2+1^2} = \frac{4}{6} = \frac{2}{3}\,, \\
p_2 &= \frac{1^2}{1^2+2^2+1^2} = \frac{1}{6}\,.
\end{aligned}
$$

The average value of L_z in the given state is

$$\langle L_z \rangle = \frac{1}{6}\,(-2)\hbar + \frac{2}{3}\,0\hbar + \frac{1}{6}\,2\hbar = 0\,.$$

4.2 The wavefunction of a particle subjected to a spherically symmetrical potential $V(r)$ is given by

$$\psi(\boldsymbol{r}) = (x + y + 3z) f(r)\,.$$

(a) Prove that this wavefunction is an eigenfunction of $\hat{L}^2$.

(b) Determine the probabilities of the particle to be found in various m states.

Solution. (a) We first express the wavefunction in terms of spherical coordinates:

$$\psi(\boldsymbol{r}) = (\sin\theta\cos\varphi + \sin\theta\sin\varphi + 3\cos\theta)\, r f(r) = [\sin\theta\,(\cos\varphi + \sin\varphi) + 3\cos\theta]\, r f(r)\,.$$

The calculus of $\hat{L}^2\psi(\boldsymbol{r})$ have to be performed. By making use of Eq. (4.14) we have

$$\sin\theta\,\frac{\partial}{\partial\theta}\,\psi(\boldsymbol{r}) = [\sin\theta\cos\theta\,(\cos\varphi + \sin\varphi) - 3\sin^2\theta]\, r f(r)\,,$$

$$\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\psi(\boldsymbol{r}) = \frac{1}{\sin\theta}\,[(\cos^2\theta - \sin^2\theta)(\cos\varphi + \sin\varphi) - 6\sin\theta\cos\theta]\, r f(r)\,,$$

$$\frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\,\psi(\boldsymbol{r}) = \frac{1}{\sin\theta}\,(-\cos\varphi - \sin\varphi)\, r f(r)\,,$$

$$\begin{aligned}
&\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]\psi(\boldsymbol{r}) \\
&\qquad = \frac{1}{\sin\theta}[(\cos^2\theta - \sin^2\theta - 1)(\cos\varphi + \sin\varphi) - 6\sin\theta\cos\theta]\, r f(r) \\
&\qquad\qquad = [-2\sin\theta\,(\cos\varphi + \sin\varphi) - 6\cos\theta]\, r f(r) = -2\psi(\boldsymbol{r})\,,
\end{aligned}$$

and finally

$$\hat{L}^2\psi(\boldsymbol{r}) = 2\hbar^2\psi(\boldsymbol{r}) = 1(1+1)\hbar^2\psi(\boldsymbol{r})$$

indicating that $\psi(\boldsymbol{r})$ is an eigenfunction of $\hat{L}^2$ with eigenvalue $l = 1$.

(b) As $l = 1$, the possible values of m are -1, 0, and 1; we express the angular part of $\psi(\boldsymbol{r})$ as a linear combination of $\hat{L}_z$ eigenfunctions, here $Y_1^{-1}(\theta,\varphi)$, $Y_1^0(\theta,\varphi)$, and $Y_1^1(\theta,\varphi)$ (see Table 4.1):

$$\begin{aligned}
\psi(\boldsymbol{r}) &= [\sin\theta\,(\cos\varphi+\sin\varphi)+3\cos\theta]\,rf(r)\\
&= \left[\sin\theta\left(\frac{\mathrm{e}^{\mathrm{i}\varphi}+\mathrm{e}^{-\mathrm{i}\varphi}}{2}+\frac{\mathrm{e}^{\mathrm{i}\varphi}-\mathrm{e}^{-\mathrm{i}\varphi}}{2\mathrm{i}}\right)+3\cos\theta\right]rf(r)\\
&= \left[\sin\theta\left(\frac{1+\mathrm{i}}{2}\,\mathrm{e}^{-\mathrm{i}\varphi}+\frac{1-\mathrm{i}}{2}\,\mathrm{e}^{\mathrm{i}\varphi}\right)+3\cos\theta\right]rf(r)\\
&= \left[\left(\frac{2\pi}{3}\right)^{1/2}(1+\mathrm{i})Y_1^{-1}(\theta,\varphi)+(12\pi)^{1/2}Y_1^0(\theta,\varphi)+\left(\frac{2\pi}{3}\right)^{1/2}(-1+\mathrm{i})Y_1^1(\theta,\varphi)\right]rf(r)\\
&= \left(\frac{2\pi}{3}\right)^{1/2}\Big[(1+\mathrm{i})Y_1^{-1}(\theta,\varphi)+\sqrt{18}\,Y_1^0(\theta,\varphi)+(-1+\mathrm{i})Y_1^1(\theta,\varphi)\Big]rf(r)\,.
\end{aligned}$$

The probabilities p_m $\big(m\in\{-1,0,1\}\big)$ are

$$\begin{aligned}
p_{-1} &= \frac{|1+\mathrm{i}|^2}{|1+\mathrm{i}|^2+18+|-1+\mathrm{i}|^2}=\frac{2}{22}=\frac{1}{11}\,,\\
p_0 &= \frac{18}{|1+\mathrm{i}|^2+18+|-1+\mathrm{i}|^2}=\frac{18}{22}=\frac{9}{11}\,,\\
p_1 &= \frac{|-1+\mathrm{i}|^2}{|1+\mathrm{i}|^2+18+|-1+\mathrm{i}|^2}=\frac{2}{22}=\frac{1}{11}\,.
\end{aligned}$$

4.3 The ground state wavefunction of the hydrogen atom is of form

$$u(r,\theta,\varphi)=C\exp(-r/a_0)\,,$$

where a_0 is the first orbit Bohr radius and C is a constant.

(a) Normalize the wavefunction.

(b) Determine the radial probability density and plot it.

(c) Calculate the most probable value of r for a hydrogen atom in its ground state.

(d) Calculate the mean value of r.

Solution. (a)

$$\int_{\boldsymbol{r}}|u|^2\mathrm{d}^3r=1 \quad\Rightarrow\quad |C|^2\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty}r^2\exp(-2r/a_0)\,\mathrm{d}r=1 \quad\Rightarrow$$

$$|C|^2 4\pi\Big(\frac{a_0}{2}\Big)^3\,\Gamma(2+1)=1 \quad\Rightarrow\quad |C|=\frac{1}{\sqrt{\pi a_0^3}}\,.$$

Taking $C=1/\sqrt{\pi a_0^3}$, the normalized wavefunction is

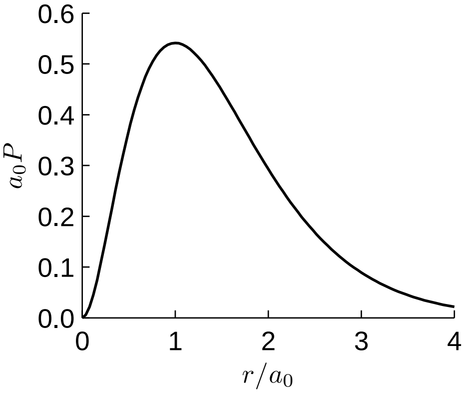
$$u(r,\theta,\varphi)=\frac{1}{\sqrt{\pi a_0^3}}\,\mathrm{e}^{-r/a_0}\,.$$

(b) The probability $\mathrm{d}p(r)$ that the electron is between r and $r+\mathrm{d}r$ regardless of the direction is

$$\mathrm{d}p(r) = \int_0^{\pi}\int_0^{2\pi} |u(r,\theta,\varphi)|^2\, r^2 \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\varphi = 4a_0^{-3} r^2 \exp(-2r/a_0)\, \mathrm{d}r\,.$$

The radial probability density is therefore

$$P(r) = 4a_0^{-3} r^2 \exp(-2r/a_0)\,.$$



The radial probability density of the electron in the ground state of the hydrogen atom.

(c) The most probable radius is found from the condition $\mathrm{d}P(r)/\mathrm{d}r = 0$. We find

$$4a_0^{-3}(2r - 2r^2/a_0)\exp(-2r/a_0) = 0$$

and the most probable value $r_{\mathrm{mp}} = a_0$. Thus, for the hydrogen atom, the most probable distance of the electron from the nucleus is equal to the radius of the first Bohr orbit.

(d)

$$\langle r\rangle = \int_0^{\infty} rP(r)\,\mathrm{d}r = \frac{4}{a_0^3}\int_0^{\infty} r^3 \mathrm{e}^{-2r/a_0}\,\mathrm{d}r = \frac{4}{a_0^3}\left(\frac{a_0}{2}\right)^4 \int_0^{\infty} \rho^3 \mathrm{e}^{-\rho}\,\mathrm{d}\rho = \frac{1}{4}\,a_0\Gamma(3+1)$$
$$= \frac{3}{2}\,a_0\,.$$

Chapter 5

Lasers

5.1 The width of a spectral line

Up to now we have considered that atoms are characterized by energy levels that are infinitely sharp. The real case is that an atom in a given energy level can actually have any energy within a finite range; we say that the energy level is *broadened.* At the transition between two energy levels, the frequency of the radiation is not unique, but has a spectrum characterized by the *lineshape funtion* $g(\nu)$ whose physical significance is given by: $g(\nu)\,\mathrm{d}\nu$ is the probability that the radiation emitted or absorbed has the frequency in the range between ν and $\nu + \mathrm{d}\nu$. It follows that

$$\int_0^\infty g(\nu)\,\mathrm{d}\nu = 1\,.$$

The lineshape function is usually sharply peaked near some frequency ν_0; for this reason, the function is frequently written $g(\nu_0, \nu)$. The values of the lineshape function are practically unsignificant for frequencies close to zero. It is mathematically convenient to extend the function for negative frequencies and to write the normalization condition as

$$\int_{-\infty}^\infty g(\nu)\,\mathrm{d}\nu = 1\,. \tag{5.1}$$

The measure of the width of the lineshape function is taken the full width at half maximum, written $\Delta\nu$ or FWHM.

The calculation of $\Delta\nu$ will be exemplified for the *natural broadening* mechanism. Suppose an atom in an excited state. It can decay to a lower energy level by spontaneous emission. Let us denote by τ the lifetime of the excited level. In the classical theory of radiation emission, the natural width of a spectral line is explained based on the finite wavetrain emitted by the atom. We will find this by analyzing the frequency spectrum of the emitted radiation.

We can represent the electric field of the decaying atom as

$$\mathcal{E}(t) = \begin{cases} 0\,, & \text{for } t < 0 \\ \mathcal{E}_0 \exp(-t/2\tau)\cos(2\pi\nu_0 t)\,, & \text{for } t \geq 0\,. \end{cases}$$

Here $t = 0$ is the instant of time when the atom is pushed into the excited state. The choice for the decaying term is determined by the condition that the intensity of radiation—which is proportional to the amplitude of the electric field intensity—is proportional to $\exp(-t/\tau)$.

The Fourier transform of the electric field is

$$\begin{aligned} \mathcal{E}(\nu) &= \int_{-\infty}^{\infty} \mathcal{E}(t)\exp(\mathrm{i}2\pi\nu t)\,\mathrm{d}t \\ &= \frac{1}{2}\mathcal{E}_0 \int_0^{\infty} \exp(-t/2\tau)\left[\exp(-\mathrm{i}2\pi\nu_0 t) + \exp(\mathrm{i}2\pi\nu_0 t)\right]\exp(\mathrm{i}2\pi\nu t)\,\mathrm{d}t \\ &= \frac{1}{2}\mathcal{E}_0 \left[-\frac{1}{-(1/2\tau) + \mathrm{i}2\pi(\nu-\nu_0)} - \frac{1}{-(1/2\tau) + \mathrm{i}2\pi(\nu+\nu_0)}\right] \\ &= \frac{\mathrm{i}}{4\pi}\mathcal{E}_0 \left(\frac{1}{\nu - \nu_0 + \mathrm{i}/4\pi\tau} + \frac{1}{\nu + \nu_0 + \mathrm{i}/4\pi\tau}\right). \end{aligned}$$

Let us compare the two terms. As $\nu_0 \gg 1/\tau$ (typical values: $\nu_0 \sim 10^{14}\,\mathrm{Hz}$ and $\tau \sim 10^{-8}\,\mathrm{s}$), for all positive frequencies the second term is negligible compared to the first. It follows that

$$|\mathcal{E}(\nu)|^2 \propto \frac{1}{(\nu-\nu_0)^2 + (1/4\pi\tau)^2}\,.$$

The spectral distribution of the radiated energy is described by the function

$$g(\nu) = \frac{\text{const}}{(\nu-\nu_0)^2 + (1/4\pi\tau)^2}\,, \quad \nu \geq 0\,. \tag{5.2}$$

It has a maximum for $\nu = \nu_0$ and decreases simmetrically to zero. Frequencies $\nu_\pm$ at half intensity are given by

$$\nu_\pm = \nu_0 \pm 1/4\pi\tau\,, \tag{5.3}$$

so the full witdth at half maximum is

$$\Delta\nu = \nu_+ - \nu_- = 1/2\pi\tau\,. \tag{5.4}$$

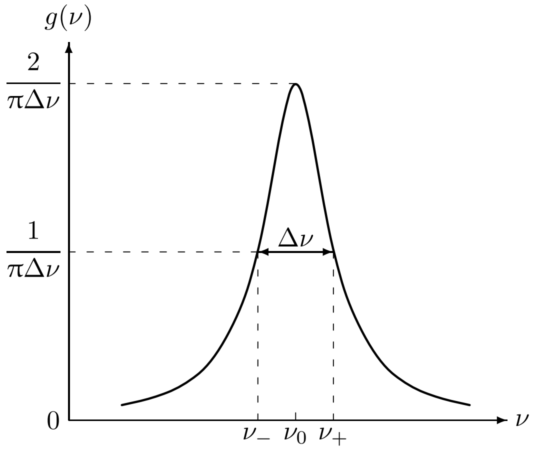


Fig. 5.1 Lorentzian lineshape. The function peaks at the line centre ν_0 and has FWHM = $\Delta\nu$. The function is normalized so that the area between its graph and the frequency axis is unity.

For small (positive) frequencies $g(\nu)$ takes on neglijible values compared to $g(\nu_0)$; we can extend the function for negative frequencies up to $-\infty$. The normalization condition (5.1) gives const $= 1/4\pi^2\tau = \Delta\nu/2\pi$, thus the lineshape function acquires the final form

$$g(\nu) = \frac{\Delta\nu/2\pi}{(\nu-\nu_0)^2 + (\Delta\nu/2)^2}\,, \quad \nu \in (-\infty, \infty)\,. \tag{5.5}$$

This type of function is called a *Lorentzian* (see Fig. 5.1).

The width $\Delta\nu$ of the lineshape function, given by Eq. (5.4), is called *natural width* of the spectral line. The natural width is inversely proportional to the lifetime τ of the excited state.

As an example, let us consider the typical value $\tau = 10^{-8}\,\mathrm{s}$. The natural width of the spectral line is $\Delta\nu = 1/2\pi\tau \approx 1.6 \times 10^7\,\mathrm{Hz} \ll \nu_0$.

Practically, the observed spectral lines do not exhibit the natural width just described. This is because other, usually more pronounced effects are present. For example, in a gas there two other broadening mechanisms: the collision broadening and the Doppler broadening.

5.2 Radiation attenuation in a two-level medium

Ordinary optical materials tend to absorb or scatter the light, so that the light intensity out of the medium is less than the intensity that went in.

To be more specific, let us consider a medium of identical atoms and two atomic energy levels 1 and 2 as in Fig. 1.8. For simplicity, we assume here that the energy levels are non-degenerate. The spectral line at the transition

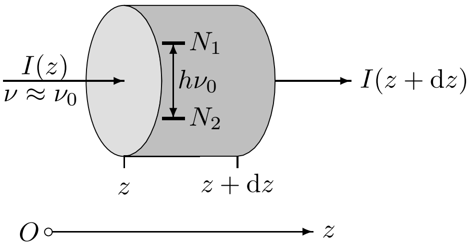


Fig. 5.2 The interaction of a monochromatic radiation of frequency ν and a thin layer containing atoms with the ground state denoted as 1 and an excited state 2 such that $E_2 - E_1 = h\nu_0 \approx h\nu$.

$2 \to 1$ has the central frequency ν_0 and the profile $g(\nu)$. Suppose a beam of monochromatic light of frequency ν close to ν_0 is incident on a thin layer of this medium placed between the coordinates z and $z + \mathrm{d}z$ (see Fig. 5.2). It can be proven that the change in intensity $\mathrm{d}I$ due to the interactions between the atoms and the the radiation field is

$$\mathrm{d}I = -\alpha(\nu)\, I \,\mathrm{d}z\,, \tag{5.6}$$

where

$$\alpha(\nu) = \frac{\lambda^2}{8\pi n^2 \tau}(N_1 - N_2)g(\nu)\,, \tag{5.7}$$

$\lambda = c/\nu$, τ is the lifetime of level 2, and n is the refractive index of the medium. At thermal equilibrium $N_1 > N_2$, thus $\alpha > 0$; $\alpha(\nu)$ is called the *attenuation coefficient* of the medium at the frequency ν .

5.3 The amplification of radiation

Suppose now that by pumping energy into the atomic medium we can maintain $N_2 > N_1$; we say that a *population inversion* between the energy levels 1 and 2 is created. For such a system the attenuation coefficient becomes negative, i.e., the atomic medium is amplifying the light. The process responsible for the light amplification is the *stimulated emission.*

It can be proven that a stationary population inversion can not be obtained with 2-level atoms, i.e., in case only two energy levels are implied in the atom transitions.

In a 4-level atomic system (Fig. 5.3), atoms in ground state (0) are excited by pumping to the energy level 3. This is usually done with a bright flash lamp or by an electrical discharge. An atom in state 3 performs a rapid decay to the level 2; this condition ensures that the population of the level 3 can be neglected. Then, the atom can decay spontaneously to state 1, and this in turn decays to the ground state. Let us denote by τ_1 and τ_2 the lifetime of level 1 and 2, respectively. To obtain population inversion between levels

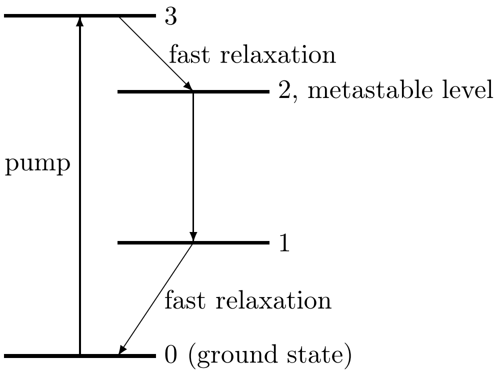


Fig. 5.3 Realization of population inversion in a system of 4-level atoms. The population inversion is obtained between levels 2 and 1.

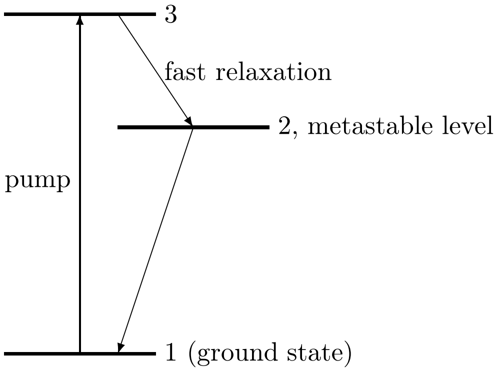


Fig. 5.4 Realization of population inversion in a system of 3-level atoms. The population inversion is obtained between levels 2 and 1.

1 and 2, it is necessary that $\tau_2 > \tau_1$. Practically, population inversion is obtained with a level 2 which has a very long lifetime; it is said that level 2 is *metastable*.

The realization of the population inversion in a 3-level atomic system is presented in Fig. 5.4.

The key difference between the two cases originates from the fact that the lower level is the ground state for a 3-level atomic system: it is much more difficult to obtain population inversion in 3-level atoms because the the lower level initially has a very large population.

5.4 The laser

LASER = Light Amplification by Stimulated Emission of Radiation

A laser is actually an *oscillator* rather than a simple amplifier. The difference is that an oscillator has positive feedback in addition to the amplifier.

Light is understood in a general sense: electromagnetic radiation with

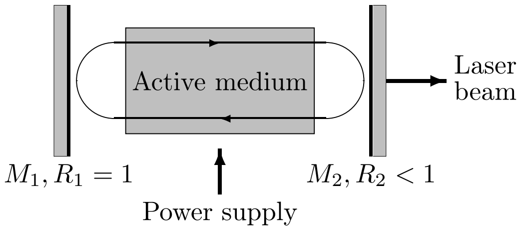


Fig. 5.5 Schematic diagram of a laser.

wavelength around 1 µm. Thus one can have infrared, visible or ultraviolet lasers.

The atomic medium with population inversion used in the laser is called *active medium.* The positive optical feedback is obtained by placing the active medium between two mirrors (see Fig. 5.5). One of them (M_1) totally reflects back the light (The mirror reflectivity is $R_1 = 1$) to the active medium, while the other one (M_2, called the *output coupler*) has a reflectivity less than unity ($R_2 < 1$) and allows some of the light to be transmitted as the output of the laser. The two mirrors form a *resonant cavity* for the optical radiation.

5.5 Types of lasers

Lasers come in many shapes and sizes. They are classified by various criteria:

- Gain medium is solid, liquid or gas
- Wavelength is in the infrared, visible or ultraviolet spectral region
- Mode of operation is continuous or pulsed
- Wavelength is fixed or tuneable

The present state of the art includes:

- Peak powers $> 10^{12}$ W
- Pulses shorter than 10^{-15} s
- Cheap, efficient diode lasers available at blue (400 nm), red (620 nm—670 nm), and near-infrared wavelengths (700 nmŰ–1600 nm)
- Other readily-available fixed-wavelengths include:

Infrared: CO_2 (10.6 µm), erbium (1.55 µm), Nd:YAG (1.064 µm)

Visible: ruby (693 nm), He–Ne (633 nm), Ar^+ (514 nm, 488 nm), doubled Nd:YAG (532 µm)

Ultraviolet: Ar^+ (364 nm, 351 nm), tripled Nd:YAG (355 µm), N_2 (337 µm), quadrupled Nd:YAG (266 nm), excimer (308 nm, 248 nm, 193 nm, 150 nm)

- Tuneable lasers:

  Dye (typical tuning range ∼100 nm, dyes available from UV to near infrared)

  Ti: sapphire (700 nm–Ű1000 nm, doubled: 350 nm–Ű500 nm);

  Free electron (far infrared to ultraviolet)

5.6 Properties of laser light

1. Monochromatic

The emission of the laser generally corresponds to just one of the atomic transitions of the gain medium, in contrast to discharge lamps, which emit on all the transitions. The spectral line width can be much smaller than that of the atomic transition. This is because the emission is affected by the optical cavity. In certain cases, the laser can be made to operate on just one of the modes of the cavity. Since the quality factor of the cavity is generally rather large, the mode is usually much narrower than the atomic transition, and the spectral line width is orders of magnitude smaller than the atomic transition. This is particularly useful for high resolution spectroscopy and applications such as interferometry and holography that require high coherence.

2. Coherence

In discussing the coherence of an optical beam, we must distinguish between spatial and temporal coherence. Laser beams have a high degree of both.

Spatial coherence refers to whether there are irregularities in the optical phase in a cross-sectional slice of the beam.

Temporal coherence refers to the time duration over which the phase of the beam is well defined. In general, the temporal coherence time t_c is given by the reciprocal of the spectral linewidth $\Delta\nu$. Thus the coherence length l_c is given by:

$$l_c = ct_c = c/\Delta\nu\,. \tag{5.8}$$

Table 5.1 Coherence length of several light sources.

Source	$\Delta\nu/\text{Hz}$	t_c/s	l_c/m
Sodium discharge lamp (D-lines at 589 nm)	5×10^{11}	2×10^{-12}	6×10^{-4}
Multi-mode He–Ne laser (632.8 nm line)	1.5×10^{9}	6×10^{-10}	0.2
Single-mode He–Ne laser (632.8 nm line)	1×10^{6}	1×10^{-6}	300

Typical values of the coherence length for a number of light sources are given in Table 5.1.

3. Directionality

This is perhaps the most obvious aspect of a laser beam: the light comes out as a highly directional beam. This contrasts with light bulbs and discharge lamps, in which the light is emitted in all directions. The directionality is a consequence of the cavity.

4. Brightness

The brightness of lasers arises from two factors. First of all, the fact that the light is emitted in a well-defined beam means that the power per unit area is very high, even though the total amount of power can be rather low. Then we must consider that all the energy is concentrated within the narrow spectrum of the active atomic transition. This means that the spectral brightness (i.e., the intensity in the beam divided by the width of the emission line) is even higher in comparison with a white light source like a light bulb. For example, the spectral brightness of a 1 mW laser beam could easily be millions times greater than that of a 100 W light bulb.

Properties 1–4 are common to all lasers. There is a fifth property which is found in only some:

5. Ultrashort pulse generation

Lasers can be made to operate continuously or in pulses. The time duration of the pulses t_p is linked to the spectral bandwidth of the laser light $\Delta\nu$ by the “uncertainty”product $\Delta t\,\Delta\nu \sim 1$:

$$t_p \geq 1/\Delta\nu\,. \tag{5.9}$$

This follows from taking the Fourier transform of a pulse of duration t_p. As an example, the bandwidth of the 632.8 nm line in the He–Ne laser is 1.5 GHz (see Table 5.1), so that the shortest pulses a He–Ne laser can produce would be 0.67 ns duration. This is not particularly short by modern standards. Dye lasers typically have gain bandwidths greater than 10^{13} Hz, and can be used to generate pulses shorter than 100 fs ($1\,\mathrm{fs} = 10^{-15}\,\mathrm{s}$). This is achieved by a technique called "mode-locking". The present world record for a light pulse is less than 1 fs. These short pulsed lasers are very useful for studying fast processes in physics, chemistry and biology, and are also being developed for high data rate transmission using optical fibre networks.

5.7 Problems

5.1 Calculate $\int_{-\infty}^{0} g(\nu)\,\mathrm{d}\nu$ for a Lorentzian spectral line with the central wavelength $\lambda_0 = 600\,\mathrm{nm}$ and the linewidth $\Delta\nu = 10^9\,\mathrm{Hz}$.

Solution. The central frequency of the spectral line is $\nu_0 = c/\lambda_0 = 5\times 10^{14}\,\mathrm{Hz}$. By use of the Lorentzian lineshape function [see Eq. (5.5)], we have

$$\begin{aligned}\int_{-\infty}^{0} g(\nu)\,\mathrm{d}\nu &= \int_{-\infty}^{0} \frac{\Delta\nu/2\pi}{(\nu-\nu_0)^2+(\Delta\nu/2)^2}\,\mathrm{d}\nu = \frac{1}{\pi}\arctan\frac{\nu-\nu_0}{\Delta\nu/2}\bigg|_{-\infty}^{0}\\ &= \frac{1}{\pi}\left(-\arctan\frac{\nu_0}{\Delta\nu/2}+\frac{\pi}{2}\right) = \frac{1}{\pi}\arctan\left[\tan\left(-\arctan\frac{\nu_0}{\Delta\nu/2}+\frac{\pi}{2}\right)\right]\\ &= \frac{1}{\pi}\arctan\frac{\Delta\nu/2}{\nu_0} \approx \frac{1}{\pi}\,\frac{\Delta\nu/2}{\nu_0} \approx 3.2\times 10^{-7}.\end{aligned}$$

The value of the integral is negligible compared to unity, thus the normalization condition $\int_0^{\infty} g(\nu)\,\mathrm{d}\nu = 1$ may be replaced by the condition $\int_{-\infty}^{\infty} g(\nu)\,\mathrm{d}\nu = 1$, which is more convenient for analytical reasons.

5.2 The $\lambda_0 = 632.8\,\mathrm{nm}$ emission line of neon has the Doppler linewidth $\Delta\nu_{\mathrm{D}} = 1.5\,\mathrm{GHz}$ at $T = 400\,\mathrm{K}$. (This is the approximate temperature of the gas mixture in the He–Ne laser.) Determine the linewidth $\Delta\lambda_{\mathrm{D}}$ corresponding to the frequency linewidth $\Delta\nu_{\mathrm{D}}$.

Solution. By use of the link relation between wavelength and frequency, $\lambda = c/\nu$, for the small frequency interval $\Delta\nu_{\mathrm{D}}$, the wavelength interval is

$$\Delta\lambda_{\mathrm{D}} = \left|\left(\frac{\mathrm{d}\lambda}{\mathrm{d}\nu}\right)_{\nu=\nu_0}\right|\Delta\nu_{\mathrm{D}} = \frac{c}{\nu_0^2}\Delta\nu_{\mathrm{D}} = \frac{\lambda_0^2}{c}\Delta\nu_{\mathrm{D}} \approx 2\times 10^{-12}\,\mathrm{m}\,.$$

Appendix A

The derivation of Eqs. (4.13) and (4.14)

By use of the gradient operator expression in sperical polar coordinates,

$$\nabla = \boldsymbol{e}_r\frac{\partial}{\partial r} + \boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \boldsymbol{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}\,, \tag{A.1}$$

the operator $\hat{\boldsymbol{L}}$ writes

$$\hat{\boldsymbol{L}} = -\mathrm{i}\hbar\begin{vmatrix} \boldsymbol{e}_r & \boldsymbol{e}_\theta & \boldsymbol{e}_\varphi \\ r & 0 & 0 \\ \dfrac{\partial}{\partial r} & \dfrac{1}{r}\dfrac{\partial}{\partial\theta} & \dfrac{1}{r\sin\theta}\dfrac{\partial}{\partial\varphi} \end{vmatrix} = \mathrm{i}\hbar\left(\boldsymbol{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - \boldsymbol{e}_\varphi\frac{\partial}{\partial\theta}\right). \tag{A.2}$$

The Cartesian components of the operator $\hat{\boldsymbol{L}}$ are obtained by projecting succesively on the Ox, Oy, and Oz direction. By help of Eq. (4.11), we get

$$\begin{aligned}\hat{L}_x = \boldsymbol{i}\cdot\hat{\boldsymbol{L}} &= \mathrm{i}\hbar\left[(\boldsymbol{i}\cdot\boldsymbol{e}_\theta)\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - (\boldsymbol{i}\cdot\boldsymbol{e}_\varphi)\frac{\partial}{\partial\theta}\right] \\ &= \mathrm{i}\hbar\left(\cos\theta\cos\varphi\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\varphi} + \sin\varphi\,\frac{\partial}{\partial\theta}\right) = \mathrm{i}\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\,\frac{\partial}{\partial\varphi}\right),\end{aligned}$$

$$\begin{aligned}\hat{L}_y = \boldsymbol{j}\cdot\hat{\boldsymbol{L}} &= \mathrm{i}\hbar\left[(\boldsymbol{j}\cdot\boldsymbol{e}_\theta)\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - (\boldsymbol{j}\cdot\boldsymbol{e}_\varphi)\frac{\partial}{\partial\theta}\right] \\ &= \mathrm{i}\hbar\left(\cos\theta\sin\varphi\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\varphi} - \cos\varphi\,\frac{\partial}{\partial\theta}\right) = -\mathrm{i}\hbar\left(\cos\varphi\,\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\,\frac{\partial}{\partial\varphi}\right),\end{aligned}$$

$$\hat{L}_z = \boldsymbol{k}\cdot\hat{\boldsymbol{L}} = \mathrm{i}\hbar\left[(\boldsymbol{k}\cdot\boldsymbol{e}_\theta)\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - (\boldsymbol{k}\cdot\boldsymbol{e}_\varphi)\frac{\partial}{\partial\theta}\right] = \mathrm{i}\hbar\left(-\sin\theta\,\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - 0\right)$$
$$= -\mathrm{i}\hbar\,\frac{\partial}{\partial\varphi}\,.$$

We calculate $\hat{L}^2$ based on Eq. (A.2):

$$\hat{L}^2 = -\hbar^2\left(\boldsymbol{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - \boldsymbol{e}_\varphi\frac{\partial}{\partial\theta}\right)\cdot\left(\boldsymbol{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} - \boldsymbol{e}_\varphi\frac{\partial}{\partial\theta}\right). \tag{A.3}$$

In calculation the derivatives we must take into account that the unit vectors $\boldsymbol{e}_\theta$ and $\boldsymbol{e}_\theta$ depend on θ and φ:

$$\begin{aligned}\frac{\partial\boldsymbol{e}_\theta}{\partial\theta} &= \frac{\partial}{\partial\theta}(\boldsymbol{i}\cos\theta\cos\varphi + \boldsymbol{j}\cos\theta\sin\varphi - \boldsymbol{k}\sin\theta)\\ &= -\boldsymbol{i}\sin\theta\cos\varphi - \boldsymbol{j}\sin\theta\sin\varphi - \boldsymbol{k}\cos\theta = -\boldsymbol{e}_r,\end{aligned}$$

$$\begin{aligned}\frac{\partial\boldsymbol{e}_\theta}{\partial\varphi} &= \frac{\partial}{\partial\varphi}(\boldsymbol{i}\cos\theta\cos\varphi + \boldsymbol{j}\cos\theta\sin\varphi - \boldsymbol{k}\sin\theta)\\ &= -\boldsymbol{i}\cos\theta\sin\varphi + \boldsymbol{j}\cos\theta\cos\varphi = \boldsymbol{e}_\varphi\cos\theta,\end{aligned}$$

$$\frac{\partial\boldsymbol{e}_\varphi}{\partial\theta} = \frac{\partial}{\partial\theta}(-\boldsymbol{i}\sin\varphi + \boldsymbol{j}\cos\varphi) = 0\,,$$

$$\begin{aligned}\frac{\partial\boldsymbol{e}_\varphi}{\partial\varphi} =& \frac{\partial}{\partial\varphi}(-\boldsymbol{i}\sin\varphi + \boldsymbol{j}\cos\varphi) = -\boldsymbol{i}\cos\varphi - \boldsymbol{j}\sin\varphi\\ =& -(\boldsymbol{e}_r\sin\theta\cos\varphi + \boldsymbol{e}_\theta\cos\theta\cos\varphi - \boldsymbol{e}_\varphi\sin\varphi)\cos\varphi\\ &-(\boldsymbol{e}_r\sin\theta\sin\varphi + \boldsymbol{e}_\theta\cos\theta\sin\varphi + \boldsymbol{e}_\varphi\cos\varphi)\sin\varphi\\ =& -\boldsymbol{e}_r\sin\theta - \boldsymbol{e}_\theta\cos\theta\,.\end{aligned}$$

The use of these derivatives in Eq. (A.3) yields

$$\begin{aligned}\hat{L}^2 &= -\hbar^2\left(\cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\ &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right].\end{aligned}$$

Appendix B

Fundamental physical constants

The tables give values of some basic physical constants recommended by the Committee on Data for Science and Technology (CODATA) based on the 2006 adjustment [11, 12]. The standard uncertainty in the last two digits is given in parenthesis.

Table B.1 An abbreviated list of the CODATA recommended values of the fundamental constants of physics and chemistry.

Quantity	Symbol	Value
speed of light in vacuum	c, c_0	$299\,792\,458\,\mathrm{m\,s^{-1}}$ (exact)
magnetic constant	μ_0	$4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}}$
electric constant $1/\mu_0 c^2$	ϵ_0	$8.854\,187\,817... \times 10^{-12}\,\mathrm{F\,m^{-1}}$
Newtonian constant of gravitation	G	$6.674\,28(67) \times 10^{-11}\,\mathrm{m^3\,kg^{-1}\,s^{-2}}$
Avogadro constant	N_A	$6.022\,141\,79(30) \times 10^{23}\,\mathrm{mol^{-1}}$
molar gas constant	R	$8.314\,472(15)\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Boltzmann constant R/N_A	k	$1.380\,6504(24) \times 10^{-23}\,\mathrm{J\,K^{-1}}$
		$8.617\,343(15) \times 10^{-5}\,\mathrm{eV\,K^{-1}}$
molar volume of ideal gas		
$(T = 273.15\,\mathrm{K},\ p = 101.325\,\mathrm{kPa})$	V_m	$22.413\,996(39) \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$
Loschmidt constant $N_\mathrm{A}/V_\mathrm{m}$	n_0	$2.686\,7774(47) \times 10^{25}\,\mathrm{m^{-3}}$
elementary charge	e	$1.602\,176\,487(40) \times 10^{-19}\,\mathrm{C}$
Faraday constant $N_\mathrm{A}e$	F	$96\,485.3399(24)\,\mathrm{C\,mol^{-1}}$
Planck constant	h	$6.626\,068\,96(33) \times 10^{-34}\,\mathrm{J\,s}$
		$4.135\,667\,33(10) \times 10^{-15}\,\mathrm{eV\,s}$
$h/2\pi$	$\hbar$	$1.054\,571\,628(53) \times 10^{-34}\,\mathrm{J\,s}$
		$6.582\,118\,99(16) \times 10^{-16}\,\mathrm{eV\,s}$
electron mass	m_e	$9.109\,382\,15(45) \times 10^{-31}\,\mathrm{kg}$
energy equivalent in MeV	$m_\mathrm{e}c^2$	$0.510\,998\,910(13)\,\mathrm{MeV}$
electron charge to mass quotient	$-e/m_\mathrm{e}$	$-1.758\,820\,150(44) \times 10^{11}\,\mathrm{C\,kg^{-1}}$
proton mass	m_p	$1.672\,621\,637(83) \times 10^{-27}\,\mathrm{kg}$
$m_\mathrm{p} = A_\mathrm{r}(\mathrm{p})\,\mathrm{u}$		$1.007\,276\,466\,77(10)\,\mathrm{u}$
energy equivalent in MeV	$m_\mathrm{p}c^2$	$938.272\,013(23)\,\mathrm{MeV}$
neutron mass	m_n	$1.674\,927\,211(84) \times 10^{-27}\,\mathrm{kg}$
$m_\mathrm{n} = A_\mathrm{r}(\mathrm{n})\,\mathrm{u}$		$1.008\,664\,915\,97(43)\,\mathrm{u}$
energy equivalent in MeV	$m_\mathrm{n}c^2$	$939.565\,346(23)\,\mathrm{MeV}$
proton-electron mass ratio	$m_\mathrm{p}/m_\mathrm{e}$	$1836.152\,672\,47(80)$
fine-structure constant $e^2/4\pi\epsilon_0\hbar c$	α	$7.297\,352\,5376(50) \times 10^{-3}$
inverse fine-structure constant	$1/\alpha$	$137.035\,999\,679(94)$
Rydberg constant $\alpha^2 m_\mathrm{e}c/2h$	R_∞	$10\,973\,731.568\,527(73)\,\mathrm{m^{-1}}$
$R_\infty hc$ in eV		$13.605\,691\,93(34)\,\mathrm{eV}$
Wien displacement law constants		
$b = \lambda_\mathrm{max}T$	b	$2.897\,7685(51) \times 10^{-3}\,\mathrm{m\,K}$
$b' = \nu_\mathrm{max}/T$	b'	$5.878\,933(10) \times 10^{10}\,\mathrm{Hz\,K^{-1}}$
Stefan–Boltzmann constant		
$(\pi^2/60)k^4/\hbar^3c^2$	σ	$5.670\,400(40) \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$
Bohr radius $\alpha/4\pi R_\infty = 4\pi\epsilon_0\hbar^2/m_\mathrm{e}e^2$	a_0	$0.529\,177\,208\,59(36) \times 10^{-10}\,\mathrm{m}$
Compton wavelength $h/m_\mathrm{e}c$	λ_C	$2.426\,310\,2175(33) \times 10^{-12}\,\mathrm{m}$
classical electron radius $\alpha^2 a_0$	r_e	$2.817\,940\,2894(58) \times 10^{-15}\,\mathrm{m}$
Bohr magneton $e\hbar/2m_\mathrm{e}$	μ_B	$927.400\,915(23) \times 10^{-26}\,\mathrm{J\,T^{-1}}$
		$5.788\,381\,7555(79) \times 10^{-5}\,\mathrm{eV\,T^{-1}}$
nuclear magneton $e\hbar/2m_\mathrm{p}$	μ_N	$5.050\,783\,24(13) \times 10^{-27}\,\mathrm{J\,T^{-1}}$
		$3.152\,451\,2326(45) \times 10^{-8}\,\mathrm{eV\,T^{-1}}$

Table B.2 The values in SI units of some non-SI units.

Name of unit	Symbol	Value in SI units
ångström	Å	$0.1\,\mathrm{nm} = 100\,\mathrm{pm} = 10^{-10}\,\mathrm{m}$
electron volt[a]: (e/C) J	eV	$1.602\,176\,487(40) \times 10^{-19}\,\mathrm{J}$
(unified) atomic mass unit[b] $1\,\mathrm{u} = m_\mathrm{u}$ $= (1/12)m(^{12}\mathrm{C}) = 10^{-3}\,\mathrm{kg\,mol^{-1}}/N_\mathrm{A}$	u	$1.660\,538\,782(83) \times 10^{-27}\,\mathrm{kg}$

[a] The electronvolt is the kinetic energy acquired by an electron in passing through a potential difference of one volt in vacuum.

[b] The unified atomic mass unit is equal to 1/12 times the mass of a free carbon 12 atom, at rest and in its ground state.

Appendix C

Greek letters used in mathematics, science, and engineering

Name of letter	Capital letter	Lower-case letter
alpha	A	α
beta	B	β
gamma	Γ	γ
delta	Δ	δ
epsilon	E	ϵ, ε
zeta	Z	ζ
eta	H	η
theta	Θ	θ, ϑ
iota	I	ι
kappa	K	κ, $\varkappa$
lambda	Λ	λ
mu	M	μ
nu	N	ν
xi	Ξ	ξ
omicron	O	o
pi	Π	π, ϖ
rho	P	ρ, ϱ
sigma	Σ	σ, ς
tau	T	τ
upsilon	Υ	υ
phi	Φ	ϕ, φ
chi	X	χ
psi	Ψ	ψ
omega	Ω	ω

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