Lecture Notes in

Quantum Physics I

Artemio González López

Madrid, June 11, 2024

Dedicated to the loving memory of my parents, Artemio and Matilde,
to whom I owe everything I am

Artemio González López

Departamento de Física Teórica
Facultad de Ciencias Físicas
Universidad Complutense de Madrid
Plaza de las Ciencias, 1
28040 Madrid

Contents

Contents

1 The experimental basis of quantum mechanics

1.1 Black body radiation and Planck's hypothesis

An ideal **black body** is a hollow enclosure with perfectly absorbing (i.e., "black") inner and outer walls, whose surface is pierced by a tiny hole. If electromagnetic radiation falls into the enclosure, the smallness of the hole makes it extremely unlikely that any radiation coming through it will eventually come out after a certain number of reflections on the vessel's inner surface, even if this surface is not perfectly absorbing. On the other hand, the electromagnetic radiation entering the enclosure will be absorbed by the atoms in its inner surface and make them vibrate, causing them to radiate electromagnetic energy. When thermal equilibrium is reached, the energy of the electromagnetic radiation absorbed by the atoms in the enclosure's inner surface will equal the energy radiated by them. The electromagnetic radiation coming from the enclosure's walls after equilibrium is reached is called **black body radiation**, and depends only on the equilibrium temperature of the enclosure's walls. More precisely, from general thermodynamic principles it can be shown[1] that black body radiation has the following properties:

1) The energy density (i.e., energy per unit volume and frequency) of the radiation field inside the enclosure is the same function of frequency at a given temperature, regardless of the size and shape of the enclosure and of the material its walls are made of.

2) The energy flux of the radiation field inside the enclosure is *homogeneous* (i.e., is the same at all points inside the cavity) and *isotropic* (i.e., is the same in all directions).

Let us therefore denote by $u(\nu, T)$ the energy density per unit frequency of the radiation field at any point inside the enclosure for frequencies in the range $[\nu, \nu + d\nu]$ at a temperature T. In other words, the energy of the radiation in an infinitesimal volume d^3r centered on an arbitrary point $\mathbf{r}$ inside the enclosure with frequencies in the range $[\nu, \nu + d\nu]$ at a certain temperature T is $u(\nu, T) \, d^3r \, d\nu$, and the total energy (regardless of the frequency) is therefore $U(T) \, d^3r$, where

$$U(T) = \int_0^\infty u(\nu, T) \, d\nu. \tag{1.1}$$

The energy of the black body radiation field in the frequency range $[\nu, \nu + d\nu]$ hitting the hole in the enclosure emitted by an infinitesimal volume d^3r centered at a point inside the enclosure with position vector $\mathbf{r}$ with respect to the hole is thus

$$u(\nu, T) d^3r \, d\nu \cdot \frac{dA \cos\theta}{4\pi r^2},$$

where dA is the area of the hole and θ is the angle between the normal to the surface of the hole and the vector $\mathbf{r}$. Indeed, by the *isotropy* of the radiation field the fraction of the total energy $u(\nu, T) d^3r \, d\nu$ emitted by the infinitesimal volume d^3r reaching the hole must equal the *cross section* of the hole ($dA \cos\theta$) divided by the surface of a sphere of radius equal to the distance r from the emitter to the hole. The radiation in the frequency range $[\nu, \nu + d\nu]$ going through the hole in an infinitesimal time dt is emitted by points inside the enclosure in a solid hemisphere H of radius $c \, dt$ (where c is the velocity

---

[1] The original proof of this result is due to the German physicist Gustav Robert Kirchhoff (1824–1887), in 1859–62.

of light *in vacuo*) centered at the hole. The energy of this radiation is therefore given by

$$u(v, T)\, dv\, dA \int_H \frac{\cos\theta}{4\pi r^2}\, d^3r = u(v, T)\, dv\, dA \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta\, \sin\theta \int_0^{c\, dt} dr\, r^2 \frac{\cos\theta}{4\pi r^2}$$

$$= u(v, T)\, dv\, dA \cdot 2\pi \left(\int_0^{\pi/2} \sin\theta \cos\theta\, d\theta \right) \frac{c\, dt}{4\pi} = \frac{c}{4} u(v, T)\, dA\, dv\, dt.$$

Hence the *power per unit surface area* of the black body radiation coming through the hole in the frequency range $[v, v + dv]$ when the walls of the enclosure are at a temperature T is $\rho(v, T)\, dv$, with

$$\rho(v, T) = \frac{c}{4} u(v, T). \tag{1.2}$$ `enfluxBB`

At the end of the nineteenth century there was great interest in computing from first principles the energy density $u(v, T)$ —and hence the emitted power per unit frequency and surface area— of black body radiation, which could be experimentally measured with great precision. The first theoretical calculation of $u(v, T)$ was carried out by Lord Rayleigh[2] in 1900. Rayleigh argued that, since the energy density of black body radiation is independent of the shape of the enclosure, it can be computed without loss of generality for a cubic enclosure of size L and volume $V = L^3$. Since the phase of the electromagnetic waves is $\mathbf{kr} - \omega t$, where $\mathbf{k} \in \mathbb{R}^3$ is the wave vector and $\omega > 0$ is the angular frequency of the waves, imposing (for instance) periodic boundary conditions on the cube's sides we find that

$$\mathbf{k}L = 2\pi\mathbf{n},$$

where $\mathbf{n} = (n_1, n_2, n_3)$ is a vector with integer components n_i. We thus have

$$|\mathbf{n}| = \frac{L|\mathbf{k}|}{2\pi} = \frac{L\omega}{2\pi c} = \frac{Lv}{c},$$

where v is the angular frequency of the wave. Thus the number of wave vectors $\mathbf{k}$ whose corresponding frequency is in the range $[v, v + dv]$ is equal to the volume of a spherical shell of radius $|\mathbf{n}| = Lv/c$ and width $L\, dv/c$, namely

$$4\pi \left(\frac{Lv}{c} \right)^2 \frac{L\, dv}{c} = \frac{4\pi L^3}{c^3} v^2\, dv.$$

Moreover, for each wave vector $\mathbf{k}$ there are two possible independent polarizations, and thus two possible independent oscillation *modes* of the electromagnetic field, since the electric and magnetic field vectors must be perpendicular to $\mathbf{k}$ (i.e., to the direction of propagation). Thus the number $dN(v)$ of modes of the electromagnetic field inside the cavity with frequency in the range $[v, v + dv]$ is given by

$$dN(v) = \frac{8\pi L^3}{c^3} v^2\, dv = \frac{8\pi V}{c^3} v^2\, dv. \tag{1.3}$$ `dNmodes`

Rayleigh argued that each of these modes behaves like an oscillator, so that the radiation in the cavity can be regarded as an ensemble of oscillators. The energy density per unit frequency of black body radiation with frequencies in the range $[v, v + dv]$ is thus

$$u(v, T) = \frac{1}{V} \frac{dN(v)}{dv} \overline{E}(v, T) = \frac{8\pi}{c^3} v^2 \overline{E}(v, T), \tag{1.4}$$ `uBB`

where $\overline{E}(v, T)$ is the average energy of a mode (i.e., of one of the oscillators in the ensemble) with frequency v at a temperature T. On the other hand, according to the fundamental principle of statistical

---

[2]John William Strutt, 3rd Baron Rayleigh (1842-1919), British mathematician and physicist and Nobel Prize winner in 1904.

mechanics introduced by Gibbs[3], the probability that the energy of one of the oscillators in an ensemble at thermal equilibrium is in the range $[E, E + dE]$ is proportional to $e^{-\beta E} \, dE$, where $\beta = (k_B T)^{-1}$ and k_B is **Boltzmann's**[4] **constant**[5]. Hence the average energy of a mode is given by

$$\overline{E}(\nu, T) = \frac{\int_0^\infty E e^{-\beta E} \, dE}{\int_0^\infty e^{-\beta E} \, dE} = -\frac{\partial}{\partial \beta} \log \left(\int_0^\infty e^{-\beta E} \, dE \right) = -\frac{\partial}{\partial \beta} \log(\beta^{-1}) = \frac{\partial}{\partial \beta} \log \beta = \frac{1}{\beta} = k_B T. \tag{1.5}$$ `equipE`

Using this result in Eq. (1.4) one finally obtains the so called *Rayleigh–Jeans*[6] formula

$$u(\nu, T) = \frac{8\pi}{c^3} k_B T \, \nu^2. \tag{1.6}$$ `RJeq`

Although this formula is in excellent agreement with experiment at low frequencies, it cannot hold for arbitrarily large ν, since in that case the total energy density of the black body radiation field $U(T)$ would diverge (cf. Eq. (1.1)). This divergence was informally referred to as the *ultraviolet catastrophe*. In fact, the experimental measurements showed that at high frequencies

$$u(\nu, T) \approx A\nu^3 e^{-B\nu/T}, \tag{1.7}$$ `WL`

where A and B where two empirical constants. In 1900 Planck[7] guessed a simple formula for $u(\nu, T)$ that interpolates between Eqs. (1.6) and (1.7), namely

$$u(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} \tag{1.8}$$ `Planckf`

(cf. Fig. 1.1), where h a constant with units of *action* (energy $\times$ time or length $\times$ momentum) known ever since as **Planck's constant**. Note that Planck's formula leads to a finite total energy density: indeed,

$$U(T) = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 \, d\nu}{e^{h\nu/k_B T} - 1} = \frac{8\pi k_B^4}{h^3 c^3} T^4 \int_0^\infty \frac{x^3}{e^x - 1} \, dx,$$

where the last integral is convergent at both endpoints since the integrand behaves as x^2 for $x \to 0$ and as $x^3 e^{-x}$ for $x \to \infty$. In fact, this integral can be computed in closed form as follows[8]:

$$\int_0^\infty \frac{x^3}{e^x - 1} \, dx = \int_0^\infty \frac{x^3 e^{-x}}{1 - e^{-x}} \, dx = \int_0^\infty x^3 \sum_{n=1}^\infty e^{-nx} \, dx = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} \, dx = 3! \sum_{n=1}^\infty \frac{1}{n^4} = 3! \frac{\pi^4}{90} = \frac{\pi^4}{15}.$$

We thus obtain the following expression for the *total energy density* of the black body thermal radiation inside the enclosure:

$$U(T) = \frac{8\pi^5 k_B^4}{15 h^3 c^3} T^4. \tag{1.9}$$ `SBlaw`

---

[3]J. Willard Gibbs (1839–1903), American physicist.

[4]Ludwig Boltzmann, Austrian physicist (1844–1906).

[5]In the new SI system of units approved in 2019, the following physical constants have *exact* values:

$$\text{Speed of light } \textit{in vacuo } c = 299\,792\,458 \text{ m s}^{-1}$$
$$\text{Planck's constant } h = 6.626\,070\,15 \cdot 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$
$$\text{Electron's charge } e = -1.602\,176\,634 \cdot 10^{-19} \text{ C}$$
$$\text{Bolzmann's constant } k_B = 1.380\,649 \cdot 10^{-23} \text{ J K}^{-1}$$
$$\text{Avogadro's number } N_A = 6.022\,140\,76 \cdot 10^{23} \text{ mol}^{-1}.$$

[6]James Jeans, British physicist, astronomer and mathematician (1877–1946).

[7]Max Planck (1868–1947), German physicist and Nobel Prize winner in 1918.

[8]Permuting the infinite sum and the integral in the following calculation is mathematically justified by the *dominated* (or *monotone*) *convergence theorem* in (Lebesgue) integration theory.
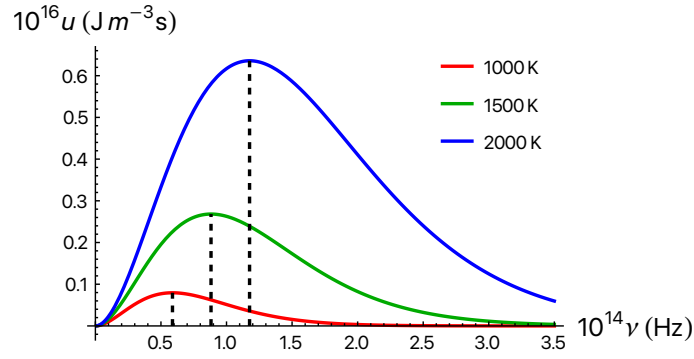
Figure 1.1. Energy density per unit frequency of the radition field inside a black body as a function of the frequency, for several values of the temperature. The dashed vertical lines indicate the frequencies for which u is maximum for a given temperature. It is apparent that this maximum frequency increases linearly with the temperature.

`fig.BBrad`

By Eq. (1.2), the total *power per unit area* $R(t)$ radiated by a black body at a temperature T is given by **Stefan's[9] law**

$$R(T) = \frac{c}{4} U(T) = \sigma T^4,$$

(1.10) `Slaw`

where

$$\sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2} = 5.670374419 \cdot 10^{-8} \, \text{W} \, \text{m}^{-2} \, \text{K}^{-4}$$

(1.11) `SBconstant`

is called the **Stefan–Boltzmann constant**.

Although Planck obtained Eq. (1.8) essentially by interpolation, he later proposed a heuristic justification thereof by postulating that the energy of an oscillation mode of frequency ν of the black body radiation field could only be an integer multiple $nh\nu$ of a minimum energy $h\nu$. That this hypothesis leads to Planck's law (1.8) can be easily proved[10] by noting that if the energy of a mode can only take the values $nh\nu$ with $n = 0, 1, \dots$ Eq. (1.5) must be replaced by

$$\overline{E}(\nu, T) = \frac{\sum\limits_{n=0}^{\infty} nh\nu e^{-\beta nh\nu}}{\sum\limits_{n=0}^{\infty} e^{-\beta nh\nu}} = -\frac{\partial}{\partial \beta} \log \left(\sum_{n=0}^{\infty} e^{-\beta nh\nu} \right) = \frac{\partial}{\partial \beta} \log \left(1 - e^{-\beta h\nu} \right) = \frac{h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} = \frac{h\nu}{e^{\beta h\nu} - 1}.$$

Substituting this expression for $\overline{E}(\nu, T)$ into Eq. (1.4) we indeed obtain Planck's distribution (1.8).

Remark. Before the introduction of Planck's constant, the dependence of $u(\nu, T)$ on ν and T could have been determined on dimensional grounds as follows. To begin with, if the existence of h is not known $u(\nu, T)$ can be expected to depend only on ν, $k_B T$, and c. Since $u(\nu, T)$ has dimensions of

$$\left[u(\nu, T) \right] = \frac{E}{L^3 t^{-1}} = ML^{-1}t^{-1},$$

and

$$[\nu] = t^{-1}, \qquad [k_B T] = ML^2 t^{-2}, \qquad [c] = Lt^{-1},$$

for $\nu^\alpha (k_B T)^\beta t^\gamma$ to have the same dimension as $u(\nu, T)$ the exponents α, β, γ must satisfy the linear system

$$\beta = 1, \qquad 2\beta + \gamma = -1, \qquad -\alpha - 2\beta - \gamma = -1,$$

---

[9]Josef Stefan (1835–1893), Slovenian physicist.
[10]The following argument is actually due to Lorentz. Planck's deduction, much more involved, was based on thermodynamical considerations.

whose unique solution is

$$\alpha = 2, \qquad \beta = 1, \qquad \gamma = -3.$$

Thus on dimensional grounds we must have

$$u(\nu, T) = a\,\frac{\nu^2 k_B T}{c^3},$$

where a is a dimensionless constant (in particular, independent of ν and T). This is essentially the Rayleigh–Jeans formula (1.6). Since this formula cannot be valid for high frequencies (as it leads to an infinite value for the total energy $U(T)$), we conclude that there must be an additional universal constant on which $u(\nu, T)$ depends. ∎

Exercise 1.1. Show that the power per unit wavelength $\rho(\lambda, T)$ radiated by a black body is given by[a]

$$\rho(\lambda, T) = \frac{2\pi h c^2 \lambda^{-5}}{e^{hc/\lambda k_B T} - 1}.$$

Find the wavelength $\lambda_{\max}(T)$ for which this power is maximum for a given temperature T.

Solution. First of all, since obviously

$$\rho(\lambda, T)\,d\lambda = -\rho(\nu, T)\,d\nu,$$

where the minus sign takes into account that $\lambda = c/\nu$ decreases when ν increases, we obtain

$$\rho(\lambda, T) = -\rho(\nu, T)\,\frac{d\nu}{d\lambda} = \frac{c}{\lambda^2}\,\rho(\nu, T) = \frac{c^2}{4\lambda^2}\,u(\nu, T) = \frac{2\pi h c^2 \lambda^{-5}}{e^{hc/\lambda k_B T} - 1}.$$

Calling $x = hc/\lambda k_B T$ we can write the previous formula as

$$\rho(\lambda, T) = \frac{2\pi}{h^4 c^3}\,(k_B T)^5 f(x), \qquad \text{with} \quad f(x) = \frac{x^5}{e^x - 1}. \qquad (1.12) \quad \boxed{\text{rhofx}}$$

It is straightforward to show that $f(x)$ has a unique maximum x_0 on the positive real axis. Indeed, $f(x)$ behaves as x^4 for small $x > 0$ and tends to 0 as $x^5 e^{-x}$ for $x \to \infty$. On the other hand,

$$f'(x) = \frac{5x^4(e^x - 1) - x^5 e^x}{(e^x - 1)^2} = \frac{x^4 e^x}{(e^x - 1)^2}\,g(x), \qquad \text{with} \quad g(x) := 5(1 - e^{-x}) - x.$$

The function $g(x)$ vanishes for $x = 0$ and tends to $-\infty$ as $x \to \infty$. Moreover, $g'(x) = 5e^{-x} - 1$ is positive for $x < \log 5$ and negative for $x > \log 5$, and vanishes for $x = \log 5$. Thus g is increasing for $0 \leqslant x \leqslant \log 5$, has a maximum at $x = \log 5$ with $g(\log 5) = 4 - \log 5 > 0$ and decreases monotonically for $x > \log 5$. Since $g(x) \to -\infty$ for $x \to \infty$, it follows that there is a unique number $x_0 > \log 5$ such that $g(x_0) = 0$. Thus $f'(x) = x^4 e^x g(x)$ is positive for $0 < x < x_0$ and negative for $x > x_0$, so that $f(x)$ has a unique global maximum at $x = x_0$. Solving numerically the equation $f'(x) = 0$, or equivalently

$$5(1 - e^{-x}) - x = 0, \qquad (1.13) \quad \boxed{\text{eqlamax}}$$

we obtain[b]

$$x_0 = 4.9651142317\cdots.$$

From Eq. (1.12) it then follows that for a fixed temperature the function $\rho(\lambda, T)$ has a unique maximum at

$$\lambda_{\max}(T) = \frac{hc}{k_B T x_0} = \frac{ahc}{k_B T}, \qquad \text{with} \quad a = x_0^{-1} = 0.201405235\cdots.$$

In particular, from the previous equation we deduce that the product

$$\lambda_{\max}(T)T = \frac{ahc}{k_B}$$

is constant, a result that is known as **Wien's law**.

Note: the frequency $\nu_{\max}(T)$ for which $\rho(\nu, T)$ is maximum for a given temperature T can be computed in the same way, expressing $\rho(\nu, T)$ as

$$\rho(\nu, T) = \frac{c}{4}u(\nu, T) = \frac{2\pi h}{c^2}\frac{\nu^3}{e^{h\nu/k_B T} - 1} = \frac{2\pi}{h^2 c^2}(k_B T)^3 h(x),$$

with

$$x = \frac{h\nu}{k_B T}, \qquad h(x) = \frac{x^3}{e^x - 1}.$$

Proceeding as above we obtain

$$\nu_{\max}(T) = y_0 \frac{k_B T}{h},$$

where

$$y_0 = 2.8214393721 \cdots$$

is the unique maximum of $h(x)$ for $x > 0$, determined by the transcendental equation

$$3(1 - e^{-x}) - x = 0.$$

In particular, the product $\nu_{\max}(T)T$ is again constant. Note, finally, that $\nu_{\max}(T) \neq c/\lambda_{\max}(T)$; indeed,

$$\frac{1}{c}\nu_{\max}(T)\lambda_{\max}(T) = \frac{y_0}{x_0} \simeq 0.568253.$$

---

[a]Strictly speaking, the power per unit wavelength is a function of its arguments (λ, T) different from the function $\rho(\nu, T)$, and should therefore be represented by a different symbol, for instance $\hat{\rho}(\lambda, T)$. Following widespread physical usage, with a slight abuse of notation we shall represent both functions by the same symbol ρ when no possible confusion can arise.

[b]A solution of the latter equation can be easily obtained recursively setting

$$x_{n+1} = 5(1 - e^{-x_n}),$$

with (for instance) $x_1 = 5$. Note that if this sequence converges its limit x must satisfy

$$\lim_{n\to\infty} x_{n+1} = x = 5\lim_{n\to\infty}(1 - e^{-x_n}) = 5(1 - e^{-x}),$$

so that x is the unique solution of the transcendental equation (1.13). Computing the first 5 terms in the sequence we obtain

$$x_2 = 4.96631027, \quad x_3 = 4.96515593, \quad x_4 = 4.96511569, \quad x_5 = 4.96511428, \quad x_6 = 4.96511423, \ldots,$$

which is accurate to 8 decimal places.

1.2 The photoelectric effect. Photons

sec.photoel

In his heuristic derivation of the black body radiation law (1.8), Planck had actually supposed that the energies of the oscillators that made up the enclosure's walls were *quantized* (i.e., took on a discrete set of values proportional to a minimum energy $h\nu$ dependent on the oscillators' frequency ν), and that this caused in turn the quantization of the energy of the Fourier modes of the electromagnetic radiation emitted by the walls. It was Albert Einstein who in 1905 actually imposed the quantization of energy *to the electromagnetic field itself*, postulating that the energy of an electromagnetic wave of frequency ν can only be an integer multiple of $h\nu$, where h is Planck's constant. The minimum energy $h\nu$ carried by an electromagnetic wave of frequency ν was called by Einstein a **quantum** of light. Although the wavelike

nature of light was well established by the end of the nineteenth century from interference and diffraction phenomena, Einstein's hypothesis suggested that light of frequency ν was made up of individual particles of energy $h\nu$ which we now call **photons**[11]. This assumption was in fact supported by his successful explanation of the **photoelectric effect,** which we shall next describe.

A metal is a lattice of atoms that have each lost one or more outer electrons —the so called *conduction electrons*. These electrons, which are able to move freely inside the metal, are responsible for the good electrical and thermal conductivity characteristic of metals. The positively charged ions fixed at the lattice sites in a metal create an electric field that keeps the conduction electrons inside the metal. Thus to extract an electron from the metal it is necessary to provide a certain energy ϕ characteristic of each metal, called the **work function**. At the end of the nineteenth century, it was observed that when a metal is illuminated by ultraviolet light a negative electric charge can be extracted from the metal's surface. It was naturally assumed that this charge was carried by electrons, which had been discovered by J. J. Thomson[12] in 1897. It was also believed that the energy of the emitted electrons should increase with the intensity of the light illuminating the metal. Precise experiments carried by Lennard[13], however, conclusively showed that this is not the case. More precisely, Lennard found that no electrons are ejected from the metal until the frequency reaches a certain threshold (usually in the ultraviolet range). When this threshold is exceeded, the energy of the electrons expelled from the metal (usually called photoelectrons) grows linearly with the frequency. Moreover, the intensity of the light only affects the number of photoelectrons emitted, not their individual energies.

Lennard's experimental findings can be elegantly explained by Einstein's light quanta hypothesis. Indeed, when an electron absorbs a photon of frequency ν its energy increases by $h\nu$, and it cannot therefore leave the metal unless this energy exceeds the work function ϕ. On the other hand, it is extremely unlikely that an electron absorbs more than one photon. Thus the frequency threshold below which no electrons are emitted is clearly ϕ/h. When ν exceeds this threshold[14] the (kinetic) energy E of a photoelectron is simply

$$E = h\nu - \phi, \tag{1.14}$$

`photoeleff`

which indeed increases linearly with ν. Millikan's[15] Chicago experiments in 1914–1916 fully confirmed Einstein's relation (1.14). In fact, the latter equation was used by Millikan to determine the value of h. To this end, when $h\nu > \phi$ an electric current of increasing voltage is applied to the metal plate until no photoelectrons are ejected when the voltage reaches a certain value V (usually referred to as the *retarding potential*). This will be the case when the energy $h\nu - eV$ (where $e > 0$ is the absolute value of the electron's charge) supplied to the electrons exactly matches the work function ϕ, so that

$$h\nu - eV = \phi.$$

---

[11]The name *photon* was coined by the American physical chemist Gilbert N. Lewis (1875–1946) in 1926.

[12]British physicist (1856–1940) and Nobel Prize winner in 1906.

[13]Philipp Lennard (1862–1947), German physicist and Nobel Prize winner in 1905.

[14]In order to trigger the emission of photoelectrons, the frequency ν of the light beam illuminating the metal must thus satisfy the condition

$$h\nu = \frac{hc}{\lambda} > \phi,$$

or in terms of the wavelength

$$\lambda < \frac{hc}{\phi}.$$

Since for most metals ϕ is typically of the order of a few eV, taking, for instance, $\phi \sim 5$ eV $\sim 8 \cdot 10^{-19}$ J we obtain

$$\lambda \lesssim \frac{6.6 \cdot 10^{-34} \cdot 3 \cdot 10^8}{8 \cdot 10^{-19}} \text{ m} \sim 2.5 \cdot 10^{-7} \text{ m} = 250 \text{ nm}.$$

A wavelength of about 250 nm (or less) corresponds to the ultraviolet region of the spectrum, since the wavelength of the visible spectrum extends from about 380 nm (violet) to about 700 nm (red).

[15]Robert Andrews Millikan (1868–1953), American physicist and Nobel Prize winner in 1923.

Repeating the experiment for two values ν_i of the frequency we obtain the linear system

$$h\nu_1 - eV_1 = \phi, \qquad h\nu_2 - eV_2 = \phi$$

which can be used to determine Planck's constant h and the metal's work function ϕ from the equations

$$h = \frac{e(V_1 - V_2)}{\nu_1 - \nu_2}, \qquad \phi = \frac{e(V_1 - V_2)}{\nu_1 - \nu_2}\nu_1 - eV_1 = \frac{e(\nu_2 V_1 - \nu_1 V_2)}{\nu_1 - \nu_2}.$$

In this way Millikan found a value for Planck's constant h in excellent agreement with the value obtained from earlier measurements of black body radiation spectra.

1.3 Compton scattering

c.Compscatt

Einstein's hypothesis of light quanta was further confirmed by the experiments on scattering of X rays (electromagnetic radiation with much shorter wavelength than visible light) by electrons in atoms performed by Compton[16] in 1922–23. Indeed, since the energy of X rays is much greater than the binding energy of electrons in light atoms[17], it is possible to regard the electrons as free particles. Moreover, since X rays are much more energetic than visible or ultraviolet light, photons are not merely absorbed but collide elastically with these electrons. As photons travel at the speed of light c they must have zero rest mass, as otherwise the relativistic relation between energy E, velocity $\mathbf{v}$ and momentum $\mathbf{p}$

$$\mathbf{p} = \frac{m\mathbf{v}}{\sqrt{1 - \frac{\mathbf{v}^2}{c^2}}}$$

would assign photons an infinite momentum. From the relativistic formula

$$E^2 - c^2\mathbf{p}^2 = m^2c^4$$

it follows that the momentum of a photon of frequency ν is

$$\mathbf{p} = \frac{h\nu}{c}\,\mathbf{n},$$

where $\mathbf{n} = \frac{\mathbf{p}}{|\mathbf{p}|}$ is a unit vector in the direction of the photon's velocity. Thus the 4-momentum p of a photon of frequency ν is given by

$$p = \left(\frac{E}{c}, \mathbf{p}\right) = \frac{h\nu}{c}\left(1, \frac{\mathbf{p}}{|\mathbf{p}|}\right).$$

If a photon of frequency ν collides with an electron at rest, conservation of energy-momentum requires that

$$p_\gamma + p_e = p_\gamma' + p_e',$$

where p_γ, p_e denote the initial four-momenta of the photon and the electron, and p_γ', p_e' their final four-momenta. Using the relativistic identity $p \cdot p \equiv p^2 = m^2c^4$, where the dot stands for Minkowski product, we easily obtain the relation

$$m_e^2c^4 = (p_\gamma - p_\gamma' + p_e)^2 = (p_\gamma - p_\gamma')^2 + 2(p_\gamma - p_\gamma') \cdot p_e + m_e^2c^4$$

$$= 2(p_\gamma - p_\gamma') \cdot p_e - 2p_\gamma \cdot p_\gamma' + m_e^2c^4 \implies p_\gamma \cdot p_\gamma' = (p_\gamma - p_\gamma') \cdot p_e,$$

---

[16] Arthur Holly Compton, American physicist (1892-1962) and Noble Prize winner in 1927.

[17] Typically, (hard) X rays have energies of a few keV (i.e., thousands of eV), while the ionization energy of (say) the electron in a hydrogen atom is about 13.6 eV. In terms of wavelengths, for X rays

$$\lambda = \frac{c}{\nu} = \frac{hc}{E} \sim \frac{6.6 \cdot 10^{-34} \cdot 3 \cdot 10^8}{1.6 \cdot 10^{-16}}\,\mathrm{m} \sim \frac{10^{-25}}{10^{-16}}\,\mathrm{m} = 1\,\mathrm{nm},$$

while the visible part of the electromagnetic spectrum starts at wavelengths of about 380 nm.

where m_e denotes the electron's mass. Choosing the x axis along the direction of motion of the incoming photon, and calling θ the photon's scattering angle and ν' the frequency of the scattered photon, we can write

$$p_\gamma = \frac{h\nu}{c}\,(1,1,0,0)\,, \qquad p'_\gamma = \frac{h\nu'}{c}\,(1,\cos\theta,\sin\theta,0), \qquad p_e = (m_e c,0,0,0)\,,$$

and therefore

$$\frac{h^2\nu\nu'}{c^2}(1-\cos\theta) = hm_e(\nu-\nu').$$

Expressed in terms of the wavelengths $\lambda = c/\nu$, $\lambda' = c/\nu'$, the previous identity yields Compton's formula

$$\lambda' - \lambda = \lambda_e(1-\cos\theta), \tag{1.15}$$

`Compton`

where

$$\lambda_e = \frac{h}{m_e c} = 2.42631023867(73)\cdot 10^{-12}\ \text{m} \tag{1.16}$$

`elComp`

is called the electron's **Compton wavelength**. Compton's experiments established the validity of the previous formula, thus lending further support to the existence of photons.

   Although the photoelectric and Compton effects fully supported Einstein's light quanta hypothesis, which amounted to a corpuscular theory of light, for several decades it remained a mystery how this hypothesis could be reconciled with the results of interference and diffraction experiments, all of which supported a wave theory of light. This apparent contradiction could not be satisfactorily explained till the discovery of quantum mechanics in the mid nineteen-twenties, as we shall see in the sequel.

1.4 Bohr's atomic model

`ec.Bohratom`

When an electric current is made to go through a gas like hydrogen or helium, the gas is excited and as a consequence emits light —or, in general, electromagnetic radiation— of characteristic frequencies. The set of these frequencies is called the **emission spectrum** of the gas. These *emission spectra* were intensively studied at the end of the nineteenth century since, as we shall see, they throw considerable light on the fundamental structure of the gas under study at the atomic level. For hydrogen, the wavelengths of the emission spectrum known in the early twentieth century obeyed the simple empiric formula

$$\lambda_n^{-1} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right), \qquad n = 3,4,\dots, \tag{1.17}$$

`Balmer`

where

$$R_H \simeq 1.09677576\cdot 10^7\ \text{m}^{-1}. \tag{1.18}$$

`RyH`

is the so called **Rydberg**[18] **constant**. This set of wavelengths, called the *Balmer series* after the discoverer[19] of Eq. (1.17), is entirely in the visible spectrum, since it is in the range

$$(\lambda_\infty, \lambda_3] = (364.705, 656.47]\ \text{nm}.$$

   By 1911, the experiments carried out by Rutherford[20], Geiger[21] and Marsden[22] had conclusively established that atoms consisted of a positively charged nucleus around which orbited the negatively charged electrons, bound to the nucleus by their mutual electromagnetic attraction. For example, in the case of

---

[18]Johannes Robert Rydberg (1854–1919), Swedish physicist.

[19]Johann Jakob Balmer (1825–1898), Swiss mathematician.

[20]Ernest Rutherford (1871–1937), British physicist and Nobel Prize winner in Chemistry in 1908.

[21]Hans Wilhelm Geiger (1882–1945), German physicist.

[22]Sir Ernest Marsden (19 February 1889–1970), British physicist.

hydrogen there is a single electron of charge $-e$ orbiting around the nucleus with charge $e > 0$, so that the interaction potential binding the electron to the nucleus is the Coulomb one:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}.$$

In the SI unit system the constant ε_0 appearing in the previous formula, called the *vacuum permittivity*, has the value[23]

$$\varepsilon_0 = 8.8541878128(13) \cdot 10^{-12} \mathrm{F\,m}^{-1}.$$

According to a standard result in classical electrodynamics, a particle (in this case, the electron) moving along a circular orbit with frequency ν will emit electromagnetic radiation of the same frequency ν. It could be thought that this radiation accounts for the emission spectrum of hydrogen detected experimentally. This explanation is however unsatisfactory, since classically the frequency of the electron's orbital motion, and hence of the radiation emitted by it, could be *any* positive number. More importantly, the classical model of the atom described above is clearly inconsistent, since the fact that the orbiting electron must radiate electromagnetic energy implies that it is steadily losing energy. Since the radius a of a circular orbit (or, more generally, the major semiaxis of an elliptic orbit) in the Coulomb potential is related to its energy by the formula

$$E = -\frac{e^2}{8\pi\varepsilon_0 a} < 0,$$

a decrease of the electron's energy (i.e., an *increase* in $|E|$) implies a decrease in the radius of its orbit. In other words, classical electrodynamics predicts that the electron in the hydrogen atom will fall onto the nucleus following a spiral trajectory. The time τ taken by the electron to fall into the nucleus —i.e., the classical lifetime of a hydrogen atom— can also be computed combining classical electrodynamics with classical mechanics, with the result

$$\tau = \frac{4c^3\pi^2\varepsilon_0^2 m_e^2 r_0^3}{e^4}, \tag{1.19} \quad \boxed{\text{Hlifet}}$$

where r_0 is the electron's initial distance to the nucleus. Taking r_0 as what is nowadays called the **Bohr radius** of the atom, namely

$$r_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} \simeq 5.29177210903(80) \cdot 10^{-11} \ \mathrm{m},$$

we obtain the estimate

$$\tau = \frac{4c^3 h^6 \varepsilon_0^5}{\pi m_e e^{10}} \simeq 1.55618 \cdot 10^{-11} \ \mathrm{s}.$$

Thus Rutherford's atomic model is *inconsistent*, since it predicts that hydrogen should disintegrate in a very short time.

Exercise 1.2. Prove Eq. (1.19) using *Larmor's[a] formula* for the power P radiated by a charge q moving with an acceleration a:

$$P = \frac{q^2 a^2}{6\pi\varepsilon_0 c^3}.$$

Solution. When the electron moves along a circular orbit of radius r, its acceleration and energy are respectively given by

$$a = \frac{F}{m_e} = \frac{e^2}{4\pi\varepsilon_0 m_e r^2}, \qquad E = -\frac{e^2}{8\pi\varepsilon_0 r}.$$

By energy conservation, the power P radiated by the electron must equal the rate $-\frac{\mathrm{d}E}{\mathrm{d}t}$ at which the

---

[23]The Farad (abbreviated F) is the unit of capacitance, and has dimensions of $\mathrm{kg}^{-1}\mathrm{m}^{-2}\mathrm{s}^4\mathrm{A}^2$.

electron loses its mechanical energy. We thus obtain the differential equation

$$-\frac{dE}{dt} = -\frac{e^2}{8\pi\varepsilon_0 r^2}\frac{dr}{dt} = \frac{e^2 a^2}{6\pi\varepsilon_0 c^3} = \frac{e^6}{96\pi^3\varepsilon_0^3 m_e^2 c^3 r^4} \implies \frac{dt}{dr} = -\frac{12\pi^2\varepsilon_0^2 m_e^2 c^3}{e^4}r^2.$$

Integrating between $r = r_0$ for $t = 0$ and $r = 0$ for $t = \tau$ we obtain

$$\tau = \frac{12\pi^2\varepsilon_0^2 m_e^2 c^3}{e^4}\int_0^{r_0} r^2\,dr = \frac{4\pi^2\varepsilon_0^2 m_e^2 c^3 r_0^3}{e^4},$$

as claimed.

---

[a]Sir Joseph Larmor (1857–1942), Irish physicist.

In 1913, Bohr[24] developed a heuristic model of the atom which addressed the deficiencies of the Rutherford model mentioned above. Bohr realized that the fact that the frequencies in the emission spectrum of hydrogen and other gases were *quantized* (i.e., formed discrete sequences like the Balmer series for hydrogen) suggested that the frequencies, and therefore the radii, of the circular orbits of electrons in atoms should also be quantized. In other words, electrons could only orbit around the nucleus along circular orbits whose radii belonged to a certain discrete set $\{r_n : n = 1, 2, \dots\}$. For a *hydrogen-like* (ionized) *atom*, consisting of a nucleus of charge Ze and a single electron, the energy of the electron along one of these allowed orbits of radius r_n is

$$E_n = -\frac{kZe^2}{2r_n}, \qquad n = 1, 2, \dots, \tag{1.20}$$ `EnBohr`

where

$$k := \frac{1}{4\pi\varepsilon_0}.$$

Thus the quantization of the radius of circular orbits leads to the quantization of the electron's energy. To avoid the instability problem of Rutherford's model of the atom, Bohr further postulated that these allowed circular orbits were *stable*, i.e., that when the electron moved along them it *did not radiate*. Emission of light —or, in general, of electromagnetic radiation— occurred instead when the electron fell from one of these stable orbits of radius r_n and energy E_n to a less energetic orbit of radius $r_l < r_n$ and energy $E_l < E_n$. More precisely, following Einstein's hypothesis of light quanta, Bohr assumed that in the transition from the orbit of energy E_n to the orbit of energy E_l the atom emitted a photon of energy $E_n - E_l$ and frequency

$$\nu_{n\to l} = \frac{E_n - E_l}{h} = \frac{kZe^2}{2h}\left(\frac{1}{r_l} - \frac{1}{r_n}\right). \tag{1.21}$$ `nunl`

To determine the radii r_k of the allowed circular orbits, Bohr observed that Planck's constant h has the same dimensions as an angular momentum, which lead him to hypothesize that the angular momentum of the electron's allowed circular orbits must be an integer multiple of an elementary angular momentum $\hbar$ expected to be proportional to h. In other words, the electron's allowed angular momenta are

$$L_n = n\hbar, \qquad n = 1, 2, \dots. \tag{1.22}$$ `LnBohr`

The above relation is easily transformed into a formula for the radii of the stable circular orbits by noting that the electron's centripetal acceleration along a circular orbit of radius r is given by

$$a_r = \frac{v^2}{r} = \frac{kZe^2}{m_e r^2},$$

---

[24]Niels Bohr (1885–1962), Danish physicist and Nobel Prize winner in 1922.

and therefore

$$v^2 = \frac{kZe^2}{m_e r}.$$

We thus have

$$L_n^2 = n^2\hbar^2 = m_e^2 v^2 r_n^2 = m_e^2 \frac{kZe^2}{m_e r_n} r_n^2 = kZe^2 m_e r_n.$$

The radii of the stable orbits in Bohr's atom are therefore

$$r_n = \frac{n^2\hbar^2}{kZe^2 m_e}, \qquad n = 1, 2, \dots,$$

(1.23)   `rnBohr`

whose corresponding energies are obtained from Eq. (1.20):

$$E_n = -\frac{k^2 m_e Z^2 e^4}{2n^2\hbar^2}, \qquad n = 1, 2, \dots.$$

(1.24)   `EnBohrfinal`

The wavelength of the photon emitted by the atom in the transition $E_n \to E_l$ (where $n > l$) is computed combining Eqs. (1.21) and (1.23), namely

$$\frac{1}{\lambda_{n\to l}} = \frac{\nu_{l\to n}}{c} = R_\infty Z^2 \left(\frac{1}{l^2} - \frac{1}{n^2}\right), \qquad n > l,$$

(1.25)   `laBohr`

where

$$R_\infty = \frac{k^2 m_e e^4}{2ch\hbar^2}.$$

(1.26)   `Ryinfhh`

Equation (1.26) determines the emission spectrum of hydrogen-like atoms in terms of the unknown constant $\hbar$. To compute this constant Bohr applied what he called the **correspondence principle**, according to which the predictions of the new quantum theory should coincide with the classical results for large quantum numbers. Indeed, when $n \to \infty$ the quotient

$$\frac{E_{n+1} - E_n}{|E_n|} = 1 - \frac{E_{n+1}}{E_n} = 1 - \frac{n^2}{(n+1)^2} = \frac{2n+1}{(n+1)^2} \simeq \frac{2}{n}$$

tends to zero, and thus the energies are virtually continuous. In this case, according to classical electrodynamics the frequency of the electromagnetic radiation emitted by the atom should coincide with the frequency of the electron's motion, which for a circular orbit of radius r_n can be easily computed from the law of areas and Eqs. (1.22)-(1.23):

$$\frac{L_n}{2m_e \nu_n} = \pi r_n^2 \implies \nu_n = \frac{L_n}{2\pi m_e r_n^2} = \frac{n\hbar}{2\pi m_e} \frac{k^2 Z^2 e^4 m_e^2}{n^4\hbar^4} = \frac{k^2 Z^2 e^4 m_e}{2\pi n^3\hbar^3} = \frac{cR_\infty Z^2}{\pi n^3} \frac{h}{\hbar}.$$

According to Bohr's correspondence principle, this frequency should coincide with the frequency $\nu_{n+1\to n}$ of the photon emitted by the ion in the transition from the n-th to the $(n-1)$-th energy level, given by

$$\nu_{n\to n-1} = cR_\infty Z^2 \left(\frac{1}{(n-1)^2} - \frac{1}{n^2}\right) = cR_\infty Z^2 \frac{2n-1}{n^2(n-1)^2} \simeq \frac{2cR_\infty Z^2}{n^3}.$$

Imposing that $\nu_{n\to n-1} = \nu_n$ we deduce that the unknown constant $\hbar$, nowadays called the **reduced Planck constant**, is given by

$$\hbar = \frac{h}{2\pi}.$$

(1.27)   `hbar`

From this equation we obtain the following explicit expression for the Rydberg constant R_∞:

$$R_\infty = \frac{k^2 m_e e^4}{4\pi\hbar^3 c} = \frac{m_e e^4}{64\pi^3 \varepsilon_0^2 \hbar^3 c} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \simeq 1.0973731568160(21) \cdot 10^7 \text{ m}^{-1}. \qquad (1.28) \quad \boxed{\text{Ryinf}}$$

In the special case $Z = 1$ and $l = 2$ Eqs. (1.25)-(1.28) yield the Balmer series (1.17) with $\lambda_n = \lambda_{n\to 2}$, together with the value $R_H = R_\infty$ for the empiric constant R_H. We thus see that the n-th wavelength in the Balmer series correspond to the transition of the electron from the n-th allowed orbit to the second one. Moreover, Bohr's formula (1.25) predicts the existence of other spectral series corresponding to $l = 1, 3, 4$, etc. In fact, the spectral series for $l = 1, 3, 4, 5$ (the so called Lyman, Paschen, Brackett and Pfund series) were discovered shortly after Bohr proposed his atomic model, lending it strong experimental support. Further confirmation of the existence of quantized energy levels in atomic spectra came from the experiment with vapor of mercury performed in 1914 by Franck[25] and Hertz[26], who offered compelling evidence of the existence of a gap of 4.9eV between the first excited state and the ground state of mercury.

Remark 1. According to Eqs. (1.23)-(1.24), the *ground state* —i.e., the state of *minimum* energy— of the hydrogen atom corresponds to the circular orbit of minimum radius

$$r_1 = \frac{\hbar^2}{k e^2 m_e} = \frac{4\pi\varepsilon_0 \hbar^2}{e^2 m_e} = \frac{\varepsilon_0 h^2}{\pi e^2 m_e}, \qquad (1.29) \quad \boxed{\text{Bohrrad}}$$

called the **Bohr radius**. The ground state energy of the hydrogen atom is

$$E_1 = -\frac{k^2 m_e e^4}{2\hbar^2} = -\frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \simeq -13.6057 \text{ eV}. \qquad (1.30) \quad \boxed{\text{GSHyd}}$$

This is also the electron's *binding energy* or *ionization energy* of the hydrogen atom, i.e., the energy needed to remove the electron from the atom. ∎

Remark 2. The small discrepancy between the values of R_∞ and R_H is due to the fact that in the argument leading to Eqs. (1.25)-(1.28) we ignored the motion of the nucleus, or equivalently regarded its mass as infinite. To take into account the finite value of the mass of the nucleus we should replace in the equations derived above the mass of the electron by the *reduced mass* of the electron-nucleus system. For hydrogen, this reduced mass is given by

$$\mu = \frac{m_e m_p}{m_e + m_p} = \left(1 + \frac{m_e}{m_p}\right)^{-1} m_e \simeq 0.999456 \, m_e,$$

where m_p is the proton's mass. The Rydberg constant for hydrogen is therefore

$$R_H = \left(1 + \frac{m_e}{m_p}\right)^{-1} R_\infty \simeq 1.09677583 \cdot 10^7 \text{ m}^{-1},$$

in excellent agreement with Eq. (1.18). ∎

Remark 3. In the previous deductions we have regarded the electron as non-relativistic. This is consistent for light hydrogen-like atoms ($Z \ll 100$, say), since for the electron in the n-th atomic orbital we have

$$\frac{v^2}{c^2} = \frac{kZe^2}{m_e c^2 r_n} = \frac{kZe^2}{m_e c^2} \frac{kZe^2 m_e}{n^2 \hbar^2} = \frac{\alpha^2 Z^2}{n^2} \implies \frac{v}{c} = \frac{\alpha Z}{n} \leqslant \alpha Z,$$

---

[25]James Franck (1882–1964), German physicist and Nobel prize winner in 1925.
[26]Gustav Hertz (1887–1975), German physicist and Nobel prize winner in 1925.

where

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{e^2}{2\varepsilon_0 h c} \simeq 7.2973525693(11) \cdot 10^{-3} \qquad (1.31)$$

`finestcons`

is the **fine structure constant**[27]. ∎

In the previous discussion of hydrogen-like atoms we assumed for simplicity's sake (as originally done by Bohr himself) that the electron was moving along a *circular* orbit. Bohr's quantization rule (1.22) has to be modified for the more general case of motion along an elliptic orbit. In 1915–16 Sommerfeld[28], Wilson[29] and Ishiwara[30] independently proposed a generalization of Bohr's quantization of angular momentum for hydrogen-like atoms to conservative N-dimensional multi-periodic Hamiltonian systems admitting action-angle variables. Roughly speaking, this means that there is a set of generalized coordinates $(q_1, \ldots, q_N)$ with corresponding canonical momenta $(p_1, \ldots, p_N)$ such that along any trajectory of the system each canonical momentum p_i is a function of the corresponding generalized coordinate q_i alone, and the motion in the (q_i, p_i) plane is periodic[31]. The Sommerfeld–Wilson–Ishiwara (SWI) general quantization rules[32] read

$$\oint p_i \, \mathrm{d}q_i = n_i h, \qquad 1 \leqslant i \leqslant N, \qquad (1.32)$$

`SWIquant`

where n_i is a non-negative integer for all i and the integrals are extended along a period of the motion in the (q_i, p_i) plane. For a hydrogen-like atom the Lagrangian governing the electron's motion in polar coordinates (r, φ) can be taken as

$$\mathcal{L} = \frac{1}{2} m_e (\dot{r}^2 + r^2 \dot{\varphi}^2) + \frac{kZe^2}{r}.$$

The canonical momenta are therefore

$$p_r = m_e \dot{r}, \qquad p_\varphi = m_e r^2 \dot{\varphi},$$

and the Hamiltonian is the total energy expressed in terms of the canonical momenta:

$$H = \frac{1}{2m_e} \left(p_r^2 + \frac{p_\varphi^2}{r^2} \right) - \frac{kZe^2}{r}.$$

Note that Hamilton's equation of motion for p_φ is

$$\dot{p}_\varphi = -\frac{\partial H}{\partial \varphi} = 0,$$

and thus p_φ is conserved. In fact, p_φ is equal to the angular momentum L. The Sommerfeld–Wilson–Ishiwara quantization rules are in this case

$$\oint p_r \, \mathrm{d}r = n_r h, \qquad \oint p_\varphi \, \mathrm{d}\varphi = n_\varphi h. \qquad (1.33)$$

`AAvarcentra`

---

[27] The value of the fine structure constant is very close to 1/137.

[28] Arnold Sommerfeld (1868–1951), British physicist.

[29] William Wilson (1875–1965), British physicist.

[30] Jun Ishiwara (1881–1947), Japanese physicist

[31] More precisely, either the projection of the orbit to the (q_i, p_i) plane is a closed curve (*libration*) or p_i is a periodic function of q_i (*rotation*). See, e.g., H. Goldstein, *Classical Mechanics*, 2nd ed. (Addison Wesley, 1980), p. 463.

[32] Also known as Bohr–Sommerfeld, or Sommerfeld–Wilson, quantization rules.

The system is multi-separable, since p_φ is constant and from the energy equation

$$\frac{1}{2m_e}\left(p_r^2 + \frac{L^2}{r^2}\right) - \frac{kZe^2}{r} = E$$

we deduce that

$$p_r = \pm\sqrt{2m_e\left(E + \frac{kZe^2}{r}\right) - \frac{L^2}{r^2}}$$

is a function of r alone. If we parametrize the orbits with the angle φ, the line integrals become ordinary integrals over the interval $[0, 2\pi]$ (since the angle φ goes from 0 to 2π in a period of the motion). In particular, the last equation (1.33) becomes

$$p_\varphi \int_0^{2\pi} \mathrm{d}\varphi = 2\pi p_\varphi = 2\pi L = n_\varphi h \quad\Longrightarrow\quad L = n_\varphi \hbar,$$

so that angular momentum is quantized as in Bohr's original theory. On the other hand, the quantization condition for the variables (r, p_r) can be written as

$$\int_0^{2\pi} p_r \frac{\mathrm{d}r}{\mathrm{d}\varphi}\,\mathrm{d}\varphi = n_r h, \tag{1.34}$$ `rprSWI`

where it is understood that p_φ and r should be expressed in terms of φ. Note than in circular orbits $p_r = m_e\dot{r} = 0$ implies that $n_r = 0$. Taking into account that

$$p_r = m_e\dot{r} = m_e\frac{\mathrm{d}r}{\mathrm{d}\varphi}\dot{\varphi} = \frac{L}{r^2}\frac{\mathrm{d}r}{\mathrm{d}\varphi} = \frac{n_\varphi\hbar}{r^2}\frac{\mathrm{d}r}{\mathrm{d}\varphi},$$

the quantization rule (1.34) becomes

$$\int_0^{2\pi}\left(\frac{1}{r}\frac{\mathrm{d}r}{\mathrm{d}\varphi}\right)^2 \mathrm{d}\varphi = 2\pi\frac{n_r}{n_\varphi}. \tag{1.35}$$ `rprSWI2`

The equation of the classical orbits is

$$r = \gamma(1 + \varepsilon\cos\varphi)^{-1},$$

where

$$\gamma = \frac{L^2}{km_eZe^2} = \frac{n_\varphi^2\hbar^2}{km_eZe^2},$$

ε is the eccentricity of the orbit,

$$\varepsilon = \sqrt{1 - \frac{b^2}{a^2}} = \sqrt{1 + \frac{2EL^2}{k^2m_eZ^2e^4}} = \sqrt{1 + \frac{2En_\varphi^2\hbar^2}{k^2m_eZ^2e^4}},$$

and a and b are respectively its major and minor semiaxes. From these equations we obtain

$$\frac{1}{r}\frac{\mathrm{d}r}{\mathrm{d}\varphi} = \frac{\varepsilon\sin\varphi}{1 + \varepsilon\cos\varphi} \quad\Longrightarrow\quad \int_0^{2\pi}\frac{\varepsilon^2\sin^2\varphi}{(1 + \varepsilon\cos\varphi)^2}\,\mathrm{d}\varphi = 2\pi\left(\frac{1}{\sqrt{1 - \varepsilon^2}} - 1\right) = 2\pi\frac{n_r}{n_\varphi},$$

and therefore

$$1 - \varepsilon^2 = \frac{b^2}{a^2} = \frac{n_\varphi^2}{(n_r + n_\varphi)^2} \quad\Longrightarrow\quad \frac{a}{b} = 1 + \frac{n_r}{n_\varphi}, \tag{1.36}$$ `baSWI`

$$E = -\frac{k^2m_e^2Z^2e^4}{2n_\varphi^2\hbar^2}(1 - \varepsilon^2) = -\frac{k^2m_e^2Z^2e^4}{2(n_\varphi + n_r)^2\hbar^2}. \tag{1.37}$$ `ESWI`

We thus obtain the same equation for the allowed energies as with Bohr's original approach, together with the relation $n = n_\varphi + n_r$ between the quantum numbers n, n_φ and n_r. In particular, $n = n_\varphi$ only for $n_r = 0$, i.e., when the electron moves along a circular orbit. From the classical formula relating the energy of an elliptical orbit with its major semiaxis,

$$E = -\frac{kZe^2}{2a},$$

we deduce the following quantization rules for the semiaxes a and b of an arbitrary elliptic orbit:

$$a = (n_\varphi + n_r)^2 \frac{r_1}{Z}, \qquad b = n_\varphi(n_\varphi + n_r) \frac{r_1}{Z},$$

where r_1 denotes the Bohr radius (1.29). The ground state energy is obtained when $n_r = 0$ and $n_\varphi = 1$, i.e., when the electron moves along a circular orbit of radius r_1/Z. This, of course, coincides with the prediction obtained from Bohr's original quantization procedure. Note also that from Eq. (1.37) it follows that the n-th energy level is n times degenerate, since for a fixed natural number n the possible values of the quantum number n_φ are $1, \ldots, n$ (and for each of these values $n_r = n - n_\varphi$). ∎

`exa.SWI`

Example 1.1. *SWI quantization of one-dimensional systems.*

The SWI quantization method is particularly simple to apply to one-dimensional systems. Indeed, in Cartesian coordinates we have

$$H = \frac{p^2}{2m} + V(x), \qquad p = m\dot{x},$$

where the last equation follows directly from Hamilton's equation of motion of the coordinate x. For a periodic orbit of energy E with turning points $x_{1,2}$, we have

$$\oint p\,dx = 2\int_{x_1}^{x_2} p(x)\,dx = 2\sqrt{2m}\int_{x_1}^{x_2} \sqrt{E - V(x)}\,dx = nh, \qquad (1.38)$$ `SWI1d`

where the last equality follows form the energy equation

$$\frac{p^2}{2m} + V(x) = E.$$

Applying Green's theorem to the trajectory $H(x, p) = E$ in phase space we obtain the alternative formula

$$\int_{H(x,p) \leqslant E} dx\,dp = nh, \qquad (1.39)$$ `SWI1darea`

where the double integral is extended to the interior of the curve $H(x, p) = E$.

For example, for the *harmonic oscillator* we have

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2,$$

and the orbits $H(x, p) = E$ in phase space are ellipses with semiaxes

$$\sqrt{2mE}, \quad \sqrt{\frac{2E}{m\omega^2}}.$$

From Eq. (1.39) we therefore get the quantization condition

$$\pi\sqrt{2mE}\sqrt{\frac{2E}{m\omega^2}} = 2\pi\frac{E}{\omega} = nh \quad \Longleftrightarrow \quad E = n\hbar\omega, \qquad n = 0, 1, \ldots. \qquad (1.40)$$ `HOspecSWI`

Incidentally, this formula for the allowed energies of a harmonic oscillator provides a theoretical justification of Planck's derivation of the black body radiation formula (1.8) which originated quantum mechanics. We shall see in the next chapters that Eq. (1.40) actually differs by a constant energy $\hbar\omega/2$ from the correct formula for the energy levels of a quantum harmonic oscillator. In particular, the ground state energy of a quantum harmonic oscillator is $\hbar\omega/2$ instead of 0.

Likewise, for a particle in a box of length L we can formally take $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ for $x \leqslant 0$ or $x \geqslant L$. Inside the box the Hamiltonian is simply

$$H = \frac{p^2}{2m},$$

and the energy equation reads

$$E = \frac{p^2}{2m}.$$

Hence the SWI quantization condition is in this case

$$2\int_0^L p\,\mathrm{d}x = 2\sqrt{2mE}\int_0^L \mathrm{d}x = 2L\sqrt{2mE} = nh \quad\Longrightarrow\quad E = \frac{n^2h^2}{8mL^2}, \qquad n = 0, 1, \dots.$$

We shall again see in the sequel that the above formula coincides with the result derived using modern quantum mechanics, except that the value $n = 0$ must be excluded. In other words, the ground state energy is $h^2/(8mL^2)$ instead of 0.

Bohr's model of the atom, and the more general quantization scheme of Sommerfeld, Wilson and Ishiwara, is the core of what is often referred to as the *Old Quantum Theory*. Although this theory was undeniably successful in explaining the emission spectrum of simple systems like the hydrogen atom, and was widely accepted by 1916, it was however plagued by several fundamental flaws. For instance:

- The theory is not able to predict correctly the degeneracy of the energy levels of atoms, which can be experimentally verified by exposing them to external electric and magnetic fields causing the splitting of the spectral lines.

- In fact, the SWI quantization rule only applies to a very restricted class of Hamiltonian systems admitting action-angle variables with multi-periodic orbits, and is thus unable to deal even with relatively simple systems like the helium atom. In particular, it cannot quantitatively explain the quantization of atomic energy levels in the Franck–Hertz experiment.

- The theory is clearly inconsistent with the classical concept of a continuous trajectory, which only applies when the electron moves along an allowed orbit but must be abandoned when it "jumps" discontinuously from one allowed orbit to another.

- Much more importantly, the main hypotheses on which Bohr's atomic model is based, namely that electrons in atoms can only move along a discrete set of stable orbits, and that they do not radiate electromagnetic energy while they move but only when they jump from one stable orbit to another, were completely *ad hoc assumptions* for which no justification was provided.

1.5 De Broglie's matter waves

c.deBroglie

As explained in Section 1.2, although since the development of modern electromagnetic theory by Maxwell light had long been thought to have a wave-like nature, experiments like the photoelectric effects uncovered a dual particle-like behavior. In his 1923 Ph. D. thesis, de Broglie[33] speculated that

---

[33]Louis de Broglie (1892–1987), French physicist and Nobel Prize winner in 1929.

matter could also exhibit this dual particle-wave nature. De Broglie noted that, since photons of frequency ν are massless particles with energy $E = h\nu$, from the relativistic relation $E^2 = p^2c^2 + m^2c^4$ the magnitude $p \equiv |\mathbf{p}|$ of their three-momentum should be given by

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda},$$

where $\lambda = c/\nu$ is the wavelength. De Broglie then went on to postulate that *a material particle with three momentum p should have an associated wave of wavelength λ given by the previous formula,* namely

$$\lambda = \frac{h}{p}. \tag{1.41}$$

dBwavel

This wavelength is nowadays called the particle's **de Broglie wavelength**. From equation (1.41) we obtain the relation

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

where $k \equiv |\mathbf{k}|$ is the magnitude of the wave vector. It is therefore natural to assume that the relation between the particle's (relativistic) three momentum $\mathbf{p}$ and the wave vector $\mathbf{k}$ is given by the formula

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar}. \tag{1.42}$$

bpbk

De Broglie further assumed that the relation between the energy and the frequency of a photon, given by Einstein's equation

$$E = h\nu = \hbar\omega,$$

where $\omega = 2\pi\nu$ is the circular frequency, also holds for material particles. Since the energy of a free particle with three-momentum $\mathbf{p}$ is given by

$$E = c\sqrt{p^2 + m^2c^2} = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = mc^2 + \frac{p^2}{2m} + O\left(\frac{p^4}{m^3c^2}\right), \tag{1.43}$$

Erel

in the non-relativistic limit $p \ll mc$ the particle's energy (disregarding the zero point energy mc^2, which plays no role in non-relativistic physics) should be related to the circular frequency ω of the associated wave by the formula

$$\omega = \frac{p^2}{2m\hbar}. \tag{1.44}$$

dBom

Combining the previous formulas we obtain the following equation for the amplitude of the (complex) **matter wave** associated to a free material particle of mass m and three-momentum $\mathbf{p}$:

$$\Psi(\mathbf{r}, t) = A\exp\left[\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t\right)\right], \tag{1.45}$$

dBwave

with A a complex constant and

$$E(\mathbf{p}) = \frac{p^2}{2m}.$$

Note that the **phase velocity** (i.e., the velocity of propagation of the planes of constant phase) of the plane wave (1.45) is simply

$$v_\varphi = \frac{E(\mathbf{p})}{p} = \frac{p}{2m},$$

i.e., *half* the particle's velocity. On the other hand, if instead of a pure wave with well-defined frequency we consider a **wave packet**[34]

$$\Psi(\mathbf{r}, t) = \int d^3p \, A(\mathbf{p}) \exp\left(\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{r} - E(\mathbf{p})t)\right), \tag{1.46}$$

<div style="text-align:right">`wavepack`</div>

with $A(\mathbf{p})$ (assumed to be real, for simplicity) sharply peaked at a momentum $\mathbf{p} = \mathbf{p}_0$, expanding $E(\mathbf{p})$ around $\mathbf{p} = \mathbf{p}_0$ we obtain

$$\mathbf{p} \cdot \mathbf{r} - E(\mathbf{p})t \simeq \mathbf{p} \cdot \mathbf{r} - \left[E(\mathbf{p}_0) + \nabla E(\mathbf{p}_0) \cdot (\mathbf{p} - \mathbf{p}_0)\right]t = \mathbf{p} \cdot \left(\mathbf{r} - \nabla E(\mathbf{p}_0)t\right) + t\left(\nabla E(\mathbf{p}_0) \cdot \mathbf{p}_0 - E(\mathbf{p}_0)\right),$$

and therefore

$$\Psi(\mathbf{r}, t) \simeq \exp\left[\frac{it}{\hbar}\left(\nabla E(\mathbf{p}_0) \cdot \mathbf{p}_0 - E(\mathbf{p}_0)\right)\right] \int d^3p \, A(\mathbf{p}) \exp\left(\frac{i\mathbf{p}}{\hbar}\left(\mathbf{r} - \nabla E(\mathbf{p}_0)t\right)\right)$$

$$\implies |\Psi(\mathbf{r}, t)| \simeq \left|\int d^3p \, A(\mathbf{p}) \exp\left(\frac{i\mathbf{p}}{\hbar}\left(\mathbf{r} - \nabla E(\mathbf{p}_0)t\right)\right)\right|.$$

Since the *intensity* $|\Psi(\mathbf{r}, t)|^2$ of the wave packet (1.46) is (approximately) a function of $\mathbf{r}$ and t through the linear combination

$$\mathbf{r} - \nabla E(\mathbf{p}_0)t,$$

if (for instance) the wave packet is concentrated at a point $\mathbf{r}_0$ at $t = 0$ it will be concentrated at the point

$$\mathbf{r}(t) = \mathbf{r}_0 + \nabla E(\mathbf{p}_0)t \tag{1.47}$$

<div style="text-align:right">`r0wp`</div>

at any other time t. Thus the peak of the wave packet, located at $\mathbf{r}(t)$ at time t, moves with a velocity

$$\boxed{\mathbf{v}_g = \nabla E(\mathbf{p}_0) = \frac{\mathbf{p}_0}{m}}$$

called the wave packet's **group velocity**. Remarkably, this velocity coincides with the velocity of the material particle associated to the wave packet. In fact, this is also true if we use the relativistic formula (1.43) for the energy, since in this case

$$\nabla E(\mathbf{p}) = \frac{c\mathbf{p}}{\sqrt{p^2 + m^2c^2}} = \frac{c^2\mathbf{p}}{E},$$

where the right-hand side is the well-known relativistic formula for the velocity in terms of the energy and three-momentum.

The equality between the particle velocity $\mathbf{v}$ and the group velocity $\mathbf{v}_g$ of the associated wave packet (1.46) lends some support to de Broglie's hypothesis of the existence of matter waves. Further theoretical confirmation of this hypothesis comes from the fact that Bohr's quantization rule (1.22) for the angular momentum an electron in a hydrogen-like atom moving along a circular orbit can be recast as follows:

$$L_n = pr = \frac{rh}{\lambda} = \frac{nh}{2\pi} \iff n\lambda = 2\pi r, \tag{1.48}$$

<div style="text-align:right">`deBBohr`</div>

where r is the radius of the orbit and p is the electron's momentum. We thus see that Bohr's rule for the quantization of angular momentum is equivalent to imposing that the circumference of an allowed orbit contain an *exact* number of de Broglie wavelengths. Equation (1.48), which is strongly reminiscent of the condition for *standing waves* in a vibrating string with both ends clamped, provides an elegant theoretical explanation of the possible origin of Bohr's quantization hypothesis.

---

[34] In what follows we shall often omit the integration range when it coincides with the whole domain of the integration variable (in this case, $\mathbb{R}^3$).

According to a widespread anecdote, when de Broglie was asked during his Ph. D. thesis defense how could the existence of matter waves be experimentally ascertained, he answered that it should be possible under appropriate conditions to observe diffraction phenomena involving matter waves, just as for ordinary (electromagnetic) waves. More precisely, de Broglie suggested to analyze the diffraction of electron waves by crystals, analogous to the diffraction of X-rays well known at the time. Since the typical distance between atoms in a crystal is of the order of 10^{-10} m $= 1$ Å, the electrons' de Broglie wavelength λ should be of the same order of magnitude for diffraction phenomena to be observable. On the other hand, according to de Broglie's formula (1.41), the de Broglie wavelength of a non-relativistic electron (i.e., an electron with kinetic energy $E \ll m_e c^2$) is given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E}} = \frac{h}{\sqrt{2m_e \frac{E}{1\text{eV}} \cdot 1\text{eV}}} = \frac{12.2643 \text{ Å}}{\sqrt{E/1\text{eV}}}. \tag{1.49}$$

<div style="text-align:right">`elwavel`</div>

Thus, to obtain de Broglie wavelengths of the order of 1 Å the electron's energy should be of the order of 100 eV. (By comparison, X-rays have wavelengths between approximately 0.1 Å and 100 Å, or energies between approximately 100 eV and 100 keV.) The experiment suggested by de Broglie was carried out in 1927 by Davisson[35] and Germer[36], who indeed found that electrons scattered by a single crystal of nickel gave rise to a diffraction pattern similar to that observed in X-ray diffraction. More precisely, for any wave of wavelength λ scattered by a crystal with interatomic distance d, reflection is enhanced when the angle θ between the direction of propagation of the incident and reflected waves takes certain values θ_n (with $n \in \mathbb{N}$) determined by Bragg's formula

$$n\lambda = 2d \cos(\theta_n/2), \qquad n = 1, 2, \dots .$$

Davisson and Germer used a beam of electrons of energy $E = 54$ eV, and found that the first angle for which reflection was enhanced was $\theta_1 = 50°$. Since $d = 0.92$ Å for nickel, using Bragg's formula with $n = 1$ we obtain the following value for the wavelength of the electron's matter wave:

$$\lambda = 2 \cdot 0.92 \cdot 0.906308 \cdots \text{ Å} \simeq 1.6676 \text{ Å},$$

in excellent agreement with the value

$$\lambda = \frac{12.2643 \text{ Å}}{\sqrt{54}} \simeq 1.66896 \text{ Å}$$

computed from de Broglie's formula (1.49). A similar experiment performed by G. P. Thomson[37] in 1928 confirmed Davisson and Germer's result, thus conclusively establishing the existence of the matter waves postulated by de Broglie.

Remark. The relation between the de Broglie wavelength of an electron and the wavelength of a photon of the same energy E is given by

$$\frac{\lambda_e}{\lambda_\gamma} = \frac{h/\sqrt{2m_e E}}{hc/E} = \sqrt{\frac{E}{2m_e c^2}}.$$

Since $2m_e c^2 \sim 1$ MeV, for (non-relativistic) energies in the range 10 eV to 10 keV this quotient is at most 10^{-1}. This is the idea behind the *electron microscope*, able to achieve much greater resolutions than an ordinary (optical) microscope using photons of the same energy. ∎

`pref`

---

[35]Clinton Davisson (1881–1958), American physicist and Nobel Prize winner in 1937.
[36]Lester Germer (1896–1971), American physicist and Nobel Prize winner in 1937.
[37]Sir George Paget Thomson (1892–1975), British physicist and Nobel Prize winner in 1937.

exe.wp

Exercise 1.3. Consider a one-dimensional wave packet of the form

$$\Psi(x,t) = \int \mathrm{d}p A(p) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(px - E(p)t\right)},$$

where $\left|A(p)\right|$ is slowly varying and concentrated on an interval of width Δp centered at $p = p_0$.

 i) Find the coordinate x_m of the maximum of $\left|\Psi(x,t)\right|$ (this point is usually called the *center* of the wave packet).

 ii) Show that $\Psi(x,t)$ is concentrated on an interval of width Δx around x_m, where Δx satisfies $\Delta x \Delta p \gtrsim 2\pi\hbar$.

 iii) Generalize these results to a three-dimensional wave packet.

Solution.

i) Let us write

$$A(p) = f(p) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\alpha(p)},$$

where $f(p) = \left|A(p)\right| \geq 0$ and $\alpha(p)/\hbar \in \mathbb{R}$ is the argument of $A(p)$. We thus have

$$\Psi(x,t) = \int \mathrm{d}p f(p) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\varphi(x,p,t)}, \tag{1.50}$$

intphase

with

$$\varphi(x,p,t) = px - E(p)t + \alpha(p).$$

Since by hypothesis $f(p)$ is slowly varying and negligible outside the interval $[p_0 - \Delta p/2, \, p_0 + \Delta p/2]$, we can write

$$\Psi(x,t) \simeq f(p_0) \int_{p_0 - \frac{\Delta p}{2}}^{p_0 + \frac{\Delta p}{2}} \mathrm{d}p \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\varphi(x,p,t)} \simeq f(p_0) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\varphi(x,p_0,t)} \int_{p_0 - \frac{\Delta p}{2}}^{p_0 + \frac{\Delta p}{2}} \mathrm{d}p \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\frac{\partial\varphi}{\partial p}(x,p_0,t)(p-p_0)}$$

$$= f(p_0) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\varphi(x,p_0,t)} \int_{-\frac{\Delta p}{2}}^{\frac{\Delta p}{2}} \mathrm{d}p \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\frac{\partial\varphi}{\partial p}(x,p_0,t)p}, \tag{1.51}$$

wpexpand

where for simplicity we have assumed that the terms of order $(p - p_0)^2$ and higher in the Taylor expansion of $\varphi(p)$ about p_0 are negligible[a] for $|p - p_0| \leq \Delta p/2$. Thus at points (x,t) for which $\varphi(x,p,t)$ has nonzero partial derivative with respect to p at p_0 the integrand in Eq. (1.50) is wildly oscillatory (due to the smallness of $\hbar$), and therefore the integral is very small in absolute value due to cancellations. Hence the condition for a maximum of the absolute value of the integral is that

$$\frac{\partial}{\partial p}\varphi(x,p,t)\bigg|_{p=p_0} = 0.$$

This is the so called **principle of stationary phase** for integrals of the type (1.50). Computing the partial derivative we obtain the condition

$$x_m - E'(p_0)t + \alpha'(p_0) = 0 \quad \Longrightarrow \quad x_m = -\alpha'(p_0) + E'(p_0)t.$$

In other words, the peak (center) of the wave packet is located at the point $-\alpha'(p_0)$ for $t = 0$, and moves with constant velocity $v_g = E'(p_0) = p_0/m$.

ii) The variation of the phase $\varphi(x,p,t)/\hbar$ when p ranges from $p_0 - \frac{\Delta p}{2}$ to $p_0 + \frac{\Delta p}{2}$ is approximately given by

$$\frac{\Delta\varphi}{\hbar} \simeq \frac{\partial}{\partial p}\varphi(x,p,t)\bigg|_{p=p_0} \frac{\Delta p}{\hbar} = \left(x - E'(p_0)t + \alpha'(p_0)\right)\frac{\Delta p}{\hbar} = (x - x_m)\frac{\Delta p}{\hbar}.$$

For the integral (1.50) not to be vanishingly small at x, $|\Delta\varphi|/\hbar$ can be at most of the order of (say) half a period (in modulus) of the complex exponential, or equivalently

$$|x - x_m|\frac{\Delta p}{\hbar} \sim \pi.$$

For this condition to hold for all x in an interval of width Δx centered at x_m we must have

$$\frac{\Delta x}{2}\frac{\Delta p}{\hbar} \sim \pi \iff \Delta x\,\Delta p \sim 2\pi\hbar.$$

In other words, the intensity of the wave packet $\Psi(x,t)$ is concentrated on an interval centered at x_m of width Δx *at least* $2\pi\hbar/\Delta p$, i.e., such that

$$\Delta x\,\Delta p \gtrsim 2\pi\hbar. \tag{1.52}$$

Heiswp

iii) In the three-dimensional case we have

$$\Psi(\mathbf{r}, t) = \int \mathrm{d}^3 p\, f(\mathbf{p}) \mathrm{e}^{\frac{i}{\hbar}\varphi(\mathbf{r}, \mathbf{p}, t)}, \tag{1.53}$$

intphase3D

with $f(\mathbf{p}) \geqslant 0$ slowly varying and concentrated on a solid sphere of radius $|\Delta\mathbf{p}|/2$ centered at $\mathbf{p}_0$, $\alpha(\mathbf{p}) \in \mathbb{R}$ and

$$\varphi(\mathbf{r}, \mathbf{p}, t) = \mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t + \alpha(\mathbf{p}).$$

The stationary phase condition becomes

$$\nabla_{\mathbf{p}}\varphi(\mathbf{r}, \mathbf{p}, t)\bigg|_{\mathbf{p}=\mathbf{p}_0} = \mathbf{r} - (\nabla_{\mathbf{p}}E)(\mathbf{p}_0)t + (\nabla_{\mathbf{p}}\alpha)(\mathbf{p}_0),$$

where

$$\nabla_{\mathbf{p}} := \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \frac{\partial}{\partial p_3}\right).$$

Hence the center of the wave packet is the point

$$\mathbf{r}_m = -(\nabla_{\mathbf{p}}\alpha)(\mathbf{p}_0) + (\nabla_{\mathbf{p}}E)(\mathbf{p}_0)t.$$

Reasoning as before, we find that the wave packet is concentrated on a solid sphere centered at $\mathbf{r}_m$ whose radius $|\Delta\mathbf{r}|/2$ satisfies

$$\left|\Delta\mathbf{r}\right|\left|\Delta\mathbf{p}\right| \gtrsim 2\pi\hbar.$$

Note. In fact, the integral (1.51) can be easily evaluated, with the result[b]

$$\int_{-\frac{\Delta p}{2}}^{\frac{\Delta p}{2}} \mathrm{d}p\, \mathrm{e}^{\frac{i}{\hbar}\frac{\partial\varphi}{\partial p}(x, p_0, t)p} = \int_{-\frac{\Delta p}{2}}^{\frac{\Delta p}{2}} \mathrm{d}p\, \mathrm{e}^{\frac{i}{\hbar}p(x - x_m)}$$

$$= \frac{\hbar}{i(x - x_m)}\left(\mathrm{e}^{\frac{i\Delta p}{2\hbar}(x-x_m)} - \mathrm{e}^{-\frac{i\Delta p}{2\hbar}(x-x_m)}\right) = \frac{2\hbar\sin\left(\frac{\Delta p}{2\hbar}(x - x_m)\right)}{x - x_m} \equiv \Delta p\frac{\sin\xi}{\xi},$$

where we have set

$$\xi := \frac{\Delta p}{2\hbar}(x - x_m).$$

Thus the intensity of the wave packet can be approximated by

$$\left|\Psi(x,t)\right|^2 \simeq f(p_0)^2 \Delta p^2 \left(\frac{\sin\xi}{\xi}\right)^2 \equiv f(p_0)^2 \Delta p^2 g(\xi).$$

From the graph of the function $g(\xi)$ in Fig. 1.2 it is apparent that $\left|\Psi(x,t)\right|^2$ will be significant only for (say) $|\xi| \gtrsim \pi/2$ (indeed, $g(\pi/2) = 4/\pi^2 \simeq 0.405285$), i.e., for

$$\frac{\Delta p}{2\hbar}|x - x_m| \gtrsim \frac{\pi}{2}.$$

For this to hold for all x in an interval of width $\Delta x/2$ centered at x_m we need that

$$\frac{\Delta p}{2\hbar}\frac{\Delta x}{2} \gtrsim \frac{\pi}{2},$$

which is the same condition derived above.
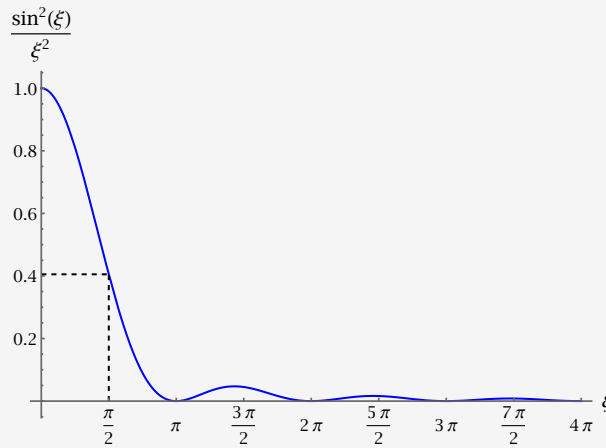
Figure 1.2. Graph of the function $g(\xi) = \sin^2\xi/\xi^2$ for $\xi > 0$. The first secondary maximum of this function is located at $\xi = 4.49341$, and is equal to 0.0471904.

---

[a]Note that, due to the term $E(p)t$ in $\varphi(x, p, t)$, this simplifying assumption can only be valid for sufficiently small $|t|$ even if it folds for $t = 0$.

[b]The following calculation is only valid for $x \neq x_m$, but letting x tend to x_m in the final result we obtain the correct value of the integral also for $x = x_m$.

1.6 Wave-particle duality. The wave function

By the mid and late 1920's, experimental phenomena like the photoelectric effect or the diffraction of electrons by crystals had convincingly shown that both light —or, in general, electromagnetic waves— and material particles like electrons exhibited a dual, and seemingly contradictory, wave-particle nature. More precisely, in certain experiments (for example, the photoelectric or Compton effects) light behaves as a stream of individual particles (photons), while in diffraction experiments it behaves as a wave. The situation is similar for material particles like the electron, which exhibit wavelike behavior when their de Broglie wavelength is comparable to the characteristic length of their surroundings (for instance, the interatomic distance of the crystal in diffraction experiments), and otherwise behaves as particles. Moreover, while for photons the associated wave is clearly the electromagnetic field[38], the physical nature of de Broglie's matter waves and their precise relation with the associated particle is not clear at all.

---

[38]Classically, the intensity of light is proportional to the time average of $\mathbf{E}^2$ or of $\mathbf{B}^2$, where $\mathbf{E}$ and $\mathbf{B}$ are respectively the electric and magnetic induction vector fields (both averages being proportional).

Figure 1.3. Setup of the double slit experiment. A monochromatic and unpolarized beam of light orig-
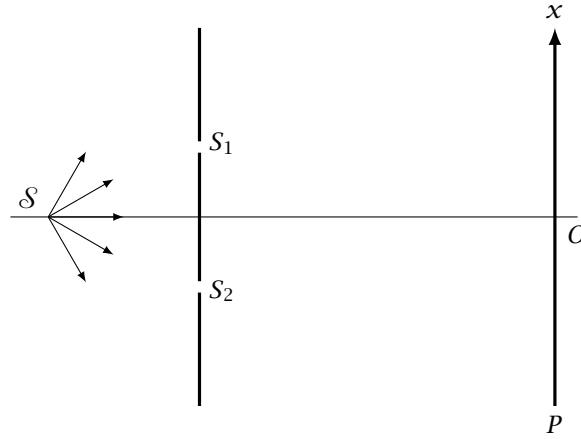inating from a point source at $\mathcal{S}$ strikes an opaque screen in which two narrow slits S_1 and
S_2 have been cut very close to each other and equidistant from $\mathcal{S}$. The beam's intensity on a
plane parallel to the screen is then measured by the photographic plate P.

fig.DSexp

In order to better understand the interplay between the wave and particle aspects of matter and radia-
tion, let us analyze in some detail the so called **double slit experiment** (see Fig. 1.3). The results of this
experiment can be summarized as follows:

1) If we block the slit S_2 (resp. S_1) the intensity $I_1(x)$ (resp. $I_2(x)$) of the light reaching the photo-
graphic plate P exhibits a characteristic diffraction pattern (see Fig. 1.4 left).

2) On the other hand, when both slits are open the intensity $I(x)$ of the light reaching the photographic
plate is *not* simply the sum $I_1(x) + I_2(x)$, but rather the oscillating function shown in Fig. 1.4.

To interpret these observations note first that, since the light used in this experiment is not polarized,
we can ignore the vector character of the (time averaged) electric field and represent it by a complex[39]
scalar function $E(x)$, whose modulus squared $\left|E(x)\right|^2$ is proportional to the light intensity at the point
(with vertical coordinate) x on the plate P. The results of the double slit experiment are then easily
explained by the wave theory. Indeed, according to this theory the slits act as secondary light sources.
Consequently, when the slit S_i is open and the other one is closed the intensity measured at P can be
taken (apart from an irrelevant constant factor) as

$$I_i(x) = \left|E_i(x)\right|^2,$$

where $E_i(x)$ is the electric field created by S_i. It can be shown that this formula correctly accounts for
the diffraction pattern observed at P. On the other hand, when both slits are open the total electric field
$E(x)$ at a point x on the plate is the sum of the electric fields created by both slits, namely

$$E(x) = E_1(x) + E_2(x),$$

and consequently the intensity at this point is given by

$$\begin{aligned}
I(x) = \left|E_1(x) + E_2(x)\right|^2 &= \left|E_1(x)\right|^2 + \left|E_2(x)\right|^2 + 2\operatorname{Re}\left(E_1(x)E_2^*(x)\right) \\
&= I_1(x) + I_2(x) + 2\operatorname{Re}\left(E_1(x)E_2^*(x)\right),
\end{aligned} \tag{1.54}$$

IJ12

---

[39]More precisely, for an oscillating electric field of the form $\mathcal{E}(x,t) = \operatorname{Re}\left(E(x)\mathrm{e}^{-\mathrm{i}\omega t}\right)$, with $E(x)$ complex valued, the
time average of $\mathcal{E}(x,t)^2$ is $\frac{1}{2}\left|E(x)\right|^2$. Moreover, if $\mathcal{E}_1(x,t) = \operatorname{Re}(E_1(x)\mathrm{e}^{-\mathrm{i}\omega t})$ and $\mathcal{E}_2(x,t) = \operatorname{Re}(E_2(x)\mathrm{e}^{-\mathrm{i}\omega t})$ are two such
fields with the same frequency ω, the time average of $\left(\mathcal{E}_1(x,t) + \mathcal{E}_2(x,t)\right)^2$ is $\frac{1}{2}\left|E_1(x) + E_2(x)\right|^2$. Since the respective light
intensities are proportional to these time averages, and thus to the squared modulus of $E(x)$ or $E_1(x) + E_2(x)$, it is customary
to represent the vector field $\mathcal{E}(x,t)$ by its *complex amplitude* $E(x)$. See, e.g., M. Born and E. Wolf, *Principles of Optics* (5th
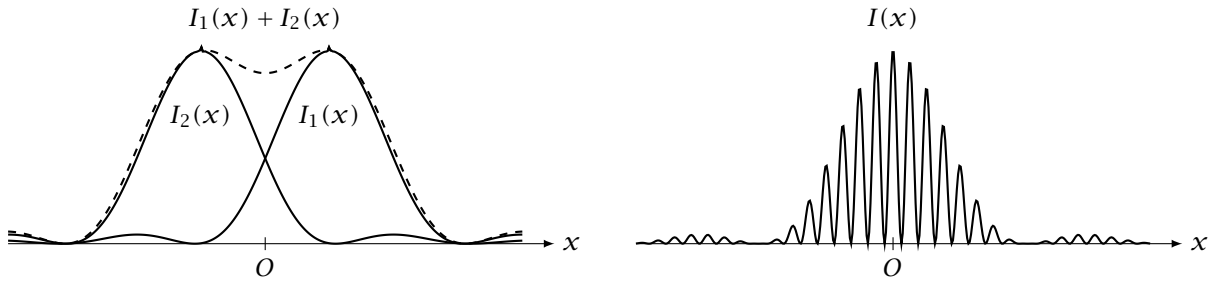ed.), Pergamon Press, 1975.

Figure 1.4. Left: light intensities $I_1(x)$ and $I_2(x)$ (black lines) and their sum $I_1(x) + I_2(x)$ (dashed line) in the double slit experiment. Right: light intensity $I(x)$ when both slits are unblocked.

which differs form $I_1(x) + I_2(x)$ by the *interference term*

$$J_{12}(x) = 2 \operatorname{Re} \left(E_1(x) E_2^*(x) \right).$$

In other words, according to the wave theory the intensity pattern observed when both slits are open is due to the *interference* between the waves originating at each slit.

From the point of view of the corpuscular theory of light, the intensity at a point x on the plate P is proportional to the number $N(x)$ of photons hitting this point per unit time, i.e,

$$I(x) = a N(x)$$

for some irrelevant constant a. Although the result of the first experiment (with one slit blocked) could perhaps be explained by the interaction between the individual photons in the beam and the edges of the slit, when both slits are open the number of photons per unit time hitting the point x is the sum of the photons going through each slit, namely

$$I(x) = a N(x) = a \left(N_1(x) + N_2(x) \right) = I_1(x) + I_2(x).$$

This result is clearly inconsistent with the intensity pattern actually observed, described by Eq. (1.54). The corpuscular theory of light is thus unable to account for the interference term $J_{12}(x)$.

In point of fact, in the previous argument we assumed that the number of photons hitting a point on the plate which pass through one of the slits S_i is the *same* whether the other slit is blocked or not. This assumption, however, may not be true if the photons passing through one slit interact with those passing through the other one. In order to suppress this effect, the beam's intensity can be diminished till ideally the source emits only *one photon at a time.* The naive prediction of the corpuscular theory is that, since in this limit there is no possible interaction between photons passing through different slits, the intensity fringes disappear and $I(x) = I_1(x) + I_2(x)$. On the other hand, according to the wave theory if the beam's intensity diminishes the intensity of the interference fringes will just diminish accordingly, but the fringes will not disappear. Remarkably, *neither the wave nor the corpuscular theory predictions are supported by experiment.* More precisely, when the source $\mathcal{S}$ emits one photon at a time the following is observed:

1) If the exposure time is so short that only a few photons hit the photographic plate, the *individual* impacts of these photons on seemingly random points on the plate can be clearly observed. This result is *inconsistent with the wave theory,* which predicts instead a very weak interference pattern.

2) On the other hand, if the exposure time is increased so as to ensure that a large number of photons hit the plate, the locations of the random individual impacts of the photons on the plate accumulate, and over time give rise to a visible pattern of interference fringes described by Eq. (1.54). This result is *incompatible with the corpuscular theory prediction* of an absence of interference fringes for a sufficiently low beam intensity. It is essential to realize, however, that the pattern of interference fringes arises *gradually,* as the individual impacts of the photons at random locations on the plate

build up. In other words, the intensity at a point x on the plate is proportional to the number of photons hitting the plate at this point. We thus conclude that the emergence of the interference fringes is ultimately a *statistical* phenomenon. Note, however, that this statistical phenomenon affects *each individual photon,* since it manifests itself even when only one photon at a time is emitted.

The previous analysis of the double slit experiment thus clearly points at a *statistical connection* between the wavelike and the particle aspects of photons. More precisely:

- The square of the modulus of the electric field at a point x on the photographic plate, $\left|E(x)\right|^2$, is proportional to the density of photon impacts at x. In other words, the *probability* that a photon strikes the plate at a point in the interval $[x, x + \mathrm{d}x]$ is proportional to $\left|E(x)\right|^2 \mathrm{d}x$.

- Moreover, to explain the existence of the interference fringes when both slits are unblocked we must accept that, contrary to classical thought and everyday experience, the probability that a photon strikes the plate at a point inside the interval $[x, x+\mathrm{d}x]$ is *not* the sum of the probabilities $\left|E_{1,2}(x)\right|^2$ of the photon going through the slit $S_{1,2}$ before hitting the interval, but is instead given by $\left|E_1(x) + E_2(x)\right|^2$. In other words, it is the (in general *complex*) *probability amplitudes* $E_i(x)$ of each of the independent events

$$\mathscr{E}_i = \text{photon strikes the plate inside the interval } [x, x + \mathrm{d}x] \text{ after passing}$$
$$\text{through the slit } S_i \ (i = 1, 2),$$

  that are added up to obtain the *probability amplitude $E_1(x) + E_2(x)$* of the event

$$\mathscr{E}_1 \cup \mathscr{E}_2 = \text{photon strikes the plate inside the interval } [x, x + \mathrm{d}x].$$

  The probability of the latter event is then obtained by computing the *square of the modulus of this probability amplitude*, thus giving rise to interference fringes described by Eq. (1.54).

It should be stressed that the *addition of probability amplitudes instead of probabilities,* although essential in order to explain the genesis of the interference fringes in the double slit experiment, flatly contradicts our intuition based on everyday experience. Indeed, we may intuitively think that when the beam intensity is so low that there is no interaction between photons passing through different slits, the fact that one slit is blocked or not cannot affect the number of photons passing through the other (open) slit. If this were true the intensity at a point x on the plate would be simply the sum $I_1(x) + I_2(x)$ of the intensities obtained when either slit is blocked, and no interference fringes would therefore be observed. In fact:

- In order to avoid a contradiction with classical logic, according to which the probability of the union of two independent events (i.e., a photon passing through either slit and striking a certain region of the plate) is the sum of their individual probabilities, *the belief that photons pass through either one or the other slit must be abandoned.*

- This in turn entails that *it is impossible to assign a definite classical trajectory to photons* in the double slit experiment, since otherwise we would be forced to conclude that each photon must pass through one and only one of the open slits.

Another fundamental consequence of the previous analysis is the following:

- Contrary to classical lines of thought, the explanation of the emergence of interference fringes in the double slit experiment is ultimately of a *probabilistic nature*. In other words, the theory cannot predict where on the plate will an individual photon strike, but only provides a *probability* for the

photon hitting a point on the plate (proportional to the square of the modulus of the electric field at that point). *The interference fringes arise as the individual impacts of photons on the plate build up following this probability distribution.* Put differently, the interference fringes in the double slit experiment are caused by a *statistical property of a* single *photon,* rather than by an interaction between photons.

The previous analysis of the double slit experiment can be summarized as follows:

1) The particle and wave aspects of light are inseparable: light behaves simultaneously like a wave and like a stream of particles (photons). The energy E and momentum $\mathbf{p}$ of the photon are related to the frequency ν and wave vector $\mathbf{k}$ of the associated wave by the **Einstein–de Broglie relations**

$$E = h\nu = \hbar\omega, \qquad \mathbf{p} = \hbar\mathbf{k}. \tag{1.55}$$

2) The wave and the particle aspects of light are connected as follows: the probability of finding a photon at time t inside an infinitesimal volume $\mathrm{d}^3 r$ centered at a point $\mathbf{r}$ in space is proportional to $\left|\mathbf{E}(\mathbf{r}, t)\right|^2$, where $\mathbf{E}$ is the field vector of the associated electromagnetic wave.

3) Predictions about the behavior of a photon are thus necessarily of a probabilistic nature.

As a matter of fact, the double slit experiment can be performed with *material particles* (electrons, neutrons, protons, etc.) instead of photons[40], and the results are exactly the same as discussed above. Namely, when the particle beam has a sufficiently high intensity a continuous interference fringe is observed on a plate (actually, a detector of some kind) placed behind the slits, whereas for low intensities the individual impacts of particles at seemingly random positions on the plate can be detected, the interference fringes eventually appearing as these impacts accumulate[41]. Just as in the case of photons, we conclude that these interference fringes are not caused by an interaction between the particles, but are rather a *statistical property of a* single *particle.* In other words, we cannot predict the precise point on the plate each particle is going to strike, but only the *probability* of a particle hitting the plate at a particular point. It is natural to assume that *the role played by the electric field in determining this probability for photons should now be played by de Broglie's matter wave* $\Psi(\mathbf{r}, t)$ *associated to the particle.* In other words:

The probability of finding a material particle at a time t inside an infinitesimal volume $\mathrm{d}^3 r$ centered at a point $\mathbf{r}$ in space is proportional to $\left|\Psi(\mathbf{r}, t)\right|^2 \mathrm{d}^3 r$, where the complex valued smooth function $\Psi(\mathbf{r}, t)$ is de Broglie's matter wave for the particle in question.

In general, since the probability of finding the particle *anywhere* in space must equal 1, the actual probability is given by

$$dP(\mathbf{r}, t) = \frac{\left|\Psi(\mathbf{r}, t)\right|^2 \mathrm{d}^3 r}{\displaystyle\int \mathrm{d}^3 r \left|\Psi(\mathbf{r}, t)\right|^2}, \tag{1.56}$$

where as usual the integral is extended over the whole space $\mathbb{R}^3$. In particular, the latter integral must be finite:

$$\int \mathrm{d}^3 r \left|\Psi(\mathbf{r}, t)\right|^2 < \infty. \tag{1.57}$$

---

[40]The double slit experiment has been performed with electrons, neutrons, atoms, and even some heavy molecules.

[41]See `https://www.hitachi.com/rd/research/materials/quantum/doubleslit/index.html` for a practical demonstration of the double slit experiment with electrons.

Remark. The linear space of (complex valued) scalar functions $\phi(\mathbf{r})$ whose modulus squared $\left|\phi(\mathbf{r})\right|^2$ is integrable over $\mathbb{R}^3$ is called the *Lebesgue space* $L^2(\mathbb{R}^3)$. Thus Eq. (1.57) states that $\Psi(\mathbf{r}, t)$ is in $L^2(\mathbb{R}^3)$ for each fixed $t \in \mathbb{R}$. We shall see in the sequel that under certain conditions this requirement can be relaxed. ∎

Equation (1.56) furnishes an *interpretation of de Broglie's matter wave* $\Psi(\mathbf{r}, t)$ as proportional to the **probability amplitude** for the particle being found inside an infinitesimal volume centered at a point $\mathbf{r}$ at time t. In more modern terminology $\Psi(\mathbf{r}, t)$ is called the particle's **wave function**, and *completely determines its state* at a certain instant t through equation (1.56). Indeed, as mentioned above we can only expect to know the *probability* of finding the particle inside a certain infinitesimal volume at any time t, given by the latter equation. Thus, whereas in classical mechanics the state of a particle is determined by 6 real variables (the particle's coordinates and momentum), and is thus a point in the finite-dimensional vector space $\mathbb{R}^6$, in quantum mechanics the particle's state is an element of the *infinite-dimensional* linear space $L^2(\mathbb{R}^3)$. In other words, in quantum mechanics the number of degrees of freedom of a single particle is *infinite*. To determine the state of a particle, we must compute its wave function $\Psi(\mathbf{r}, t)$ for all times t. As we shall explain in the next chapter, in mathematical terms this amounts to solving a certain (linear) partial differential equation (Schrödinger's wave equation) with appropriate initial and boundary conditions (usually, that the wave function vanish fast enough at spatial infinity so that Eq. (1.57) is satisfied). Even for a single particle, this is in general an extremely difficult problem which can be exactly solved only in a handful of simple yet physically important situations, that we shall study in some detail in the following chapters.

Example 1.2. *De Broglie wavelength of conduction electrons in copper.*

Whether the particle or the wave aspect of material particles is relevant in a given physical situation respectively depends on whether the particle's de Broglie wavelength is very small compared to the problem's characteristic length or is comparable to it. In the former case we can treat the particle as a point particle following the laws of classical mechanics, while in the latter we must use the quantum wave function to properly describe the particle's behavior.

Consider, for instance, conduction electrons in a copper wire carrying a 220 V current. The characteristic length in this problem is copper's interatomic distance $d = 2.54$ Å. The energy of the conduction electrons is

$$E = 220 \, \text{eV} \simeq 3.52479 \cdot 10^{-17} \, \text{J},$$

and their momentum is therefore

$$p = \sqrt{2 m_e E} \simeq 8.01357 \cdot 10^{-24} \, \text{kg m s}^{-1}.$$

Note that the conduction electrons can be considered non-relativistic, since their potential energy is very small compared to their rest mass energy $m_e c^2 \sim 0.5 \cdot 10^6$ eV. Thus the de Broglie wavelength of a conduction electron is

$$\lambda = \frac{h}{p} \simeq 8.26856 \cdot 10^{-11} \, \text{m},$$

which is of the same order of magnitude as copper's interatomic spacing $d = 2.54 \cdot 10^{-10}$ m. Hence conduction electrons in copper wires at 220 V must be treated as quantum mechanical, i.e., must be described by their quantum wave function and exhibit a wavelike behavior.

On the other hand, for a dust speck of diameter $1 \, \mu$ and mass 10^{-15} kg moving at a speed of $1 \, \text{mm s}^{-1}$ we have

$$\lambda = \frac{h}{mv} \simeq \frac{6.6 \cdot 10^{-34} \, \text{kg m}^2 \, \text{s}^{-1}}{10^{-15} \, \text{kg} \times 10^{-3} \, \text{m s}^{-1}} = 6.6 \cdot 10^{-16} \, \text{m} = 6.6 \cdot 10^{-10} \mu.$$

Since the de Broglie's wavelength of the speck of dust is ten orders of magnitude less than its diameter, we conclude that a description of the speck as a point particle following the laws of classical mechanics is appropriate.

1.7 Heisenberg's uncertainty principle

`sec.HUP`

As pointed out in the previous section, the results of the double slit experiment make it unavoidable to abandon the classical notion of trajectory, and in particular the intuitive idea that the photon (or the material particle used in the experiment) must pass through either slit before hitting the photographic plate. From the quantum mechanical point of view, the fact that we cannot determine through which slit the photon has passed does not contradict any fundamental physical principle. Indeed, physics deals ultimately with *experimentally measurable* properties, and in the double slit experiment no attempt is made to detect the passage of a photon or particle through the slits. A crude way of experimentally detecting through which slit the photons pass is to place a photomultiplier behind both slits. It is found in this way that approximately half the photons go through each slit. However, in the process of measuring the passage of a photon through either slit we have fundamentally altered the original experiment, since the photons are destroyed after being detected by the photomultiplier, and obviously the photographic plate does not register any intensity. To remedy this problem, we could place a photomultiplier behind only one of the slits, say S_2. The result of this experiment is that the photomultiplier records approximately the passage of half of the incoming photons through S_2, so that we can assume that the other half have passed through S_1 on their way to the plate. However, since the slit S_2 is effectively *blocked* the photographic plate shows only the *diffraction pattern* of the other slit, and no interference pattern is observed. Again, we find that the attempt to measure the number of photons going through S_2 has fundamentally affected the original experiment. Although several other more sophisticated experiments can be performed to detect the passage of photons through the slits in the double slit experiment, in all cases it has been found that *it is impossible to achieve this objective without destroying the interference pattern.* This result underscores what has been acknowledged as one of the fundamental principles of modern quantum mechanics, namely

> Any measure performed on a system inevitably alters its physical state in a fundamental way.

A related, but more quantitative, fundamental principle of quantum mechanics was formulated by Heisenberg[42] in 1927:

> **Heisenberg's uncertainty principle:** if two *canonically conjugate* dynamical variables q and p are *simultaneously* measured, their respective uncertainties Δq and Δp must satisfy the approximate inequality
>
> $$\Delta q \, \Delta p \gtrsim \hbar. \tag{1.58}$$

`Heisuncp`

We shall provide a formal proof of this relation in the next Chapter. In fact, we shall precisely define the uncertainty of any dynamical variable, and show that with this definition we have the more precise inequality

$$\Delta q \, \Delta p \geqslant \frac{\hbar}{2}. \tag{1.59}$$

`HeisURprec`

An immediate consequence of the uncertainty principle is that *it is impossible to measure* simultaneously *with arbitrary precision two canonically conjugate dynamical variables*. This is prevented by the laws of quantum mechanics as presently understood, and has nothing to do with any practical limitation of our experimental setup. In fact, nothing prevents us in principle from measuring with arbitrary precision *one* of a pair of canonically conjugate dynamical variables, but in doing so the uncertainty of the other variable will increase without bound due to Eq. (1.58).

Recall that in Lagrangian mechanics the canonical momentum associated to a generalized coordinate q_i is

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \qquad i = 1, \dots, N, \tag{1.60}$$

`piqi`

---

[42]Werner Heisenbreg (1901–1976), German physicist and Nobel Prize winner in 1932.

where $L(t, q_1, \ldots, q_N, \dot{q}_1, \ldots, \dot{q}_N)$ is the system's Lagrangian. The dynamical variables q_i and p_i are said to be *canonically conjugate*. From the Lagrangian L we construct the system's Hamiltonian

$$H(t, q_1, \ldots, q_N, p_1, \ldots, p_N) = \sum_{i=1}^{N} p_i \dot{q}_i - L,$$

where it is understood that in the RHS the variables $\dot{q}_k$ are expressed in terms of the canonical momenta p_j using Eq. (1.60). The equations of motion of two canonically conjugate variables (q_i, p_i) are then Hamilton's canonical equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}.$$

In particular, for a single particle of mass m moving subject to a potential $V(\mathbf{r})$ the Lagrangian in Cartesian coordinates is simply

$$L(\mathbf{r}, \dot{\mathbf{r}}) = \frac{1}{2}m\dot{\mathbf{r}}^2 - V(\mathbf{r}).$$

The canonical coordinates are the particle's three Cartesian coordinates (x_1, x_2, x_3), i.e., the components of its position vector $\mathbf{r}$. The canonical momentum p_i conjugate to the coordinate x_i is then

$$p_i = \frac{\partial L}{\partial \dot{x}_i} = m\dot{x}_i,$$

i.e., the i-th component of the linear momentum. Therefore in this case Heisenberg's uncertainty relation (1.58) reads

$$\Delta x_i \, \Delta p_i \gtrsim \hbar, \qquad 1 \leqslant i \leqslant 3. \tag{1.61}$$

It follows that:

> It is impossible to measure *simultaneously* with arbitrary precision one of the particle's coordinates and the corresponding component of its linear momentum.

(Of course, nothing prevents us from measuring simultaneously and with arbitrary precision a coordinate x_i and a *different* momentum component p_j with $j \neq i$). An immediate consequence of this fact is that, as we already knew from our analysis of the double slit experiment in the previous section, is that:

> In quantum mechanics, it is impossible to determine (with arbitrary precision) the trajectory of a particle.

Indeed, this would require knowing *simultaneously* the particle's position and velocity (and hence momentum) at all times. In practice, however, given the smallness of the constant $\hbar$ compared to typical actions of macroscopic particles, *this restriction is only effective in the microscopic realm* (see, e.g., Exercise 1.4).

Remark. Heisenberg's uncertainty principle always applies to a pair of *canonically conjugate* variables. For instance, in Cartesian coordinates the Lagrangian of a particle of charge e and mass m moving under the influence of an external electromagnetic field is given by

$$L(t, \mathbf{r}, \dot{\mathbf{r}}) = \frac{1}{2}m\dot{\mathbf{r}}^2 + e\big(\dot{\mathbf{r}} \cdot \mathbf{A}(\mathbf{r}, t) - \phi(\mathbf{r}, t)\big),$$

where $\phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potentials generating the electromagnetic field through the equations

$$\mathbf{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \frac{\partial \mathbf{A}}{\partial t}(\mathbf{r}, t), \qquad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t),$$

In this case the canonical momentum conjugate to the Cartesian coordinate x_i is

$$p_i = \frac{\partial L}{\partial \dot{x}_i} = m\dot{x}_i + eA_i(\mathbf{r}, t),$$

which in general differs from the i-th component of the particle's linear momentum $m\dot{x}_i$. Of course, even in this case it is impossible to measure simultaneously with arbitrary precision the coordinate x_i and the corresponding linear momentum component $m\dot{x}_i$, since by the previous formula this would require determining with arbitrary precision both x_i and its conjugate momentum p_i. ∎

Example 1.3. As seen in Section 1.5, the wave function of a particle of mass m moving *freely* (i.e., subject to no external force) in one dimension can be taken as

$$\Psi(x, t) = A\, e^{\frac{i}{\hbar}(p_0 x - E(\mathbf{p}_0)t)},$$

where $A > 0$, p_0 is the particle's momentum and $E(\mathbf{p}_0) = \frac{p_0^2}{2m}$ its momentum. Note that Ψ is not in $L^2(\mathbb{R})$, since $|\Psi(x, t)| = A$ is constant. In fact, in this case the probability density of finding the particle at a point x is the *constant* A^2. In other words, it is equally likely to find the particle anywhere on the real line, and thus the position uncertainty Δx is infinite. This is in agreement with Heisenberg's uncertainty principle, since $p = p_0$ is *exactly* known and therefore $\Delta p = 0$.

More realistically, if the particle's momentum is only known with an uncertainty Δp its wave function can be taken as the *wave packet*

$$\Psi(x, t) = \int dp\, A(p) e^{\frac{i}{\hbar}(px - E(\mathbf{p})t)},$$

where $|A(p)|$ is slowly varying, sharply peaked at $p = p_0$ and vanishingly small outside an interval of width Δp centered at p_0. As we saw in Exercise 1.3, at any time t the function $|\Psi(x, t)|$ (and hence the particle's *probability density*, which is proportional to $|\Psi(x, t)|^2$) is concentrated on an interval centered at the point

$$x_m(t) = \frac{p_0 t}{m} - \alpha'(p_0),$$

where $\alpha(p)/\hbar$ is the argument of $A(p)$. Moreover, the width Δx of this interval, i.e., the uncertainty in the particle's position, satisfies

$$\Delta x\, \Delta p \gtrsim 2\pi\hbar$$

(cf. Eq. (1.52)). This is again in full agreement with Heisenberg's uncertainty principle.

exe.traj

Exercise 1.4. Discuss whether it is possible to attribute a classical trajectory to the following particles: i) a dust speck of diameter $1\,\mu$ and mass 10^{-15} kg moving at a speed of $1\,\text{mm}\,\text{s}^{-1}$, and ii) an electron in Bohr's model of the atom.

Solution. For the classical trajectory of a particle to be well defined, both its position and momentum uncertainties must be small enough so that the particle's position and momentum can be simultaneously measured with sufficient accuracy.

By Heisenberg's uncertainty relation, to be able to measure both the position and the momentum of a particle with a relative error ε we must have

$$\Delta x\, \Delta p = \varepsilon^2 xp \gtrsim \hbar \quad \Longleftrightarrow \quad \varepsilon \gtrsim \sqrt{\frac{\hbar}{xp}}.$$

Thus the maximum relative precision in a simultaneous measurement of position and momentum al-

lowed by Heisenberg's uncertainty relation is (of the order of)

$$\varepsilon_{max} \sim \sqrt{\frac{\hbar}{xp}} \sim \frac{10^{-17}}{\sqrt{xp\ (SI)}},$$

if x and p are measured in SI units. In order to be able to assign a classical trajectory to the particle, ε_{max} should be much less than 1.

i) For the dust particle we can take

$$x = 1\,\mu = 10^{-6}\,\text{m}, \quad p = 10^{-15}\,\text{kg} \times 10^{-3}\,\text{m\,s}^{-1} = 10^{-18}\,\text{kg\,m\,s}^{-1}$$
$$\implies \quad xp \simeq 10^{-24}\,\text{J\,s} \quad \implies \quad \varepsilon_{max} \simeq 10^{-5}.$$

Thus it would be reasonable to attribute a classical trajectory to the dust particle.

ii) On the other hand, for an electron in the n-th allowed circular orbit of a Bohr atom we have

$$rp = L = n\hbar \quad \implies \quad \varepsilon_{max} \sim \sqrt{\frac{\hbar}{rp}} = \frac{1}{\sqrt{n}}\,.$$

Thus it is not possible to assign a classical trajectory to an electron in Bohr's model of the atom unless the quantum number n is very large (of the order of 10^6 for a relative precision of only 10^{-3}).

2 The Schrödinger wave equation

2.1 The wave function and Born's rule

As we saw in the previous chapter, in quantum mechanics the state of a material particle at a certain time t is represented by a (nonzero) *wave function* $\Psi(\mathbf{r}, t)$ satisfying

$$\int \mathrm{d}^3 r \left|\Psi(\mathbf{r}, t)\right|^2 < \infty.$$

More precisely, what this statement means is that when the particle is in the state $\Psi(\mathbf{r}, t)$ the *probability* of finding the particle at any time t in a volume element $\mathrm{d}^3 r$ centered at a point $\mathbf{r}$ is given by

$$\mathrm{d}P(\mathbf{r}, t) = \frac{\left|\Psi(\mathbf{r}, t)\right|^2}{\int \left|\Psi(\mathbf{r}, t)\right|^2 \mathrm{d}^3 r}\, \mathrm{d}^3 r. \tag{2.1}$$

If we define the (L^2) **norm** of $\Psi(\cdot, t)$ as[1]

$$\left\|\Psi\right\|(t) := \left(\int \mathrm{d}^3 r \left|\Psi(\mathbf{r}, t)\right|^2\right)^{1/2} > 0,$$

the function

$$\widetilde{\Psi}(\mathbf{r}, t) = \frac{\Psi(\mathbf{r}, t)}{\left\|\Psi\right\|(t)}$$

has unit norm, i.e.,

$$\int \mathrm{d}^3 r \left|\widetilde{\Psi}(\mathbf{r}, t)\right|^2 = 1, \tag{2.2}$$

and by Eq. (2.1) the probability $\mathrm{d}P(\mathbf{r}, t)$ is simply

$$\mathrm{d}P(\mathbf{r}, t) = \left|\widetilde{\Psi}(\mathbf{r}, t)\right|^2 \mathrm{d}^3 r. \tag{2.3}$$

From now on, unless otherwise stated we shall always assume that the wave function obeys the normalization (2.2). With this proviso, we can state what is usually called **Born's rule**[2]:

Born's rule. The state of a material particle is represented by a (normalized) wave function $\Psi(\mathbf{r}, t)$ satisfying

$$\int \mathrm{d}^3 r \left|\Psi(\mathbf{r}, t)\right|^2 = 1,$$

in the sense that the probability of finding the particle at a time t in a volume element $\mathrm{d}^3 r$ centered at a point $\mathbf{r}$ is given by

$$\mathrm{d}P(\mathbf{r}, t) = \left|\Psi(\mathbf{r}, t)\right|^2 \mathrm{d}^3 r.$$

---

[1]The notation $\Psi(\cdot, t)$ stands for $\Psi(\mathbf{r}, t)$ considered as a function of $\mathbf{r}$ with t fixed.

[2]After Max Born (1882–1970), German physicist and Nobel prize winner in 1954.

Remarks.

- We thus see that in quantum mechanics knowing the state of a particle at a certain time does *not* determine (as in classical mechanics) the particle's position, but only the *probability* of finding the particle anywhere in space.

- The function $|\Psi(\mathbf{r}, t)|^2$ is the **probability density** of finding the particle at some time t in a volume element $d^3 r$ centered at $\mathbf{r}$. The wave function $\Psi(\mathbf{r}, t)$ is thus the **probability amplitude** (per unit volume) of finding the particle inside this volume element. In particular, since $|\Psi|^2 d^3 r$ is *dimensionless*, the wave function Ψ has dimensions of $L^{-3/2}$ (or, more generally, $L^{-d/2}$ in d-dimensional space for $d = 1, 2$).

- We shall show in the sequel that the wave function $\Psi(\mathbf{r}, t)$ is *defined up to a global* constant *phase* $e^{i\alpha}$, with $\alpha \in \mathbb{R}$ independent of $\mathbf{r}$ and t. In other words, $\Psi(\mathbf{r}, t)$ and $e^{i\alpha}\Psi(\mathbf{r}, t)$ define the *same* quantum state. In particular, the respective probability densities $|\Psi(\mathbf{r}, t)|^2$ and $|e^{i\alpha}\Psi(\mathbf{r}, t)|^2$ obviously coincide.

- It should, however, be stressed that *the quantum state is determined by the wave function $\Psi(\mathbf{r}, t)$, not just by the probability density* $|\Psi(\mathbf{r}, t)|^2$. This is essential, since interference effects are of paramount importance in quantum mechanics. In other words, although $\Psi(\mathbf{r}, t)$ and $\widetilde{\Psi}(\mathbf{r}, t) = e^{i\alpha(\mathbf{r}, t)}\Psi(\mathbf{r}, t)$ (with $\alpha(\mathbf{r}, t)$ a non-constant real valued function) give rise to the same probability density $|\Psi(\mathbf{r}, t)|^2 = |\widetilde{\Psi}(\mathbf{r}, t)|^2$, these wave functions *represent different physical states*. For example, we shall see below that the probability density of finding the particle with a certain linear momentum $\mathbf{p}$ is *not* the same for the state Ψ than for the state $\widetilde{\Psi}$.

- Suppose that at a certain time t we measure the position of a particle, and find it to be at a point $\mathbf{r}_0$ (more precisely, inside a small volume element centered at $\mathbf{r}_0$). *Where was the particle* just before *we measured its position?* The classical, or *realist*, answer to this question is that the particle was at $\mathbf{r}_0$. If this answer were correct, quantum mechanics would provide an essentially *incomplete* description of nature, since even knowing the state of the particle it is impossible to predict were it is at any time t. The proponents of the realist answer, among others Einstein and de Broglie, counter that the incompleteness of quantum mechanics stems from the fact that there are certain *hidden variables* governing the particle's motion whose values are unknown. This explanation, however, has been conclusively disproved by experiment[3]. Another problem with the realist point of view is that if the particle is at a certain point at every instant t (even if quantum mechanics is not able to predict where) then it is following some continuous trajectory, a notion contradicted for example by the double slit experiment. The "orthodox" answer to the question of where was the particle immediately before we measured its position, defended by most (though not all!) modern day physicists, is that this question actually *does not make sense*. Indeed, we can only find where a particle is at a certain instant by measuring its position, so all we can *experimentally* know is where is the particle going to be immediately *after* we measure its position, not *before*. In a way, it is as if the particle is *nowhere in particular* before we measure its position, and it only manifests itself at some point in space when we *force* it to do so by *measuring* its position. This is the so called *Copenhagen school* point of view, named after Niels Bohr, one of the first physicists to advance it.

- Suppose, again, that we measure the position of a particle at a certain time t_0, finding it inside a small volume element centered at $\mathbf{r}_0$. *What is the result of a position measurement performed* immediately

---

[3]Indeed, in 1964 the British physicist John Bell (1928–1990) proved a now famous inequality relating the probabilities of three events that must be satisfied in all (local) hidden variable theories. Several experiments carried out, among others, by the 2022 Nobel Prize winners Alain Aspect, John F. Clauser and Anton Zeilinger have conclusively shown that this inequality is violated in exactly the way predicted by quantum mechanics. This invalidates all (local) hidden variable theories, and providing a strong experimental confirmation of quantum mechanics. See [GS18, Section 12.2] for an elementary discussion of Bell's theorem.

afterwards? It is intuitively clear (and can be experimentally verified) that we should find the particle at the *same* point if the interval between both measurements is sufficiently small, since otherwise the position of a particle would become meaningless. In other words, even if the probability density $\left|\Psi(\mathbf{r}, t_0)\right|^2$ at the time of the first position measurement is spread out over the whole space, its probability density $\left|\Psi(\mathbf{r}, t)\right|^2$ at a time $t = t_0 + \Delta t$ with $\Delta t > 0$ small enough must be *sharply peaked* at $\mathbf{r}_0$. In other words, our measurement of the particle's position *forces its state to change discontinuously*, becoming located (for a sufficiently small time) inside a small volume element centered at the point $\mathbf{r}_0$ obtained as a result of the first position measurement. This is an instance of the general phenomenon called **collapse of the wave function**, which as we shall see is characteristic of measurements of observables in quantum mechanics. ∎

2.2 Schrödinger's wave equation

`sec.Schr`

Our next objective is to derive a differential equation satisfied by the wave function $\Psi(\mathbf{r}, t)$ of a particle, that will allows us to determine Ψ imposing appropriate initial and boundary conditions. We shall start by the simplest case of a particle of mass m moving freely (i.e., not acted upon by any forces) in space, whose linear momentum $\mathbf{p}$ and energy E are classically related by the familiar equation[4]

$$E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}. \tag{2.4}$$ `enmomrel`

As we saw in Section (1.5), the particle's wave function in this case is the plane wave with wave vector $\mathbf{k}$ and frequency $\omega(\mathbf{k})$ satisfying the Einstein–de Broglie relations

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar}, \qquad \omega = \frac{E}{\hbar} \tag{2.5}$$ `EdBom`

(cf. Eq. (1.55)). In other words,

$$\Psi(\mathbf{r}, t) = A\, e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t\right)}, \tag{2.6}$$ `wffree`

where A is a constant that we can take as real and positive without loss of generality (why?). If the wave function is of the latter form we have

$$i\hbar\,\partial_t \Psi = E\Psi, \qquad -i\hbar\nabla\Psi = \mathbf{p}\Psi, \tag{2.7}$$ `Emomop`

where

$$\nabla \equiv (\partial_{x_1}, \partial_{x_2}, \partial_{x_3}), \qquad \partial_{x_i} \equiv \frac{\partial}{\partial x_i}, \qquad \partial_t \equiv \frac{\partial}{\partial t}\,.$$

In the latter equation

$$\nabla^2 \equiv \nabla \cdot \nabla = \sum_{i=1}^{3} \partial_{x_i}^2$$

---

[4]In what follows we shall assume that the speeds of all particles involved are small compared to the speed of light, so that by "classical mechanics" we shall usually mean non-relativistic classical mechanics. The corresponding quantum theory that we shall develop in these notes is accordingly called "non-relativistic quantum mechanics". As in non-relativistic classical mechanics, in non-relativistic quantum mechanics particles cannot be created or destroyed. By contrast, relativity theory allows for particle creation or annihilation, provided that the total energy of the system is conserved. The relativistic version of quantum mechanics, which is able to accommodate particle creation and annihilation, is called "quantum field theory". It is essentially a field theory (like, e.g., electromagnetism) in which the value of a field at a point in spacetime is an operator instead of a complex number.

© *Artemio González López*

is the **Laplacian** operator in Cartesian coordinates. Moreover, from the non-relativistic energy-momentum relation (2.4) and the previous equation it follows that

$$i\hbar\partial_t\Psi = \frac{\mathbf{p}^2}{2m}\Psi = \frac{1}{2m}\left(-i\hbar\nabla\right)^2\Psi,$$

i.e.,

$$i\hbar\partial_t\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi. \tag{2.8}$$

Since the latter equation does not contain explicitly the momentum $\mathbf{p}$, it is satisfied by *all* wave functions (2.6) regardless of the particle's momentum. Equation (2.8) is **Schrödinger's**[5] **wave equation** for a free particle of mass m.

It might be objected that the plane waves (2.6) are not acceptable as wave functions, since they are obviously not normalizable; indeed, for these functions

$$\int d^3r\left|\Psi(\mathbf{r},t)\right|^2 = |A|^2\int d^3r = \infty.$$

This is a valid objection, since the momentum of a particle cannot be experimentally determined with infinite accuracy. More realistically, if the linear momentum of a free particle is only known to be $\mathbf{p}_0$ with a certain accuracy $\left|\Delta\mathbf{p}\right|$ the particle's wave function will be a *wave packet* of the form

$$\Psi(\mathbf{r},t) = \int d^3p\, A(\mathbf{p})\, e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)}, \tag{2.9}$$

where $A(\mathbf{p})$ is an (in general complex valued) function concentrated on a solid sphere of radius $\left|\Delta\mathbf{p}\right|$ centered at $\mathbf{p}_0$ in momentum space. According to the theory of the *Fourier transform*, the squared norm of the latter wave function is equal to

$$\left\|\Psi\right\|^2(t) = (2\pi\hbar)^3\int d^3p\left|A(\mathbf{p})\right|^2,$$

and is thus finite (and independent of t) for such a function $A(\mathbf{p})$. Moreover, since the Schrödinger equation (2.8) is *linear*, and the wave packet (2.9) is a linear combination[6] of the solutions (2.6), it follows that (2.9) is also a solution. More explicitly, from Eq. (2.8) immediately obtain

$$\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2\right)\Psi = \left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2\right)\int d^3p\, A(\mathbf{p})\, e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)}$$

$$= \int d^3p\, A(\mathbf{p})\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2\right)e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)} = 0.$$

Remark. If instead of the classical energy-momentum relation we had used the relativistic one

$$E^2 = c^2\mathbf{p}^2 + m^2c^4,$$

instead of Schrödinger's equation (2.8) we would have obtained the *Klein–Gordon* equation[7]

$$\partial_t^2\Psi - c^2\nabla^2\Psi + \frac{m^2c^4}{\hbar^2}\Psi = 0.$$

This relativistically covariant equation was considered by Schrödinger as early as 1925, but it was soon discarded by him because it lead to negative energy solutions, which are unacceptable in relativity theory (and would imply the instability of all matter). It is, however, relevant in the context of quantum field theory. ∎

---

[5] Erwin Schrödinger (1887–1961), German physicist and Nobel Prize winner in 1933

[6] Although in mathematics linear combinations involve only a finite number of terms, it is common in the physics literature to use this terminology for infinite sums or even integrals.

[7] Named after the Swedish physicist Oskar Klein (1894–1977) and the German physicist Walter Gordon (1893–1939).

Our next aim is to write down the analogue of the free Schrödinger equation (2.8) when the particle moves subject to a potential $V(\mathbf{r})$. To this end, note that in non-relativistic mechanics the energy of a particle is defined up to an arbitrary constant. Thus for a free particle, instead of the usual relation (2.4) we could have taken

$$E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V_0,$$

where V_0 is any real constant. Proceeding as before we obtain

$$\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2\right)e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)} = \left(E(\mathbf{p}) - \frac{\mathbf{p}^2}{2m}\right)e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)} = V_0 e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t\right)},$$

so that the plane waves (2.6) now satisfy the equation

$$i\hbar\partial_t\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V_0\Psi \qquad (2.10)$$

<div style="text-align:right">`SchrV0`</div>

instead of (2.8). The same is true, by linearity, of the more general wave packets (2.9). Equation (2.10) strongly suggests that the appropriate generalization of the free particle Schrödinger equation when the potential $V(\mathbf{r})$ is not constant is

$$i\hbar\partial_t\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\Psi. \qquad (2.11)$$

<div style="text-align:right">`SchreqV`</div>

This is the celebrated **time-dependent Schrödinger equation**, proposed by Erwin Schrödinger in 1926[8]. Equation (2.11) is the fundamental equation of non-relativistic quantum mechanics, in many ways comparable to Newton's second law $\mathbf{F} = m\mathbf{a}$ for classical mechanics. The previous derivation of Schrödinger's equation is only a heuristic argument, not a formal or rigorous proof. Equation (2.11) can in fact be considered as one of the *axioms* of non-relativistic quantum mechanics. Its best "proof" is ultimately the total agreement so far of its predictions with experiment.

The Schrödinger equation (2.11) is a linear partial differential equation of *evolutionary type*, since does not contain terms with time derivatives of order greater than one. What this entails is that, under appropriate smoothness conditions for the potential $V(\mathbf{r})$, there is a *unique* solution satisfying the initial condition

$$\Psi(\mathbf{r},0) = \psi(\mathbf{r}),$$

where ψ is any (sufficiently smooth, in general complex valued) function. Note, however, that if at a certain time $t_0 > 0$ the position of the particle is measured and found to be[9] $\mathbf{r}_0$, the particle's state immediately after this measurement is performed *jumps discontinuously* from $\Psi(\mathbf{r}, t_0)$ to a wave function sharply peaked at $\mathbf{r}_0$. This is the so called *collapse of the wave function*, which is one of the most controversial and least understood aspects of quantum mechanics. The collapse of the wave function is clearly a consequence of the *inevitable and uncontrollable perturbation* produced by measuring — or, as is often said, *observing*— the particle's position. In fact, as we shall see in more detail in the next chapters, it takes place whenever a measurement of any dynamical variable (position, momentum, energy, angular momentum, spin . . .) is performed on the particle. Summarizing:

> The knowledge of the particle's state at the initial time $t = 0$ completely determines its state at any other time $t > t_0$ *provided that no measurement is performed* on the particle during the interval $[0, t]$.

In this sense, even if the information on the particle's state provided by the wave function is of a probabilistic or statistical nature, *quantum mechanics is a deterministic theory.* It should be stressed, however,

---

[8]Schrödinger's derivation of Eq. (2.11) was based on the classical Hamilton–Jacobi equation in Hamiltonian mechanics.

[9]When no confusion is possible, we shall simply say that "the particle's position is found to be $\mathbf{r}_0$," instead of the more correct statement "the particle's position is found to lie inside a volume element d^3r centered at $\mathbf{r}_0$."

that in quantum mechanics there are *two different types* of evolutions: the *deterministic and continuous* evolution governed by Schrödinger's time-dependent equation (when no intermediate measurement is performed on the particle), and the *discontinuous collapse of the wave function* immediately after a measurement is performed. The latter type of evolution is of course *not deterministic* in nature, since as we shall see in the sequel (and have already remarked for position measurements) it is impossible in general to predict the outcome of a measurement even when the state of the particle is known (the theory only provides the *probability* of obtaining a certain value of the dynamical variable measured).

In our heuristic derivation of the Schrödinger equation, we noted that

$$-i\hbar\nabla = \mathbf{p}$$

when both sides act on a momentum wave function (2.6). For this reason, we shall define the **linear momentum** operator **P** as

$$\mathbf{P} = -i\hbar\nabla,$$ (2.12) `lmomdef`

with components

$$P_k = -i\hbar\partial_{x_k}, \qquad k = 1, 2, 3.$$

We thus have

$$\mathbf{P}\,e^{-\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t)} = \mathbf{p}\,e^{-\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t)},$$

for any constant vector $\mathbf{p} \in \mathbb{R}^3$. Another justification for the previous definition of the linear momentum operator in quantum mechanics is that **P** is the *generator of translations*. (Recall that in classical mechanics the linear momentum of a particle is the quantity that is conserved when the particle's Lagrangian is invariant under translations.) Indeed, if $\mathbf{a} \in \mathbb{R}^3$ is a constant vector and $\Psi(\cdot, t)$ is an analytic function, by Taylor's theorem in multivariable calculus we have

$$e^{\frac{i}{\hbar}\mathbf{a}\cdot\mathbf{P}}\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i}{\hbar}\mathbf{a}\cdot\mathbf{P}\right)^n\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty}\frac{1}{n!}(\mathbf{a}\cdot\nabla)^n\Psi(\mathbf{r}, t) = \Psi(\mathbf{r} + \mathbf{a}, t).$$

We shall also define the **position operator R** as the *multiplication operator* by the vector **r**. In other words, if $\Psi(\mathbf{r}, t)$ is any wave function the (vector valued) function $\mathbf{R}\Psi$ is defined by

$$\mathbf{R}\Psi(\mathbf{r}, t) := \mathbf{r}\Psi(\mathbf{r}, t).$$

The components of the vector-valued operator **R**, denoted by X_k, are accordingly defined by

$$X_k\Psi(\mathbf{r}, t) = x_k\Psi(\mathbf{r}, t).$$

In general, if $f(\mathbf{r})$ is any smooth function of the vector variable **r**, we defined the corresponding multiplication operator $f(\mathbf{R})$ by

$$f(\mathbf{R})\Psi(\mathbf{r}, t) := f(\mathbf{r})\Psi(\mathbf{r}, t).$$

With these definitions, the time-dependent Schrödinger equation (2.11) can be written as

$$i\hbar\partial_t\Psi = H\Psi,$$

where the quantum **Hamiltonian** H is the *linear operator*

$$H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R}).$$

In other words, the quantum Hamiltonian is formally obtained from the classical Hamiltonian of a particle of mass m (in *Cartesian* coordinates)

$$H_{\mathrm{cl}} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

by the replacement

$$\mathbf{p} \to \mathbf{P} = -\mathrm{i}\hbar\nabla, \qquad \mathbf{r} \to \mathbf{R}.$$

The passage from the classical to the quantum Hamiltonian through the previous replacement is called **canonical quantization**. In other words, in canonical quantization we replace the classical dynamical variables $\mathbf{r}$ and $\mathbf{p}$ by their corresponding *linear operators* $\mathbf{R}$ and $\mathbf{P}$ (see p. 40 for further details).

The linear space $L^2(\mathbb{R}^3)$ to which the wave functions of a quantum particle belong is endowed with a natural *scalar product*, defined by[10]

$$(\psi, \phi) := \int \mathrm{d}^3 r\, \psi^*(\mathbf{r})\phi(\mathbf{r}), \qquad \forall \psi, \phi \in L^2(\mathbb{R}^3),$$

where the integral is extended as usual to the whole space $\mathbb{R}^3$. This product has the usual properties of a complex scalar product, namely

i) $\|\psi\|^2 := (\psi, \psi) \geqslant 0$, and $\|\psi\| = 0$ if and only if[11] $\psi = 0$.

ii) $(\phi, \psi) = (\psi, \phi)^*$.

iii) $(\psi, \lambda_1\phi_1 + \lambda_2\phi_2) = \lambda_1(\psi, \phi_1) + \lambda_2(\psi, \phi_2)$, for all $\lambda_{1,2} \in \mathbb{C}$.

Note that properties ii) and iii) imply that

$$(\lambda_1\psi_1 + \lambda_2\psi_2, \phi) = \lambda_1^*(\psi_1, \phi) + \lambda_2^*(\psi_2, \phi).$$

The space $L^2(\mathbb{R}^3)$, with the norm $\|\cdot\|$ defined by i), is *complete*, by which it is meant that every *Cauchy sequence*[12] of functions $\psi_n \in L^2(\mathbb{R}^3)$ is convergent. Moreover, it can be shown that $L^2(\mathbb{R}^3)$ is *separable*, i.e., it contains a countable dense[13] subset (actually, there is an infinite number of such subsets). Thus $L^2(\mathbb{R}^3)$ is an infinite dimensional **Hilbert space**.

As in the finite-dimensional case, given a linear operator $A : L^2(\mathbb{R}^3) \to \mathbb{C}$, we define its **adjoint** $A^\dagger$ as the linear operator satisfying[14]

$$(\psi, A\phi) = (A^\dagger\psi, \phi), \qquad \forall \phi, \psi \in L^2(\mathbb{R}^3).$$

---

[10]Using *Hölder's inequality*, it can be shown that when $\psi, \phi \in L^2(\mathbb{R}^3)$ the integral of $\psi^*\phi$ is absolutely convergent.

[11]In fact, the elements of $L^2(\mathbb{R}^3)$ are *equivalence classes* of complex valued functions, with two functions considered to be equivalent if they differ on a set of measure zero. In particular, $\psi = 0$ actually means that ψ vanishes except at most on a set of measure zero. This statement is often abbreviated by saying that ψ vanishes *almost everywhere*, or a. e. for short.

[12]A sequence of functions $\{\psi_n\}_{n=1}^\infty \subset L^2(\mathbb{R}^3)$ is a Cauchy sequence if for every $\varepsilon > 0$ there exists a natural number $N \in \mathbb{N}$ such that $\|\psi_n - \psi_m\| < \varepsilon$ for all $n, m \geqslant N$. The sequence is convergent if there is an element $\psi \in L^2(\mathbb{R}^3)$ such that $\|\psi - \psi_n\|$ tends to zero as n tends to infinity.

[13]A set S in a topological space X is *dense* in X if the closure of S (i.e., the union of S and the set of its accumulation points of S) is the whole space X. Intuitively, S is dense in X if there is a point of S arbitrarily close to every point of X. For instance, the set $\mathbb{Q}$ of rational numbers is dense in the set $\mathbb{R}$ of real numbers with its standard topology.

[14]More precisely, if the domain of A is only a dense proper subset $\mathscr{D}(A)$ of $L^2(\mathbb{R}^3)$ we say that ψ is in the domain of $A^\dagger$ if there exists an element $\psi_1 \in L^2(\mathbb{R}^3)$ such that

$$(\psi, A\phi) = (\psi_1, \phi), \qquad \forall \phi \in \mathscr{D}(A).$$

When this is the case, we define $A^\dagger\psi := \psi_1$. It is immediate to show that the operator thus defined is *linear*.

A linear operator $A : L^2(\mathbb{R}^3) \to \mathbb{C}$ is **self-adjoint** if $A^\dagger = A$, or equivalently if the following equality holds[15]:

$$(\psi, A\phi) = (A\psi, \phi), \qquad \forall \phi, \psi \in L^2(\mathbb{R}^3). \tag{2.13}$$

<div style="float:right">selfadj</div>

As in the finite-dimensional case, a complex number λ is an **eigenvalue** of a linear operator $A : L^2(\mathbb{R}^3) \to \mathbb{C}$ if there exists a *nonzero* element $\psi \in L^2(\mathbb{R}^3)$ such that

$$A\psi = \lambda\psi.$$

We then say that ψ is an *eigenvector* —or, more commonly in this context, **eigenfunction**— of A with eigenvalue λ. An important property of self-adjoint operators is that their eigenvalues must be *real numbers*. Indeed, if $\lambda \in \mathbb{C}$ is an eigenvalue of $A : L^2(\mathbb{R}^3) \to \mathbb{C}$ and $\psi \in L^2(\mathbb{R}^3)$ is an eigenfunction of A with eigenvalue λ we have

$$(\psi, A\psi) = \lambda(\psi, \psi) \equiv \lambda \|\psi\|^2 = (A\psi, \psi) = (\lambda\psi, \psi) = \lambda^*(\psi, \psi) = \lambda^* \|\psi\|^2 \implies \lambda = \lambda^*,$$

since $\|\psi\| \neq 0$ by definition of eigenfunction. This property is essential in quantum mechanics since, as we shall see in the next chapters, the eigenvalues of an operator representing a classical dynamical variable are the possible values that can be obtained when we measure that variable, and thus must be real numbers. For instance, it is straightforward to check that *the position and momentum operators are self-adjoint.* Indeed, for the position operator it suffices to note that

$$(\psi, X_k\phi) = \int d^3r\, \psi^*(\mathbf{r}) x_k \phi(\mathbf{r}) = \int d^3r \Big(x_k \psi(\mathbf{r}) \Big)^* \phi(\mathbf{r}) = (x_k\psi, \phi).$$

Likewise, for the momentum operator we have

$$(\psi, P_k\phi) = \int d^3r\, \psi^*(\mathbf{r})(-i\hbar\partial_{x_k})\phi(\mathbf{r}) = i\hbar \int d^3r \Big(\partial_x \psi^*(\mathbf{r}) \Big)\phi(\mathbf{r}) = \int d^3r \Big(-i\hbar\partial_x\psi(\mathbf{r}) \Big)^* \phi(\mathbf{r})$$
$$= (P_k\psi, \phi),$$

where in the second equality we have integrated by parts taking into account that ϕ and ψ vanish at infinity (as they are both in $L^2(\mathbb{R}^3)$)[16]. As a matter of fact, the previous calculation only shows that the position and momentum operators are symmetric, *not* self-adjoint. It can be shown, however, that they are self-adjoint in their natural domains. In what follows we shall avoid these technical issues, for whose resolution a knowledge of functional analysis is indispensable, and use the terms "self-adjoint" and "symmetric" (or "Hermitian") almost interchangeably.

<div style="float:left">ge.canquant</div>

The process of canonical quantization can in principle be performed with any dynamical variable $f(\mathbf{r}, \mathbf{p})$, with the following important proviso. While the classical coordinates x_i and momenta p_j are commutative variables, i.e., $x_i p_j = p_j x_i$ for all i, j, the same is *not* true for the corresponding quantum operators X_i and P_j unless $i \neq j$. More precisely, we clearly have

$$X_i X_j = X_j X_i, \qquad P_i P_j = P_j P_i$$

for all i, j, the latter equality expressing the commutativity of the partial derivatives:

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\psi(\mathbf{r}) = \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i}\psi(\mathbf{r})$$

---

[15]As a matter of fact, the previous definition assumes that the domain of the operator A is the whole Hilbert space $L^2(\mathbb{R}^3)$, which in practice (for instance, for the position and linear momentum operators) is often not the case. If A is only defined on a dense subset $\mathcal{D}(A) \subset L^2(\mathbb{R}^3)$ and (2.13) holds for all $\phi, \psi \in \mathcal{D}(A)$, the operator A is said to be *symmetric* (or *Hermitian*). A symmetric operator A is self-adjoint if

$$(\psi, A\phi) = (\psi_1, \phi)$$

for *all* $\phi \in \mathcal{D}(A)$ if and only if $\psi \in \mathcal{D}(A)$ and $\psi_1 = A\psi$. A is symmetric but not self-adjoint if and only if the adjoint operator $A^\dagger$ is a *proper extension* of A, i.e. it is defined on a domain $\mathcal{D}(A^\dagger) \supsetneq \mathcal{D}(A)$ and $A^\dagger = A$ on $\mathcal{D}(A)$. Whether a symmetric operator is actually self-adjoint depends crucially on its domain, i.e., on the precise *boundary conditions* used to define it.

[16]As a matter of fact, there are (pathological) examples of square integrable functions not vanishing at infinity. It can be shown, however, that none of these functions can belong to the domain of the momentum operator.

---

for all functions ψ of class C^2. On the other hand,

$$X_i P_j \psi(\mathbf{r}) = -i\hbar x_i \frac{\partial \psi}{\partial x_j}(\mathbf{r}), \quad P_j X_i \psi(\mathbf{r}) = -i\hbar \frac{\partial}{\partial x_j}(x_i \psi(\mathbf{r})) = -i\hbar x_i \frac{\partial \psi}{\partial x_j}(\mathbf{r}) - i\hbar \delta_{ij} \psi(\mathbf{r})$$

and therefore

$$[X_i, P_j]\psi(\mathbf{r}) := (X_i P_j - P_j X_i)\psi(\mathbf{r}) = i\hbar \delta_{ij} \psi(\mathbf{r}).$$

Since the latter equality holds for any (sufficiently smooth) wave function, we have proved the operator identity

$$[X_i, P_j] = i\hbar \delta_{ij}. \tag{2.14}$$

`HeisCR`

The latter identities are called the **canonical commutation relations**, and play a similar role in quantum mechanics as the fundamental *Poisson bracket* identities

$$\{x_i, p_j\} = \delta_{ij}$$

in classical mechanics. We thus see that the canonical quantization prescription

$$f(\mathbf{r}, \mathbf{p}) \to f(\mathbf{R}, \mathbf{P})$$

is ambiguous in most cases. For example, classically

$$x_k^2 p_k = x_k p_k x_k = p_k x_k^2 = \frac{1}{2}(x_k^2 p_k + p_k x_k^2),$$

while the corresponding quantum mechanical operators are not all equal:

$$X_k P_k X_k = X_k[P_k, X_k] + X_k^2 P_k = X_k^2 P_k - i\hbar X_k, \qquad P_k X_k^2 = X_k P_k X_k + [P_k, X_k]X_k = X_k^2 P_K - 2i\hbar X_k,$$

$$\frac{1}{2}(X_k^2 P_k + P_k X_k^2) = X_k^2 P_K - i\hbar X_k = X_k P_k X_k.$$

Since the linear operator associated to a classical dynamical variable must be self-adjoint, the operators $X_k^2 P_k$ and $P_k X_k^2$ are clearly unsuitable, as

$$(X_k^2 P_k)^\dagger = P_x X_k^2 = X_k^2 P_K - 2i\hbar X_k \neq X_k^2 P_K, \qquad (P_k X_k^2)^\dagger = X_k^2 P_k = P_K X_k^2 + 2i\hbar X_k \neq P_k X_k^2.$$

On the other hand, $X_k P_k X_k$ is obviously self-adjoint, and hence is the only quantum operator that can represent the classical dynamical variable $x_k^2 p_k$. Thus in this case the self-adjointness requirement removes the ambiguity in canonical quantization. Unfortunately, this is *not* true in general. For instance, both self-adjoint operators

$$X_k P_k^2 X_k, \qquad \frac{1}{2}(X_k^2 P_k^2 + P_k^2 X_k^2)$$

reduce to the classical canonical variable $x_k^2 p_k^2$ under $(X_k, P_k) \to (x_k, p_k)$, but they are *different*:

$$\frac{1}{2}(X_k^2 P_k^2 + P_k^2 X_k^2) = X_k P_k^2 X_k + \frac{1}{2}\left(X_k[X_k, P_k^2] + [P_k^2, X_k]X_k\right) = X_k P_k^2 X_k + i\hbar(X_k P_k - P_k X_k)$$

$$= X_k P_k^2 X_k - \hbar^2.$$

This shows that the self-adjointness requirement is in general not enough to remove the ambiguity in canonical quantization. In practice, however, one seldom needs to quantize monomials of order greater than 2 containing both coordinates x_i and momenta p_j. Of these monomials, the only one for which canonical quantization is ambiguous is $x_k p_k$, but in this case the prescription

$$x_k p_k \to \frac{1}{2}(X_k P_k + P_k X_k)$$

is the only possible canonical quantization yielding a self-adjoint operator. Thus any observable of the form

$$a(\mathbf{r}) + b(\mathbf{p}) + \sum_{i,j=1}^{3} c_{ij} x_i p_j,$$

with $c_{ij} = c_{ji} \in \mathbb{R}$ constant, can be canonically quantized in a unique way as

$$a(\mathbf{R}) + b(\mathbf{P}) + \frac{1}{2} \sum_{i,j=1}^{3} c_{ij} (X_i P_j + P_j X_i).$$

For instance, for the components of the *angular momentum* $l_k = x_i p_j - x_j p_i$, with (i, j, k) a cyclic permutation of $(1, 2, 3)$, the canonical quantization procedure yields the operator

$$L_k := \frac{1}{2}(X_i P_j + P_j X_i - X_j P_i - P_i X_j) = X_i P_j - X_j P_i + \frac{1}{2}([P_j, X_i] - [P_i, X_j]) = X_i P_j - X_j P_i,$$

where in the last equality we have used the canonical commutation relations (2.14).

Example 2.1. *Schrödinger equation for a system of particles.*
The classical Hamiltonian (in Cartesian coordinates) of a system of N particles subject to a potential $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is given by

$$H_{\mathrm{cl}} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \ldots, \mathbf{r}_N),$$

where m_i, $\mathbf{r}_i$ and $\mathbf{p}_i$ are respectively the mass, position vector and linear momentum of the i-th particle. To canonically quantize this system, we replace the classical (vector) dynamical variables $\mathbf{r}_k$, $\mathbf{p}_k$ by the linear operators $\mathbf{R}_k$, $\mathbf{P}_k$, where $\mathbf{R}_k$ is the multiplication operator by $\mathbf{r}_k$,

$$\mathbf{P}_k = -\mathrm{i}\hbar \nabla_{\mathbf{r}_k},$$

and $\nabla_{\mathbf{r}_k}$ is the gradient with respect to the coordinates $\mathbf{r}_k = (x_{k1}, x_{k2}, x_{k3})$ of the k-th particle. These operators act on wave functions $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \in L^2(\mathbb{R}^{3N})$ satisfying the normalization condition

$$\int \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N |\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 = 1.$$

The system's quantum Hamiltonian is then

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2m_i} + V(\mathbf{R}_1, \ldots, \mathbf{R}_N);$$

note that in this case canonical quantization is not ambiguous, since clearly

$$[X_{ik}, X_{jl}] = [P_{ik}, P_{jl}] = 0, \qquad \forall i, j, k, l.$$

Accordingly, the time-dependent Schrödinger equation for this system reads

$$\mathrm{i}\hbar \partial_t \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) = H\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t),$$

or in expanded form

$$\mathrm{i}\hbar \partial_t \Psi = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2 \Psi + V(\mathbf{r}_1, \ldots, \mathbf{r}_N)\Psi.$$

Example 2.2. *Non-covariance of canonical quantization.*

Canonical quantization is *not* covariant, by which we mean that it must be performed in *Cartesian* coordinates. In other words, suppose that $\mathbf{q} = (q_1, q_2, q_3)$ is any set of generalized coordinates, and let $\mathbf{p} = (p_1, p_2, p_3)$ denote the corresponding canonical momenta (in general different from the components of the particle's linear momentum). If the classical Hamiltonian is a certain function $H_{\mathrm{cl}}(\mathbf{q}, \mathbf{p})$ of the non-Cartesian canonical variables $(\mathbf{q}, \mathbf{p})$, Schrödinger's equation is *not*

$$i\hbar \partial_t \Psi(\mathbf{q}, t) = H_{\mathrm{cl}}(\mathbf{q}, -i\hbar \nabla_{\mathbf{q}}) \Psi(\mathbf{q}, t).$$

The correct procedure for obtaining Schrödinger's equation in the new coordinate system $\mathbf{q}$ is, of course, to perform the change of variables $\mathbf{q} = \mathbf{q}(\mathbf{r})$ in Schrödinger's equation in *Cartesian* coordinates (2.11).

To illustrate this important point, let us write down Schrödinger's time-dependent equation for a particle of mass m in cylindrical coordinates $\mathbf{q} = (\rho, \varphi, z)$, where

$$x_1 = \rho \cos \varphi, \qquad x_2 = \rho \sin \varphi, \qquad x_3 = z.$$

As is well known, the Laplacian ∇^2 is expressed in cylindrical coordinates as follows:

$$\nabla^2 = \partial_\rho^2 + \frac{1}{\rho} \partial_\rho + \frac{1}{\rho^2} \partial_\varphi^2 + \partial_z^2.$$

Substituting into Eq. (2.11) we immediately obtain the equation

$$i\hbar \partial_t \Psi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial \Psi}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2 \Psi}{\partial \varphi^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(\rho, \varphi, z) \Psi,$$

with Ψ regarded as a function of (ρ, φ, z, t). On the other hand, the classical Hamiltonian of a particle of mass m in cylindrical coordinates can be taken as

$$H_{\mathrm{cl}}(\rho, \varphi, z, p_\rho, p_\varphi, p_z) = \frac{1}{2m} \left(p_\rho^2 + \frac{p_\varphi^2}{\rho^2} + p_z^2 \right) + V(\rho, \varphi, z).$$

The naive canonical quantization using the replacements

$$p_\rho \to -i\hbar \partial_\rho, \qquad p_\varphi \to -i\hbar \partial_\varphi, \qquad p_z \to -i\hbar \partial_z$$

in $H_{\mathrm{cl}}(\rho, \varphi, z, p_\rho, p_\varphi, p_z)$ would have led to the *wrong* equation

$$i\hbar \partial_t \Psi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial^2 \Psi}{\partial \varphi^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(\rho, \varphi, z) \Psi,$$

in which the term proportional to $\frac{1}{\rho} \frac{\partial \Psi}{\partial \rho}$ is missing.

2.3 The continuity equation

sec.cont

The wave function $\Psi(\mathbf{r}, t)$ of a particle must satisfy the normalization condition (2.2) at *all* times t, since the probability of finding the particle anywhere in space must obviously be 1. At the same time, Ψ must satisfy Schrödinger's equation (2.11), which determines $\Psi(\mathbf{r}, t)$ from the initial data $\Psi(\mathbf{r}, 0)$ if no measurement is performed on the particle in the time interval $[0, t]$. Indeed, the Schrödinger equation can be written in operator form as

$$i\hbar \partial_t \Psi = H\Psi, \tag{2.15}$$

TDSEop

where the Hamiltonian $H : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ is a linear operator independent of the time t (since we are assuming that the potential V is time independent). Formally, the solution of the latter equation is

$$\Psi(\mathbf{r}, t) = e^{-\frac{it}{\hbar}H} \Psi(\mathbf{r}, 0), \qquad (2.16) \quad \boxed{\texttt{eiHt}}$$

where the exponential of an operator is defined as in the finite-dimensional case (i.e., when H is a *matrix*):

$$e^{-\frac{it}{\hbar}H} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{itH}{\hbar} \right)^n. \qquad (2.17) \quad \boxed{\texttt{expitH}}$$

The operator H is *self-adjoint*, since it can be expressed in terms of the self-adjoint operators $\mathbf{R}$ and $\mathbf{P}$ as

$$H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R}),$$

and

$$(\mathbf{P}^2)^\dagger = \left(\mathbf{P}^\dagger \right)^2 = \mathbf{P}^2, \qquad V(\mathbf{R})^\dagger = V(\mathbf{R}^\dagger) = V(\mathbf{R}),$$

where in the penultimate equality we have taken into account that the potential V is real valued. By a standard result in functional analysis, it follows that the RHS of Eq. (2.17) converges to a *unitary* operator $U(t) = e^{-\frac{it}{\hbar}H}$. Note that the unitarity of $U(t)$ can be formally proved as follows:

$$U(t)^\dagger = e^{\left(-\frac{it}{\hbar}H \right)^\dagger} = e^{\frac{it}{\hbar}H^\dagger} = e^{\frac{it}{\hbar}H} = U(t)^{-1}.$$

Calling $\psi(\mathbf{r}) = \Psi(\mathbf{r}, 0)$ we then have

$$\left\| \Psi \right\|^2 = (\Psi, \Psi) = (U(t)\psi, U(t)\psi) = (\psi, U^\dagger(t)U(t)\psi) = (\psi, \psi) = 1.$$

This establishes the following fundamental result:

> If initially the wave function is normalized, and we let it evolve in time according to the time-dependent Schrödinger equation (2.15), the wave function will remain normalized at all times.

In other words, *probability is globally conserved*.

Exercise 2.1. Show that probability is conserved by differentiating the squared norm of the wave function Ψ and applying the Schrödinger equation.

Solution. We have

$$\begin{aligned} i\hbar \partial_t \left\| \Psi \right\|^2 &= i\hbar \partial_t (\Psi, \Psi) = i\hbar \left[(\partial_t \Psi, \Psi) + (\Psi, \partial_t \Psi) \right] = (-i\hbar \partial_t \Psi, \Psi) + (\Psi, i\hbar \partial_t \Psi) \\ &= (-H\Psi, \Psi) + (\Psi, H\Psi) = 0, \end{aligned}$$

where in the third equality we have used Schrödinger's equation and in the last one the self-adjointness of H.

In fact, it can be shown that probability is also *locally conserved*, i.e., that it cannot disappear from some region in space and appear in a different region, even if this would not violate global probability conservation. Indeed, we have

$$\begin{aligned} i\hbar \partial_t |\Psi|^2 &\equiv i\hbar \partial_t (\Psi^* \Psi) = (-i\hbar \partial_t \Psi)^* \Psi + \Psi^* i\hbar \partial_t \Psi = \Psi^*(H\Psi) - (H\Psi)^* \Psi \\ &= \frac{\hbar^2}{2m} \left[(\nabla^2 \Psi^*)\Psi - \Psi^* \nabla^2 \Psi \right] = \frac{\hbar^2}{2m} \nabla \cdot \left[(\nabla \Psi^*)\Psi - \Psi^* \nabla \Psi \right], \end{aligned}$$

where in the fourth equality we have used Schrödinger's equation taking into account that the potential $V(\mathbf{r})$ is real valued. Defining the probability density $\rho(\mathbf{r}, t)$ and the **probability current** (density) $\mathbf{j}(\mathbf{r}, t)$ by

$$\rho(\mathbf{r}, t) := \big|\Psi(\mathbf{r}, t)\big|^2, \qquad \mathbf{j}(\mathbf{r}, t) := \frac{\mathrm{i}\hbar}{2m}\big[(\nabla\Psi^*)\Psi - \Psi^*\nabla\Psi\big], \tag{2.18}$$

`rhoj`

we have thus established the **continuity equation**

$$\partial_t \rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0. \tag{2.19}$$

`conteq`

Integrating the continuity equation over a fixed (time independent) volume Ω and applying the divergence theorem we immediately obtain the identity

$$\partial_t \int_\Omega \rho(\mathbf{r}, t)\,\mathrm{d}^3 r = -\int_{\partial\Omega} \mathbf{j}(\mathbf{r}, t)\cdot\mathbf{n}\,\mathrm{d}S,$$

where $\partial\Omega$ is the boundary of Ω, $\mathbf{n}$ denotes the *outer* normal to $\partial\Omega$ and $\mathrm{d}S$ its surface element. In other words, *the increase in the probability contained in the volume Ω must equal the probability flowing into Ω through its boundary*[17]. Of course, if in the previous equation we take as Ω a sphere of radius a then in the limit $a \to \infty$ the RHS vanishes (since the wave function, being square integrable, must vanish together with its first partial derivatives at spatial infinity[18]), and we recover the law of global probability conservation derived above.

Remark.

- The probability current for a plane wave

$$\Psi(\mathbf{r}, t) = A\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)}$$

of momentum $\mathbf{p}$ and intensity proportional to $\big|A\big|^2$ is given by

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

The vector $\mathbf{j}$ is therefore proportional to the product of the *intensity* of the wave and the particle's *velocity* $\mathbf{p}/m$. Thus $\mathbf{j}\cdot\mathbf{n}$ is proportional to the *particle flux* (i.e., number of particles per unit time and area) crossing an infinitesimal surface centered at $\mathbf{r}$ perpendicular to the unit vector $\mathbf{n}$ (and in the direction of the latter vector) at a time t.

2.4 Position and momentum eigenfunctions

`.posmomeigf`

In a finite-dimensional Hilbert space (i.e., $\mathbb{C}^n$ with its standard complex scalar product) all self-adjoint operators are diagonalizable, and in fact possess an orthonormal basis of eigenvectors. In infinite-dimensional Hilbert spaces the situation is far more complex. In particular, a self-adjoint operator may not have any eigenvalues.

An important example of the latter fact is provided by the position and momentum operators in the Hilbert space $L^2(\mathbb{R}^3)$. Indeed, if (for example) $\psi(\mathbf{r})$ is an eigenfunction of the momentum operator $\mathbf{P}$ with eigenvalue[19] $\mathbf{p} = (p_1, p_2, p_3) \in \mathbb{R}^3$ it must satisfy the differential equation

$$-\mathrm{i}\hbar\nabla\psi = \mathbf{p}\psi.$$

---

[17] Note that a negative value of the surface integral in Eq. (2.19) means that probability is entering the volume Ω through its boundary $\partial\Omega$, since by definition the normal vector $\mathbf{n}$ points *outside* Ω.

[18] As pointed out above, there are square integrable functions that do not vanish at infinity. However, it is always assumed that *physical* wave functions, together with their first partial derivatives, vanish sufficiently fast at spatial infinity.

`foot.L2`

[19] Recall that the eigenvalues of a self-adjoint operator must be real.

This vector equation is equivalent to the three scalar equations

$$-i\hbar \frac{\partial \psi}{\partial x_k} = p_k \psi, \qquad k = 1, 2, 3,$$

whose general solution is

$$\psi(\mathbf{r}) = A e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}, \tag{2.20}$$

with $A = \psi(0)$ an arbitrary complex constant. Since

$$\left| \psi(\mathbf{r}) \right|^2 = \left| A \right|^2$$

is constant, the probability of finding the particle anywhere in space is uniform. (This is in agreement with Heisenberg's uncertainty principle, since when the particle's momentum is perfectly known the uncertainty in its position must be infinite so as not to violate the inequality (1.61).) However, the plane wave (2.20) is *not* a true eigenfunction of $\mathbf{P}$, since it is *not* normalizable (i.e., is *not* in $L^2(\mathbb{R}^3)$):

$$\int d^3 r \left| \psi(\mathbf{r}) \right|^2 = \int d^3 r \left| A \right|^2 = \infty.$$

Thus strictly speaking the momentum operator has no eigenvalues. On the other hand, a plane wave of the form $A e^{\frac{i}{\hbar} \mathbf{p}_0 \cdot \mathbf{r}}$ can be considered as a limiting case of a wave packet

$$\psi(\mathbf{r}) = \int d^3 p \, A(\mathbf{p}) \, e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}$$

with $|A|$ narrowly concentrated near a certain momentum $\mathbf{p}_0$, which as we have remarked above is a physical state as long as

$$\int d^3 p \left| A(\mathbf{p}) \right| < \infty.$$

Such a wave packet is clearly an *approximate eigenfunction* of the linear momentum operator $\mathbf{P}$, since

$$\mathbf{P} \psi(\mathbf{r}) = -i\hbar \nabla \int d^3 p \, A(\mathbf{p}) \, e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} = -i\hbar \int d^3 p \, A(\mathbf{p}) \, \nabla e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} = \int d^3 p \, A(\mathbf{p}) \, \mathbf{p} \, e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}$$

$$\simeq \mathbf{p}_0 \int d^3 p \, A(\mathbf{p}) \, e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} = \mathbf{p}_0 \psi(\mathbf{r})$$

if $\left| A(\mathbf{p}) \right|$ is narrowly concentrated around $\mathbf{p}_0$. From the mathematical point of view plane waves are extremely useful, as we shall see below, and as a matter of fact we shall use them extensively in what follows.

> **Definition 2.3.** When a nonzero function ψ that is not normalizable is a solution of the equation
>
> $$A\psi = a\psi,$$
>
> where A is a linear operator A and a a complex number, we shall say that ψ is a **formal eigenfunction** of A with eigenvalue a. For instance, from the above discussion it follows that the plane wave (2.20) is a formal eigenfunction of the linear momentum operator $\mathbf{P}$ with eigenvalue $\mathbf{p}$.

The situation is similar for position eigenfunctions. Indeed, if ψ is an eigenfunction of the position operator $\mathbf{R}$ with eigenvalue $\mathbf{r}_0 = (x_{01}, x_{02}, x_{03}) \in \mathbb{R}^3$ then

$$\mathbf{r}\psi(\mathbf{r}) = \mathbf{r}_0 \psi(\mathbf{r}).$$

This equation implies that $\psi(\mathbf{r}) = 0$ for all $\mathbf{r} \neq \mathbf{r}_0$, and hence

$$\int d^3 r \left| \psi(\mathbf{r}) \right|^2 = 0$$

however we define $\psi(\mathbf{r_0})$, which is incompatible with the normalization condition (2.2). Thus the position operator $\mathbf{R}$ does not possess any eigenfunctions.

Note, however, that any square integrable function ψ concentrated on a small region around the point $\mathbf{r_0}$ is an approximate eigenfunction of the position operator $\mathbf{r}$ with approximate eigenvalue $\mathbf{r_0}$. For example, we can take

$$\psi_\varepsilon(\mathbf{r}) = \begin{cases} 0, & |\mathbf{r} - \mathbf{r_0}| > \varepsilon \\ \left(\frac{3}{4\pi\varepsilon^3}\right)^{1/2}, & |\mathbf{r} - \mathbf{r_0}| \leqslant \varepsilon, \end{cases}$$

which fails to satisfy the eigenvalue equation only inside the infinitesimal (as $\varepsilon \to 0$) region $|\mathbf{r} - \mathbf{r_0}| < \varepsilon$ and is normalized:

$$\int \mathrm{d}^3 r \left|\psi_\varepsilon(\mathbf{r})\right|^2 = \int_{|\mathbf{r} - \mathbf{r_0}| \leqslant \varepsilon} \mathrm{d}^3 r \frac{3}{4\pi\varepsilon^3} = 1.$$

A similar example is provided by the family of smooth functions

$$\psi_\varepsilon(\mathbf{r}) = (\pi\varepsilon^2)^{-3/4} \mathrm{e}^{-\frac{(\mathbf{r} - \mathbf{r_0})^2}{2\varepsilon^2}},$$

which is non-negligible only for $|\mathbf{r} - \mathbf{r_0}| \lesssim \varepsilon$ and also satisfies the normalization condition:

$$\int \mathrm{d}^3 r \left|\psi_\varepsilon(\mathbf{r})\right|^2 = (\pi\varepsilon^2)^{-3/2} \int \mathrm{d}^3 r \, \mathrm{e}^{-\frac{(\mathbf{r} - \mathbf{r_0})^2}{\varepsilon^2}} = (\pi\varepsilon^2)^{-3/2} \int \mathrm{d}^3 r \, \mathrm{e}^{-\frac{r^2}{\varepsilon^2}} = (\pi\varepsilon^2)^{-3/2} \varepsilon^3 \pi^{3/2} = 1.$$

Note that in both cases $\psi_\varepsilon(\mathbf{r_0})$ is of the order of $\varepsilon^{-3/2}$, and thus tends to infinity as $\varepsilon \to 0$. This is reasonable, since as $\varepsilon \to 0$ the wave function ψ_ε is concentrated inside a sphere centered at $\mathbf{r_0}$ with a radius of the order of ε, whose volume is proportional to ε^3, $|\psi|^2$ must be of the order of ε^{-3} so that the normalization condition (2.2) is fulfilled. Although the family of wave functions $\{\psi_\varepsilon(\mathbf{r}) : \varepsilon > 0\}$ are approximate eigenfunctions of the position operator $\mathbf{R}$ with increasing accuracy as $\varepsilon \to 0+$, their limit

$$\lim_{\varepsilon \to 0+} \psi(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \neq \mathbf{r_0} \\ \infty, & \mathbf{r} = \mathbf{r_0} \end{cases}$$

vanishes for all $\mathbf{r} \neq \mathbf{r_0}$ but blows up at $\mathbf{r} = \mathbf{r_0}$, and its squared norm vanishes. On the other hand, if $\phi(\mathbf{r})$ is a smooth function vanishing (together with its partial derivatives of all orders) sufficiently fast at infinity —usually called a *test function*— and $\varepsilon > 0$ is small enough then

$$\int \mathrm{d}^3 r \phi(\mathbf{r}) \left|\psi_\varepsilon(\mathbf{r})\right|^2 \simeq \phi(\mathbf{r_0}) \int \mathrm{d}^3 r \left|\psi_\varepsilon(\mathbf{r})\right|^2 = \phi(\mathbf{r_0}),$$

or more rigorously

$$\lim_{\varepsilon \to 0+} \int \mathrm{d}^3 r \phi(\mathbf{r}) \left|\psi_\varepsilon(\mathbf{r})\right|^2 = \phi(\mathbf{r_0}). \qquad (2.21) \quad \boxed{\texttt{psieplim}}$$

We can thus write

$$\lim_{\varepsilon \to 0+} \int \mathrm{d}^3 r \phi(\mathbf{r}) \left|\psi_\varepsilon(\mathbf{r})\right|^2 = \delta_{\mathbf{r_0}}(\phi),$$

where $\delta_{\mathbf{r_0}}$ is a *linear functional* acting on the linear space of test functions as follows:

$$\delta_{\mathbf{r_0}}(\phi) = \phi(\mathbf{r_0}).$$

In mathematical terms, we say that as $\varepsilon \to 0+$ the function $\left|\psi_\varepsilon(\mathbf{r})\right|^2$ converges *in the sense of distributions* to **Dirac's delta function** $\delta_{\mathbf{r_0}}$. In practical terms, one uses the notation $\delta(\mathbf{r} - \mathbf{r_0})$ instead of $\delta_{\mathbf{r_0}}$, and proceeds formally as if

$$\delta_{\mathbf{r_0}}(\phi) = \int \mathrm{d}^3 r \phi(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r_0})$$

for some ordinary function $\delta_{\mathbf{r}_0}$. In other words, the identity

$$\int d^3r\, \phi(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_0) = \phi(\mathbf{r}_0) \tag{2.22}$$

deltadef

for any test function $\phi(\mathbf{r})$ is regarded as the *defining property* of the symbol $\delta(\mathbf{r} - \mathbf{r}_0)$. In the same vein, any identity of the form $A(\mathbf{r}) = B(\mathbf{r})$ involving Dirac's delta function is taken to mean

$$\int d^3r\, A(\mathbf{r})\phi(\mathbf{r}) = \int d^3r\, B(\mathbf{r})\phi(\mathbf{r})$$

for *all* test functions ϕ. For example,

$$f(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_0) = f(\mathbf{r}_0)\delta(\mathbf{r} - \mathbf{r}_0) \tag{2.23}$$

deeigf

for any function f, since by the defining property of $\delta(\mathbf{r} - \mathbf{r}_0)$ we have

$$\int d^3r\, f(\mathbf{r})\phi(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_0) = f(\mathbf{r}_0)\phi(\mathbf{r}_0) = \int d^3r\, f(\mathbf{r}_0)\phi(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_0)$$

for all test functions ϕ. In particular,

$$\mathbf{r}\delta(\mathbf{r} - \mathbf{r}_0) = \mathbf{r}_0\delta(\mathbf{r} - \mathbf{r}_0),$$

so that *formally* $\delta(\mathbf{r} - \mathbf{r}_0)$ is an eigenfunction of the position operator $\mathbf{R}$ with eigenvalue $\mathbf{r}_0$.

Exercise 2.2. Show that $\delta(a\mathbf{r}) = |a|^{-3}\delta(\mathbf{r})$, where $a \neq 0$ is a real number.

Solution. For any test function $\phi(\mathbf{r})$ we have

$$\int d^3r\, \phi(\mathbf{r})\delta(a\mathbf{r}) = |a|^{-3} \int d^3r\, \phi(\mathbf{r}/a)\delta(\mathbf{r}) = \frac{\phi(0)}{|a|^3} = \int d^3r\, \phi(\mathbf{r})\frac{\delta(\mathbf{r})}{|a|^3},$$

which by definition is equivalently to the identity we had to proof. Note that the same argument shows that in one dimension we have $\delta(ax) = |a|^{-1}\delta(x)$.

2.5 Expectation values. Ehrenfest's theorem

sec.Ehre

From the probabilistic interpretation of the wave function it follows that if at a certain time t a particle is in the state described by the wave function $\Psi(\mathbf{r}, t)$ and we measure its position, the *average value* we shall obtain for any (real) dynamical variable $f(\mathbf{r})$ depending only on the particle's position is given by the formula

$$\mathrm{av}_\Psi\big(f(\mathbf{r})\big) = \int d^3r\, f(\mathbf{r})\big|\Psi(\mathbf{r}, t)\big|^2 = (\Psi, f(\mathbf{r})\Psi) = (\Psi, f(\mathbf{R})\Psi). \tag{2.24}$$

avfr

Note that by "average value of $f(\mathbf{r})$ in the state Ψ" we mean the average

$$\frac{1}{N} \sum_{i=1}^{N} f(\mathbf{r}_i),$$

where $\mathbf{r}_1, \ldots, \mathbf{r}_N$ are the values of the position obtained after performing a large number N of position measurements on an ensemble of particles of the same type all of which are in the same state Ψ. Alternatively, $\mathbf{r}_i$ can represent the value obtained measuring the position of the particle for the i-th time *if*

prior to each measurement we prepare the particle in the state Ψ. In general, given an operator A acting on the Hilbert space of states of a particle we define its **expectation value** in the state Ψ by the formula

$$\langle A\rangle_\Psi := (\Psi, A\Psi).$$

Note that the expectation value of a self-adjoint operator is automatically *real*, since

$$(\Psi, A\Psi)^* = (A\Psi, \Psi) = (\Psi, A\Psi).$$

By Eq. (2.24), the average of $f(\mathbf{r})$ is the expectation value of the multiplication operator $f(\mathbf{R})$:

$$\mathrm{av}_\Psi\big(f(\mathbf{r})\big) = \big\langle f(\mathbf{R})\big\rangle_\Psi;$$

in particular, the average value of the particle's position when the particle is in a state Ψ is $\langle \mathbf{R}\rangle_\Psi$.

Let us next determine how the expectation value of an operator A *not depending explicitly on time* (for example, one of the components of the particle's position or momentum, or a function thereof) varies with time. To this end, note that

$$i\hbar\partial_t\langle A\rangle_\Psi = i\hbar\partial_t\big(\Psi, A\Psi\big) = \big(-i\hbar\partial_t\Psi, A\Psi\big) + \big(\Psi, i\hbar\partial_t(A\Psi)\big) = \big(-H\Psi, A\Psi\big) + \big(\Psi, A(i\hbar\partial_t\Psi)\big)$$
$$= \big(\Psi, -H(A\Psi) + AH\Psi\big) = \big(\Psi, [A, H]\Psi\big),$$

where we have applied the time-dependent Schrödinger equation in the third and fourth equalities and the self-adjoint character of H in the fourth one. We thus have proved the relation

$$i\hbar\partial_t\langle A\rangle_\Psi = (\Psi, [A, H]\Psi) \equiv \big\langle[A, H]\big\rangle_\Psi. \tag{2.25}$$

`pdtava`

This formula should be compared with its classical analogue

$$\dot{a} = \{a, H_{\mathrm{cl}}\}$$

for a dynamical variable $a(\mathbf{q}, \mathbf{p})$, where $\{\cdot, \cdot\}$ is the classical *Poisson bracket* defined by

$$\{a(\mathbf{q}, \mathbf{p}), b(\mathbf{q}, \mathbf{p})\} := \sum_{i=1}^N \left(\frac{\partial a}{\partial q_i}\frac{\partial b}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial b}{\partial q_i}\right).$$

In particular, applying Eq. (2.25) to a component of the position operator we have

$$i\hbar\partial_t\langle X_k\rangle_\Psi = (\Psi, [X_k, H]\Psi).$$

The commutator is easily computed[20]:

$$[X_k, H]\Psi = \left[X_k, -\frac{\hbar^2}{2m}\nabla^2\right]\Psi = \frac{\hbar^2}{2m}\big(\nabla^2(x_k\Psi) - x_k\nabla^2\Psi\big) = \frac{\hbar^2}{2m}\left(x_k\nabla^2\Psi + 2\frac{\partial\Psi}{\partial x_k} - x_k\nabla^2\Psi\right)$$
$$= \frac{\hbar^2}{m}\frac{\partial\Psi}{\partial x_k}.$$

---

[20]Alternatively, taking into account that $[X_k, V(\mathbf{R})] = 0$ we have

$$2m[X_k, H] = [X_k, \mathbf{P}^2] = [X_k, P_k^2] = P_k[X_k, P_k] + [X_k, P_k]P_k = 2i\hbar P_k,$$

where we have used the canonical commutation relations and the operator identity

$$[A, BC] = B[A, C] + [A, B]C.$$

Substituting in the previous formula for $i\hbar\partial_t\langle X_k\rangle_\Psi$ we obtain the identity

$$\partial_t\langle X_k\rangle_\Psi = \left(\Psi, -\frac{i\hbar}{m}\frac{\partial\Psi}{\partial x_k}\right) = \frac{1}{m}\left(\Psi, P_k\Psi\right) \equiv \frac{1}{m}\langle P_k\rangle_\Psi,$$

or in vector form

$$\partial_t\langle\mathbf{R}\rangle_\Psi = \frac{1}{m}\langle\mathbf{P}\rangle_\Psi. \tag{2.26}$$

`dtavr`

Since, as mentioned above, the average value of the position vector when the particle is in the state Ψ coincides with the expectation value $\langle\mathbf{R}\rangle_\Psi$, comparing this formula with the classical identity

$$\dot{\mathbf{r}} = \frac{\mathbf{p}}{m}$$

we are led to the conclusion that *the RHS of Eq.* (2.26) *should coincide with the average value of the particle's momentum in the state Ψ*:

$$\mathrm{av}_\Psi(\mathbf{p}) = \langle\mathbf{P}\rangle_\Psi.$$

The above analysis strongly suggests the following general property:

> The average value of *any* dynamical variable $a(\mathbf{r}, \mathbf{p})$ when a particle is in a quantum state Ψ is equal to the *expectation value*
> $$\langle A(\mathbf{R}, \mathbf{P})\rangle_\Psi \equiv \left(\Psi, A(\mathbf{R}, \mathbf{P})\Psi\right) \tag{2.27}$$
> of the self-adjoint *operator* $A(\mathbf{R}, \mathbf{P})$ representing $a(\mathbf{r}, \mathbf{p})$, obtained by canonical quantization (with a suitable ordering of the operators involved, as explained in Section 2.2).

`expApos`

The previous property establishes a *correspondence between classical dynamical variables and self-adjoint operators A*. For this reason, in quantum mechanics self-adjoint operators are usually called **observables**. Note that the self-adjointness of the operator A representing an observable is essential to guarantee that the expectation value of A in any state, which is the average value of the corresponding dynamical variable, is *real*. In these notes we shall usually assume that we are dealing with *scalar* particles, which have no *internal degrees of freedom* (like, for instance, *spin*). When this is the case the relevant observables are obtained by canonical quantization (with a suitable ordering of the operators involved) from classical dynamical variables (i.e., ordinary functions) $a(\mathbf{r}, \mathbf{p})$. On the other hand, when there are internal degrees of freedom there are quantum observables —for example, the spin components— not obtained by canonical quantization from a corresponding classical dynamical variable $a(\mathbf{r}, \mathbf{p})$. The most important observables we shall deal with in these notes are the following:

$$
\begin{aligned}
&\text{Position:} && \mathbf{R} \ \ (\text{multiplication by } \mathbf{r})\\
&\text{Linear momentum:} && \mathbf{P} = -i\hbar\nabla\\
&\text{Angular momentum:} && \mathbf{R}\times\mathbf{P} = -i\hbar\mathbf{r}\times\nabla\\
&\text{Kinetic energy:} && \frac{\mathbf{P}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2\\
&\text{Potential energy:} && V(\mathbf{R}) \ \ (\text{multiplication by } V(\mathbf{r}))
\end{aligned}
$$

Applying Eq. (2.25) to a component $P_k = -i\hbar\partial_{x_k}$ of the linear momentum we obtain the equation

$$i\hbar\partial_t\langle P_k\rangle_\Psi = (\Psi, [P_k, H]\Psi)$$

for the rate of variation of the average value of p_k in the state Ψ. Taking into account that the momentum components commute with one another we easily obtain

$$\left[P_k, H\right] = \left[P_k, V(\mathbf{R})\right] = -i\hbar\left[\partial_{x_k}, V(\mathbf{R})\right] = -i\hbar\frac{\partial V}{\partial x_k}(\mathbf{R})$$

(for the last equality, just apply both sides to an arbitrary wave function ϕ), or in vector form

$$\left[\mathbf{P}, H\right] = -i\hbar \nabla V(\mathbf{R}).$$

From the general formula. (2.25) we conclude that

$$\partial_t \langle \mathbf{P} \rangle_\Psi = -\langle \nabla V(\mathbf{R}) \rangle_\Psi. \tag{2.28}$$

<div style="float:right">`pdtP`</div>

Equations (2.26) and (2.28) are the content of **Ehrenfest's**[21] **theorem**. Although these equations are similar to the classical equations of motion

$$\dot{\mathbf{r}} = \frac{\mathbf{p}}{m}, \qquad \dot{\mathbf{p}} = -\nabla V(\mathbf{r}),$$

they do *not* imply that the average position $\langle \mathbf{R} \rangle_\Psi$ moves as a classical particle of mass m subject to the potential $V(\langle \mathbf{R} \rangle_\Psi)$, since in general

$$\langle \nabla V(\mathbf{R}) \rangle_\Psi \neq \nabla V\left(\langle \mathbf{R} \rangle_\Psi\right).$$

The latter equality is approximately true at some instant t_0 if the wave function is concentrated near a point $\mathbf{r}_0$, since in that case

$$\langle \mathbf{R} \rangle_\Psi \simeq \mathbf{r}_0 \quad \Longrightarrow \quad \langle \nabla V(\mathbf{R}) \rangle_\Psi \simeq \nabla V(\mathbf{r}_0) \simeq \nabla V\left(\langle \mathbf{R} \rangle_\Psi\right).$$

However, as the wave function $\Psi(\mathbf{r}, t)$ evolves in time according to the time-dependent Schrödinger equation it will in general *spread out*, so that after a sufficiently long time it will no longer be concentrated near any point in space, and the approximate equality of $\langle \nabla V(\mathbf{R}) \rangle_\Psi$ and $V\left(\langle \mathbf{R} \rangle_\Psi\right)$ will cease to hold. This can be clearly seen in the following example:

<div style="float:left">`exa.Gaussian`</div>

Example 2.4. Consider a particle moving freely (i.e., subject to no forces) in space, and suppose that for $t = 0$ the particle's wave function is the Gaussian

$$\psi(\mathbf{r}, 0) = \psi(\mathbf{r}) = (a^2 \pi)^{-3/4} e^{-\frac{r^2}{2a^2}},$$

where $a > 0$ is a constant. It can be easily checked that ψ is normalized:

$$\|\psi\|^2 = (a^2 \pi)^{-3/2} \int e^{-\frac{r^2}{a^2}} d^3 r = (a^2 \pi)^{-3/2} \left(\int e^{-\frac{x^2}{a^2}} dx \right)^3 = 1.$$

Moreover, ψ is concentrated on a sphere of radius of the order of a centered at the origin. On the other hand, integrating the time-dependent Schrödinger equation

$$i\hbar \partial_t \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t)$$

with the initial condition $\Psi(\mathbf{r}, 0) = \psi(\mathbf{r})$ it is found that[a]

$$\Psi(\mathbf{r}, t) = N A(t)^{-3/2} e^{-\frac{r^2}{2A(t)}}, \qquad \text{with} \quad N := \left(\frac{a^2}{\pi} \right)^{3/4}, \quad A(t) := a^2 + \frac{i\hbar t}{m},$$

---

[21]Paul Ehrenfest (1880–1933), Austrian physicist.

© Artemio González López

where[b] $z^{3/2} = |z|^{3/2}e^{\frac{3i}{2}\operatorname{Arg} z}$. This can be easily checked by differentiation:

$$i\hbar\partial_t(\Psi/N) = e^{-\frac{r^2}{2A}}\left(-\frac{3}{2}A^{-5/2} + A^{-3/2}\frac{r^2}{2A^2}\right)\left(-\frac{\hbar^2}{m}\right) = -\frac{\hbar^2}{2m}A^{-7/2}(r^2 - 3A)e^{-\frac{r^2}{2A}},$$

$$\nabla(\Psi/N) = A^{-3/2}e^{-\frac{r^2}{2A}}\left(-\frac{\mathbf{r}}{A}\right) = -A^{-5/2}e^{-\frac{r^2}{2A}}\,\mathbf{r},$$

$$\nabla^2(\Psi/N) = -A^{-5/2}e^{-\frac{r^2}{2A}}\left(3 - \frac{r^2}{A}\right) = A^{-7/2}(r^2 - 3A)e^{-\frac{r^2}{2A}}.$$

Note that $\Psi(\mathbf{r}, t)$ is automatically normalized for all t, since it is a solution of the time-dependent Schrödinger equation with $\Psi(0, \mathbf{r}) = \psi(\mathbf{r})$ of unit norm. This can also be checked directly:

$$|\Psi|^2 = \left(\frac{a^2}{\pi}\right)^{3/2}|A|^{-3}e^{-\frac{r^2}{2}\left(\frac{1}{A}+\frac{1}{A^*}\right)} = \left(\frac{a^2}{\pi}\right)^{3/2}|A|^{-3}e^{-\frac{\operatorname{Re}A\cdot r^2}{|A|^2}} = \left(\frac{a^2}{\pi}\right)^{3/2}|A|^{-3}e^{-\frac{a^2r^2}{|A|^2}} \qquad (2.29)$$

$$\implies \int d^3r\,|\Psi|^2 = \left(\frac{a^2}{\pi}\right)^{3/2}|A|^{-3}\left(\frac{\sqrt{\pi}\,|A|}{a}\right)^3 = 1.$$

<div style="text-align:right">rhogauss</div>

Note that the state $\Psi(\mathbf{r}, t)$ has zero average momentum, since

$$\langle\mathbf{P}\rangle_\Psi = (\Psi, \mathbf{P}\Psi) = (\Psi, -i\hbar\nabla\Psi) = N^2|A|^{-3}\int d^3r\,e^{-\frac{r^2}{2A^*}}(-i\hbar\nabla)e^{-\frac{r^2}{2A}}$$

$$= i\hbar N^2|A|^{-3}A^{-1}\int d^3r\,\mathbf{r}\left|e^{-\frac{r^2}{2A}}\right|^2 = 0$$

(the integrand is antisymmetric under $\mathbf{r} \mapsto -\mathbf{r}$). According to Ehrenfest's equation (2.26), the average position of the particle is therefore independent of time; in fact, it can be easily checked that $\langle\mathbf{R}\rangle_\Psi = 0$ for all t. More importantly, from Eq. (2.29) it follows that at an arbitrary time $t > 0$ the probability density $|\Psi(\mathbf{r}, t)|^2$ is concentrated on a sphere centered at the origin (i.e., at the average position $\langle\mathbf{R}\rangle_\Psi$) whose radius

$$\Delta r(t) = \frac{|A|}{a} = a\sqrt{1 + \frac{\hbar^2 t^2}{m^2 a^4}}$$

increases without bound as $t \to \infty$. Note also that the rate of increase of this radius, given by

$$\frac{d}{dt}\Delta r(t) = \frac{\hbar^2 t/m^2 a^2}{\sqrt{a^2 + \frac{\hbar^2 t^2}{m^2 a^2}}},$$

is approximately equal to $\frac{\hbar}{ma}$ as $a \to 0$. In other words, *the more concentrated the wave function is initially the faster it spreads out.*

---

[a]See Example 2.6.

[b]In these notes $\operatorname{Arg} z \in (-\pi, \pi]$ will always denote the *principal argument* of the complex number z.

2.6 Eigenfunctions and eigenvalues of observables

Let us suppose that at a certain time t a particle is in a state $\psi(\mathbf{r})$ which is an *eigenfunction* of an observable A with eigenvalue λ, i.e.,

$$A\psi = \lambda\psi.$$

Note that λ is necessarily real, as A is self-adjoint. Since

$$\langle A^n\rangle_\psi = (\psi, A^n\psi) = (\psi, \lambda^n\psi) = \lambda^n(\psi, \psi) = \lambda^n,$$

the *uncertainty* (root mean square deviation) of the observable A in the state ψ, denoted by $\Delta_\psi A$, vanishes:

$$\left(\Delta_\psi A\right)^2 \equiv \left\langle A^2\right\rangle_\psi - \left\langle A\right\rangle_\psi^2 = \lambda^2 - \lambda^2 = 0.$$

Thus A has a *well-defined value*, which must be equal to λ since $\left\langle A\right\rangle_\psi = \lambda$. Hence:

> If at a certain time the particle is in a state ψ which is an eigenfunction of an observable A with eigenvalue λ, a measurement of the observable A performed at this time will yield with certainty the value λ.

Conversely, suppose that when we measure the value of an observable A at a certain time t_0 we obtain the value λ. If we measure again the observable A at a later time $t_0 + \Delta t$ with $\Delta t \to 0+$, by consistency we should obtain the same value λ. It follows that the state of the particle immediately after the measurement of A is such that the uncertainty of A vanishes. Since

$$0 = \left(\Delta_\psi A\right)^2 = \left\langle \left(A - \langle A\rangle_\psi\right)^2\right\rangle_\psi = \left(\psi, (A - \langle A\rangle_\psi)^2 \psi\right) = \left\| (A - \langle A\rangle_\psi)\psi \right\|^2$$
$$\implies \quad (A - \langle A\rangle_\psi)\psi = 0,$$

we conclude that ψ is an *eigenstate* of A with eigenvalue $\lambda = \langle A\rangle_\psi$. In other words:

> If an observable A is measured at a certain time and the value λ is obtained, the state of the particle *immediately after the measurement* is an eigenstate of A with eigenvalue λ. In particular, the *only possible values* that can be obtained when an observable is measured are its *eigenvalues*.

2.7 The momentum representation

According to Born's rule, the square of the modulus of the wave function $\Psi(\mathbf{r}, t)$ of a quantum particle represents the probability density of finding the particle at the time t in an infinitesimal volume $\mathrm{d}^3 r$ centered at the point $\mathbf{r}$. We now ask ourselves how to obtain the probability density of finding the particle's momentum inside an infinitesimal volume $\mathrm{d}^3 p$ in momentum space about a given momentum $\mathbf{p}$. To this end, we shall start by recalling some fundamental facts about the Fourier transform. Given a function $\psi(\mathbf{r})$ in $L^2(\mathbb{R}^3)$, we define its **Fourier transform** $\hat{\psi}(\mathbf{p})$ by the formula[22]

$$\hat{\psi}(\mathbf{p}) = (2\pi\hbar)^{-3/2} \int \mathrm{d}^3 r \, \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}} \psi(\mathbf{r}). \tag{2.30}$$

It can be shown that $\hat{\psi}$ is in $L^2(\mathbb{R}^3)$ if and only if ψ is, and that the Fourier transform is in fact a *unitary mapping* from $L^2(\mathbb{R}^3)$ into itself. In other words,

$$(\psi, \phi) = (\hat{\psi}, \hat{\phi}), \qquad \forall \psi, \phi \in L^2(\mathbb{R}^3). \tag{2.31}$$

Moreover, the inverse $\psi(\mathbf{r})$ of the Fourier transform of a function $\hat{\psi}(\mathbf{p})$ can be computed from the formula

$$\psi(\mathbf{r}) = (2\pi\hbar)^{-3/2} \int \mathrm{d}^3 p \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}} \hat{\psi}(\mathbf{p}). \tag{2.32}$$

---

[22]In point of fact, the integral in Eq. (2.30) is only guaranteed to converge if $\psi \in L^1(\mathbb{R}^3)$ (i.e., if $|\psi|$ is integrable), and there are functions in $L^2(\mathbb{R}^3)$ that are not in $L^1(\mathbb{R}^3)$ (for instance, $(r^4+1)^{-1/2}$). If ψ is any such function, it can be shown that there is a sequence of functions ψ_j ($j \in \mathbb{N}$) with compact support (i.e., vanishing outside a compact set) such that $\left\| \psi - \psi_j \right\| \to 0$ as $j \to \infty$. It is also shown that the sequence $\hat{\psi}_j$ ($j \in \mathbb{N}$) is a Cauchy sequence, and therefore (since $L^2(\mathbb{R}^3)$ is complete) it has a limit, denoted by $\hat{\psi}$, which is shown to be independent of the sequence ψ_j chosen to approximate ψ. It is this function $\hat{\psi} = \lim_{j\to\infty} \hat{\psi}_j$ that is then *defined* as the Fourier transform of the function $\psi \in L^2(\mathbb{R}^3) \setminus L^1(\mathbb{R}^3)$.

Remark. In one dimension, the Fourier transform of a wave function $\psi(x)$ in $L^2(\mathbb{R})$ is defined by the analogous formula

$$\hat{\psi}(p) = (2\pi\hbar)^{-1/2} \int dx \, e^{-\frac{i}{\hbar}px} \psi(x).$$

With this normalization the Fourier transform is still unitary, i.e.,

$$(\psi, \phi) = (\hat{\psi}, \hat{\phi}), \qquad \forall \psi, \phi \in L^2(\mathbb{R}),$$

and the inverse Fourier transform is given by

$$\psi(x) = (2\pi\hbar)^{-1/2} \int dp \, e^{\frac{i}{\hbar}px} \hat{\psi}(p).$$ ∎

Suppose that at a certain time t the state of a particle is described by a wave function $\psi(\mathbf{r})$. We wish to find the probability density $\hat{\rho}(\mathbf{p})$ in momentum space when the particle is in the state ψ. A well known result in probability theory states that $\hat{\rho}(\mathbf{p})$ is uniquely determined by its *moments*

$$\text{av}_\psi\left(p_k^n\right) = \int d^3 p \, p_k^n \hat{\rho}(\mathbf{p}), \qquad k = 1, 2, 3, \quad n \in \mathbb{N}.$$

As we saw in the previous section, the average value of any function $f(\mathbf{p})$ of the particle's momentum can be computed by taking the expectation value of the corresponding quantum operator $f(\mathbf{P})$. Thus the sought for probability density is the unique function $\hat{\rho}(\mathbf{p})$ satisfying

$$\left\langle P_k^n \right\rangle_\psi \equiv (\psi, P_k^n \psi) = \int d^3 p \, p_k^n \hat{\rho}(\mathbf{p}), \qquad k = 1, 2, 3, \quad n \in \mathbb{N}. \tag{2.33}$$ `hrhodet`

On the other hand, from Eq. (2.32) we easily obtain

$$P_k^n \psi(\mathbf{r}) = (2\pi\hbar)^{-3/2} \int d^3 p \, \left(-i\hbar\partial_{x_k}\right)^n e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \hat{\psi}(\mathbf{p}) = (2\pi\hbar)^{-3/2} \int d^3 p \, e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} p_k^n \hat{\psi}(\mathbf{p}),$$

and therefore

$$p_k^n \hat{\psi}(\mathbf{p}) = \left(P_k^n \psi\right)^{\hat{}}(\mathbf{p}).$$

From Eq. (2.31) it then follows that

$$\left\langle P_k^n \right\rangle_\psi = \left(\psi, P_k^n \psi\right) = \left(\hat{\psi}, \left(P_k^n \psi\right)^{\hat{}}\right) = \left(\hat{\psi}, p_k^n \hat{\psi}\right),$$

and thus

$$\left\langle P_k^n \right\rangle_\psi = \int d^3 p \, p_k^n \left|\hat{\psi}(\mathbf{p})\right|^2. \tag{2.34}$$ `hrho`

Comparing Eqs. (2.33) and (2.34) we conclude that

$$\hat{\rho}(\mathbf{p}) = \left|\hat{\psi}(\mathbf{p})\right|^2.$$

In other words, $\left|\hat{\psi}(\mathbf{p})\right|^2$ is the probability density in momentum space. In the above discussion we have kept the time t fixed, and have accordingly dropped it from Eqs. (2.30) and (2.32). Restoring it we obtain the analogous equations

$$\hat{\Psi}(\mathbf{p}, t) = (2\pi\hbar)^{-3/2} \int d^3 r \, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \Psi(\mathbf{r}, t), \quad \Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3/2} \int d^3 p \, e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \hat{\Psi}(\mathbf{p}, t), \tag{2.35}$$ `Foutrinv`

and similarly for the one-dimensional case. In summary:

If a quantum particle is in a state $\Psi(\mathbf{r}, t)$, the function $\left|\hat{\Psi}(\mathbf{p}, t)\right|^2$ represents the *probability density* of finding the particle's momentum in an infinitesimal volume $\mathrm{d}^3 p$ about $\mathbf{p}$ in momentum space at the time t.

Exercise 2.3. Using the unitarity of the Fourier transform, prove the identity

$$\int \frac{\mathrm{d}^3 k}{(2\pi)^3}\, e^{i\mathbf{k}\cdot\mathbf{r}} = \delta(\mathbf{r}).$$

Solution. We have:

$$(\psi, \phi) = \int \mathrm{d}^3 r\, \psi^*(\mathbf{r})\phi(\mathbf{r}) = (2\pi\hbar)^{-3}\int \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3 p\, \mathrm{d}^3 p'\, \hat{\psi}^*(\mathbf{p})e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\hat{\phi}(\mathbf{p}')e^{\frac{i}{\hbar}\mathbf{p}'\cdot\mathbf{r}}$$

$$= \int \mathrm{d}^3 p\, \mathrm{d}^3 p'\, \hat{\psi}^*(\mathbf{p})\hat{\phi}(\mathbf{p}')\int \mathrm{d}^3 r\, (2\pi\hbar)^{-3}e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}} = (\hat{\psi}, \hat{\phi}) \equiv \int \mathrm{d}^3 p\, \hat{\psi}^*(\mathbf{p})\hat{\phi}(\mathbf{p})$$

$$= \int \mathrm{d}^3 p\, \mathrm{d}^3 p'\, \hat{\psi}^*(\mathbf{p})\hat{\phi}(\mathbf{p}')\delta(\mathbf{p}' - \mathbf{p}).$$

Thus

$$\int \mathrm{d}^3 p\, \mathrm{d}^3 p'\, \hat{\psi}^*(\mathbf{p})\hat{\phi}(\mathbf{p}')\int \mathrm{d}^3 r\, (2\pi\hbar)^{-3}e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}} = \int \mathrm{d}^3 p\, \mathrm{d}^3 p'\, \hat{\psi}^*(\mathbf{p})\hat{\phi}(\mathbf{p}')\delta(\mathbf{p}' - \mathbf{p}),$$

and hence

$$\delta(\mathbf{p}' - \mathbf{p}) = (2\pi\hbar)^{-3}\int \mathrm{d}^3 r\, e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}}. \tag{2.36}$$

`deppp`

Setting $\hbar = 1$ and $\mathbf{p}' - \mathbf{p} = \mathbf{k}$ we obtain

$$\int \frac{\mathrm{d}^3 r}{(2\pi)^3}\, e^{i\mathbf{k}\cdot\mathbf{r}} = \delta(\mathbf{k}),$$

which yields the sought for identity exchanging the roles of $\mathbf{r}$ and $\mathbf{k}$. A similar argument shows that in one dimension

$$\int \frac{\mathrm{d}k}{2\pi}\, e^{ikx} = \delta(x). \tag{2.37}$$

`eikxdel`

Remark. Equation (2.37) can be directly established as follows. To begin with, we have

$$\int_{-L}^{L} \frac{\mathrm{d}k}{2\pi}\, e^{ikx} = \frac{\sin(Lx)}{\pi x},$$

and thus we need to prove that

$$\lim_{L\to\infty} \frac{\sin(Lx)}{\pi x} = \delta(x)$$

in the sense of distributions. In other words, we must show that for any test function $\phi(x)$ the following equality holds:

$$\lim_{L\to\infty} \int_{-\infty}^{\infty} \mathrm{d}x\, \frac{\sin(Lx)}{\pi x}\phi(x) = \phi(0).$$

And indeed,

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \frac{\sin(Lx)}{\pi x}\phi(x) = \int_{-\infty}^{\infty} \mathrm{d}s\, \frac{\sin s}{\pi s}\phi(s/L) \xrightarrow[L\to\infty]{} \phi(0)\int_{-\infty}^{\infty} \mathrm{d}s\, \frac{\sin s}{\pi s} = \phi(0),$$

where in the last step we have made use of the well-known integral

$$\int_{-\infty}^{\infty} \mathrm{d}s\, \frac{\sin s}{s} = \pi.$$

which can be computed using residue theory. ∎

If the Fourier transform $\hat{\Psi}(\mathbf{p}, t)$ of a state $\Psi(\mathbf{r}, t)$ is known, we can compute the average (i.e., expectation value) of any observable $A(\mathbf{R}, \mathbf{P})$ in the state Ψ. Indeed, we have already seen that the Fourier transform of $\mathbf{P}\Psi(\mathbf{r}, t)$ is $\mathbf{p}\hat{\Psi}(\mathbf{p}, t)$, or expressed symbolically

$$\mathbf{P}\Psi(\mathbf{r}, t) \quad \overset{\frown}{\longrightarrow} \quad \mathbf{p}\hat{\Psi}(\mathbf{p}, t).$$

On the other hand, we have

$$\left(X_k \Psi\right)\hat{\,}(\mathbf{p}) = (2\pi\hbar)^{-3/2} \int \mathrm{d}^3 r \, x_k \Psi(\mathbf{r}, t) \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}} = (2\pi\hbar)^{-3/2} \mathrm{i}\hbar\partial_{p_k} \int \mathrm{d}^3 r \, \Psi(\mathbf{r}, t) \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}}$$
$$= \mathrm{i}\hbar\partial_{p_k} \hat{\Psi}(\mathbf{p}, t),$$

and therefore

$$\mathbf{R}\Psi(\mathbf{r}, t) \quad \overset{\frown}{\longrightarrow} \quad \mathrm{i}\hbar\nabla_{\mathbf{p}}\hat{\Psi}(\mathbf{p}, t).$$

It follows that, more generally,

$$A(\mathbf{R}, \mathbf{P})\Psi(\mathbf{r}, t) \quad \overset{\frown}{\longrightarrow} \quad A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p})\hat{\Psi}(\mathbf{p}, t),$$

whence

$$\left\langle A(\mathbf{R}, \mathbf{P})\right\rangle_{\Psi} = \left(\Psi, A(\mathbf{R}, \mathbf{P})\Psi\right) = \left(\hat{\Psi}, [A(\mathbf{R}, \mathbf{P})\Psi]\hat{\,}\right) = \left(\hat{\Psi}, A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p})\hat{\Psi}\right).$$

Thus the average of any observable $A(\mathbf{R}, \mathbf{P})$ can be computed either as

$$\left\langle A(\mathbf{R}, \mathbf{P})\right\rangle_{\Psi} = \left(\Psi, A(\mathbf{r}, -\mathrm{i}\hbar\nabla)\Psi\right), \tag{2.38}$$ `avpos`

i.e., in the so called *position representation*, or equivalently from

$$\left\langle A(\mathbf{R}, \mathbf{P})\right\rangle_{\Psi} = \left(\hat{\Psi}, A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p})\hat{\Psi}\right), \tag{2.39}$$ `avmom`

i.e., in the *momentum representation*). We conclude that

The Fourier transform $\hat{\Psi}(\mathbf{p}, t)$ represents the particle's *wave function* (i.e., *probability amplitude*) in the momentum representation. In particular, in this representation the operators $\mathbf{R}$ and $\mathbf{P}$ are respectively given by

$$\mathbf{R} = \mathrm{i}\hbar\nabla_{\mathbf{p}}, \qquad \mathbf{P} = \mathbf{p}$$

(the latter regarded as a multiplication operator).

Example 2.5. *Normalization of momentum "eigenfunctions".*
We saw in Section (2.4) that the plane waves

$$\psi_{\mathbf{p}}(\mathbf{r}) := A \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}}$$

are formal eigenfunctions of the momentum operator $\mathbf{P}$ with eigenvalue $\mathbf{p}$. Although these functions are *not* normalizable in the usual sense, i.e.,

$$\int \mathrm{d}^3 r \, |\psi_{\mathbf{p}}(\mathbf{r})|^2 = |A|^2 \int \mathrm{d}^3 r = \infty,$$

it is of interest to find a prescription for choosing the value of the constant A in a convenient way. To begin with, since a global (i.e., position independent) phase does not change the state, we can take A as real and positive without loss of generality. Secondly, using Eq. (2.36) we obtain

$$(\psi_{\mathbf{p}}, \psi_{\mathbf{p}'}) = A^2 \int d^3r \, e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}} = (2\pi\hbar)^3 A^2 \delta(\mathbf{p}' - \mathbf{p}).$$

It follows that the functions

$$\psi_{\mathbf{p}}(\mathbf{r}) := (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \qquad (2.40)$$

`normmomeigf`

obey the normalization condition

$$(\psi_{\mathbf{p}}, \psi_{\mathbf{p}'}) = \delta(\mathbf{p} - \mathbf{p}'). \qquad (2.41)$$

`Diracnorm`

This condition, usually known as **Dirac's** (or **delta function**) **normalization**, is the analogue for (formal) eigenfunctions depending on a continuous parameter (in this case, the momentum $\mathbf{p}$) of the usual normalization for a discrete set $\{\psi_n : n \in \mathbb{N}\}$ of (genuine) eigenfunctions of a self-adjoint operator:

$$(\psi_n, \psi_m) = \delta_{nm}.$$

With the above normalization, Eq. (2.32) can be written as

$$\psi(\mathbf{r}) = \int d^3p \, \hat{\psi}(\mathbf{p})\psi_{\mathbf{p}}(\mathbf{r}), \qquad (2.42)$$

`Fourierexp`

which is again the continuous analogue of the expansion

$$\psi(\mathbf{r}) = \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r})$$

of a function $\psi \in L^2(\mathbb{R}^3)$ in terms of an orthonormal basis $\{\psi_n : n \in \mathbb{N}\}$ of eigenfunctions of a self-adjoint operator. We thus see that the value of the momentum wave function $\hat{\psi}(\mathbf{p})$ at a point $\mathbf{p}$ can be interpreted as the coefficient of the plane wave (2.40) with momentum $\mathbf{p}$ in the expansion (2.42) of a *normalized* wave function.

Of course, similar statements can be made for the formal position eigenfunctions

$$\varphi_{\mathbf{r}_0} := \delta(\mathbf{r} - \mathbf{r}_0),$$

which formally satisfy the eigenvalue equation

$$\mathbf{R}\varphi_{\mathbf{r}_0} = \mathbf{r}\delta(\mathbf{r} - \mathbf{r}_0) = \mathbf{r}_0\delta(\mathbf{r} - \mathbf{r}_0) = \mathbf{r}_0\varphi_{\mathbf{r}_0}(\mathbf{r}).$$

Indeed, by the defining equation (2.22) of the Dirac delta they also obey the Dirac normalization

$$(\varphi_{\mathbf{r}_0}, \varphi_{\mathbf{r}_1}) = \int d^3r \, \delta(\mathbf{r} - \mathbf{r}_0)\delta(\mathbf{r} - \mathbf{r}_1) = \delta(\mathbf{r}_0 - \mathbf{r}_1),$$

analogous to (2.41), as well as the identity

$$\psi(\mathbf{r}) = \int d^3r' \, \psi(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') \equiv \int d^3r' \, \psi(\mathbf{r}')\varphi_{\mathbf{r}'}(\mathbf{r}).$$

2.8 The free particle. Wave packets

`sec.freep`

The position and momentum representations are equivalent descriptions of the state of a quantum particle, each of which is useful in different situations. For example, since the momentum operator $\mathbf{P}$ is

© Artemio González López

simply a multiplication operator in the momentum representation, i.e.,

$$\mathbf{P}\hat{\Psi}(\mathbf{p}, t) = \mathbf{p}\hat{\Psi}(\mathbf{p}, t),$$

the momentum representation is especially suited to describe a free particle. Indeed, the time-dependent Schrödinger equation for a free particle in the momentum representation,

$$\mathrm{i}\hbar\partial_t\hat{\Psi}(\mathbf{p}, t) = \frac{\mathbf{p}^2}{2m}\hat{\Psi}(\mathbf{p}, t),$$

is easily solved:

$$\hat{\Psi}(\mathbf{p}, t) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E(\mathbf{p})t}\hat{\Psi}(\mathbf{p}, 0), \qquad \text{with} \quad E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}.$$

From the Fourier transform relation (2.32) we then easily obtain the particle's wave function in the position representation:

$$\Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3/2}\int \mathrm{d}^3 p\, \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E(\mathbf{p})t}\hat{\Psi}(\mathbf{p}, 0)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}} = (2\pi\hbar)^{-3/2}\int \mathrm{d}^3 p\, \hat{\Psi}(\mathbf{p}, 0)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t\right)}. \quad (2.43) \qquad \boxed{\text{psifree}}$$

We thus see that $\Psi(\mathbf{r}, t)$ is a wave packet made up of a (continuous) superposition of de Broglie matter waves

$$\psi_{\mathbf{p}}(\mathbf{r}, t) = (2\pi\hbar)^{-3/2}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t\right)}$$

with well defined momentum $\mathbf{p}$. Moreover, as we saw in the previous section the corresponding weight $\hat{\Psi}(\mathbf{p}, 0)$ multiplying $\psi_{\mathbf{p}}(\mathbf{r}, t)$ in Eq. (2.43) represents the *probability amplitude* for the particle having a momentum $\mathbf{p}$ at the initial time $t = 0$. On the other hand, Ehrenfest's theorem with $V = 0$ implies that

$$\partial_t\langle\mathbf{R}\rangle_{\Psi} = \frac{\langle\mathbf{P}\rangle_{\Psi}}{m}, \qquad \partial_t\langle\mathbf{P}\rangle_{\Psi} = 0;$$

in particular, the particle's average momentum $\langle\mathbf{P}\rangle_{\Psi}$ is *constant* (like the classical momentum of a free particle). We thus have

$$\langle\mathbf{R}\rangle_{\Psi} = \langle\mathbf{R}\rangle_{\psi} + \frac{\langle\mathbf{P}\rangle_{\psi}}{m}t, \qquad (2.44) \qquad \boxed{\text{wpmotion}}$$

where $\psi(\mathbf{r}) = \Psi(\mathbf{r}, 0)$. In other words, the average position of the particle moves as a classical particle with constant momentum $\langle\mathbf{P}\rangle_{\psi}$. If $\hat{\psi}$ is sharply peaked at $\mathbf{p}_0$ then $\langle\mathbf{P}\rangle_{\psi} \simeq \mathbf{p}_0$, and from the Eq. (2.44) we obtain

$$\langle\mathbf{R}\rangle_{\Psi} \simeq \langle\mathbf{R}\rangle_{\psi} + \frac{t\mathbf{p}_0}{m}, \qquad \text{with} \quad \mathbf{r}_0 = \langle\mathbf{R}\rangle_{\psi}.$$

This is in agreement with the analysis in Section 1.5, since $\langle\mathbf{R}\rangle_{\psi}$ obviously coincides with the center of the wave packet at $t = 0$ (denoted by $\mathbf{r}_0$ in Eq. (1.47)).

Equation (2.43) allows one to compute the wave function $\Psi(\mathbf{r}, t)$ in the position representation if the momentum wave function $\hat{\Psi}$ is known at the initial time $t = 0$. We can easily express $\Psi(\mathbf{r}, t)$ in terms of the initial wave function $\Psi(\mathbf{r}, 0)$ in the position representation using the definition (2.30) of the Fourier transform, namely

$$\Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3}\int \mathrm{d}^3 p\, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - E(\mathbf{p})t\right)}\int \mathrm{d}^3 r'\, \Psi(\mathbf{r}', 0)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\mathbf{p}\cdot\mathbf{r}'}$$

$$= (2\pi\hbar)^{-3}\int \mathrm{d}^3 r'\, \Psi(\mathbf{r}', 0)\int \mathrm{d}^3 p\, \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\left(\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}') - \frac{tp^2}{2m}\right)}.$$

The Gaussian integral in momentum space is easily computed by completing the square:

$$\mathbf{p}\cdot(\mathbf{r} - \mathbf{r}') - \frac{tp^2}{2m} = -\frac{t}{2m}\left(\mathbf{p} - \frac{m(\mathbf{r} - \mathbf{r}')}{t}\right)^2 + \frac{m(\mathbf{r} - \mathbf{r}')^2}{2t}, \qquad t \neq 0,$$

and using the general formula

$$\int d^3 p \, e^{-a(\mathbf{p}-\mathbf{p}_0)^2} = \left(\frac{\pi}{a}\right)^{3/2},$$

where $\operatorname{Re} a \geqslant 0$ (with $a \neq 0$) and $a^{3/2} = |a|^{3/2} e^{\frac{3i}{2} \operatorname{Arg} a}$. We thus obtain

$$\int d^3 p \, e^{\frac{i}{\hbar}\left(\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}') - \frac{tp^2}{2m}\right)} = \left(\frac{2m\pi\hbar}{it}\right)^{3/2} e^{\frac{im(\mathbf{r}-\mathbf{r}')^2}{2\hbar t}}, \qquad t \neq 0.$$

Inserting the value of this integral into the previous equation for $\Psi(\mathbf{r}, t)$ we finally arrive at the following explicit formula for the general solution of the time-dependent Schrödinger equation for a free particle:

$$\Psi(\mathbf{r}, t) = \int d^3 \mathbf{r}' G\left(|\mathbf{r} - \mathbf{r}'|, t\right) \Psi(\mathbf{r}', 0), \qquad t \neq 0, \qquad (2.45) \quad \boxed{\text{Green}}$$

where

$$G(s, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} e^{\frac{im s^2}{2\hbar t}}.$$

The function $G(s, t)$ is the so called **Green function** (or *propagator*) for the free time-dependent Schrödinger equation

$$i\hbar \partial_t \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t).$$

Note also that comparing Eq. (2.45) with the general equation (2.16) we obtain the following explicit formula for the exponential of the operator $-it\mathbf{P}^2/(2m\hbar)$ in the position representation:

$$e^{-\frac{it\mathbf{P}^2}{2m\hbar}} \psi(\mathbf{r}) \equiv e^{\frac{i\hbar t}{2m}\nabla^2} \psi(\mathbf{r}) = \int d^3 r' G\left(|\mathbf{r} - \mathbf{r}'|, t\right) \psi(\mathbf{r}').$$

Remark. If initially $\Psi(\mathbf{r}, 0) = \delta(\mathbf{r})$, from Eq. (2.45) we obtain

$$\Psi(\mathbf{r}, t) = G\left(|\mathbf{r}|, t\right).$$

Thus $G\left(|\mathbf{r}|, t\right)$ is the wave function at a time t of a particle that at $t = 0$ was located precisely at the origin. Note that, even if initially the uncertainty in the position vanishes, at any subsequent time $t > 0$ the particle's wave function $G(|\mathbf{r}|, t)$ has modulus 1, and is thus uniformly spread out throughout the whole space. In particular, the uncertainty in the position is *infinite* for $t > 0$. This is in fact an extreme instance of the general phenomenon observed in Example 2.4, namely that the more concentrated is the wave function at a certain time the faster it will start spreading out as time elapses. ∎

Example 2.6. Let us apply Eq. (2.45) to compute the wave function of a free particle if initially

$$\Psi(\mathbf{r}, 0) = (a^2\pi)^{-3/4} e^{-\frac{r^2}{2a^2}}$$

(cf. Example 2.4). Note, first of all, that $\Psi(\mathbf{r}, 0)$ is normalized. According to Eq. (2.45),

$$\Psi(\mathbf{r}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} (a^2\pi)^{-3/4} \int d^3 r' e^{\frac{im(\mathbf{r}-\mathbf{r}')^2}{2\hbar t} - \frac{r'^2}{2a^2}}, \qquad t \neq 0.$$

To evaluate the Gaussian integral, we complete the square of the exponent. To this end, let

$$A = a^2 + \frac{i\hbar t}{m},$$

so that

$$\frac{im(\mathbf{r} - \mathbf{r}')^2}{2\hbar t} - \frac{r'^2}{2a^2} = \frac{1}{2}\left(\frac{im}{\hbar t} - \frac{1}{a^2}\right)r'^2 + \frac{im}{2\hbar t}(r^2 - 2\mathbf{r}\cdot\mathbf{r}') = \frac{im}{2\hbar t a^2}\left(Ar'^2 - 2a^2\mathbf{r}\cdot\mathbf{r}' + a^2 r^2\right)$$

$$= -\frac{m}{2i\hbar t a^2}\left[A\left(\mathbf{r}' - \frac{a^2}{A}\mathbf{r}\right)^2 + \frac{i\hbar t a^2}{mA}r^2\right] = -\frac{mA}{2i\hbar t a^2}\left(\mathbf{r}' - \frac{a^2}{A}\mathbf{r}\right)^2 - \frac{r^2}{2A},$$

where we have made use of the elementary identities

$$\frac{im}{\hbar t} - \frac{1}{a^2} = \frac{im}{\hbar t a^2}A, \qquad a^2 - \frac{a^4}{A} = \frac{a^2}{A}(A - a^2) = \frac{i\hbar t a^2}{mA}.$$

We thus have

$$\Psi(\mathbf{r}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2}(a^2\pi)^{-3/4}e^{-\frac{r^2}{2A}}\int d^3 r' e^{-\frac{mA}{2i\hbar t a^2}\left(\mathbf{r}' - \frac{a^2}{A}\mathbf{r}\right)^2}$$

$$= \left(\frac{m}{2\pi i\hbar t}\right)^{3/2}(a^2\pi)^{-3/4}e^{-\frac{r^2}{2A}}\left(\frac{2\pi i\hbar t a^2}{mA}\right)^{3/2} = \left(\frac{a^2}{\pi}\right)^{3/4}A^{-3/2}e^{-\frac{r^2}{2A}}.$$

2.9 General uncertainty relation

In this section we shall state and prove a general and precise version of Heisenberg's uncertainty principle discussed informally in Section 1.7. To this end, we shall start by formulating a precise definition of the uncertainty of a dynamical variable $a(\mathbf{r}, \mathbf{p})$ represented by a self-adjoint operator A (usually obtained by canonical quantization from $a(\mathbf{r}, \mathbf{p})$). We have seen in the previous sections that when a particle is in a state $\Psi(\mathbf{r}, t)$ the average value of $a(\mathbf{r}, \mathbf{p})$ is given by the expectation value

$$\langle A\rangle_\Psi = (\Psi, A\Psi).$$

The **standard deviation** (root mean square deviation) $\Delta_\Psi a$ of the dynamical variable a is therefore given by

$$\Delta_\Psi A := \sqrt{\left\langle \left(A - \langle A\rangle_\Psi\right)^2\right\rangle_\Psi} = \sqrt{\langle A^2\rangle_\Psi - \langle A\rangle_\Psi^2}. \tag{2.46}$$

sdevA

We shall take the standard deviation $\Delta_\Psi A$ as a precise measure of the **uncertainty** in the value of the dynamical variable represented by the self-adjoint operator A when the particle is in the state Ψ.

Given two self-adjoint operators $\tilde{A}$ and $\tilde{B}$, we shall next prove a general inequality satisfied by the product[23] $\langle \tilde{A}^2\rangle\langle \tilde{B}^2\rangle$. To this end, note that

$$\langle \tilde{A}^2\rangle = (\Psi, \tilde{A}^2\Psi) = (\tilde{A}\Psi, \tilde{A}\Psi) = \|\tilde{A}\Psi\|^2,$$

and similarly for $\langle \tilde{B}^2\rangle$. We then have

$$\langle \tilde{A}^2\rangle\langle \tilde{B}^2\rangle = \|\tilde{A}\Psi\|^2\|\tilde{B}\Psi\|^2 \geqslant \left|(\tilde{A}\Psi, \tilde{B}\Psi)\right|^2,$$

---

[23]For convenience, in this section we shall often drop the subscript Ψ when no confusion can arise.

where the last inequality follows from the **Cauchy–Schwarz inequality** for the inner product. On the other hand,

$$\left|(\tilde{A}\Psi, \tilde{B}\Psi)\right|^2 = \left|(\Psi, \tilde{A}\tilde{B}\Psi)\right|^2 \geqslant \left(\mathrm{Im}\,(\Psi, \tilde{A}\tilde{B}\Psi)\right)^2 = \left\{\frac{1}{2\mathrm{i}}\left[(\Psi, \tilde{A}\tilde{B}\Psi) - (\tilde{A}\tilde{B}\Psi, \Psi)\right]\right\}^2$$

$$= -\frac{1}{4}\left(\Psi, [\tilde{A}, \tilde{B}]\Psi\right)^2 \equiv -\frac{1}{4}\left\langle[\tilde{A}, \tilde{B}]\right\rangle^2.$$

Combining this formula with the previous one we arrive at the inequality

$$\langle\tilde{A}^2\rangle\langle\tilde{B}^2\rangle \geqslant -\frac{1}{4}\left\langle[\tilde{A}, \tilde{B}]\right\rangle^2.$$

Note that the RHS of this inequality is non-negative, since the expectation value of the commutator of two self-adjoint operators is pure imaginary (exercise). We can therefore simplify the previous inequality as follows:

$$\langle\tilde{A}^2\rangle^{1/2}\langle\tilde{B}^2\rangle^{1/2} \geqslant \frac{1}{2}\left|\langle[\tilde{A}, \tilde{B}]\rangle\right|. \tag{2.47}$$ $\boxed{\text{Huppre}}$

If A and B are two observables the expectation values $\langle A\rangle$ and $\langle B\rangle$ are both real, and thus the operators $\tilde{A} = A - \langle A\rangle$ and $\tilde{B} = B - \langle B\rangle$ are self-adjoint. Taking into account that

$$[\tilde{A}, \tilde{B}] \equiv [A - \langle A\rangle, B - \langle B\rangle] = [A, B]$$

and applying Eq. (2.47) we deduce the following general inequality relating the uncertainties of the observables A and B in any state Ψ:

$$\Delta_\Psi A\,\Delta_\Psi B \geqslant \frac{1}{2}\left|\langle[A, B]\rangle_\Psi\right|. \tag{2.48}$$ $\boxed{\text{Heisgen}}$

Equation (2.48) is a general form of the uncertainty principle discussed in Section 1.7. Indeed, if we apply it to the operators $A = X_i$ and $B = P_i$ and make use of the canonical commutation relation (2.14) we immediately arrive at the inequality

$$\Delta_\Psi X_i\,\Delta_\Psi P_i \geqslant \frac{\hbar}{2}. \tag{2.49}$$ $\boxed{\text{Heisuncrelx}}$

Note that the passage from the general Eq. (2.48) to the previous equation relies only on the canonical commutation relations (2.14). Therefore if P and Q are any observables satisfying

$$[Q, P] = \mathrm{i}\hbar \tag{2.50}$$ $\boxed{\text{CCR}}$

then their uncertainties in any state Ψ will also verify the inequality

$$\Delta_\Psi P\,\Delta_\Psi Q \geqslant \frac{\hbar}{2}. \tag{2.51}$$ $\boxed{\text{CCRHeis}}$

We shall say in this case that Q and P are *canonically conjugate*, since Eq. (2.50) is usually obtained as a result of canonically quantizing two classical canonically conjugate variables q and p (i.e., two dynamical variables satisfying $\{q, p\} = 1$). From Eq. (2.51) it then follows that:

Two canonically conjugate observables cannot be simultaneously measured with infinite precision.

This is the import of Heisenberg's uncertainty principle as originally formulated.

We shall say that two observables A and B are **compatible** if $[A, B] = 0$, and **incompatible**) if $[A, B] \neq 0$. An important consequence of the general uncertainty principle (2.48) is the following:

Two incompatible observables A and B cannot be simultaneously measured with infinite precision unless the system is in a state Ψ such that $\langle [A, B] \rangle_\Psi = 0$.

Example 2.7. *Minimum-uncertainty wave function.*

The position-momentum uncertainty relation (2.49) is *optimal*, in the sense that there are states $\psi(\mathbf{r})$ for which

$$\Delta_\psi X_i \, \Delta_\psi P_i = \frac{\hbar}{2}, \qquad \forall i = 1, 2, 3. \tag{2.52}$$

`minunc3D`

To find such states, we start by looking for one-dimensional states $\psi(x)$ such that

$$\Delta_\psi X \, \Delta_\psi P = \frac{\hbar}{2}. \tag{2.53}$$

`minunc`

From the proof of the general inequality (2.48) it follows that a necessary condition for (2.53) to hold is that

$$\left\| (X - \langle X \rangle_\psi) \right\| \left\| (P - \langle P \rangle_\psi) \right\| = \left| \left((X - \langle X \rangle_\psi)\psi, (P - \langle P \rangle_\psi)\psi \right) \right|,$$

or equivalently that the "vectors" $(X - \langle X \rangle_\psi)\psi$ and $(P - \langle P \rangle_\psi)\psi$ be parallel. Thus

$$(P - p_0)\psi = i\hbar a(x - x_0)\psi \quad \Longleftrightarrow \quad (i\hbar\partial_x + p_0)\psi = -i\hbar a(x - x_0)\psi$$

for some complex constant $a := a_1 + i a_2$, where we have set $x_0 = \langle X \rangle_\psi$, $p_0 = \langle P \rangle_\psi$. Integrating this differential equation for $\psi(x)$ we find

$$\psi(x) = N e^{-\frac{a}{2}(x-x_0)^2} e^{\frac{i}{\hbar} p_0 x}, \tag{2.54}$$

`psimin`

where N can be taken as real and positive without loss of generality. Note that $\operatorname{Re} a = a_1$ must be positive in order that ψ be square integrable. Imposing that ψ have unit norm we obtain

$$\int dx \, |\psi(x)|^2 = N^2 \int dx \, e^{-\frac{a+a^*}{2}(x-x_0)^2} = N^2 \int dx \, e^{-a_1(x-x_0)^2} = N^2 \sqrt{\frac{\pi}{a_1}} = 1 \implies N = \left(\frac{a_1}{\pi}\right)^{\frac{1}{4}}.$$

Let us now find under what conditions the wave function (2.54) does indeed verify Eq. (2.53). To this end, we first compute the averages of the particle's position and momentum in the state ψ:

$$\langle X \rangle_\psi = \int dx \, x |\psi(x)|^2 = N^2 \int dx \, x e^{-a_1(x-x_0)^2} = x_0 + N^2 \int dx \, (x - x_0) e^{-a_1(x-x_0)^2} = x_0,$$

$$\langle P \rangle_\psi = \int dx \, \psi^*(x)(-i\hbar\partial_x)\psi(x) = N^2 \int dx \, e^{-\frac{a^*}{2}(x-x_0)^2} e^{-\frac{i}{\hbar}p_0 x}(-i\hbar\partial_x)\left(e^{-\frac{a}{2}(x-x_0)^2} e^{\frac{i}{\hbar}p_0 x}\right)$$

$$= N^2 \int dx \, e^{-a_1(x-x_0)^2}\left(p_0 + ia\hbar(x - x_0)\right) = p_0 + ia\hbar N^2 \int dx \, (x - x_0)e^{-a_1(x-x_0)^2} = p_0,$$

since the integrand in the last integrals is odd in $x - x_0$. We next compute the uncertainties in X and P. To begin with,

$$(\Delta_\psi X)^2 = \left\| (x - x_0)\psi \right\|^2 = N^2 \int dx \, (x - x_0)^2 e^{-a_1(x-x_0)^2} = -N^2 \frac{\partial}{\partial a_1} \int dx \, e^{-a_1(x-x_0)^2}$$

$$= -\left(\frac{a_1}{\pi}\right)^{\frac{1}{2}} \frac{\partial}{\partial a_1}\left(\frac{\pi}{a_1}\right)^{\frac{1}{2}} = \frac{1}{2a_1}.$$

Likewise,

$$(\Delta_\psi P)^2 = \left\| (P - p_0)\psi \right\|^2,$$

---

with

$$(P-p_0)\psi = -(i\hbar\partial_x+p_0)\psi = -N(i\hbar\partial_x+p_0)\left(e^{-\frac{a}{2}(x-x_0)^2}e^{\frac{i}{\hbar}p_0 x}\right) = ia\hbar N(x-x_0)e^{-\frac{a}{2}(x-x_0)^2}e^{\frac{i}{\hbar}p_0 x}.$$

We thus obtain

$$(\Delta_\psi P)^2 = |a|^2\hbar^2 N^2 \int dx\,(x-x_0)^2 e^{-a_1(x-x_0)^2} = |a|^2\hbar^2(\Delta_\psi X)^2 = \frac{|a|^2\hbar^2}{2a_1},$$

and therefore

$$\Delta_\psi X \Delta_\psi P = \frac{\hbar}{2}\frac{|a|}{a_1}.$$

Hence Eq. (2.53) will hold if and only if $|a| = a_1$, i.e., if a is real and positive. This shows that *in one dimension the only wave function $\psi(x)$ verifying Eq.* (2.53) *is the Gaussian wave packet* (2.54) *with $a > 0$.* Using this result it is straightforward to show that in three dimensions the only wave function verifying the minimum uncertainty relations (2.52) is the Gaussian wave packet

$$\psi(\mathbf{r}) = \left(\frac{a}{\pi}\right)^{3/4} e^{-\frac{a}{2}(\mathbf{r}-\mathbf{r}_0)^2}e^{\frac{i}{\hbar}\mathbf{p}_0\cdot\mathbf{r}}, \tag{2.55}$$

`psimin3D`

with $a > 0$ and $\mathbf{r}_0, \mathbf{p}_0 \in \mathbb{R}^3$, for which

$$\langle\mathbf{R}\rangle_\psi = \mathbf{r}_0, \quad \langle\mathbf{P}\rangle_\psi = \mathbf{p}_0, \quad (\Delta_\psi X_i)^2 = \frac{1}{2a}, \quad (\Delta_\psi P_i)^2 = \frac{a\hbar^2}{2}.$$

Exercise 2.4. Study the time evolution of the uncertainty product $\Delta_\psi X\,\Delta_\psi P$ for the Gaussian wave packet (2.54) with $x_0 = p_0 = 0$ in the absence of external forces.

Solution. Proceeding as in Example 2.6, we find that

$$\Psi(x,t) = \left(\frac{a}{\pi}\right)^{1/4} f(t)^{-1/2}e^{-\frac{ax^2}{2f(t)}}, \qquad \text{with}\quad f(t) := 1 + \frac{i\hbar a}{m}t \tag{2.56}$$

`Gausswpt`

and $f(t)^{-1/2} \equiv |f(t)|^{-1/2}e^{-\frac{i}{2}\text{Arg}\,f(t)}$. It is easy to see that (apart from a time-dependent overall phase) $\Psi(x,t)$ is obtained from Eq. (2.54) (with complex a) by the replacement

$$a \to \frac{a}{f}.$$

Indeed, under this replacement we have

$$N = \left(\frac{a_1}{\pi}\right)^{1/4} \equiv \left(\frac{\text{Re}\,a}{\pi}\right)^{1/4} \to \left(\frac{\text{Re}(a/f)}{\pi}\right)^{1/4} = \left(\frac{a}{\pi}\,\text{Re}\left(\frac{f^*}{|f|^2}\right)\right)^{1/4} = \left(\frac{a}{\pi}\right)^{1/4}|f|^{-1/2}$$

$$= \left(\frac{a}{\pi}\right)^{1/4}f^{-1/2}e^{\frac{i}{2}\text{Arg}\,f}.$$

Although the (time dependent) phase $e^{\frac{i}{2}\text{Arg}\,f}$ is necessary in order that $\Psi(x,t)$ satisfy the time-dependent Schrödinger equation, since it does not depend on the x coordinate it can be dropped when computing expectation values. We thus conclude that $\langle X\rangle_\psi$, $\langle P\rangle_\psi$, $\Delta_\psi X$ and $\Delta_\psi P$ can be obtained from the previous example (in the general case of complex a) replacing a by a/f, and hence $a_1 = \text{Re}\,a$ by

$$\text{Re}\left(\frac{a}{f}\right) = \frac{a}{|f|^2}.$$

We thus obtain

$$\langle X \rangle_\Psi = \langle P \rangle_\Psi = 0, \qquad (\Delta_\Psi X)^2 = \frac{|f|^2}{2a}, \qquad (\Delta_\Psi P)^2 = \frac{\hbar^2}{2} \frac{a^2}{|f|^2} \frac{|f|^2}{a} = \frac{a\hbar^2}{2}.$$

We thus see that, although the momentum uncertainty does not change with time, the position uncertainty is time-dependent. In particular, the uncertainty product

$$\Delta_\Psi X \, \Delta_\Psi P = \frac{\hbar}{2} |f| = \frac{\hbar}{2} \sqrt{1 + \frac{\hbar^2 a^2}{m^2} t^2}$$

steadily increases with time for $t > 0$, and is equal to $\hbar/2$ only for $t = 0$. In other words, the Gaussian wave packet (2.56) minimizes the uncertainty product only at $t = 0$.

Remark. The fact that $\Delta_\Psi P$ is constant is a direct consequence of Ehrenfest's general theorem. Indeed, the momentum operator P commutes with the free Hamiltonian $H = P^2/(2m)$, so that by Eq. (2.25) the expectation value of any power of P must be time-independent. On the other hand, since

$$[X, H] = \frac{1}{2m}[X, P^2] = \frac{1}{2m}\left(P[X,P] + [X,P]P\right) = \frac{i\hbar}{m} P,$$

$$[X^2, H] = X[X, H] + [X, H]X = \frac{i\hbar}{m}(XP + PX)$$

we have

$$i\hbar\partial_t\langle X^2 \rangle_\Psi = \frac{i\hbar}{m}\langle XP + PX \rangle_\Psi \implies m\partial_t\langle X^2 \rangle_\Psi = \langle XP + PX \rangle_\Psi = (\Psi, XP\Psi) + (\Psi, PX\Psi)$$

$$= (X\Psi, P\Psi) + (P\Psi, X\Psi) = 2\,\mathrm{Re}(X\Psi, P\Psi)$$

and therefore

$$\frac{m}{2}\partial_t\langle X^2 \rangle_\Psi = \left(\frac{a}{\pi}\right)^{1/2} \mathrm{Re} \int \mathrm{d}x \, |f|^{-1} x \left(\mathrm{e}^{-\frac{ax^2}{2f}}\right)^* \left(-i\hbar\partial_x \mathrm{e}^{-\frac{ax^2}{2f}}\right)$$

$$= a^{3/2}\pi^{-1/2}\hbar|f|^{-1} \mathrm{Re}\left(\frac{i}{f}\right) \int \mathrm{d}x \, x^2 \left|\mathrm{e}^{-\frac{ax^2}{2f}}\right|^2 = a^{3/2}\pi^{-1/2}\hbar|f|^{-1}\frac{\mathrm{Im}\,f}{|f|^2} \int \mathrm{d}x \, x^2 \mathrm{e}^{-\frac{ax^2}{|f|^2}}$$

$$= a^{5/2}\pi^{-1/2}\hbar^2|f|^{-3}\frac{t}{m} \cdot \frac{\sqrt{\pi}}{2}|f|^3 a^{-3/2} = \frac{a\hbar^2}{2m}t.$$

Integrating the differential equation

$$\partial_t\langle X^2 \rangle_\Psi = \frac{a\hbar^2}{m^2}t$$

with the initial condition

$$\langle X^2 \rangle_\Psi \bigg|_{t=0} = \frac{1}{2a}$$

we obtain

$$\langle X^2 \rangle_\Psi = \frac{1}{2a} + \frac{a\hbar^2}{2m^2}t^2 = \frac{1}{2a}\left(1 + \frac{a^2\hbar^2}{m^2}t^2\right) = \frac{|f|^2}{2a},$$

as before.

2.10 The time-energy uncertainty principle

The general Heisenberg uncertainty relation (2.48) can be used to derive an uncertainty relation involving the particle's energy E and the time t. This is natural from a relativistic point of view, since E/c and ct are respectively the zero components of the particle's four-momentum p and spacetime "position" vector x. Note, however, that in non-relativistic quantum mechanics time is *not* an observable (i.e., a self-adjoint operator), but rather a universal independent variable labeling the evolution of the system.

To formulate the energy-time uncertainty relation, we apply the general uncertainty principle (2.48) to the Hamiltonian H and any other observable A:

$$\Delta_\Psi E \, \Delta_\Psi A \geqslant \frac{1}{2} \left| \langle [H, A] \rangle_\Psi \right|, \tag{2.57} \quad \boxed{\text{DeEA}}$$

where (as is customary) we have written $\Delta_\Psi E$ instead of $\Delta_\Psi H$ (indeed, recall that in a conservative natural Hamiltonian system $H = E$). On the other hand, from Ehrenfest's general theorem (2.25) we have

$$\left| \langle [H, A] \rangle_\Psi \right| = \hbar \left| \partial_t \langle A \rangle_\Psi \right|.$$

If $\partial_t \langle A \rangle_\Psi$ is slowly varying with time, the average value of the observable will change by one standard deviation $\Delta_\Psi A$ in a time $\Delta_\Psi t_A$ given by

$$\Delta_\Psi t_A = \frac{\Delta_\Psi A}{\left| \partial_t \langle A \rangle_\Psi \right|}.$$

Thus

$$\left| \langle [H, A] \rangle_\Psi \right| = \hbar \frac{\Delta_\Psi A}{\Delta_\Psi t_A},$$

which combined with Eq. (2.57) yields the following time-energy uncertainty relation[24]:

$$\Delta_\Psi E \, \Delta_\Psi t_A \geqslant \frac{\hbar}{2}. \tag{2.58} \quad \boxed{\text{uncETA}}$$

In spite of its obvious similarity with the position-momentum uncertainty relation (2.49), it should be noted that $\Delta_\Psi t_A$ is *not* the uncertainty in time, but, roughly speaking, the time that must elapse for the average value of the observable A to change appreciably (more precisely by one standard deviation). In particular, this lapse depends on the observable A. In practice, however, this relation is written more informally as

$$\Delta_\Psi E \, \Delta_\Psi t \geqslant \frac{\hbar}{2}, \tag{2.59} \quad \boxed{\text{uncET}}$$

where $\Delta_\Psi t$ is loosely interpreted as a characteristic time lapse required for the system's state to change appreciably when it is in a given state Ψ.

An important particular case of the time-energy uncertainty relation ensues when Ψ is a **stationary state**, i.e., an eigenstate of the Hamiltonian H. In this case

$$H\Psi = E\Psi \quad \implies \quad \langle H^n \rangle_\Psi = (\Psi, H^n \Psi) = (\Psi, E^n \Psi) = E^n (\Psi, \Psi) = E^n,$$

and therefore

$$\langle H^2 \rangle_\Psi = E^2 = \left(\langle H \rangle_\Psi \right)^2 \quad \implies \quad \Delta H \equiv \Delta E = 0.$$

---

[24]This version of the time-energy uncertainty relation is due to the Russian physicists Leonid Mandelstam (1879–1944) and Igor Tamm (1895–1971, Nobel prize winner in 1958).

Thus in this case $\Delta E = 0$, and therefore $\Delta t = \infty$. To understand what this means, note that if Ψ is a stationary state and A is any observable (not explicitly depending on time) we have

$$\big\langle [A, H] \big\rangle_\Psi = (\Psi, (AH - HA)\Psi) = (\Psi, AH\Psi) - (AH\Psi, \Psi) = E(\Psi, A\Psi) - E(A\Psi, \Psi) = 0,$$

since A is by hypothesis self-adjoint[25]. From Eq. (2.25) it then follows that

$$\partial_t \big\langle A \big\rangle_\Psi = 0.$$

In other words:

> In a stationary state Ψ the averages of *all* (time-independent) observables are time independent.

In particular, for any observable A the time $\Delta_\Psi t_A$ required for $\big\langle A \big\rangle_\Psi$ to change by one standard deviation is infinite (since $\big\langle A \big\rangle_\Psi$ is *not* changing at all!). It is in this sense that in a stationary state the characteristic time Δt of the system is infinite.

2.11 Summary

Let us briefly summarize the main results obtained in this chapter:

i) The *state* of a particle is represented by a square integrable *wave function* (or *probability amplitude*) $\Psi(\mathbf{r}, t)$ of unit norm. The *probability density* of finding the particle at a certain time t inside an infinitesimal volume d^3r around $\mathbf{r}$ is equal to $\big|\Psi(\mathbf{r}, t)\big|^2$.

ii) If the particle is subject to a potential $V(\mathbf{r})$ and we do not perform any measurements on it over a certain time interval, the *evolution of the wave function* is governed by the *time-dependent Schrödinger equation*

$$i\hbar \partial_t \Psi = H\Psi,$$

where the Hamiltonian H is the differential operator

$$H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

obtained from the classical Hamiltonian

$$H_{\mathrm{cl}}(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

by the replacement

$$\mathbf{r} \to \mathbf{R}, \qquad \mathbf{p} \to \mathbf{P} = -i\hbar\nabla \tag{2.60}$$

canquant

with $\mathbf{R}\Psi(\mathbf{r}, t) = \mathbf{r}\Psi(\mathbf{r}, t)$.

iii) In the momentum representation, the state of the particle is represented by the *Fourier transform*

$$\hat{\Psi}(\mathbf{p}, t) = (2\pi\hbar)^{-3/2} \int d^3r \, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \Psi(\mathbf{r}, t)$$

of the position space wave function $\Psi(\mathbf{r}, t)$. The probability density of finding the particle at a certain time t inside an infinitesimal volume d^3p around a momentum $\mathbf{p}$ is equal to $\big|\hat{\Psi}(\mathbf{p}, t)\big|^2$. The particle's position and momentum operator in the momentum representation are given by

$$\mathbf{R} = i\hbar\nabla_{\mathbf{p}}, \qquad \mathbf{P} = \mathbf{p}.$$

---

[25]Note that in the third equality we have used the fact that the eigenvalue E is real, since H is self-adjoint.

iv) A classical dynamical variable $a(\mathbf{r}, \mathbf{p})$ is represented by a *self-adjoint operator* $A(\mathbf{R}, \mathbf{P})$ obtained from a through the prescription (2.60) with a suitable ordering of the operators involved.

v) If a particle is in a quantum state Ψ, the *average value* of a dynamical variable a represented by a quantum observable A is given by the *expectation value* of A in the state ψ, namely

$$\langle A \rangle_{\Psi} = (\Psi, A\Psi).$$

Note that $\langle A \rangle_{\Psi}$ is necessarily real, since A is self-adjoint.

vi) If A does not depend explicitly on time, the *time evolution of the average of A* is given by *Ehrenfest's general theorem*

$$i\hbar \partial_t \langle A \rangle_{\Psi} = \langle [A, H] \rangle_{\Psi}.$$

vii) If at a certain time the particle is in a state ψ which is an eigenfunction of an observable A with eigenvalue λ, a measurement of the observable A performed at this time will yield with certainty the value λ.

viii) If an observable A is measured at a certain time and the value λ is obtained, the state of the particle *immediately after the measurement is performed* is an eigenstate of A with eigenvalue λ.

ix) The only possible values that can be obtained when an observable A is measured are the *eigenvalues* of A.

3 One-dimensional problems

3.1 The time-independent Schrödinger equation

From the mathematical point of view, the Schrödinger equation for a particle of mass m subject to a *time independent* potential $V(\mathbf{r})$,

$$\mathrm{i}\partial_t \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + V(\mathbf{r})\Psi(\mathbf{r}, t) \equiv H\Psi(\mathbf{r}, t), \tag{3.1}$$

is a second-order *linear* partial differential equation whose general solution can be formally obtained by the method of *separation of variables*. Indeed, since the potential V is time-independent, we look for solutions of the latter equation of the form

$$\Psi(\mathbf{r}, t) = \tau(t)\psi(\mathbf{r}).$$

Substituting into Eq. (3.1) and dividing by Ψ we arrive at the equation

$$\mathrm{i}\hbar\frac{\tau'(t)}{\tau(t)} = \frac{H\psi(\mathbf{r})}{\psi(\mathbf{r})} \tag{3.2}$$

in the nonempty open set defined by the inequalities

$$\tau(t) \neq 0, \qquad \psi(\mathbf{r}) \neq 0.$$

Since the LHS of Eq. (3.2) depends only on t and the RHS is a function of $\mathbf{r}$, both sides of the latter equation must be *constant*. Thus there exists a number E (the so-called *separation constant*) such that

$$\mathrm{i}\hbar\tau'(t) = E\tau(t), \qquad H\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

The general solution of the first equation is

$$\tau(t) = c\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et},$$

where $c = \tau(0)$ is an arbitrary constant that can be absorbed in $\psi(\mathbf{r})$. We thus have shown that the function

$$\Psi(\mathbf{r}, t) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}\psi(\mathbf{r}) \tag{3.3}$$

is a solution of the time-dependent Schrödinger equation (3.1) provided that the function $\psi(\mathbf{r})$ is a solution of the second-order partial differential equation

$$H\psi(\mathbf{r}) \equiv -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{3.4}$$

Moreover, since

$$\big|\Psi(\mathbf{r}, t)\big| = \big|\psi(\mathbf{r})\big|,$$

we must have

$$\big\|\Psi\big\|(t) = \big\|\psi\big\| = 1;$$

in other words, the function $\psi(\mathbf{r})$ must be in $L^2(\mathbb{R}^3)$ and have unit norm. Thus equation (3.4), which is known as the **time-independent Schrödinger equation**, simply states that the function $\psi(\mathbf{r})$ is an *eigenfunction* of the Hamiltonian operator H with eigenvalue E. This implies that the separation constant E must be *real*, since it is an eigenvalue of the *self-adjoint* operator H. As to the physical significance of this constant, note that for any time t the wave function $\Psi(\mathbf{r}, t)$ is also an eigenfunction of H with eigenvalue E. In other words, $\Psi(\mathbf{r}, t)$ is a *stationary state* (cf. Section (2.9)). From item vii) in Section 2.11 it then follows that:

> In a stationary state (3.3), where ψ is an eigenfunction of H with eigenvalue E, the particle has a *well-defined* and *constant* energy E.

As we shall see in more detail below, for a generic value of the parameter $E \in \mathbb{R}$ the time-independent equation (3.4) has no normalizable solutions. Indeed, in general the set of energies E for which Eq. (3.4) has normalizable solutions is a *discrete*[1] set. This set is called the **point spectrum**[2] of the Hamiltonian H. By item ix) in Section 2.11, the elements of the point spectrum of H are the possible values of the particle's energy. Thus the set of allowed energies is necessarily a discrete set. This observation provides a simple and clear explanation of the quantization of energy, which Bohr's old quantum theory was unable to account for:

> In quantum mechanics the *quantization of energy* need not be *imposed* (as in Bohr's old quantum theory), but is an automatic consequence of the discrete character of the point spectrum of the Hamiltonian operator H.

A fundamental property of the eigenfunctions of any self-adjoint operator that we shall often use in the sequel is the following:

> Two eigenfunctions $\psi_{1,2}$ of a self-adjoint operator A with *different* eigenvalues $\lambda_1 \neq \lambda_2$ are *orthogonal*.

Proof. Indeed,

$$(\psi_1, A\psi_2) = (\psi_1, \lambda_2 \psi_2) = \lambda_2 (\psi_1, \psi_2) = (A\psi_1 \psi_2) = (\lambda_1 \psi_1 \psi_2) = \lambda_1 (\psi_1, \psi_2)$$
$$\implies (\lambda_2 - \lambda_1)(\psi_1, \psi_2) = 0 \implies (\psi_1, \psi_2) = 0. \qquad \blacksquare$$

In particular, two eigenfunctions of H with different energies must be orthogonal. Let us now assume that, as is the case in many problems of physical interest, there is an *orthonormal basis*

$$\{\psi_n : n \in \mathbb{N}\} \tag{3.5}$$

of the Hilbert space $L^2(\mathbb{R}^3)$ whose elements are *eigenfunctions* of the Hamiltonian operator H. In other words, the functions ψ_n satisfy[3]

$$H\psi_n = E_n \psi_n, \qquad (\psi_n, \psi_m) = \delta_{nm},$$

and each function $\psi(\mathbf{r})$ in $L^2(\mathbb{R}^3)$ admits an expansion

$$\psi(\mathbf{r}) = \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}). \tag{3.6}$$

---

[1] A subset S of the real line is *discrete* if all of its points are *isolated*, i.e., if for every point x in the set there is a neighborhood U of x such that $U \cap S = \{x\}$. Equivalently, S is discrete if it does not contain its accumulation points. It can be shown that discrete subsets of $\mathbb{R}$ are either finite or countably infinite.

[2] The term *discrete spectrum* is used sometimes as a synonym, but we shall avoid it in these notes since some authors give it a slightly different meaning.

[3] Note that we are not assuming that $E_n \neq E_m$ for $n \neq m$.

The coefficients $c_k \in \mathbb{C}$ can be computed by taking the scalar product of the previous equation with the eigenfunction ψ_k:

$$c_k = (\psi_k, \psi) \equiv \int \mathrm{d}^3 r \, \psi_k^*(\mathbf{r}) \psi(\mathbf{r}), \tag{3.7}$$ `ckexpeigf`

and they must verify the condition (usually called *Parseval's relation*)

$$\|\psi\|^2 = (\psi, \psi) = \left(\sum_{n=0}^{\infty} c_n \psi_n, \sum_{m=0}^{\infty} c_m \psi_m \right) = \sum_{n.m=0}^{\infty} c_n^* c_m (\psi_n, \psi_m) = \sum_{n.m=0}^{\infty} c_n^* c_m \delta_{nm}$$

$$= \sum_{n=1}^{\infty} |c_n|^2 = 1. \tag{3.8}$$ `cnnorm`

Remark. If the point spectrum of H is *non-degenerate,* i.e., if $E_m \neq E_n$ for $m \neq n$, we shall show in the next chapter that the probability p_k of obtaining the value E_k when measuring the particle's energy in the state ψ is given by

$$p_k = |c_k|^2 = |(\psi_k, \psi)|^2.$$

$\blacksquare$

When there exists an orthonormal basis $\{\psi_n : n \in \mathbb{N}\}$ of $L^2(\mathbb{R}^3)$ whose elements are eigenfunctions of the Hamiltonian H, we can find the solution of the time dependent Schrödinger equation (3.1) with an arbitrary initial condition

$$\Psi(\mathbf{r}, 0) = \psi(\mathbf{r}) = \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) \tag{3.9}$$ `inidat`

as follows. As we have remarked above, each function

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-\frac{i}{\hbar} E_n t} \tag{3.10}$$ `Psinpsin`

is a solution of Eq. (3.1). By *linearity*, so is the infinite sum

$$\Psi(\mathbf{r}, t) = \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) e^{-\frac{i}{\hbar} E_n t}. \tag{3.11}$$ `gensolSchr`

Since $\Psi(\mathbf{r}, 0) = \psi(\mathbf{r})$ by Eq. (3.9), we conclude that (3.11) is the unique solution of the initial value problem (3.1)-(3.9). In other words:

The function $\Psi(\mathbf{r}, t)$ in Eq. (3.11) with coefficients $c_n \in \mathbb{C}$ satisfying Eq. (3.8) is the *general solution* of the Schrödinger equation (3.1).

Remark. The previous result can be also proved in a more abstract way as follows. As we saw in the previous chapter, the solution of (3.1) with the initial condition (3.9) is given by Eq. (2.16). Using the expansion (3.6) of $\psi(\mathbf{r})$ in terms of the eigenfunctions ψ_n of H and the identity

$$e^{-\frac{i}{\hbar} t H} \psi_n = e^{-\frac{i}{\hbar} t E_n} \psi_n$$

we easily obtain

$$\Psi(\mathbf{r}, t) = e^{-\frac{i}{\hbar} t H} \sum_{n=1}^{\infty} c_n \psi_n = \sum_{n=1}^{\infty} c_n e^{-\frac{i}{\hbar} t H} \psi_n = \sum_{n=1}^{\infty} c_n e^{-\frac{i}{\hbar} E_n t} \psi_n,$$

3.2 Stationary states. Bound and scattering states

Recall that a stationary state is an eigenstate $\Psi(\mathbf{r}, t)$ of the Hamiltonian H. From the eigenvalue equation

$$H\Psi = E\Psi$$

and the time independent equation (3.1) we obtain

$$\mathrm{i}\hbar\partial_t\Psi = E\Psi \quad\Longrightarrow\quad \boxed{\Psi(\mathbf{r}, t) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}\psi(\mathbf{r}), \qquad \text{with } H\psi = E\psi \text{ and } \psi(\mathbf{r}) \equiv \Psi(\mathbf{r}, 0).}$$

$$(3.12)$$

Thus the only stationary states are the separable solutions of the time-dependent Schrödinger equation found in the previous section. Let us briefly summarize the main properties of the *stationary states* (3.3):

1. The stationary state (3.12) has a well-defined and constant energy E.
2. Two eigenfunctions $\psi_{1,2}$ of H with *different* energies $E_1 \neq E_2$ must necessarily be *orthogonal*.
3. The probability density $\left|\Psi(\mathbf{r}, t)\right|^2$ associated to a stationary state is *time-independent*:

$$\left|\Psi(\mathbf{r}, t)\right|^2 = \left|\psi(\mathbf{r})\right|^2, \qquad \forall t \in \mathbb{R}.$$

4. In fact, since for each fixed time t the factor $\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}$ is a *global* (i.e., position independent) *phase*, $\Psi(\mathbf{r}, t_1)$ and $\Psi(\mathbf{r}, t_2)$ actually describe the *same* quantum state. In other words, *in a stationary state the state of the particle does not change in time.* This is, in fact, the reason for the terminology "stationary state".

5. An immediate consequence of this fact is that *in a stationary state the averages of all observables not explicitly depending on time must be constant* (i.e., time-independent). We had already proved this property of stationary states in Section 2.9 using Ehrenfest's general formula (2.25), but it can also be established directly as follows:

$$\langle A\rangle_\Psi = \left(\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}\psi, A(\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}\psi)\right) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}Et}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Et}(\psi, A\psi) = (\psi, A\psi) \equiv \langle A\rangle_\psi.$$

6. As we saw in the previous section, when the Hilbert space $L^2(\mathbb{R}^3)$ admits an orthonormal basis of eigenstates ψ_n of the Hamiltonian H the *general* solution of the time-dependent Schrödinger equation (3.1) can be expanded in terms of the corresponding stationary states (3.10) as

$$\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty} c_n\Psi_n(\mathbf{r}, t) \equiv \sum_{n=0}^{\infty} c_n\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_n t}\psi_n(\mathbf{r}), \qquad (3.13)$$

for appropriate (in general complex) constants c_n satisfying Eq. (3.8). Note that, although each state Ψ_n is stationary and has a well-defined energy, it is clear that $\Psi(\mathbf{r}, t)$ will neither be a stationary state nor have well-defined energy unless all the nonzero coefficients c_n in the latter expansion correspond to states Ψ_n having the *same* energy. On the other hand, the probability $p_k(t)$ of finding the value E_k when measuring the particle's energy at a time t,

$$p_k(t) = \left|(\psi_k, \Psi(\cdot, t))\right|^2 = \left|c_n\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_n t}\right|^2 = |c_k|^2,$$

is *time-independent*.

Example 3.1. Consider, for instance, a linear combination of two stationary states $\Psi_{1,2}$ with different energies $E_1 \neq E_2$, i.e.,

$$\Psi(\mathbf{r},t) = c_1 e^{-\frac{i}{\hbar}E_1 t} \psi_1(\mathbf{r}) + c_2 e^{-\frac{i}{\hbar}E_2 t} \psi_2(\mathbf{r}),$$

with

$$H\psi_i = E_i \psi_i, \qquad i = 1, 2.$$

Since $E_1 \neq E_2$ implies $(\psi_1, \psi_2) = 0$, if the states $\psi_{1,2}$ are normalized then Ψ will have unit norm provided that

$$(\Psi, \Psi) = |c_1|^2 + |c_2|^2 = 1.$$

The probability density of the state Ψ is

$$
\begin{aligned}
|\Psi|^2 &= \left(c_1^* e^{\frac{i}{\hbar}E_1 t}\psi_1^* + c_2^* e^{\frac{i}{\hbar}E_2 t}\psi_2 \right) \left(c_1 e^{-\frac{i}{\hbar}E_1 t}\psi_1 + c_2 e^{-\frac{i}{\hbar}E_2 t}\psi_2 \right) \\
&= |c_1|^2 |\psi_1|^2 + |c_2|^2 |\psi_2|^2 + c_1^* c_2 e^{\frac{i}{\hbar}(E_1-E_2)t}\psi_1^*\psi_2 + c_1 c_2^* e^{-\frac{i}{\hbar}(E_1-E_2)t}\psi_1\psi_2^* \\
&= |c_1|^2 |\psi_1|^2 + |c_2|^2 |\psi_2|^2 + 2\operatorname{Re}\left(c_1^* c_2 e^{\frac{i}{\hbar}(E_1-E_2)t}\psi_1^*\psi_2 \right).
\end{aligned}
$$

The latter term is clearly oscillating in time with the **Bohr frequency**

$$\omega_{12} = \frac{|E_1 - E_2|}{\hbar};$$

indeed,

$$\operatorname{Re}\left(c_1^* c_2 e^{\frac{i}{\hbar}(E_1-E_2)t}\psi_1^*\psi_2 \right) = \operatorname{Re}\left(c_1^* c_2 \psi_1^*\psi_2 \right)\cos(\omega_{12}t) + \operatorname{Im}\left(c_1^* c_2 \psi_1^*\psi_2 \right)\sin(\omega_{12}t),$$

where we have assumed that $E_1 < E_2$. For instance, if the coefficients $c_{1,2}$ and the wave functions $\psi_{1,2}(\mathbf{r})$ are real, the probability density

$$|\Psi(\mathbf{r},t)|^2 = c_1^2 \psi_1(\mathbf{r})^2 + c_2^2 \psi_2(\mathbf{r})^2 + 2c_1 c_2 \psi_1(\mathbf{r})\psi_2(\mathbf{r})\cos(\omega_{12}t)$$

oscillates at a fixed point $\mathbf{r}$ between the two extreme values

$$\rho_\pm(\mathbf{r}) = \left(c_1\psi_1(\mathbf{r}) \pm c_2\psi_2(\mathbf{r}) \right)^2$$

with frequency ω_{12}. The same is true for the average value of any observable not explicitly depending on time. For instance, the average value of the position $\mathbf{r}$ in the state Ψ (assuming, again, that c_{12} and $\psi_{1,2}$ are real) is given by

$$\langle \mathbf{R} \rangle_\Psi = \int d^3 r\, \mathbf{r}\, |\Psi(\mathbf{r},t)|^2 = c_1^2 \langle \mathbf{R} \rangle_{\psi_1} + c_2^2 \langle \mathbf{R} \rangle_{\psi_2} + 2c_1 c_2 \left(\psi_1, \mathbf{r}\psi_2 \right)\cos(\omega_{12}t).$$

The stationary states we have considered so far, which are *genuine* (i.e., square integrable) eigenfunctions of the Hamiltonian, are called **bound states**. The reason is that, since $|\Psi|^2 = |\psi|^2$ is integrable, $|\psi|$ must decay sufficiently fast at infinity[4]. Hence the probability of finding the particle at infinity (or, more precisely, far away from a given finite point in space) is vanishingly small. Quantum bound states thus roughly correspond to classical *bounded* orbits. It is also of practical interest, however, to consider *generalized* stationary states (3.12) which are only *formal* eigenfunctions (i.e., *bounded* but not square integrable) of the Hamiltonian. For example, if $H = \frac{\mathbf{P}^2}{2m}$, then the plane waves (normalized according

---

[4]See footnote 18 on Chapter 2.

to Eq. (2.40))

$$\Psi_{\mathbf{p}}(\mathbf{r},t) := \psi_{\mathbf{p}}(\mathbf{r})e^{-\frac{i}{\hbar}E(\mathbf{p})t} = (2\pi\hbar)^{-3/2}e^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r}-E(\mathbf{p})t)}, \qquad \text{with} \quad E(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}, \qquad (3.14) \quad \boxed{\text{Psirt}}$$

are generalized stationary states of H satisfying the equations

$$i\hbar\partial_t\Psi_{\mathbf{p}} = H\Psi_{\mathbf{p}} = E(\mathbf{p})\Psi_{\mathbf{p}}.$$

Generalized stationary states of this type (i.e., bounded but not square integrable) are called **scattering states**. The reason for this terminology is that, since scattering states are not normalizable, there is a nonvanishing probability for the particle to be at infinity. Therefore these stationary states are the quantum analogues of classical unbounded motion, in which a particle comes from infinity, is scattered by the potential, and returns to infinity.

Although strictly speaking scattering states are *not* physical states (as they are not normalizable), one can construct out of them *wave packets* that are square integrable and thus represent genuine physical states. For example, the function

$$\Psi(\mathbf{r},t) = \int d^3p \, c(\mathbf{p})\Psi_{\mathbf{p}}(\mathbf{r},t) \qquad (3.15) \quad \boxed{\text{gensolfreeS}}$$

is a solution of the free Schrödinger equation

$$i\hbar\partial_t\Psi = \frac{\mathbf{P}^2}{2m}\Psi,$$

since it is a linear combination[5] of solutions $\Psi_{\mathbf{p}}(\mathbf{r},t)$ and the equation is obviously *linear*. As we saw in Section 2.7, the norm of this wave packet is equal to that of the function $c(\mathbf{p})$, which represents the particle's probability amplitude in momentum space at $t = 0$. This can be easily verified noting that

$$(\Psi_{\mathbf{p}},\Psi_{\mathbf{p}'}) = \left(e^{-\frac{i}{\hbar}E(\mathbf{p}')t}\psi_{\mathbf{p}}, e^{-\frac{i}{\hbar}E(\mathbf{p})t}\psi_{\mathbf{p}'}\right) = e^{\frac{i}{\hbar}(E(\mathbf{p})-E(\mathbf{p}'))t}(\psi_{\mathbf{p}},\psi_{\mathbf{p}'}) = e^{\frac{i}{\hbar}(E(\mathbf{p})-E(\mathbf{p}'))t}\delta(\mathbf{p}-\mathbf{p}')$$
$$= \delta(\mathbf{p}-\mathbf{p}'),$$

and therefore

$$\|\Psi\|^2 = \left(\int d^3p \, c(\mathbf{p})\Psi_{\mathbf{p}}, \int d^3p' \, c(\mathbf{p}')\Psi_{\mathbf{p}'}\right) = \int d^3p \, d^3p' \, c^*(\mathbf{p})c(\mathbf{p}') (\Psi_{\mathbf{p}},\Psi_{\mathbf{p}'})$$
$$= \int d^3p \, d^3p' \, c^*(\mathbf{p})c(\mathbf{p}')\delta(\mathbf{p}-\mathbf{p}') = \int d^3p |c(\mathbf{p})|^2 = \|c\|^2.$$

Equation (3.15) provides a representation of the general solution of the time-dependent Schrödinger equation with zero potential akin to Eq. (3.13) when the Hamiltonian possesses an orthonormal basis of eigenfunctions $\{\psi_n : n \in \mathbb{N}\}$. Indeed, as remarked above in this case $\Psi(\mathbf{r},t)$ in Eq. (3.15) is a solution of the free Schrödinger equation, and verifies any given initial condition $\Psi(\mathbf{r},0) = \psi(\mathbf{r})$ provided that $c(\mathbf{p}) = \hat{\psi}(\mathbf{p})$:

$$\Psi(\mathbf{r},0) = \int d^3p \, c(\mathbf{p})\psi_{\mathbf{p}}(\mathbf{r}) = (2\pi\hbar)^{-3/2}\int d^3p \, c(\mathbf{p})e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} = (2\pi\hbar)^{-3/2}\int d^3p \, \hat{\psi}(\mathbf{p})e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} = \psi(\mathbf{r})$$

$$(3.16) \quad \boxed{\text{psiexpplwav}}$$

(cf. Eqs. (2.30)-(2.32)). Formally, the free particle Hamiltonian $H = \frac{\mathbf{P}^2}{2m}$ has a *continuous spectrum* of nonnegative "eigenvalues" —the energies $E(\mathbf{p})$— with (3.14) as *formal* (bounded but not normalizable) eigenfunctions. Note the similarities between the spatial part of the formal eigenfunctions, i.e., the functions $\psi_{\mathbf{p}}(\mathbf{r})$, labeled by the *continuous* index $\mathbf{p}$, and the eigenfunctions $\psi_n(\mathbf{r})$ in Eqs. (3.6)-(3.7). Indeed, the expansion (3.16) of an arbitrary square integrable wave function in terms of the eigenfunctions $\psi_{\mathbf{p}}(\mathbf{r})$ of the free Hamiltonian $\frac{\mathbf{P}^2}{2m}$ can be regarded as the continuous analogue of the series (3.13).

---

[5]Strictly speaking, in mathematics by a "linear combination" it is always understood a *finite sum* of certain functions (or vectors, in a general vector space) multiplied by appropriate scalar coefficients (complex numbers, in our case). However, in the physics terminology this requirement is usually relaxed, and infinite sums or even integrals —as in Eq. (3.15)— are allowed in linear combinations.

3.3 One-dimensional problems

`sec.1D`

In the rest of this chapter we shall focus on studying in some detail the time-independent Schrödinger equation in one dimension, namely

$$H\psi(x) \equiv -\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x), \tag{3.17}$$

`Schr1D`

or equivalently

$$\psi''(x) + \Big(\varepsilon - v(x)\Big)\psi(x) = 0, \tag{3.18}$$

`Schr1Dred`

with

$$v(x) = \frac{2m}{\hbar^2}V(x), \qquad \varepsilon = \frac{2mE}{\hbar^2}. \tag{3.19}$$

`vvep`

Note that in one dimension the wave function $\psi(x)$ has dimensions of $L^{-1/2}$ (indeed, $|\psi(x)|^2\,dx$ is a probability, which is dimensionless), and v and ε have dimensions of L^{-2} (why?). For the time being, we shall suppose that the potential $V(x)$, and hence $v(x)$, is a *piecewise continuous*[6] *function.* By the standard uniqueness and existence theorems for linear homogeneous second-order ordinary differential equations (ODEs), this guarantees that for every real E equation (3.19) has two linearly independent (piecewise C^2) solutions $\psi_{1,2}(x)$. These solutions can be taken as real, since E and $v(x)$ are both real. The general solution of Eq. (3.19) is a linear combination of the two linearly independent solutions $\psi_{1,2}$ with arbitrary complex coefficients:

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x), \qquad c_{1,2} \in \mathbb{C}.$$

Note that, although the coefficient function $\varepsilon - v(x)$ in the Schrödinger equation (3.18) is real, it is essential to allow ψ to be complex-valued so as not to destroy the *interference effects* characteristic of quantum mechanics.

In order that a certain energy E belong to the *point spectrum* of the Hamiltonian H, equation (3.17) must admit at least one linearly independent *square integrable* solution $\psi(x)$, which in particular must satisfy the boundary conditions[7] at $\pm\infty$

$$\lim_{|x|\to\infty}\psi(x) = 0.$$

In most practical problems the latter condition does in fact imply the square integrability of ψ. Similarly, for E to belong to the *continuous spectrum* of H equation (3.17) must admit at least one linearly independent solution *bounded at infinity but not square integrable,* i.e., satisfying

$$\int \big|\psi(x)\big|^2\,dx = \infty, \qquad \big|\psi(x)\big| \text{ bounded as } |x| \to \infty.$$

In practice, the first of the latter two conditions can be replaced by either

$$\lim_{x\to\infty}\psi(x) \neq 0$$

or

$$\lim_{x\to-\infty}\psi(x) \neq 0$$

(or both).

---

[6]A function defined on the real line is called piecewise continuous if it has a finite number of jump discontinuities, and piecewise C^r if it is piecewise continuous and of class C^r in any open interval not containing any discontinuities.

[7]See footnote 18 on Chapter 2.

© Artemio González López

> **Definition 3.2.** The **spectrum** $\sigma(H)$ of a Hamiltonian H is the union of its point and its continuous spectrum, respectively denoted by $\sigma_p(H)$ and $\sigma_c(H)$.

Thus the spectrum of H is made up of all real numbers E such that the time-independent Schrödinger equation (3.17) has at least one linearly independent solution which is (at least) bounded at $\pm\infty$.

Remark. Although it is not obvious from the definition, it can be shown that the point and the continuous spectrum of a self-adjoint operator H are *disjoint sets,* i.e.,

$$\sigma_p(H) \cap \sigma_c(H) = \emptyset. \qquad \blacksquare$$

Before dealing with specific examples, we shall briefly discuss the continuity requirements on the wave function $\psi(x)$ (a solution of the time-independent Schrödinger equation) and its first derivative. Clearly, ψ and ψ' must be continuous in regions on which the potential $V(x)$ is continuous (indeed, in these regions ψ is of class C^2 by the standard existence and uniqueness theorems for *linear* ODEs).

> 1) If the potential V is *piecewise continuous*, both the wave function and its derivative must be *continuous* at points of discontinuity of V.

Proof. Indeed, since the potential (and hence the function $v(x)$) is piecewise continuous, it has at most a finite number of jump discontinuities. If $v(x)$ has a jump discontinuity at a point x_0, clearly the wave function ψ can have at most a jump discontinuity at this point (since to the right and to the left of x_0 we can apply the existence and uniqueness theorem for linear second-order ODEs). Restricting ourselves to an open interval around x_0 not containing any discontinuities of $V(x)$ other than x_0 we can represent $\psi(x)$ as

$$\psi(x) = \psi_+(x)\theta(x - x_0) + \psi_-(x)\theta(x_0 - x),$$

where

$$\theta(s) = \begin{cases} 0, & s < 0 \\ 1, & s > 0 \end{cases}$$

is *Heaviside's step function*[8], and $\psi_\pm(x)$ are smooth (C^2) functions equal to the restrictions of the wave function to the regions $x > x_0$ (in the case of ψ_+) or $x < x_0$ (for ψ_-). Differentiating with respect to x we obtain

$$\psi'(x) = \psi_+(x)'\theta(x - x_0) + \psi_-(x)'\theta(x_0 - x) + \psi_+(x)\delta(x - x_0) - \psi_-(x)\delta(x_0 - x)$$

$$= \psi_+(x)'\theta(x - x_0) + \psi_-(x)'\theta(x_0 - x) + \Big(\psi_+(x) - \psi_-(x)\Big)\delta(x - x_0)$$

$$= \psi_+(x)'\theta(x - x_0) + \psi_-(x)'\theta(x_0 - x) + \Big(\psi_+(x_0) - \psi_-(x_0)\Big)\delta(x - x_0),$$

where we have used the identities $\delta(s) = \delta(-s)$ and

$$\theta'(s) = \delta(s)$$

(see next exercise). Differentiating again we obtain

$$\psi''(x) = \psi_+(x)''\theta(x - x_0) + \psi_-(x)''\theta(x_0 - x) + \Big(\psi'_+(x_0) - \psi'_-(x_0)\Big)\delta(x - x_0)$$

$$+ \Big(\psi_+(x_0) - \psi_-(x_0)\Big)\delta'(x - x_0) = \Big(\varepsilon - v(x)\Big)\psi(x).$$

Since the RHS has at most a jump discontinuity at x_0, the coefficients of the singular terms $\delta(x - x_0)$ and $\delta'(x - x_0)$ in the LHS must vanish, i.e.,

$$\psi_+(x_0) - \psi_-(x_0) = \psi'_+(x_0) - \psi'_-(x_0) = 0,$$

which establishes the continuity of ψ and ψ' at x_0. $\qquad \blacksquare$

---

[8]Although the value of $\theta(s)$ at $s = 0$ is immaterial. it is usually defined as $1/2$.

Remark. An important consequence of the previous result is that if the potential is piecewise continuous, *both the probability density and the probability current are continuous.*

Exercise 3.1. Show that $\theta'(s) = \delta(s)$.

Proof. We must show that

$$\int_{-\infty}^{\infty} ds\, \phi(s)\delta'(s) = \int_{-\infty}^{\infty} ds\, \phi(s)\delta(s)$$

for all test functions $\phi(s)$. The right-hand side evaluates to $\phi(0)$. As to the left-hand side, integrating by parts we obtain

$$\int_{-\infty}^{\infty} ds\, \phi(s)\theta'(s) = \phi(s)\theta(s)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} ds\, \phi'(s)\theta(s) = -\int_0^{\infty} ds\, \phi'(s) = -\phi(\infty) + \phi(0) = \phi(0),$$

as was to be proved. ∎

---

2) If the potential V is *infinite* on the half line $(-\infty, x_0]$ or $[x_0, \infty)$, the wave function must *vanish* on this half line.

Proof. Suppose, for instance, that $V(x) = +\infty$ for $x \leqslant x_0$. To investigate the behavior of the wave function at x_0, we shall instead take $V(x) = V_0$ for $x \leqslant x_0$ and then let V_0 tend to infinity. Since the boundary condition at x_0 is only going to be affected by the behavior of the potential in an arbitrarily small neighborhood of x_0, we can further assume that $V(x)$ is constant for $x_0 < x < x_0 + \delta$ with $\delta > 0$. This constant can be taken equal to zero without loss of generality (it can be absorbed in V_0 and ε). It is also clear that the value of x_0 is immaterial for the result (indeed, if $\psi(x)$ solves the Schrödinger equation for $V(x)$ then $\psi(x - x_0)$ solves the Schrödinger equation for $V(x - x_0)$), so we shall take $x_0 = 0$. We thus have to solve the differential equation

$$\psi''(x) = \begin{cases} (v_0 - \varepsilon)\psi(x), & x \leqslant 0 \\ -\varepsilon\psi(x), & 0 \leqslant x < \delta, \end{cases} \tag{3.20}$$ `deinfV`

where we have set $v_0 = 2mV_0/\hbar^2$. Since v_0 is eventually going to tend to infinity, we can assume that $v_0 > \varepsilon$. Although this is not essential, we shall also take $\varepsilon > 0$ (the cases $\varepsilon = 0$ and $\varepsilon < 0$ are dealt with similarly). Calling

$$\eta = \sqrt{v_0 - \varepsilon},$$

the solution $\psi(x)$ of the differential equation (3.20) is

$$\psi(x) = \begin{cases} ae^{\eta x} + be^{-\eta x}, & x \leqslant 0, \\ c\sin(\sqrt{\varepsilon}\,x) + d\cos(\sqrt{\varepsilon}\,x), & 0 \leqslant x < \delta, \end{cases}$$

where a, b, c, d are complex constants. Since the wave function (both for the point and the continuous spectrum) must be bounded at $x = -\infty$, the constant b must vanish. Imposing the continuity of ψ and ψ' at x_0 (which is necessary, since V is piecewise continuous) we obtain the equalities

$$a = d, \qquad \eta a = \sqrt{\varepsilon}\,c.$$

We thus have

$$\psi(x) = \begin{cases} \frac{c\sqrt{\varepsilon}}{\eta} e^{\eta x}, & x \leqslant 0, \\ c\left(\sin(\sqrt{\varepsilon}\,x) + \frac{\sqrt{\varepsilon}}{\eta}\cos(\sqrt{\varepsilon}\,x)\right), & 0 < x < \delta. \end{cases}$$

Since $\eta \to \infty$ as $v_0 \to \infty$ with ε fixed, in this limit we obtain

$$\psi(x) = \begin{cases} 0, & x \leqslant 0, \\ c\sin(\sqrt{\varepsilon}\,x), & 0 \leqslant x < \delta. \end{cases}$$

which vanishes for $x \leqslant 0$ as claimed. Note, however, that in this case ψ' has a *jump discontinuity* at $x = 0$, since

$$\lim_{x \to 0-} \psi'(x) = 0, \qquad \lim_{x \to 0+} \psi'(x) = c\sqrt{\varepsilon} \neq 0. \qquad \blacksquare$$

The following two general results shall also be useful in the sequel:

> 3) The eigenfunctions (genuine or formal) of a one-dimensional Hamiltonian H can be taken as real valued without loss of generality.

Proof. Indeed, if ψ is a solution of the one-dimensional Schrödinger equation (3.1) so is its complex conjugate ψ^*. By linearity, the linear combinations

$$\operatorname{Re}\psi = \frac{1}{2}(\psi + \psi^*), \qquad \operatorname{Im}\psi = \frac{1}{2i}(\psi - \psi^*)$$

are both real solutions of the Schrödinger equation. Moreover, ψ is square integrable or bounded if and only if $\operatorname{Re}\psi$ and $\operatorname{Im}\psi$ are square integrable or bounded. $\qquad \blacksquare$

> 4) If ψ is an eigenfunction of H with eigenvalue E (belonging either to the point or the continuous spectrum), then
> $$E \geqslant \min V(x).$$
> Moreover, if ψ is a genuine eigenfunction (i.e, if E belongs to the point spectrum), then
> $$E > \min V(x).$$

age.EgeVmin

Proof. Indeed, suppose that ψ is a (genuine or formal) eigenfunction of H with eigenvalue E satisfying

$$E < \min V(x).$$

Then ψ is a solution of the Schrödinger equation

$$\psi''(x) = \Big(v(x) - \varepsilon\Big)\psi(x),$$

where by hypothesis

$$v(x) - \varepsilon > 0$$

for all x. By the third result at the end of the last section, we can assume without loss of generality that $\psi(x)$ is real. Setting

$$\rho(x) = |\psi(x)|^2 = \psi(x)^2$$

we then have

$$\rho'(x) = 2\psi(x)\psi'(x),$$
$$\rho''(x) = 2\big(\psi(x)\psi''(x) + \psi'(x)^2\big) = 2\big(\psi'(x)^2 + (v(x) - \varepsilon)\psi(x)^2\big) \geqslant 0.$$

Moreover, since $v(x) - \varepsilon > 0$ by hypothesis, $\rho''(x_0) = 0$ if and only if $\psi(x_0) = \psi'(x_0) = 0$, which implies that $\psi(x)$ is identically zero by the existence and uniqueness theorem for linear second-order ODEs. Hence $\rho''(x) > 0$ for all x, which integrated twice leads to

$$\rho(x) > \rho(x_0) + \rho'(x_0)(x - x_0) \quad \forall x. \tag{3.21}$$

rhopp

We can choose x_0 such that $\rho'(x_0) \neq 0$, since otherwise $\rho'(x) = 0$ for all x would imply that $\rho''(x) = 0$ for all x, which as seen above is only possible if ψ vanishes identically. From Eq. (3.21) it then follows that $\rho = |\psi|^2$ is unbounded at $\pm\infty$, so that ψ cannot be a (genuine or formal) eigenfunction.

Suppose next that ψ is a genuine eigenfunction, and thus is square integrable. We then have

$$(\psi, H\psi) = E(\psi, \psi) = \frac{1}{2m}(\psi, P^2\psi) + (\psi, V(x)\psi) = \frac{1}{2m}\|P\psi\|^2 + (\psi, V(x)\psi)$$

$$\implies \frac{1}{2m}\|P\psi\|^2 = \int dx \left(E - V(x)\right)|\psi(x)|^2.$$

Since P has no genuine eigenfunctions $\|P\psi\| \neq 0$, and therefore

$$\int dx \left(E - V(x)\right)|\psi(x)|^2 > 0.$$

This implies that $E > \min V(x)$, since otherwise

$$E \leqslant \min V(x) \implies \int dx \left(E - V(x)\right)|\psi(x)|^2 \leqslant 0. \qquad \blacksquare$$

Remark. The fact that $E > \min V(x)$ for a bound state energy E is essentially a consequence of the uncertainty principle. Indeed, if $E = \min V(x) = V(x_0)$ then classically $x = x_0$ is an equilibrium solution, and therefore $p = 0$. Quantum mechanically, if the particle's position has an uncertainty Δx then the uncertainty Δp in the momentum must be at least $\hbar/(2\Delta x)$, and thus the particle's energy is at least

$$\frac{\Delta p^2}{2m} + V(x_0) > V(x_0) \equiv \min V(x).$$

3.4 Potential wells and barriers

3.4.1 The infinite well

In this case the potential is

$$V(x) = \begin{cases} \infty, & x \in (-\infty, 0] \cup [L, \infty) \\ 0, & x \in (0, L). \end{cases}$$

Classically, this potential describes the motion inside the interval $[0, L]$ of a particle subject to no forces, the endpoints $0, L$ being two impenetrable barriers. Thus the particle's energy is non-negative, and the two endpoints $0, L$ are *turning points* for any energy $E \geqslant 0$. Moreover, since the energy of the particle is equal to $p^2/(2m) = mv^2/2$, the absolute value of the particle's velocity must be constant. Hence when the particle hits the endpoints of the interval $[0, L]$ its velocity is instantly reversed.

Let us next analyze the corresponding quantum problem. By the second framed result in the previous section, the wave function must vanish on the intervals $(-\infty, 0)$ and (L, ∞), and must satisfy the Schrödinger equation

$$\psi''(x) + \varepsilon\psi(x) = 0, \qquad 0 < x < L, \tag{3.22}$$

inside the interval $(0, L)$ with the *boundary conditions*

$$\psi(0) = \psi(L) = 0. \tag{3.23}$$

Equations (3.22)-(3.23) are a very simple instance of what in mathematics is known as a *Sturm–Liouville* problem. The type of solutions of Eq. (3.22) depends on the sign of the *eigenvalue*

$$\varepsilon \equiv \frac{2mE}{\hbar^2}$$

(cf. Eq. (3.19)). Indeed, the general solution of this equation is

$$
\psi(x) = \begin{cases} a\cos(\sqrt{\varepsilon}\,x) + b\sin(\sqrt{\varepsilon}\,x), & \varepsilon > 0 \\ a + bx, & \varepsilon = 0 \\ a\cosh(\sqrt{-\varepsilon}\,x) + b\sinh(\sqrt{-\varepsilon}\,x), & \varepsilon < 0. \end{cases}
$$

As in the classical case, the energy (i.e., the eigenvalue ε) cannot be negative. Indeed, imposing the boundary conditions (3.23) to the solution with negative ε we obtain

$$
a = 0, \qquad b\sinh(\sqrt{-\varepsilon}\,L) \quad \Longrightarrow \quad b = 0,
$$

and thus $\psi = 0$. Although the energy can be zero classically, the same is not true in the quantum case. Indeed, imposing again the boundary conditions to the solution for $\varepsilon = 0$ we obtain

$$
a = 0, \qquad bL = 0 \quad \Longrightarrow \quad b = 0 \quad \Longrightarrow \quad \psi = 0.
$$

Thus in this case the eigenvalues of H are positive, in agreement with the framed statement 4) on p. 78.

Let us next turn to the positive energy solutions. Imposing the boundary conditions at $x = 0, L$ we now obtain

$$
a = 0, \qquad b\sin(\sqrt{\varepsilon}\,L) = 0 \quad \Longrightarrow \quad \sin(\sqrt{\varepsilon}\,L) = 0
$$

and thus[9]

$$
\sqrt{\varepsilon}\,L = n\pi, \qquad n \in \mathbb{N}.
$$

or

$$
E = \frac{\hbar^2 \varepsilon}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \equiv E_n, \qquad n = 1, 2, \dots. \tag{3.24}
$$

`infwellen`

Thus the energy is *quantized*, since it can only take the discrete set of values $\{E_1, E_2, \dots\}$. The corresponding eigenfunctions inside the interval $[0, L]$ are

$$
\psi_n(x) = b\sin(\sqrt{\varepsilon_n}\,x) = b\sin\left(\frac{n\pi x}{L}\right), \qquad 0 \leqslant x \leqslant L,
$$

where the constant b (which can be taken as real and positive without loss of generality) is determined by normalization:

$$
\int_{-\infty}^{\infty} \mathrm{d}x\,|\psi_n(x)|^2 = b^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x = \frac{b^2}{2} \int_0^L \left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right] \mathrm{d}x = \frac{Lb^2}{2} = 1
$$

$$
\Longrightarrow \quad b = \sqrt{\frac{2}{L}}.
$$

Hence

$$
\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \qquad 0 \leqslant x \leqslant L. \tag{3.25}
$$

`infwelleigf`

Remarks.

- Since the functions (3.25) are square integrable they are *genuine eigenfunctions*, and hence *all the quantized energies E_n belong to the point spectrum*. In particular, in this case *there is no continuous spectrum*. This is not surprising, since in the classical case the motion is bounded for any (nonnegative) energy.

---

[9]Note that the integer n must be *positive*, since $\sqrt{\varepsilon}$ is positive.

- All of the energy levels are *non-degenerate.* As we shall see in Section (3.5), this is actually a general property of the bound-state energies of all one-dimensional potentials.

- The n-th eigenfunction ψ_n has *exactly $n - 1$ zeros* in the interval $(0, L)$. Indeed:

$$\psi_n(x) = 0 \quad \Longleftrightarrow \quad n\frac{\pi x}{L} = m\pi \ (m \in \mathbb{Z}) \quad \Longrightarrow \quad x = \frac{m}{n}L \quad \text{with } m = 1, \dots, n-1,$$

where the restriction on m comes from requiring that $x \in (0, L)$. In particular, *the ground state wave function ha no zeros in the interval* $(0, L)$. We shall see that this is a general property of all one-dimensional potentials (replacing $(0, L)$ by the open interval in which the potential is finite). In other words, if we label the energies in the point spectrum of a one-dimensional potential $V(x)$ in increasing order as

$$E_1 < E_2 < \cdots < E_n < \cdots,$$

then *the eigenfunction ψ_n with eigenvalue E_n has* exactly $n - 1$ *zeros.*

- In this case the physical wave functions are functions of class C^1 on the interval $[0, L]$ vanishing at the endpoints $x = 0, L$. (Note that continuity on $[0, L]$ automatically implies square integrability.) By Dirichlet's theorem, any such function $\psi(x)$ can be expanded in a *Fourier sine series*

$$\psi(x) = \sum_{k=1}^{\infty} a_k \sin\left(\frac{k\pi x}{L}\right),$$

with

$$a_k = \frac{2}{L}\int_0^L \sin\left(\frac{k\pi x}{L}\right)\psi(x)\,\mathrm{d}x.$$

The latter equations are nothing but Eqs. (3.6)-(3.7), with ψ_k given by Eq. (3.25) and $c_k = \sqrt{L/2}\,a_k$. In fact, it can be shown that the eigenfunctions ψ_k in Eq. (3.25) make up an *orthonormal basis* of $L^2([0, L])$ (this is essentially a consequence of the Stone–Weierstrass theorem in functional analysis). It can be proved (using the spectral theorem for self-adjoint operators in functional analysis) that this is actually a general property of potentials having only point spectrum.

- When the quantum number n is very large the eigenfunction ψ_n is wildly oscillatory, as is the corresponding probability density $\rho_n(x) = \psi_n(x)^2$. In this case we can effectively replace $\rho_n(x)$ at a point $x \in (0, L)$ by its average over an interval centered at x of length equal to one period L/n of ρ_n:

$$\rho_n(x) \longrightarrow \frac{n}{L}\frac{2}{L}\int_{x-\frac{L}{2n}}^{x+\frac{L}{2n}} \sin^2\left(\frac{n\pi s}{L}\right)\mathrm{d}s = \frac{n}{L^2}\int_{x-\frac{L}{2n}}^{x+\frac{L}{2n}} \left[1 - \cos\left(\frac{2n\pi s}{L}\right)\right]\mathrm{d}s = \frac{1}{L}.$$

In other words, as $n \to \infty$ the probability density becomes approximately uniform, as in the classical case. This is yet another example of *Bohr's correspondence principle.*

3.4.2 The square well potential: bound states

Consider now the square well potential

$$V(x) = \begin{cases} -V_0, & |x| < L/2 \\ 0, & |x| > L/2, \end{cases} \tag{3.26} \quad \boxed{\texttt{sqwell}}$$

where $V_0 > 0$ is the "depth" of the well (cf. Fig. 3.1). Since the potential is an even function of x, if $\psi(x)$ is an eigenfunction so are $\psi(-x)$ and (by *linearity*) the two linear combinations

$$\psi_e(x) = \frac{1}{2}\left(\psi(x) + \psi(-x)\right), \qquad \psi_o(x) = \frac{1}{2}\left(\psi(x) - \psi(-x)\right),$$

which are respectively even and odd functions of x. Thus without loss of generality *we can look for eigenfunctions of a definite parity* (i.e., even or odd). This argument is obviously *valid for any even potential $V(x)$*.

From the fourth result at the end of the last Section, we know that the spectrum of H is contained in the set $[-V_0, \infty)$, i.e., $E \geqslant -V_0$. We shall focus our attention on energies in the range

$$-V_0 \leqslant E < 0,$$

which in classical mechanics corresponds to *bounded motion* (see Section 3.4.4 for the case $E > 0$). In the interval $[L/2, \infty)$ we must have

$$\psi''(x) = -\varepsilon \psi(x) \quad \Longrightarrow \quad \psi(x) = e^{-\eta x}, \quad \eta := \sqrt{-\varepsilon} \equiv \sqrt{|\varepsilon|} > 0, \qquad (3.27) \quad \boxed{\texttt{psiL2inf}}$$

where we have discarded the exponentially increasing solution $e^{\eta x}$ (since it blows up as $x \to \infty$) and without loss of generality have set the arbitrary constant multiplying the decreasing exponential equal to one (indeed, we shall normalize the eigenfunctions later on). Since $\psi(x)$ is exponentially decreasing as $x \to \infty$ and is either even or odd, it is also exponentially decreasing as $x \to -\infty$, and hence is normalizable. Thus E belongs to the point spectrum, and therefore (by the third result at the end of the last section) $E > \min V(x) = -V_0$, or equivalently

$$\varepsilon > -\frac{2mV_0}{\hbar^2} \equiv -v_0.$$

Likewise, in the interval $[0, L/2]$ we have

$$\psi''(x) = -(v_0 + \varepsilon)\psi(x) \quad \Longrightarrow \quad \psi(x) = a\cos(kx) + b\sin(kx), \qquad (3.28) \quad \boxed{\texttt{psi0L2}}$$

where a and b are complex constants and we have set

$$\boxed{k = \sqrt{v_0 - |\varepsilon|} > 0.}$$

Since the potential is piecewise continuous, we must impose the continuity of ψ and ψ' at $x = L/2$, obtaining the linear system

$$a\cos(kL/2) + b\sin(kL/2) = e^{-\eta L/2}, \qquad k\Big(-a\sin(kL/2) + b\cos(kL/2)\Big) = -\eta e^{-\eta L/2}. \quad (3.29) \quad \boxed{\texttt{condeo}}$$
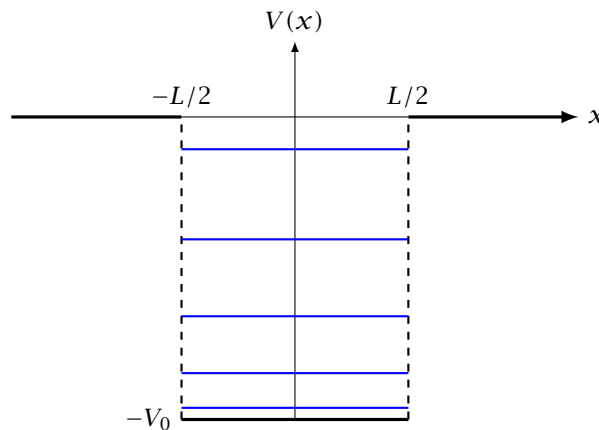
Figure 3.1. Square well potential of depth V_0 and width L. The blue lines represent the five bound state energies in the case $V_0 L^2 = 98\hbar^2/m$, listed in Eq (3.38).

If ψ is an *even* eigenfunction then $\psi(x) = \psi(-x)$ for $x < 0$. Thus ψ is automatically continuous at the origin, but the continuity of ψ' at $x = 0$ implies that $\psi'(0) = 0$, i.e.,

$$b = 0.$$

Thus for even eigenfunctions conditions (3.29) reduce to

$$a\cos(kL/2) = e^{-\eta L/2}, \qquad ka\sin(kL/2) = \eta e^{-\eta L/2}. \tag{3.30}$$ `condeven`

Eliminating a we get the *eigenvalue equation*

$$k\tan(kL/2) = \eta \quad \Longleftrightarrow \quad \boxed{\sqrt{v_0 - |\varepsilon|}\,\tan\left(\frac{L}{2}\sqrt{v_0 - |\varepsilon|}\right) = \sqrt{|\varepsilon|} \qquad \text{(even eigenfunctions)},}$$
$$\tag{3.31}$$ `eigveven`

which is a transcendental equation for the eigenvalue ε. We shall see below that this equation has a finite number (depending on L and V_0) of solutions that we shall denote by[10]

$$\varepsilon_0 < \varepsilon_2 \cdots < \varepsilon_{2n} < \cdots.$$

The eigenfunction ψ_{2n} corresponding to the eigenvalue ε_{2n} is the even extension of the function $\psi(x)$ in Eqs. (3.28)-(3.27), namely

$$\boxed{\psi_{2n}(x) = N_{2n}\begin{cases} \dfrac{e^{-\eta_{2n}L/2}}{\cos(k_{2n}L/2)}\cos(k_{2n}x), & |x| \leqslant L/2 \\ e^{-\eta_{2n}|x|}, & |x| \geqslant L/2, \end{cases}} \tag{3.32}$$ `psiesqwell`

where k_{2n} and η_{2n} are obtained from k and η replacing ε by ε_{2n}, and $N_{2n} > 0$ is a constant determined imposing that $\|\psi\| = 1$:

$$\begin{aligned} N_{2n}^{-2} &= \int_{-\infty}^{\infty} dx\, |\psi_{2n}(x)|^2 = 2\int_0^{\infty} dx\, |\psi_{2n}(x)|^2 \\ &= \frac{2e^{-\eta_{2n}L}}{\cos^2(k_{2n}L/2)}\int_0^{L/2}\cos^2(k_{2n}x)\,dx + 2\int_{L/2}^{\infty}e^{-2\eta_{2n}x}\,dx \\ &= e^{-\eta_{2n}L}\left(1 + \frac{\eta_{2n}^2}{k_{2n}^2}\right)\int_0^{L/2}\left(1 + \cos(2k_{2n}x)\right)dx + \frac{e^{-\eta_{2n}L}}{\eta_{2n}} \\ &= e^{-\eta_{2n}L}\frac{v_0}{k_{2n}^2}\left(\frac{L}{2} + \frac{\sin(k_{2n}L)}{2k_{2n}}\right) + \frac{e^{-\eta_{2n}L}}{\eta_{2n}}. \end{aligned}$$

Noting that

$$\sin(kL) = 2\tan(kL/2)\cos^2(kL/2) = \frac{2\tan(kL/2)}{1 + \tan^2(kL/2)} = \frac{2\eta/k}{1 + \frac{\eta^2}{k^2}} = \frac{2\eta k}{k^2 + \eta^2} = \frac{2\eta k}{v_0},$$

we finally obtain

$$N_{2n}^{-2} = e^{-\eta_{2n}L}\left(\frac{Lv_0}{2k_{2n}^2} + \frac{\eta_{2n}}{k_{2n}^2} + \frac{1}{\eta_{2n}}\right) = e^{-\eta_{2n}L}\left(\frac{Lv_0}{2k_{2n}^2} + \frac{\eta_{2n}^2 + k_{2n}^2}{\eta_{2n}k_{2n}^2}\right) = \frac{e^{-\eta_{2n}L}v_0}{\eta_{2n}k_{2n}^2}\left(1 + \frac{L\eta_{2n}}{2}\right),$$

and therefore

$$\boxed{N_{2n} = \sqrt{\frac{\eta_{2n}}{v_0}}\,k_{2n}e^{\eta_{2n}L/2}\left(1 + \frac{L\eta_{2n}}{2}\right)^{-1/2}.}$$

---

[10]In this problem it is convenient to number the eigenvalues and eigenfunctions of H starting with 0 instead of 1.

Similarly, for *odd* eigenfunctions the appropriate condition ensuring that both ψ and ψ' are continuous at the origin is that $\psi(0) = 0$ (indeed, if $\psi(-x) = -\psi(x)$ and ψ is continuous at the origin then automatically ψ' is continuous at the origin). Imposing this requirement we obtain $a = 0$, and therefore conditions (3.29) now reduces to

$$b\sin(kL/2) = e^{-\eta L/2}, \qquad kb\cos(kL/2) = -\eta e^{-\eta L/2},$$

from which we obtain the eigenvalue equation

$$k\cot(kL/2) = -\eta \quad \Longleftrightarrow \quad \boxed{\sqrt{v_0 - |\varepsilon|}\cot\left(\frac{L}{2}\sqrt{v_0 - |\varepsilon|}\right) = -\sqrt{|\varepsilon|}} \quad \text{(odd eigenfunctions)}.$$

(3.33) `eigvodd`

Again, we shall show that this equation has a finite number of solutions that we shall denote by

$$\varepsilon_1 < \varepsilon_3 \cdots < \varepsilon_{2n+1} < \cdots.$$

The eigenfunction ψ_{2n+1} corresponding to the eigenvalue ε_{2n+1} is the odd extension of the function $\psi(x)$ in Eqs. (3.28)-(3.27), namely

$$\psi_{2n+1}(x) = N_{2n+1}\begin{cases} \dfrac{e^{-\eta_{2n+1}L/2}}{\sin(k_{2n+1}L/2)}\sin(k_{2n+1}x), & |x| \leqslant L/2 \\ e^{-\eta_{2n+1}|x|}\,\text{sgn}\,x, & |x| \geqslant L/2, \end{cases}$$

(3.34) `psiosqwell`

where k_{2n+1} and η_{2n+1} are obtained from k and η replacing ε by ε_{2n+1}, and $N_{2n+1} > 0$ is a constant determined imposing that $\|\psi\| = 1$. Proceeding as before we obtain

$$\boxed{N_{2n+1} = \sqrt{\frac{\eta_{2n+1}}{v_0}}\,k_{2n+1}e^{\eta_{2n+1}L/2}\left(1 + \frac{L\eta_{2n+1}}{2}\right)^{-1/2}.}$$

The eigenvalue equations (3.31)-(3.33) can be somewhat simplified noting that

$$\left|\cos(kL/2)\right| = \left(1 + \tan^2(kL/2)\right)^{-1/2} = \left(1 + \frac{\eta^2}{k^2}\right)^{-1/2} = \frac{k}{v_0^{1/2}}, \qquad \text{(even eigenfunctions)},$$

$$\left|\sin(kL/2)\right| = \left(1 + \cot^2(kL/2)\right)^{-1/2} = \left(1 + \frac{\eta^2}{k^2}\right)^{-1/2} = \frac{k}{v_0^{1/2}}, \qquad \text{(odd eigenfunctions)}$$

Since $\tan(kL/2)$ must be positive (resp. negative) if Eq. (3.31) (resp. (3.33)) is satisfied, Eqs. (3.31)-(3.33) are equivalent to the following:

$$\frac{k}{v_0^{1/2}} = \begin{cases} \left|\cos(kL/2)\right|, & \tan(kL/2) > 0 \quad \text{(even eigenfunctions)} \\ \left|\sin(kL/2)\right|, & \tan(kL/2) < 0 \quad \text{(odd eigenfunctions)}. \end{cases}$$

(3.35) `eigvssqwell`

From the latter equations it immediately follows that the odd eigenvalues are intertwined with the even ones, i.e., that

$$\varepsilon_0 < \varepsilon_1 < \cdots < \varepsilon_{2n} < \varepsilon_{2n+1} < \cdots.$$

In order to get a better intuitive understanding the eigenvalue equation (3.35), it is convenient to introduce the dimensionless quantities

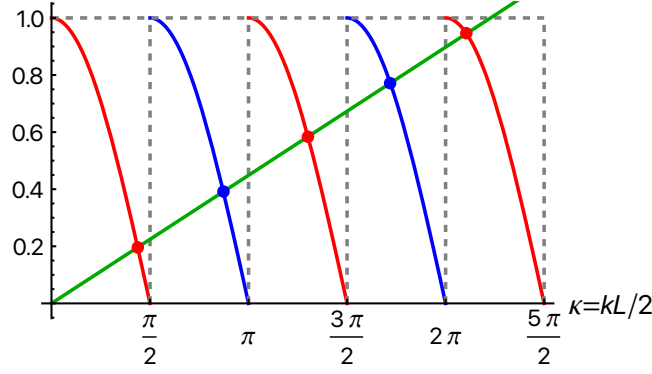$$\boxed{\kappa = \frac{kL}{2}, \qquad u_0 = \frac{Lv_0^{1/2}}{2},}$$

Figure 3.2. Eigenvalues of the square well potential (3.26) with $u_0 = 7$ (i.e., $V_0 L^2 = 98\hbar^2/m$). The red (resp. blue) curve is the graph of the function $y = \cos \kappa$ (resp. $y = \sin \kappa$) in the region $\tan \kappa > 0$ (resp. $\tan \kappa < 0$), while the green line is the straight line $y = \kappa/u_0 = \kappa/7$. The abscissas of the red (resp. blue) points are the values of κ_{2n} with $n = 0, 1, 2$ (resp. κ_{2n+1} with $n = 0, 1$).

in terms of which Eq. (3.35) is simply

$$\frac{\kappa}{u_0} = \begin{cases} \left| \cos \kappa \right|, & \tan \kappa > 0 \quad \text{(even eigenfunctions)} \\ \left| \sin \kappa \right|, & \tan \kappa < 0 \quad \text{(odd eigenfunctions).} \end{cases} \tag{3.36}$$

The physical energies E_n can be computed from the roots κ_n of the latter equation taking into account that

$$E_n = -\frac{\hbar^2}{2m} |\varepsilon_n| = \frac{\hbar^2}{2m}(-v_0 + k_n^2) = -\frac{2\hbar^2}{mL^2}(u_0^2 - \kappa_n^2). \tag{3.37}$$

Note that all of these energies verify the condition $-V_0 < E_n < 0$, since from Eqs. (3.36) it follows that $0 < \kappa_n < u_0$.

The roots κ_n of the eigenvalue equation (3.35) are the abscissas of the intersection points of the straight line $y = \kappa/u_0$ with the curves $y = |\cos \kappa|$ (in the regions where $\tan \kappa > 0$, i.e., the intervals $\left(m\pi, \frac{\pi}{2} + m\pi\right)$ with $m = 0, 1, \dots$) or $y = |\sin \kappa|$ (in the regions where $\tan \kappa < 0$, i.e., the intervals $\left(\frac{\pi}{2} + m\pi, (m+1)\pi\right)$ with $m = 0, 1, \dots$). For example, for $u_0 = 7$, or equivalently

$$V_0 = \frac{\hbar^2 v_0}{2m} = \frac{2\hbar^2 u_0^2}{mL^2} = 98 \frac{\hbar^2}{mL^2},$$

there are exactly five such points, three corresponding to even eigenfunctions and the rest to odd ones (see Fig. 3.2). Their abscissas can be computed by numerically solving the eigenvalue Eq. (3.36), namely

$$\kappa_0 = 1.37333, \quad \kappa_1 = 2.73949, \quad \kappa_2 = 4.08863, \quad \kappa_3 = 5.40172, \quad \kappa_4 = 6.61597,$$

with corresponding energies (in units of $\hbar^2/(mL^2)$)

$$E_0 = -94.228, \quad E_1 = -82.9904, \quad E_2 = -64.5662, \quad E_3 = -39.6429, \quad E_4 = -10.458. \tag{3.38}$$

The associated eigenfunctions, which can be readily computed using the above values of κ_n and Eqs. (3.32)-(3.34), are plotted in Fig. 3.3.

In general, it is apparent from Fig. 3.2 that for any value of $u_0 > 0$ there is a finite number of solutions of the eigenvalue equation (3.36), and that (as stated above) the eigenvalues corresponding to even and odd eigenfunction alternate. It is also clear from this figure that for u_0 sufficiently small there is only
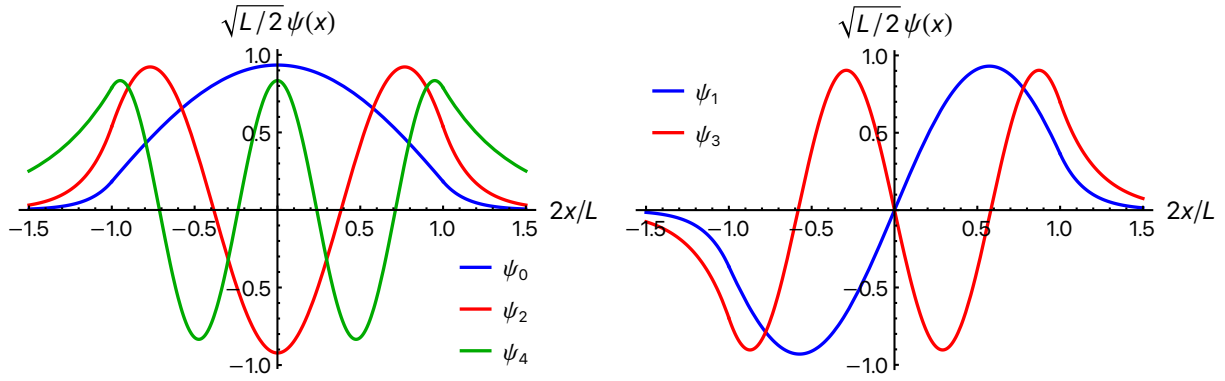
Figure 3.3. Even (left) and odd (right) eigenfunctions of the square well potential (3.26) with $u_0 = 7$ (i.e., $V_0 L^2 = 98\hbar^2/m$).

one solution of the eigenvalue equation, until the line $y = \kappa/u_0$ intersects the vertical line $\kappa = \pi/2$ at height $y = 1$, i.e, for

$$1 = \frac{\pi}{2u_0} \quad \Longleftrightarrow \quad u_0 = \frac{\pi}{2}.$$

Thus, for

$$0 < u_0 \leqslant \frac{\pi}{2}$$

the eigenvalue equation has exactly one solution. Likewise, for

$$\frac{\pi}{2} < u_0 \leqslant \pi$$

a second solution of the eigenvalue equation appears, and so on. In general, when

$$(n-1)\frac{\pi}{2} < u_0 \leqslant \frac{n\pi}{2}$$

the eigenvalue equation has exactly n solutions. Thus the *number of eigenvalues, i.e., of allowed bound state energies,* is equal to

$$\left\lceil \frac{2u_0}{\pi} \right\rceil \equiv \left\lceil \left(\frac{2m}{\pi^2\hbar^2} \right)^{1/2} \sqrt{V_0 L^2} \right\rceil,$$

where $\lceil x \rceil$ is the smallest integer greater than or equal to x.

Remarks.

- All the bound state energies are *non-degenerate.* In other words, for each bound state energy there is only one linearly independent eigenfunction. As mentioned above, this is a feature shared by *all* one-dimensional potentials.

- Each eigenfunction ψ_k has *exactly k zeros.* Again, according to a standard result in the theory of Sturm–Liouville problems this happens to be true for all one-dimensional potentials.

  Indeed, consider first an even eigenfunction ψ_{2n}. The zeros of ψ_{2n} inside the interval $[0, L/2)$ are the numbers $x_m = (L/2)\xi_m$, with $\xi_m \in [0, 1)$ satisfying

$$\cos(\kappa_{2n}\xi_m) = 0 \quad \Longrightarrow \quad \xi_m = (2m+1)\frac{\pi}{2\kappa_{2n}}, \qquad m = 0, 1, \ldots, m_{\max}.$$

From Fig. 3.2 it is apparent that[11]

$$\kappa_{2n} \in \left(n\pi, (2n+1)\frac{\pi}{2}\right),$$

and thus

$$\xi_m \in \left(\frac{2m+1}{2n+1}, \frac{2m+1}{2n}\right).$$

Since ξ must belong to the interval $[0, 1)$, the maximum value of m is $m_{\max} = n - 1$. Thus ψ_{2n} has exactly n nonzero roots in the interval $[0, L/2)$, and (being an even function) $2n$ roots in the interval $(-L/2, L/2)$. On the other hand, ψ_{2n} cannot vanish for $|x| \geq L/2$, as it is proportional to an exponential function on this region. It follows that the total number of roots of ψ_{2n} is $2n$, as claimed.

Similarly, if ψ_{2n+1} is an odd eigenfunction its zeros on the interval $[0, L/2)$ are the numbers $x_m = (L/2)\xi_m$, with $\xi_m \in [0, 1)$ satisfying

$$\sin(\kappa_{2n}\xi_m) = 0 \quad \Longrightarrow \quad \xi_m = \frac{m\pi}{\kappa_{2n}}, \qquad m = 0, 1, \ldots, m_{\max}.$$

Looking at Fig. (3.2) it is clear that now

$$\kappa_{2n+1} \in \left((2n+1)\frac{\pi}{2}, (n+1)\pi\right),$$

and therefore

$$\xi_m \in \left(\frac{m}{n+1}, \frac{2m}{2n+1}\right),$$

whence it follows that $m_{\max} = n$. Thus the number of roots of ψ_{2n+1} inside the interval $[0, L/2)$ is $n + 1$. Since ψ_{2n+1} is odd, it has exactly $2n + 1$ roots in the interval $(-L/2, L/2)$, which again proves our claim (since there are no roots in the half lines $(-\infty, -L/2] \cup [L/2, \infty)$).

- Classically, a particle with energy $E \in [-V_0, 0)$ is not allowed to move outside the interval $[-L/2, L/2]$, where its kinetic energy would become negative. Quantum mechanically, it is clear from Eqs. (3.32)-(3.34) that there is a small but non-zero probability that the particle can be found *outside* the classically allowed interval $[-L/2, L/2]$. In other words, *in quantum mechanics there is a non-vanishing probability that a particle can penetrate ("tunnel") into a classically forbidden region.* As we shall see in the sequel, this fact has far reaching consequences. ∎

Exercise 3.2. Compute the probability p_n of finding the particle outside the classically allowed region $[-L/2, L/2]$ when it is in the bound state ψ_n of the square well potential (3.26).

Solution. The probability p_n is given by

$$p_n = 2\int_{L/2}^{\infty} |\psi_n(x)|^2 \, dx = 2N_n^2 \int_{L/2}^{\infty} e^{-2\eta_n x} \, dx = \frac{N_n^2}{\eta_n} e^{-\eta_n L} = \frac{k_n^2}{v_0}\left(1 + \frac{L\eta_n}{2}\right)^{-1}.$$

This expression can be simplified by noting that

$$\frac{k_n^2}{v_0} = \frac{\kappa_n^2}{u_0^2}, \qquad \eta_n = \sqrt{|\varepsilon_n|} = \sqrt{v_0 - k_n^2} = \frac{2}{L}\sqrt{u_0^2 - \kappa_n^2},$$

and therefore

$$p_n = \frac{\kappa_n^2/u_0^2}{1 + \sqrt{u_0^2 - \kappa_n^2}}. \tag{3.39}$$

`probtun`

---

[11]Note that $\kappa = l\pi/2$ with l an integer is *not* a solution of the eigenvalue equation (3.36), since $\tan(l\pi/2)$ is either zero or $\pm\infty$.

This probability clearly increases with κ_n (i.e., with the particle's energy), as expected. For example, in the case $u_0 = 7$ discussed above we have

$$p_0 = 0.00489452, \quad p_1 = 0.0205813, \quad p_2 = 0.0510581, \quad p_3 = 0.10922, \quad p_4 = 0.271788.$$

We thus see that when the particle is in the bound state with highest energy the tunneling probability is greater than 27% !

In fact, from Eq. (3.39) and Fig. 3.2 it is apparent that p_n can be very close to one when u_0 is slightly greater than an integer multiple of $\pi/2$ and the quantum number n is the highest possible (corresponding to the highest bound state energy), since in that case $\kappa_n \lesssim u_0$. By Eq. (3.37), this is the case when the highest excited state has an energy $\lesssim 0$. For instance, for

$$u_0 = 2\pi + 10^{-3} \simeq 6.28419$$

there are 5 bound states, and $p_4 = 0.993773$. In other words, in this case the probability of finding the particle outside the classically allowed region when it is in the highest energy bound state is greater than 99%. (The highest excited energy is in this case $E_4 \simeq 7.84895 \cdot 10^{-5}$ in units of $\hbar^2/(mL^2)$, or less than 10^{-6} the depth of the potential well.) On the other hand, for

$$u_0 = 2\pi - 10^{-3} \simeq 6.28219$$

there are 4 bound states and $p_3 = 0.160854$.

3.4.3 Potential step. Reflection and transmission coefficients

Consider next the potential

$$V(x) = V_0 \theta(x) \equiv \begin{cases} 0, & x < 0 \\ V_0 & x > 0 \end{cases} \tag{3.40}$$

with $V_0 > 0$, plotted in Fig. 3.4. Classically, the motion is unbounded to the left for $0 < E < V_0$, and unbounded in both directions for $E > V_0$. For $E = 0$ (resp. $E = V_0$) all the points on the negative (resp. positive) x axis are equilibria. More precisely, for $0 < E < V_0$ the particle comes from $-\infty$ with constant velocity and is reflected by the potential barrier when it reaches the origin, changing the sign of its velocity and moving back towards $-\infty$. On the other hand, for $E > V_0$ the particle comes from $-\infty$ (resp. $+\infty$) with constant velocity, which suddenly decreases (resp. increases) as it passes through the origin, and keeps moving in the same direction.

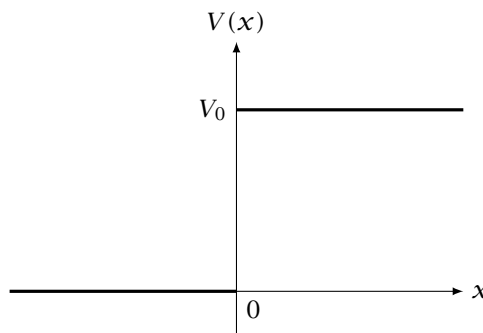Let us analyze next the quantum mechanical problem.

Figure 3.4. Potential step of height V_0.

I) $E > V_0$

Consider first the case in which the energy of the particle is greater than V_0. For $x \leqslant 0$ the Schrödinger equation reads

$$\psi''(x) + k_1^2 \psi(x) = 0, \qquad k_1 := \sqrt{\varepsilon} > 0 \qquad (x \leqslant 0),$$

and thus

$$\psi(x) = a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}, \qquad x \leqslant 0,$$

where a_1 and b_1 are two complex constants. Similarly, for $x \geqslant 0$ the Schrödinger equation reduces to

$$\psi''(x) + k_2^2 \psi(x) = 0, \qquad k_2 := \sqrt{\varepsilon - v_0} > 0 \qquad (x \geqslant 0),$$

and thus

$$\psi(x) = a_2 e^{ik_2 x} + b_2 e^{-ik_2 x}, \qquad x \geqslant 0,$$

with $a_2, b_2 \in \mathbb{C}$. Imposing the continuity of the wave function and its derivative at the origin we arrive at the system

$$a_1 + b_1 = a_2 + b_2, \qquad k_1(a_1 - b_1) = k_2(a_2 - b_2).$$

This is a linear homogeneous system in the four unknowns a_1, b_1, a_2, b_2, whose coefficient matrix

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ k_1 & -k_1 & -k_2 & k_2 \end{pmatrix}$$

has obviously rank 2. Thus the space of solutions of the system is a linear space of dimension 2. In other words, for each energy $E > V_0$ there are two linearly independent eigenfunctions, which are bounded but nor normalizable. This shows that the half line (V_0, ∞) belongs to the continuous spectrum, and that each energy in this range is twice degenerate.

For each energy $E > V_0$, the corresponding eigenfunctions are not normalizable and thus represent scattering states. In fact, the two linearly independent solutions for each energy $E > V_0$ can be chosen to describe either the scattering of the particle coming from the right $(+\infty)$ or from the left $(-\infty)$. Let us study in detail, for instance, the scattering of the particle coming from $-\infty$, i.e., moving from left to right with positive momentum $p = \hbar k_1$. We must then choose the solutions with $b_2 = 0$, so that the particle moves with momentum $p_2 = \hbar k_2$ after going through the origin. In other words, we have

$$\psi(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}, & x \leqslant 0 \\ a_2 e^{ik_2 x}, & x \geqslant 0, \end{cases}$$

where the coefficients a_1, a_2, b_1 verify the linear system

$$a_1 + b_1 = a_2, \qquad k_1(a_1 - b_1) = k_2 a_2. \tag{3.41}$$ `stepcoeff`

Although classically the particle only reduces its velocity when it goes past the origin, quantum mechanically there is a certain probability that the particle be *reflected* by the potential step. This is due to the presence of the term $b_1 e^{-ik_1 x}$ in the wave function for $x \leqslant 0$, which indeed is (when multiplied by the time-dependent factor $e^{-\frac{i}{\hbar} E t}$) a plane wave moving to the left with momentum $-\hbar k_1$. The probability currents of the *incident wave* $\psi_i = a_1 e^{ik_1 x}$, the *transmitted wave* $\psi_t = a_2 e^{ik_2 x}$ and the *reflected wave* $\psi_r = b_1 e^{-ik_1 x}$ are respectively given by

$$j_i = |a_1|^2 \frac{\hbar k_1}{m}, \qquad j_t = |a_2|^2 \frac{\hbar k_2}{m}, \qquad j_r = -|b_1|^2 \frac{\hbar k_1}{m}.$$

Physically, these currents are respectively proportional to the incoming, transmitted and reflected particle fluxes, where the minus sign in the expression for j_r simply takes into account that the reflected flux is

moving to the left (negative x direction). Accordingly, the probability that the particle be transmitted or reflected by the potential step is respectively given by

$$T = \frac{j_t}{j_i} = \frac{k_2}{k_1} \frac{|a_2|^2}{|a_1|^2}, \qquad R = -\frac{j_r}{j_i} = \frac{|b_1|^2}{|a_1|^2}.$$

These are respectively called the **transmission** and **reflection** coefficients, and are easily computed from equations (3.41). Indeed, we have

$$b_1 = \frac{k_1 - k_2}{k_1 + k_2} a_1, \qquad a_2 = \frac{2k_1}{k_1 + k_2} a_1,$$

and therefore

$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2}, \qquad R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2.$$

In particular, note that $R + T = 1$, as it should.

II) $0 < E < V_0$

The only difference with the previous case is that in the half line $x \geqslant 0$ the solutions of the Schrödinger equation are linear combinations of real exponentials $e^{\pm \eta x}$, with

$$\eta = \sqrt{v_0 - \varepsilon} > 0.$$

Only the negative exponential is physically acceptable in this region, and hence

$$\psi(x) = (a_1 + b_1)e^{-\eta x}, \qquad x \geqslant 0,$$

where we have imposed the continuity of ψ at the origin to determine the coefficient in front of the exponential. Thus in this case there is no transmitted wave. Imposing now the continuity of ψ' at the origin we obtain the relation

$$ik_1(a_1 - b_1) = -\eta(a_1 + b_1) \quad \Longleftrightarrow \quad b_1 = \frac{\eta + ik_1}{-\eta + ik_1} a_1 = \frac{k_1 - i\eta}{k_1 + i\eta} a_1.$$

Setting for simplicity, without loss of generality, $a_1 = 1$ we thus have

$$\psi(x) = \begin{cases} e^{ik_1 x} + \frac{k_1 - i\eta}{k_1 + i\eta} e^{-ik_1 x}, & x \leqslant 0 \\ \frac{2k_1}{k_1 + i\eta} e^{-\eta x}, & x \geqslant 0. \end{cases} \qquad (3.42) \quad \boxed{\texttt{psixstep}}$$

Thus there is a single formal (bounded but not normalizable) eigenfunction for each energy E in the interval $(0, V_0)$. Hence the latter interval belongs to the continuous spectrum of H, and each of these energies is non-degenerate. Furthermore, the reflection coefficient is now

$$R = |b_1|^2 = 1.$$

In other words, in this case the incoming wave is *totally reflected* by the potential, as in the classical problem.

Remark. In the region $x \leqslant 0$ the wave function can be written as

$$\psi(x) = e^{ik_1 x} + e^{-ik_1 x - 2i\varphi(k_1)}, \qquad x \leqslant 0,$$

with

$$\varphi(k_1) = \arg(k_1 + i\eta) = \arctan\left(\frac{\eta}{k_1}\right) = \arctan\left(\frac{\sqrt{v_0 - k_1^2}}{k_1}\right).$$

In other words, there is a *phase shift* $2\varphi(k_1)$ between the reflected and the incident waves. This suggests that before being reflected by the potential at $x = 0$ the particle spends some time inside the classically forbidden region $x > 0$. It can be shown (cf. [CDL20, Complement J$_\text{I}$]) that this is indeed the case by studying the *time evolution* of a *wave packet* built out of eigenfunctions of the form (3.42), namely

$$\Psi(x,t) = \theta(-x)\int_0^{\sqrt{v_0}} dk\, g(k)\left(e^{ikx} + e^{-i(kx + 2\varphi(k))}\right)e^{-i\omega(k)t}$$

$$+ \theta(x)\int_0^{\sqrt{v_0}} dk\, \frac{2kg(k)}{\sqrt{v_0}}e^{-\sqrt{v_0 - k^2}\,x - i\varphi(k)}e^{-i\omega(k)t}, \qquad \omega(k) := \frac{\hbar k^2}{2m}, \quad (3.43) \quad \boxed{\texttt{wpstep}}$$

with $|g(k)|$ sharply peaked at a wave vector $k_0 \in (0, \sqrt{v_0}\,)$.

Exercise 3.3. Deduce Eq. (3.43).

Solution. We can more concisely write down Eq. (3.42) for the eigenfunction $\psi(x)$ of energy

$$E = \frac{\hbar^2\varepsilon}{2m} = \frac{\hbar^2 k_1^2}{2m} \equiv \hbar\omega(k_1) < V_0$$

as follows:

$$\psi(x) = \theta(-x)\left(e^{ik_1 x} + e^{-i(k_1 x + 2\varphi(k_1))}\right) + \theta(x)\frac{2k_1 g(k_1)}{\sqrt{v_0}}e^{-\sqrt{v_0 - k_1^2}\,x - i\varphi(k_1)},$$

where we have taken into account that

$$k_1 + i\eta = |k_1 + i\eta|e^{i\varphi(k_1)} = \left(k_1^2 + \eta^2\right)^{1/2}e^{i\varphi(k_1)} = \sqrt{v_0}\,e^{i\varphi(k_1)}.$$

Since $\psi(x) = \Psi(x,0)$ is a stationary state of energy $E = \hbar\omega(k_1)$, its time evolution is given by

$$\Psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et} = \psi(x)e^{-i\omega(k_1)t}$$

$$= \theta(-x)\left(e^{ik_1 x} + e^{-i(k_1 x + 2\varphi(k_1))}\right)e^{-i\omega(k_1)t} + \theta(x)\frac{2k_1 g(k_1)}{\sqrt{v_0}}e^{-\sqrt{v_0 - k_1^2}\,x - i\varphi(k_1)}e^{-i\omega(k_1)t}.$$

To form a wave packet out of these functions, we multiply by an amplitude $g(k_1)$ and integrate over k_1 from 0 (corresponding to $E = 0$) to $\sqrt{v_0}$ (corresponding to $\varepsilon = v_0$, i.e., $E = V_0$). In this way (replacing the dummy integration variable k_1 by k) Eq. (3.43) is obtained.

Exercise 3.4. Determine whether $E = 0$ and $E = V_0$ belong to the spectrum of the Hamiltonian of the step potential (3.40).

Solution. For $E = 0$, the Schrödinger equation reads

$$\psi''(x) = \begin{cases} 0, & x < 0 \\ v_0, & x > 0 \end{cases}$$

The general solution of the Schrödinger equation for negative x is therefore

$$\psi(x) = ax + b, \qquad x \leqslant 0,$$

with a and b complex constants. However, for ψ to be bounded as $x \to -\infty$ we must take $b = 0$. Similarly, for $x > 0$ the general solution of the Schrödinger equation is

$$\psi(x) = c\,\mathrm{e}^{-\sqrt{v_0}\,x} + d\,\mathrm{e}^{\sqrt{v_0}\,x}, \qquad x \geqslant 0,$$

although we must take $d = 0$ for ψ to be bounded as $x \to \infty$ and $c = a$ for ψ to be continuous at the origin. In other words, we have

$$\psi(x) = \begin{cases} a, & x \leqslant 0, \\ a\,\mathrm{e}^{-\sqrt{v_0}\,x}, & x \geqslant 0. \end{cases}$$

However, requesting that ψ' be continuous at the origin we obtain

$$0 = -\sqrt{v_0}\,a \quad \Longrightarrow \quad a = 0 \quad \Longrightarrow \quad \psi(x) = 0 \quad \forall x \in \mathbb{R}.$$

Since there are no bounded nonzero solutions of the Schrödinger equation with $E = 0$, we conclude that $E = 0$ *does not belong to the spectrum of H*.

Likewise, solving the Schrödinger equation with $E = V_0$, i.e.,

$$\psi''(x) = \begin{cases} -v_0\psi(x), & x < 0 \\ 0, & x > 0, \end{cases}$$

we obtain

$$\psi(x) = \begin{cases} a\cos(\sqrt{v_0}\,x) + b\sin(\sqrt{v_0}\,x), & x \leqslant 0, \\ cx + d, & x \geqslant 0. \end{cases}$$

For $\psi(x)$ to be bounded as $x \to \infty$ we must have $c = 0$, while the continuity of ψ and ψ' at $x = 0$ leads to the equations

$$a = d, \qquad b\sqrt{v_0} = 0 \quad \Longleftrightarrow \quad b = 0.$$

Thus the only bounded solutions of the Schrödinger equation with $E = V_0$ are the functions

$$\psi(x) = \begin{cases} a\cos(\sqrt{v_0}\,x), & x \leqslant 0, \\ a, & x \geqslant 0 \end{cases}$$

for arbitrary $a \in \mathbb{C}$. Since $\psi(x)$ is bounded but not square integrable, we conclude that $E = V_0$ *belongs to the continuous spectrum of H*, and is in fact a *non-degenerate* formal eigenvalue (indeed, all the solutions found above are proportional to the one with $a = 1$). Note that in this case we have

$$\psi(x) = \frac{a}{2}(\mathrm{e}^{\mathrm{i}\sqrt{v_0}\,x} + \mathrm{e}^{-\mathrm{i}\sqrt{v_0}\,x}),$$

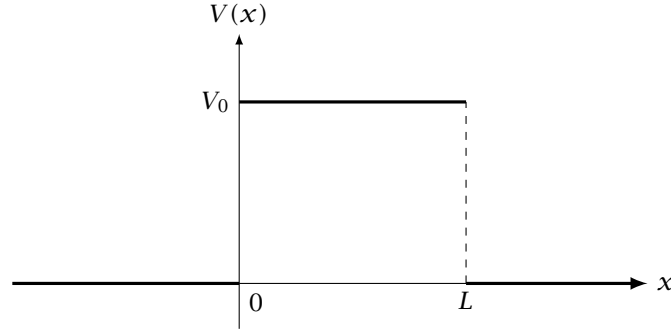and hence the reflection and transmission coefficient are

$$R = 1, \quad T = 0.$$

However, even if there is no transmitted wave (since $T = 0$) there is a uniform probability density of finding the particle to the right of the origin.

3.4.4 Potential barrier. Tunnel effect

Consider, finally, the potential barrier

$$V(x) = \begin{cases} V_0, & 0 < x < L, \\ 0, & x < 0 \text{ or } x > L \end{cases} \tag{3.44}$$

Figure 3.5. Potential barrier of height V_0 and width L.

with $V_0 > 0$, plotted in Fig. 3.5. Classically, the motion is unbounded to the left ($x \leqslant 0$) or right ($x \geqslant L$) for $0 < E < V_0$, and unbounded in both directions for $E > V_0$. For $E = 0$ all the points in the intervals $(-\infty, 0] \cup [L, x]$ are equilibria, while for $E = V_0$ the segment $[0, L]$ is made up of equilibria and the motion is unbounded to the left (resp. right) if $x(0) < 0$ (resp. $x(0) > L$). Moreover, for $0 \leqslant E < V_0$ the interval $(0, L)$ is classically forbidden.

I) $E > V_0$: **resonances**

Quantum mechanically, when $E > V_0$ the general solution of the Schrödinger equation is given by

$$\psi(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}, & x \leqslant 0 \\ a_2 e^{ik_2 x} + b_2 e^{-ik_2 x}, & 0 \leqslant x \leqslant L \\ a_3 e^{ik_1} + b_3 e^{-ik_1 x}, & x \geqslant L, \end{cases}$$

with

$$k_1 = \sqrt{\varepsilon} > 0, \qquad k_2 = \sqrt{\varepsilon - v_0} > 0.$$

There are 6 unknown coefficients a_i, b_i (with $i = 1, 2, 3$) subject to 4 conditions (continuity of both ψ and ψ' at $x = 0, L$), so that it is to be expected that there are two linearly independent eigenfunctions for each energy $E > V_0$. This is indeed the case, since the matching conditions at $x = 0, L$ can be written as

$$A \cdot (a_1, b_1, a_2, b_2, a_3, b_3)^\mathsf{T} = 0, \tag{3.45}$$

with

$$A = \begin{pmatrix} 1 & 1 & -1 & -1 & 0 & 0 \\ k_1 & -k_1 & -k_2 & k_2 & 0 & 0 \\ 0 & 0 & e^{ik_2 L} & e^{-ik_2 L} & -e^{ik_1 L} & -e^{-ik_1 L} \\ 0 & 0 & k_2 e^{ik_2 L} & -k_2 e^{-ik_2 L} & -k_1 e^{ik_1 L} & k_1 e^{-ik_1 L} \end{pmatrix} \tag{3.46}$$

clearly of rank 4. Moreover, for each energy $E > V_0$ the two linearly independent eigenfunctions with energy E are obviously formal (bounded but not normalizable), since they are oscillatory for $x \to \pm\infty$. Thus the half line (V_0, ∞) belongs to the *continuous spectrum* of the potential (3.44).

As in the previous potential, the two linearly independent eigenfunctions of each energy $E > V_0$ can be chosen to describe the scattering of the particle by the potential, either from left to right or from right to left. Let us study, for instance, the former problem, for which we must choose $b_3 = 0$ as there is no reflection at $x = L$. Solving Eqs. (3.45)-(3.46), after a straightforward calculation we readily find

$$a_1 = \frac{e^{ik_1 L} a_3}{2k_1 k_2} \left(2k_1 k_2 \cos(k_2 L) - i(k_1^2 + k_2^2) \sin(k_2 L)\right), \quad b_1 = \frac{i e^{ik_1 L} a_3}{2k_1 k_2} (k_2^2 - k_1^2) \sin(k_2 L). \tag{3.47}$$

(see next exercise). In this case the incident, reflected and transmitted waves have all wave number k_1. The corresponding probability currents are thus given by

$$j_i = |a_1|^2 \frac{\hbar k_1}{m}, \qquad j_r = -|b_1|^2 \frac{\hbar k_1}{m}, \qquad j_t = |a_3|^2 \frac{\hbar k_1}{m},$$
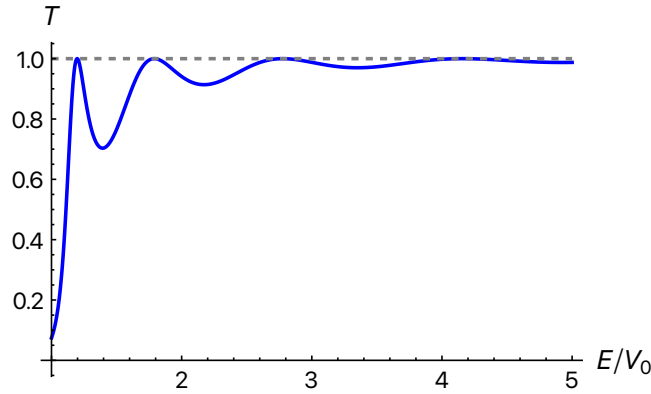
© Artemio González López

Figure 3.6. Transmission coefficient T as a function of $r = E/V_0$ for a potential barrier with $v_0 L^2 = 50$.

so that

$$R = -\frac{j_r}{j_i} = \frac{|b_1|^2}{|a_1|^2} = \frac{(k_2^2 - k_1^2)^2 \sin^2(k_2 L)}{4k_1^2 k_2^2 \cos^2(k_2 L) + (k_1^2 + k_2^2)^2 \sin^2(k_2 L)} = \frac{(k_2^2 - k_1^2)^2 \sin^2(k_2 L)}{4k_1^2 k_2^2 + (k_1^2 - k_2^2)^2 \sin^2(k_2 L)}$$

$$T = \frac{j_t}{j_i} = \frac{|a_3|^2}{|a_1|^2} = \frac{4k_1^2 k_2^2}{4k_1^2 k_2^2 \cos^2(k_2 L) + (k_1^2 + k_2^2)^2 \sin^2(k_2 L)} = \frac{4k_1^2 k_2^2}{4k_1^2 k_2^2 + (k_1^2 - k_2^2)^2 \sin^2(k_2 L)}.$$

Using the explicit values of k_1 and k_2 we arrive at the expressions

$$R = \frac{v_0^2 \sin^2\left(L\sqrt{\varepsilon - v_0}\right)}{4\varepsilon(\varepsilon - v_0) + v_0^2 \sin^2\left(L\sqrt{\varepsilon - v_0}\right)},$$

$$T = \frac{4\varepsilon(\varepsilon - v_0)}{4\varepsilon(\varepsilon - v_0) + v_0^2 \sin^2\left(L\sqrt{\varepsilon - v_0}\right)}.$$

(3.48)

In particular, as expected $R + T = 1$. It is also clear that R and T depend only on the relative energy $r := \varepsilon/v_0 = E/V_0 > 1$ and the dimensionless parameter $\lambda := v_0 L^2 = 2mV_0 L^2/\hbar^2$. Indeed,

$$T = \frac{4r(r-1)}{4r(r-1) + \sin^2\left(\sqrt{\lambda(r-1)}\right)},$$

and similarly for R. For fixed values of v_0 and L, we have

$$\lim_{\varepsilon \to v_0+} T = \left(1 + \frac{v_0 L^2}{4}\right)^{-1}, \qquad \lim_{\varepsilon \to \infty} T = 1.$$

In fact, for fixed V_0 and L the transmission coefficient T reaches its maximum value $T_{\max} = 1$ when

$$L\sqrt{\varepsilon - v_0} = n\pi \iff \varepsilon = v_0 + \frac{n^2 \pi^2}{L^2}, \qquad n = 1, 2, \ldots.$$

For these energies all the incident flux is transmitted, and hence there is no reflection. In other words, at these *resonant energies* the potential barrier becomes perfectly transparent. This phenomenon, which is called **resonance**, has important practical applications.

Remark. Nowhere in the previous calculation we have used the fact that V_0 is positive. Hence the latter analysis is valid for $E > 0$ in the square well potential (3.26) if we replace V_0 by $-V_0$. In other words, the transmission and reflection coefficients of the latter potential for $E > 0$ are given by

$$T = \frac{4\varepsilon(\varepsilon + v_0)}{4\varepsilon(\varepsilon + v_0) + v_0^2 \sin^2\left(L\sqrt{\varepsilon + v_0}\right)}, \qquad R = 1 - T. \qquad \blacksquare$$

Exercise 3.5. Prove Eqs. (3.47).

Solution. We first solve the last two Eqs. (3.45)-(3.46) with $b_3 = 0$, namely

$$e^{ik_2 L}a_2 + e^{-ik_2 L}b_2 = e^{ik_1 L}a_3, \qquad e^{ik_2 L}a_2 - e^{-ik_2 L}b_2 = \frac{k_1}{k_2}e^{ik_1 L}a_3,$$

for a_2 and b_2, obtaining

$$a_2 = \frac{1}{2}e^{i(k_1 - k_2)L}\left(1 + \frac{k_1}{k_2}\right)a_3, \qquad b_2 = \frac{1}{2}e^{i(k_1 + k_2)L}\left(1 - \frac{k_1}{k_2}\right)a_3.$$

From the first two Eqs. (3.45)-(3.46) we have

$$a_1 + b_1 = a_2 + b_2, \qquad a_1 - b_1 = \frac{k_2}{k_1}(a_2 - b_2)$$

and hence

$$
\begin{aligned}
a_1 &= \frac{1}{2}(a_2 + b_2) + \frac{k_2}{2k_1}(a_2 - b_2) = \frac{1}{2}\left(1 + \frac{k_2}{k_1}\right)a_2 + \frac{1}{2}\left(1 - \frac{k_2}{k_1}\right)b_2 \\
&= \frac{1}{4}e^{i(k_1 - k_2)L}\frac{(k_1 + k_2)^2}{k_1 k_2}a_3 - \frac{1}{4}e^{i(k_1 + k_2)L}\frac{(k_1 - k_2)^2}{k_1 k_2}a_3 \\
&= e^{ik_1 L}a_3\left(\cos(k_2 L) - \frac{i(k_1^2 + k_2^2)}{2k_1 k_2}\sin(k_2 L)\right),
\end{aligned}
$$

$$
\begin{aligned}
b_1 &= \frac{1}{2}(a_2 + b_2) - \frac{k_2}{2k_1}(a_2 - b_2) = \frac{1}{2}\left(1 - \frac{k_2}{k_1}\right)a_2 + \frac{1}{2}\left(1 + \frac{k_2}{k_1}\right)b_2 \\
&= \frac{1}{4}e^{i(k_1 - k_2)L}\frac{k_1^2 - k_2^2}{k_1 k_2}a_3 - \frac{1}{4}e^{i(k_1 + k_2)L}\frac{k_1^2 - k_2^2}{k_1 k_2}a_3 \\
&= \frac{ie^{ik_1 L}a_3}{2k_1 k_2}(k_2^2 - k_1^2)\sin(k_2 L).
\end{aligned}
$$

II) $E < V_0$: tunnel effect

The only difference with the previous case is that the wave function in the interval $[0, L]$ is a linear combination of real exponentials:

$$\psi(x) = a_2 e^{-\eta x} + b_2 e^{\eta x}, \qquad 0 \leqslant x \leqslant L,$$

with

$$\eta = \sqrt{v_0 - \varepsilon} > 0.$$

Note that we cannot drop the "positive" exponential $e^{\eta x}$, since the interval $[0, L]$ is bounded. Hence we can use the equations (3.47) with $k_2 = i\eta$, namely

$$a_1 = \frac{e^{ik_1 L}a_3}{2k_1 \eta}\left(2k_1 \eta \cosh(\eta L) - i(k_1^2 - \eta^2)\sinh(\eta L)\right), \quad b_1 = -\frac{ie^{ik_1 L}a_3}{2k_1 \eta}(\eta^2 + k_1^2)\sinh(\eta L).$$

The transmission and reflection coefficients are therefore given by

$$
\begin{aligned}
R &= \frac{|b_1|^2}{|a_1|^2} = \frac{(\eta^2 + k_1^2)^2 \sinh^2(\eta L)}{4k_1^2 \eta^2 \cosh^2(k_2 L) + (\eta^2 - k_1^2)^2 \sinh^2(\eta L)} = \frac{(\eta^2 + k_1^2)^2 \sinh^2(\eta L)}{4k_1^2 \eta^2 + v_0^2 \sinh^2(\eta L)} \\
T &= \frac{|a_3|^2}{|a_1|^2} = \frac{4k_1^2 \eta^2}{4\varepsilon\eta^2 \cosh^2(k_2 L) + (\eta^2 - k_1^2)^2 \sinh^2(\eta L)} = \frac{4k_1^2 \eta^2}{4k_1^2 \eta^2 + v_0^2 \sinh^2(\eta L)},
\end{aligned}
$$

or more explicitly

$$T = \frac{4\varepsilon(v_0 - \varepsilon)}{4\varepsilon(v_0 - \varepsilon) + v_0^2 \sinh^2\left(L\sqrt{v_0 - \varepsilon}\right)}, \qquad R = 1 - T. \tag{3.49}$$

As before, T depends on ε, v_0 and L through the dimensionless quantities

$$r = \frac{\varepsilon}{v_0} = \frac{E}{V_0} < 1, \qquad \lambda = v_0 L^2 = \frac{2mV_0 L^2}{\hbar^2},$$

namely

$$T = \frac{4r(1 - r)}{4r(1 - r) + \sinh^2\left(\sqrt{\lambda(1 - r)}\right)}.$$

The previous result is completely at odds with the classical behavior of a particle with energy in the range $0 < E < V_0$. Indeed, in classical mechanics the particle is confined to the half line $[0, \infty)$ (if $x(0) < 0$) or $[L, \infty)$ (if $x(0) > L$), since it cannot enter the interval $(0, L)$ where it would have negative kinetic energy. Thus, classically the transmission coefficient vanishes. On the other hand, we have just seen that in quantum mechanics the transmission coefficient, given by Eq. (3.49), is strictly positive. In other words, there is a non-vanishing probability (equal to T) that the particle coming from $-\infty$ will *tunnel* through the classically forbidden interval $(0, L)$ and emerge in the region $x > L$. This is the so called **tunnel effect**, which has wide ranging technological applications (inversion of the ammonia molecule, tunnel diode, Josephson effect, α decay of nuclei, etc.).

The tunneling probability depends essentially on $\lambda(1 - r) \equiv L^2(v_0 - \varepsilon)$. Indeed,

$$\lambda(1 - r) \ll 1 \quad \Longrightarrow \quad T^{-1} \simeq 1 + \frac{\lambda(1 - r)}{4r(1 - r)} \quad \Longrightarrow \quad T \simeq \left(1 + \frac{\lambda}{4r}\right)^{-1} = \left(1 + \frac{v_0^2 L^2}{4\varepsilon}\right)^{-1},$$

$$\lambda(1 - r) \gg 1 \quad \Longrightarrow \quad T \simeq 16r(1 - r)e^{-2\sqrt{\lambda(1-r)}} = \frac{16\varepsilon(v_0 - \varepsilon)}{v_0^2} e^{-2L\sqrt{v_0 - \varepsilon}}.$$

Thus T can be very large when $\lambda = v_0 L^2$ is small and $r \lesssim 1$ (i.e., $\varepsilon \lesssim v_0$), and is exponentially small when $\lambda(1 - r)$ is large (essentially, when $v_0 L^2$ is large and ε is not too close to v_0). In general, it can be shown that T increases with r for λ fixed, from $T = 0$ for $r \to 0+$ to its maximum value

$$\lim_{r \to 1-} T = \left(1 + \frac{\lambda}{4}\right)^{-1} \equiv \left(1 + \frac{v_0 L^2}{4}\right)^{-1}.$$

3.5 The spectrum of general one-dimensional potentials

In this section we shall briefly discuss the nature of the spectrum of a general (piecewise continuous) potential $V(x)$. We shall assume (as is always the case in practice, with the only exception of periodic potentials) that $V(x)$ is a *monotonic function* for both $x \to -\infty$ and $x \to \infty$. Hence there exist the two limits

$$V_\pm := \lim_{x \to \pm\infty} V(x)$$

(finite or possibly infinite). We shall accept without proof the following results (see [Mes99, pp. 101–105]):

I) If

$$E > V_+$$

(which can only happen if V_+ is finite), the real solutions of the Schrödinger equation

$$\psi''(x) + \big(\varepsilon - v(x)\big)\psi(x) = 0$$

remain *bounded* as $x \to \infty$ and *oscillate* between two opposite values. If, moreover,

$$\lim_{x \to \infty} x\big(v(x) - v_+\big) = 0$$

(i.e., if $v(x) \to v_+ \equiv 2mV_+/\hbar^2$ faster than $1/x$) then as $x \to \infty$ the general solution of the Schrödinger equation behaves as

$$\psi(x) \sim a\mathrm{e}^{\mathrm{i}k_+x} + b\mathrm{e}^{-\mathrm{i}k_+x}, \qquad k_+ := \sqrt{\varepsilon - v_+}.$$

with a and b complex constants.

II) If[12]

$$E < V_+,$$

for a sufficiently large $x_0 \in \mathbb{R}$ there is a positive constant η such that

$$v(x) - \varepsilon \geq \eta^2 > 0, \qquad \forall x > x_0.$$

(Indeed, if $V(x)$ is decreasing for $x > x_0$ we can take $\eta = \sqrt{v_+ - \varepsilon}$, while when $V(x)$ is increasing η can be any positive number strictly less than $\sqrt{v_+ - \varepsilon}$; in particular, η can be any positive real number if $V_+ = \infty$.) Then there exists a nonzero (real) solution $\psi_+(x)$ of the Schrödinger equation such that $\psi_+(x) \to 0$ as $x \to \infty$ at least as fast as $\mathrm{e}^{-\eta x}$. In other words,

$$\big|\psi_+(x)\big| \leq a\mathrm{e}^{-\eta x}$$

for some constant $a > 0$ as $x \to \infty$. All other real solutions $\phi(x)$ linearly independent from $\psi_+(x)$ tend to ∞ as $x \to \infty$ at least as fast as $\mathrm{e}^{\eta x}$. In other words, if ϕ is any solution of Schrödinger's equation with energy E linearly independent from ψ_+ we have

$$\big|\phi(x)\big| \geq b\mathrm{e}^{\eta x}$$

for some constant $b > 0$ as $x \to \infty$.

Totally analogous results hold for the behavior of the solutions of the Schrödinger equation for $x \to -\infty$. ∎

With the help of the previous results, it is straightforward to describe the spectrum of any potential satisfying the above assumptions. We shall further suppose that the potential is *bounded from below*, i.e., that there is a constant $V_0 \in \mathbb{R}$ such that

$$V(x) \geq V_0, \qquad \forall x \in \mathbb{R}.$$

Potentials that do not satisfy this condition are *physically unacceptable*, since (as we shall see below) they admit arbitrarily low eigenvalues and are therefore *unstable* (there is no *ground state* of minimum energy, and hence the particle can lose an arbitrarily large amount of energy by transitioning from one eigenstate to any other of lower energy). We shall also assume for definiteness that, as depicted in Fig. 3.7,

$$V_- \leq V_+$$

(the case $V_+ \leq V_-$ is similar). We then have:

---

[12] This case corresponds to the exponential type solutions in square well potentials.
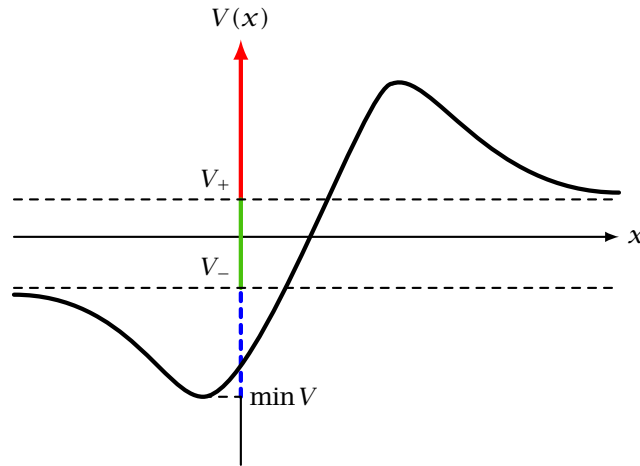
© *Artemio González López*

Figure 3.7. One dimensional potential with $-\infty < \min V(x) < V_- < V_+ < \infty$. The red and green vertical lines respectively indicate the twice degenerate and the non-degenerate continuous spectrum. The point spectrum is contained in the dashed blue vertical segment.

fig.spec1D

1) $E > V_+$

   This case is only possible if V_+ is finite. Since $V_+ \geqslant V_-$ by hypothesis, then also $E > V_-$. According to result I) above, in this case all the solutions of the Schrödinger equation are oscillating, and therefore bounded but not normalizable, both as $x \to -\infty$ and as $x \to \infty$. Hence E belongs to the *continuous spectrum* and is *twice degenerate*.

2) $V_- < E < V_+$

   This case can only arise if $V_+ > V_-$. By result II) above, the only linearly independent solution of the Schrödinger equation bounded as $x \to \infty$ is $\psi_+(x)$. However, by result I) this solution (as any other solution) is oscillatory as $x \to -\infty$, and therefore bounded but not normalizable. Hence for this energy there is only one linearly independent bounded (but not normalizable) solution of the Schrödinger equation. It follows that E belongs to the *continuous spectrum* and is *non-degenerate*.

3) $E < V_-$

   This case can occur only if $\min V(x) < V_-$. As $V_- \leqslant V_+$, we also have $E < V_+$. By result II) above, there is again only one linearly independent solution of the Schrödinger equation $\psi_+(x)$ exponentially decreasing as $x \to \infty$. Let us denote by $\psi_-(x)$ the analogous solution of the Schrödinger equation (with the same energy E) exponentially decreasing as $x \to -\infty$, and by $\phi(x)$ a second real solution linearly independent from ψ_-. Again by result II) above, the solution $\phi(x)$ is exponentially increasing as $x \to -\infty$. Moreover, since ψ_- and ϕ are two linearly independent solutions of the Schrödinger equation we must have

$$\psi_+(x) = a(E)\psi_-(x) + b(E)\phi(x),$$

for some real coefficients $a(E), b(E) \in \mathbb{R}$ (indeed, $\psi_\pm$ and ϕ are all real). Thus the necessary and sufficient condition for ψ_+ to be bounded as $x \to -\infty$ is that

$$b(E) = 0. \tag{3.50}$$

eigvgenV

This is the *eigenvalue equation*. Indeed, if E is a solution of the latter equation the eigenfunction $\psi_+(x)$ is proportional to $\psi_-(x)$, and therefore is also exponentially decaying as $x \to -\infty$. It follows that ψ_+ is normalizable, and thus E belongs to the *point spectrum* and is *non-degenerate*. ∎

   Thus the point spectrum $\sigma_p(H)$ is the set of solutions of the eigenvalue equation (3.50). The point spectrum is necessarily a *finite or at most countable set,* since eigenfunctions with different eigenvalues are orthogonal, and in a (*separable*) Hilbert space a set of mutually orthogonal vectors can be at most countable. It is also shown in courses in functional analysis that an accumulation point of the point

spectrum belongs to the spectrum. In fact, for the potentials usually occurring in quantum mechanics, *the accumulation points of the point spectrum belong to the continuous spectrum*. Since $\sigma_p(H) \cap \sigma_c(H) = \emptyset$, it follows that for these potentials the point spectrum does not contain its accumulation points, and is therefore a *discrete* set

$$\sigma_p(H) = \{E_k : k = 1, 2, \dots\}.$$

Furthermore, as shown in result 4) of Section (3.3), all of the eigenvalues E_k are strictly greater than $\min V(x)$ for all k. It can also be shown that $\sigma_p(H)$ has actually a *minimum*[13], so that if we label the eigenvalues in increasing order we have

$$\min V(x) < E_1 < E_2 < \cdots < E_k < \cdots < V_-.$$

It can also be shown that if $\sigma_p(H)$ is infinite then

$$\lim_{n \to \infty} E_n = V_-.$$

In particular, if V_- is finite then the eigenvalues E_k accumulate at V_-, and hence V_- is in the continuous spectrum. Finally, as remarked above, from standard properties of Sturm–Liouville problems it follows that the eigenfunction ψ_k corresponding to the k-th eigenvalue E_k has *exactly $k - 1$ real zeros* (see, e.g., [Mes99, p. 109–110]).

Remarks.

- The limiting values $E = V_+$ or $E = V_-$ must be dealt with on a case by case basis (i.e., whether they belong to the continuous or the point spectrum depends on the potential).

- From the previous discussion it follows that (under the assumptions on the potential stated above) the square integrable solutions of the time-independent Schrödinger equation in one dimension are those that tend to zero at $\pm\infty$. It follows that a real number E is in the point spectrum if and only if there is at least one linearly independent solution $\psi(x)$ of the Schrödinger equation with energy E such that

$$\lim_{x \to \pm\infty} \psi(x) = 0.$$

In fact, from the previous analysis it also follows that there can be *at most* one such solution.

<div style="border:1px solid green; background:#eaf5ea; padding:10px;">

Example 3.3. *Spectrum of an even potential.*

Let the potential $V(x)$ be an *even* function of x, i.e.,

$$V(-x) = V(x), \qquad \forall x \in \mathbb{R}.$$

Hence

$$V_- = V_+,$$

and therefore there is no non-degenerate continuous spectrum (except, at most, the point $V_+ = V_-$). There are essentially three possibilities (since, as usual, we are assuming that the potential is bounded from below):

1. $V_\pm = \infty$

   In this case *there is only point spectrum.* In this case the point spectrum is an *infinite set* unbounded above. Moreover, it can be shown that the eigenfunctions $\{\psi_n : n \in \mathbb{N}\}$ make up an *orthonormal basis* of $L^2(\mathbb{R})$. An example of a potential of this kind is the *harmonic oscillator* potential $V(x) = \frac{1}{2}m\omega^2 x^2$.

2. $V(x) \geqslant V_\pm, \quad \forall x \in \mathbb{R}$.

</div>

---

[13]Indeed, if the set $\sigma_p(H) = \{E_k : k = 1, 2, \dots\}$ did not have a minimum it would be an infinite set bounded below by $\min V(x)$, and hence would have an infimum $E_\infty \in [\min V(x), V_-)$ not belonging to the set. Then E_∞ would be an accumulation point of $\sigma_p(H)$, and therefore it would belong to the continuous spectrum of H. But this is impossible, since we have just shown that the continuous spectrum in this case is contained in the interval $[V_-, \infty)$.

> *There is only continuous and twice degenerate spectrum,* namely the half line $(V_\pm, \infty)$. A potential satisfying this condition is, for instance, $V(x) = V_0 \operatorname{sech}^2 x$ with $V_0 > 0$.

3. $\min V(x) < V_\pm$

   In this case *the point spectrum is contained in the segment* $(\min V(x), V_\pm)$*, while the half line* $(V_\pm, \infty)$ *makes up the continuous (and twice degenerate) spectrum* (the point $V_\pm$ could actually be either in the point or the continuous spectrum, depending on the potential considered). An important potential in this class is the *Pöschl–Teller potential* $V(x) = -V_0 \operatorname{sech}^2 x$, with $V_0 > 0$.

Let $\psi(x)$ be a genuine (i.e, normalizable) eigenfunction of $H = -\frac{\hbar^2}{2m} \partial_x^2 + V(x)$ with eigenvalue E. Since V is even, $\psi(-x)$ is also an eigenfunction of H with the same eigenvalue. As the point spectrum of a one-dimensional potential is *non-degenerate*), $\psi(-x)$ and $\psi(x)$ must be proportional, namely

$$\psi(-x) = \lambda \psi(x) = \lambda^2 \psi(-x) \quad \Longrightarrow \quad \lambda = \pm 1.$$

Thus *a genuine eigenfunction $\psi(x)$ of an even potential has a well defined parity* (i.e., is either even or odd). The above argument does not apply to *generalized* eigenfunctions whose formal eigenvalues lie in the *continuous spectrum,* since as we remarked above the continuous spectrum of an even potential (when it exists) is twice degenerate. All we can say in this case is that for every energy E in the continuous spectrum we can choose a basis of the two-dimensional eigenspace of E whose elements have well defined parity.

4 The postulates of quantum mechanics

In the previous chapters we have studied the formulation of quantum mechanics first developed by Schrödinger in 1926, based on the wave function in position (or momentum) space and the Schrödinger equation. In the present chapter we shall outline a more abstract and general formulation, essentially due to Dirac.[1] This elegant formulation, which includes Schrödinger's as a particular (though important) case, has led to a deeper understanding of the foundations of quantum mechanics and of its practical use. We shall also develop a widely used notation, also due to Dirac, to represent quantum states and their duals.

4.1 Quantum states

In classical physics, the state of a system is determined by the coordinates and momenta of all of its particles. Thus a classical state is an element of a real vector space of dimension $6N$, where N is the number of particles in the system.

Axiom 1. The **state** of any physical system at a certain time t_0 is represented by a vector in an *abstract Hilbert space* $\mathcal{H}$.

Recall that a *Hilbert space* is a complex vector space endowed with a (complex) scalar product, which is *complete* (i.e., all Cauchy sequences in it have a limit) and *separable* (i.e., there exist numerable sets which are dense in the whole space). For instance, a finite-dimensional complex vector space is automatically a Hilbert space with its standard scalar product

$$(v, w) = \sum_{i=1}^{n} v_i^* w_i,$$

where $n = \dim \mathcal{H}$. As another example, in the case of a single (spinless) particle moving in three-dimensional space the Hilbert space $\mathcal{H}$ can be taken as $L^2(\mathbb{R}^3)$.

Following Dirac, we shall denote the elements of $\mathcal{H}$ by

---

$$|\psi\rangle, \quad |\phi\rangle, \quad |\chi\rangle, \quad |a\rangle, \dots.$$

The symbol $|\cdot\rangle$ is called a **ket vector** (or simply a *ket*), and is analogous to the arrow sometimes used to denote vectors in Euclidean space $\mathbb{R}^3$. It is important to note that, although all physical states are vectors in $\mathcal{H}$, not every element of $\mathcal{H}$ can represent a physical state. For example, in the case of a single particle in $\mathbb{R}^3$, the physical states must satisfy some minimal requirements (the state and a sufficiently high number of its partial derivatives must be continuous, it must decay sufficiently fast at infinity, etc.). We shall therefore denote by $\mathcal{H}_P \subset \mathcal{H}$ the space of **physical states**. We shall assume that $\mathcal{H}_P$ is a *dense linear subspace* of $\mathcal{H}$. In other words, $\mathcal{H}_P$ is a vector space itself, and there are physical states "arbitrarily close" to any element of $\mathcal{H}$.

The fact that $\mathcal{H}_P$ (as well as $\mathcal{H}$) is a *linear space* is the basis of the **superposition principle**, which posits that *a linear combination of physical states is a physical state.* This principle is fundamental to account for the interference effects which are an essential feature of quantum mechanics.

---

[1]Paul Adrien Maurice Dirac (1902–1984), British physicist and Nobel Prize winner in 1933.

Remark. To be more precise, a quantum state must have *unit norm* since, as we shall see below, it shall be used to construct a probability density. Moreover, we shall see in the sequel that the vectors $|\psi\rangle$ and $e^{i\varphi}|\psi\rangle$, where φ is any real number, actually represent the same physical state. For this reason, to be absolutely precise a quantum state is a *unit ray* in $\mathcal{H}$, i.e., a set

$$\left\{e^{i\varphi}|\psi\rangle : \varphi \in \mathbb{R}, \quad \||\psi\rangle\| = 1\right\}.$$

In other words, any element in this ray represents the same quantum state, and hence quantum states are defined *up to a constant phase*. ∎

A continuous[2] **linear functional** is a continuous linear map $\alpha : \mathcal{H} \to \mathbb{C}$. In other words, $\alpha|\psi\rangle$ is a complex number for every ket $|\psi\rangle \in \mathcal{H}$,

$$\alpha\big(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle\big) = \lambda_1\alpha|\psi_1\rangle + \lambda_2\alpha|\psi_1\rangle, \qquad \forall\lambda_1, \lambda_2 \in \mathbb{C}, \quad \forall|\psi_1\rangle, |\psi_2\rangle \in \mathcal{H},$$

and the mapping $|\psi\rangle \mapsto \alpha(|\psi\rangle)$ depends continuously[3] on $|\psi\rangle \in \mathcal{H}$. Let us denote by $\mathcal{H}^*$ the set of all continuous linear functionals $\alpha : \mathcal{H} \in \mathbb{C}$. The space $\mathcal{H}^*$ is called the **dual** of $\mathcal{H}$, and it can be shown that it is itself a *Hilbert space*[4]. Each vector $|\psi\rangle \in \mathcal{H}$ gives rise to a linear functional, which following Dirac we shall denote by $\langle\psi|$, through the formula

$$\langle\psi|(|\phi\rangle) := (\psi, \phi), \qquad \forall|\phi\rangle \in \mathcal{H}.$$

Indeed,

$$\langle\psi|(\lambda_1|\phi_1\rangle + \lambda_2|\phi_2\rangle) = (\psi, \lambda_1|\phi_1\rangle + \lambda_2|\phi_2\rangle) = \lambda_1(\psi, |\phi_1\rangle) + \lambda_2(|\psi\rangle, |\phi_2\rangle)$$
$$\equiv \lambda_1\langle\psi|(|\phi_1\rangle) + \lambda_2\langle\psi|(|\phi_2\rangle).$$

The continuity of $\langle\psi|$ is also easily established, since if $\{\phi_n\}_{n\in\mathbb{N}}$ is a sequence such that $\lim_{n\to\infty}\phi_n = 0$ then

$$\big|\langle\psi|(|\phi\rangle_n)\big| = \big|(\psi, \phi_n)\big| \leqslant \|\psi\|\,\|\phi_n\| \xrightarrow[n\to\infty]{} 0.$$

The symbol $\langle\cdot|$ is called a **bra vector** (or, for short, a *bra*). At this point, it is very natural to introduce the **Dirac notation** $\langle\psi|\phi\rangle$ to denote the scalar product of the kets $|\psi\rangle$ and $|\phi\rangle$ or, what is the same, the image of $|\phi\rangle$ under the bra (linear functional) $\langle\psi|$ associated to the ket vector $|\psi\rangle$. In other words,

$$\langle\psi|\phi\rangle \equiv (|\psi\rangle, |\phi\rangle) \equiv \langle\psi|(|\phi\rangle).$$

In fact, according to the *Riesz–Frechet* representation theorem in functional analysis, *any* continuous linear functional $\alpha : \mathcal{H} \to \mathbb{C}$ is of this form. Moreover, the application

$$|\psi\rangle \in \mathcal{H} \to \langle\psi| \in \mathcal{H}^*$$

is a canonical *antilinear*[5] *isomorphism* (actually, an *isometry*) between $\mathcal{H}$ and its dual $\mathcal{H}^*$. In fact, it can be proved that a Hilbert space and its dual are actually *isomorphic*.

---

[2]It is essential to bear in mind that in infinite dimension not all linear maps are continuous.

[3]It can be easily shown that a linear functional (or, in general, a linear map) is continuous everywhere if and only if it is continuous at 0.

[4]The vector space operations in $\mathcal{H}^*$ are the natural ones, namely

$$(\lambda_1\alpha_1 + \lambda_2\alpha_2)|\psi\rangle := \lambda_1\alpha_1(|\psi\rangle) + \lambda_2\alpha_2(|\psi\rangle), \qquad \forall\lambda_1, \lambda_2 \in \mathbb{C}, \quad \forall|\psi\rangle \in \mathcal{H}.$$

[5]An mapping $A : X \to Y$ between two complex vector spaces X and Y is *antilinear* if $A(\lambda u + \mu v) = \lambda^* A u + \mu^* A v$ for all $u, v \in X$.

Remark. There are many *discontinuous* linear functionals that *cannot be represented by a bra vector*. One such functional is the *Dirac delta* $\delta_{\mathbf{r}_0}$, defined by the formula

$$\delta_{\mathbf{r}_0}(\psi) = \psi(\mathbf{r}_0)$$

in the linear subspace $C^0(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ of continuous functions $\psi \in L^2(\mathbb{R}^3)$. Indeed, if $\delta_{\mathbf{r}_0} = \langle\phi|$ for some function $\phi \in L^2(\mathbb{R})$ we would have

$$\delta_{\mathbf{r}_0}(\psi) = \psi(\mathbf{r}_0) = (\phi, \psi) = \int d^3r \, \phi(\mathbf{r})^* \psi(\mathbf{r}), \qquad \forall \psi \in C^0(\mathbb{R}^3) \cap L^2(\mathbb{R}^3),$$

which as we know cannot be satisfied by any ordinary function ϕ. This does not contradict the Riesz–Frechet representation theorem, since it is easy to see that this functional is discontinuous[6]. However, it is very convenient for calculations to represent $\delta_{\mathbf{r}_0}$ as the bra $\langle\mathbf{r}_0|$ of a *fictitious* (non-existent, in the sense that it is not an element of $\mathcal{H} = L^2(\mathbb{R}^3)$, or even a function) ket vector (function) $|\mathbf{r}_0\rangle$. This vector would satisfy

$$\langle\mathbf{r}_0|\psi\rangle \equiv \delta_{\mathbf{r}_0}(\psi) = \psi(\mathbf{r}_0) \equiv \int d^3r \, \delta(\mathbf{r} - \mathbf{r}_0)\psi(\mathbf{r}) \equiv \big(\delta(\mathbf{r} - \mathbf{r}_0), \psi\big), \quad \forall|\psi\rangle,$$

and hence

$$|\mathbf{r}_0\rangle = \delta(\mathbf{r} - \mathbf{r}_0).$$

In other words, the fictitious ket associated to the linear functional $\delta_{\mathbf{r}_0}$ is not a function, but rather the *distribution* (also called *generalized function*) $\delta(\mathbf{r} - \mathbf{r}_0)$.

A similar example of a (discontinuous) linear functional $\mathscr{F}_{\mathbf{p}_0}$ which is not the bra of any ket vector is given by

$$\psi \mapsto \mathscr{F}_{\mathbf{p}_0}(\psi) := \hat{\psi}(\mathbf{p}_0) \equiv (2\pi\hbar)^{-3/2} \int d^3r \, e^{-\frac{i}{\hbar}\mathbf{p}_0\cdot\mathbf{r}} \psi(\mathbf{r})$$

defined in $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$. Again, if $\mathscr{F}_{\mathbf{p}_0} = \langle\phi_{\mathbf{p}_0}|$ for some ket vector $\phi_{\mathbf{p}_0} \in L^2(\mathbb{R}^3)$ we would have

$$\langle\phi_{\mathbf{p}_0}|\psi\rangle = \mathscr{F}_{\mathbf{p}_0}(\psi) \equiv (2\pi\hbar)^{-3/2} \int d^3r \, e^{-\frac{i}{\hbar}\mathbf{p}_0\cdot\mathbf{r}} \psi(\mathbf{r}) = \int d^3r \, \phi_{\mathbf{p}_0}^*(\mathbf{r})\psi(\mathbf{r}), \quad \forall|\psi\rangle$$

$$\implies \phi_{\mathbf{p}_0}(\mathbf{r}) = (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}\mathbf{p}_0\cdot\mathbf{r}} \notin L^2(\mathbb{R}^3).$$

We thus see that the fictitious ket associated to the linear functional $\mathscr{F}_{\mathbf{p}_0}$ is in this case an ordinary function, namely the (normalized) plane wave $\phi_{\mathbf{p}_0}(\mathbf{r}) = (2\pi\hbar)^{-3/2}e^{\frac{i}{\hbar}\mathbf{p}_0\cdot\mathbf{r}}$, although it is *not* an element of $\mathcal{H} = L^2(\mathbb{R}^3)$. ∎

Given a linear operator $A : \mathcal{H} \to \mathcal{H}$ and two ket vectors $|\psi\rangle, |\phi\rangle$, we define

$$\boxed{\langle\psi|A|\phi\rangle := (\psi, A\phi),}$$

where (as we shall often do in the sequel when no confusion can arise) we are using the abbreviated notation $(\psi, A\phi)$ for $\big(|\psi\rangle, A|\phi\rangle\big)$. Note that

$$\langle\psi|A|\phi\rangle^* = (\psi, A\phi)^* = (A\phi, \psi) = (\phi, A^\dagger\psi) \equiv \langle\phi|A^\dagger|\psi\rangle.$$

---

[6]That $\delta_{\mathbf{r}_0}$ is discontinuous can be proved as follows. For any $n \in \mathbb{N}$, let $\phi_n(\mathbf{r})$ be a continuous function such that $\phi_n(\mathbf{r}_0) = 1$, $|\phi_n(\mathbf{r})| \leqslant 1$ inside the ball of radius $1/n$ centered at $\mathbf{r}_0$ and $\phi_n(\mathbf{r}) = 0$ for $|\mathbf{r} - \mathbf{r}_0| > 1/n$. The sequence $\{\phi_n\}_{n\in\mathbb{N}}$ tends to 0 in $L^2(\mathbb{R}^3)$, since

$$\|\phi_n\|^2 \leqslant \frac{4\pi}{3n^3} \xrightarrow[n\to\infty]{} 0.$$

However,

$$\delta_{\mathbf{r}_0}(\phi_n) = \phi_n(\mathbf{r}_0) = 1, \qquad \forall n \in \mathbb{N},$$

and thus $\delta_{\mathbf{r}_0}(\phi_n)$ does not converge to 0.

Exercise 4.1. If $A : \mathcal{H} \to \mathcal{H}$ is a continuous linear operator and $\langle\psi|$ a bra vector, show that $\langle\psi|A$ is a bra vector. What is the ket vector associated to it?

Solution. The product $\langle\psi|A$ is the composition of the continuous linear operators $A : \mathcal{H} \to \mathcal{H}$ and $\langle\psi| : \mathcal{H} \to \mathbb{C}$), and thus is itself a continuous linear functional (the composition of continuous mappings is continuous), i.e., a bra vector. Moreover, since

$$\big((\langle\psi|A)|\phi\rangle\big) = \langle\psi|(A|\phi\rangle) \equiv \big(|\psi\rangle, A|\phi\rangle\big) \equiv \big(A^\dagger|\psi\rangle, \phi\big), \qquad \forall\phi \in \mathcal{H},$$

we have

$$\langle\psi|A = \big\langle A^\dagger|\psi\big\rangle|,$$

which we shall usually abbreviate as $\big\langle A^\dagger\psi\big|$.

Example 4.1. Given two ket vectors $|\psi\rangle$ and $|\phi\rangle$, the product $|\psi\rangle\langle\phi|$ can be naturally interpreted as the linear operator from $\mathcal{H}$ to $\mathcal{H}$ defined by

$$\big(|\psi\rangle\langle\phi|\big)|\chi\rangle = \langle\phi|\chi\rangle|\psi\rangle, \qquad \forall|\chi\rangle \in \mathcal{H}.$$

Indeed, the RHS is clearly linear in $|\chi\rangle$, by the linearity of the second argument of the complex scalar product. It is also straightforward to prove that $|\psi\rangle\langle\phi|$ is continuous (exercise). Clearly the *range* of $|\psi\rangle\langle\phi|$ is the one-dimensional subspace generated by the vector $|\psi\rangle$, while its *kernel* is the orthogonal complement of the subspace spanned by the vector $|\phi\rangle$. It is easy to check that

$$\big(|\psi\rangle\langle\phi|\big)^\dagger = |\phi\rangle\langle\psi|;$$

in particular, $|\psi\rangle\langle\psi|$ is *self-adjoint*. Indeed, for all $|\alpha\rangle, |\beta\rangle \in \mathcal{H}$ we have

$$\Big(|\alpha\rangle, \big(|\psi\rangle\langle\phi|\big)|\beta\rangle\Big) = \big(|\alpha\rangle, \langle\phi|\beta\rangle|\psi\rangle\big) = \langle\alpha|\psi\rangle\langle\phi|\beta\rangle = \langle\psi|\alpha\rangle^*\langle\phi|\beta\rangle = \big((\langle\psi|\alpha\rangle|\phi\rangle), |\beta\rangle\big)$$

$$= \Big(\big(|\phi\rangle\langle\psi|\big)|\alpha\rangle, |\beta\rangle\Big).$$

An **orthogonal projector** is a self-adjoint operator $P : \mathcal{H} \to \mathcal{H}$ that is also *idempotent*, i.e., $P^2 = P$. The reason for this terminology is that if P is an orthogonal projector and $|\psi\rangle \in \mathcal{H}$ then $P|\psi\rangle$ is the orthogonal projection of $|\psi\rangle$ onto the range of P. Indeed, $P|\psi\rangle$ obviously belongs to the range of P, and $|\psi\rangle - P|\psi\rangle$ is orthogonal to the range of P, since

$$\big(P|\phi\rangle, |\psi\rangle - P|\psi\rangle\big) = \big(|\phi\rangle, P|\psi\rangle - P^2|\psi\rangle\big) = 0.$$

If $|\psi\rangle$ is a unit vector (and, thus, a quantum state) then $|\psi\rangle\langle\psi|$ is self-adjoint and idempotent: indeed,

$$(|\psi\rangle\langle\psi|)^2 = (|\psi\rangle\langle\psi|)(|\psi\rangle\langle\psi|) = \langle\psi|\psi\rangle|\psi\rangle\langle\psi| = \big\|\psi\big\|^2|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi|,$$

where we are again using the abbreviated notation $\big\|\psi\big\|$ instead of $\big\||\psi\rangle\big\|$. Thus $|\psi\rangle\langle\psi|$ is the *orthogonal projector* onto the one-dimensional subspace spanned by $|\psi\rangle$.

4.2 Observables

sec.obs

In classical (Hamiltonian) mechanics, a dynamical variable is any function $f(\mathbf{q}, \mathbf{p})$ defined in phase space (a $6N$-dimensional Euclidean space, where N is the number of particles in the system).

Axiom 2. A **dynamical variable** or **observable** of a quantum system is a *self-adjoint* linear operator $A : \mathcal{D}(A) \subset \mathcal{H} \to \mathcal{H}$, where $\mathcal{H}$ is the system's Hilbert space of states and the domain $\mathcal{D}(A)$ of A is a dense subspace of $\mathcal{H}$.

Remark. The precise domain of a linear operator A in an infinite-dimensional linear space is a non-trivial and crucial matter. Indeed, by the *Hellinger–Toeplitz theorem* in functional analysis, a self-adjoint operator whose domain is the whole Hilbert space is automatically continuous, which for linear operators is the same as *bounded*[7]. On the other hand, many important operators in quantum mechanics like position, momentum, angular momentum or energy are defined only in proper (dense) subspaces of the system's Hilbert space $\mathcal{H}$, and are unbounded. To simplify matters, we shall write $A : \mathcal{H} \to \mathcal{H}$ even if $\mathcal{D}(A)$ may be a proper subspace of $\mathcal{H}$, and unless otherwise stated shall tacitly assume in the sequel that all operators involved are bounded. ∎

In the case of a single particle, we saw in Section 2.11 that if the state of the system at a certain instant is described by the ket vector $|\psi\rangle$, and we measure an observable A, the average value obtained is the expectation value

$$\mathrm{av}_\psi(A) = \langle A\rangle_\psi \equiv (\psi, A\psi) \equiv \langle\psi|A|\psi\rangle.$$

We also proved that the only possible outcome in a measurement of an observable A is one of its *eigenvalues. We shall accept that this is also the case for an arbitrary quantum system.* Note that the self-adjoint character of observables guarantees that both its expectation value and any of its eigenvalues are *real*. We now ask ourselves what is the *probability* of obtaining a certain value a when measuring an observable A, where a is one of the eigenvalues of A, if the system is in a state $|\psi\rangle$. To answer this question, we shall suppose for simplicity (as is the case in many practical problems) that A has only point spectrum[8]

$$\sigma_p(A) = \{a_n : n = 1, 2, \dots\},$$

and, moreover, that all of its eigenvalues are *simple* (i.e., non-degenerate). In other words, the *eigenspace*

$$\ker(A - a_n) \equiv \ker(A - a_n\mathbb{1})$$

of each eigenvalue a_n is *one-dimensional.* Let us choose an arbitrary unit vector $|n\rangle$ in each eigenspace $\ker(A - a_n)$ (which is obviously defined up to a phase). It is easy to show that the set

$$\{|n\rangle : n = 1, 2, \dots\} \tag{4.1}$$

`orthbasis`

is an *orthonormal set.* Indeed, all its elements are by construction unit vectors, and if $n \neq m$ the eigenkets $|n\rangle$ and $|m\rangle$ are automatically *orthogonal*:

$$\langle n|A|m\rangle = \big(|n\rangle, A|m\rangle\big) = a_m\langle n|m\rangle = \big(A|n\rangle, |m\rangle\big) = a_n\langle n|m\rangle$$
$$\implies \quad (a_n - a_m)\langle n|m\rangle = 0 \quad \implies \quad \langle n|m\rangle = 0.$$

Moreover, it can be shown (using the spectral theorem for self-adjoint operators in functional analysis) that in this case the set (4.1) is an *orthonormal basis* of $\mathcal{H}$. Suppose that the system is in the state $|\psi\rangle$ at a certain time t_0. Expanding $|\psi\rangle$ in terms of the previous basis of eigenstates of the observable A we have[9]

$$|\psi\rangle = \sum_n c_n|n\rangle,$$

where the coefficients c_n can be obtained by taking the scalar product of the latter expansion with any eigenfunction $|k\rangle$:

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

---

[7]A linear operator A is bounded if there exists a constant $c \in \mathbb{R}$ such that $\|A\psi\| \leqslant c\|\psi\|$ for all $|\psi\rangle \in \mathcal{D}(A)$.

[8]It can be shown that the spectrum of a self-adjoint operator in a *separable* Hilbert space is at most countable. Indeed, if it were not so we would be able to construct an uncountable set of mutually orthogonal vectors (choosing one eigenvector for each eigenvalue), which is not possible in a separable Hilbert space.

[9]In what follows the all sums range from 1 to $\dim \mathcal{H}$, which can be either finite or infinite.

Thus we can write

$$|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle = \left(\sum_n |n\rangle\langle n|\right)|\psi\rangle;$$

since $|\psi\rangle$ is an arbitrary (unit) vector, it follows that

$$\sum_n |n\rangle\langle n| = \mathbb{1}. \tag{4.2}$$

`comprel`

Equation (4.2) is the so called **completeness** (or **closure**) **relation** satisfied by the orthonormal basis (4.1). Multiplying this relation on the right by the ket $|\psi\rangle$ an on the left by a bra $\langle\phi|$ we obtain

$$\sum_n \langle\phi|n\rangle\langle n|\psi\rangle = \langle\phi|\psi\rangle;$$

in particular,

$$\|\psi\|^2 = \langle\psi|\psi\rangle = \sum_n |\langle n|\psi\rangle|^2.$$

It follows that the numbers

$$\left\{|c_n|^2 \equiv |\langle n|\psi\rangle|^2 : n = 1, 2, \dots\right\} \tag{4.3}$$

`probdist`

define a *probability distribution*, since they are nonnegative and verify

$$\sum_n |c_n|^2 = \langle\psi|\psi\rangle = 1.$$

Since a probability distribution is determined by its *moments* (i.e., the averages of the powers of the random variable), the probability distribution $\{p_\psi(a_n) : n = 1, 2, \dots\}$ of the eigenvalues $\{a_n : n = 1, 2, \dots\}$ of A in the state $|\psi\rangle$ is uniquely determined by the equalities

$$\mathrm{av}_\psi(A^k) = \sum_n p_\psi(a_n)a_n^k, \qquad k \in \mathbb{N}. \tag{4.4}$$

`ppsidet`

On the other hand, if we assume that (as in the case of a single particle studied in Section 2.5), the average of an observable in a state $|\psi\rangle$ is the expectation value of the observable in that state, we have

$$\mathrm{av}_\psi(A^k) = \langle A^k\rangle_\psi = \langle\psi|A^k|\psi\rangle = \left(\sum_n c_n|n\rangle, \sum_m c_m a_m^k|m\rangle\right) = \sum_{n,m} c_n^* c_m a_m^k \langle n|m\rangle = \sum_n |c_n|^2 a_n^k$$

for all $k \in \mathbb{N}$. Comparing with Eq. (4.4) we conclude that the probability $p_\psi(a_n)$ of finding the value a_n when measuring the observable A if the system is in the state $|\psi\rangle$ is given by

$$p_\psi(a_n) = |c_n|^2 = |\langle n|\psi\rangle|^2.$$

Note that

$$p_\psi(a_n) = |\langle n|\psi\rangle|^2 = \big\||n\rangle\langle n|\psi\rangle\big\|^2 \equiv \big\|(|n\rangle\langle n|)|\psi\rangle\big\|^2$$

is the square of the norm of the projection of the vector $|\psi\rangle$ onto the eigenspace $\ker(A - a_n)$. In fact, a calculation totally analogous to the previous one shows that when the eigenvalues of A are degenerate the probability of finding an eigenvalue a_n is still given by the formula

$$p_\psi(a_n) = \big\|\mathscr{P}_{a_n}|\psi\rangle\big\|^2, \tag{4.5}$$

`Ppsigen`

where $\mathscr{P}_{a_n}$ denotes the orthogonal projector onto the eigenspace $\ker(A - a_n)$ of the eigenvalue a_n (no longer one-dimensional). This motivates the following axiom:

> **Axiom 3.** If the observable A has only point spectrum, a measurement of A when the system is in a state $|\psi\rangle$ can only yield as result an eigenvalue a_n of A with probability $\left\|\mathscr{P}_{a_n}|\psi\rangle\right\|^2$.

Remarks.

- From Axiom 3 it immediately follows that the average value of the observable A is its expectation value $\langle\psi|A|\psi\rangle$. Indeed (assuming again, for the sake of simplicity, that the eigenvalues of A are non-degenerate, and denoting by $|n\rangle$ a normalized eigenvector of A with eigenvalue a_n) we have

$$\langle\psi|A|\psi\rangle = (\psi, A\psi) \equiv \left(\sum_n c_n|n\rangle, \sum_m c_m A|m\rangle\right) = \sum_{m,n} c_n^* c_m a_m \langle n|m\rangle = \sum_n |c_n|^2 a_n$$
$$= \sum_n p_\psi(a_n) a_n,$$

which by definition is the average of the a_n's with respect to the probability distribution $\{p_\psi(a_n)\}$.

- Another immediate consequence of Axiom 3 is that *if an observable A is measured when the system is in an eigenstate $|\psi\rangle$ of A with eigenvalue a then the result obtained will be a.* Indeed,

$$A|\psi\rangle = a|\psi\rangle \quad\Longrightarrow\quad \mathscr{P}_a|\psi\rangle = |\psi\rangle,$$

since $|\psi\rangle$ belongs to the eigenspace $\ker(A-a)$ onto which $\mathscr{P}_a$ projects, and hence

$$p_\psi(a) = \left\|\mathscr{P}_a|\psi\rangle\right\|^2 = \left\||\psi\rangle\right\|^2 = 1.$$

(This result could also have been proved by showing that $\Delta_\psi A = 0$, as in Section 2.5.)

`exe.Ppsian`

Exercise 4.2. Suppose that an eigenvalue a_n of an observable A is d_n times degenerate (where d_n could be finite or infinite). Show that the projector $\mathscr{P}_{a_n}$ is given by

$$\mathscr{P}_{a_n} = \sum_{k=1}^{d_n} |u_k\rangle\langle u_k|,$$

where $\{|u_k\rangle : k = 1, \ldots, d_n\}$ is *any* orthonormal basis of the eigenspace $\ker(A-a_n)$. (In particular, the RHS of the previous formula is *independent of the basis chosen*.)

Solution. All we have to show is that the operator $\mathscr{P}_{a_n}$ defined by the above formula is a projector, and that its range is $\ker(A-a_n)$. That $\mathscr{P}_{a_n}$ is a projector is straightforward to prove, since it is obviously self-adjoint (each operator $|u_k\rangle\langle u_k|$ is self-adjoint), and

$$\mathscr{P}_{a_n}^2 = \sum_{j,k=1}^{d_n} |u_j\rangle\langle u_j| \cdot |u_k\rangle\langle u_k| = \sum_{j,k=1}^{d_n} \langle u_j|u_k\rangle \cdot |u_j\rangle\langle u_k| = \sum_{j,k=1}^{d_n} \delta_{jk} |u_j\rangle\langle u_k|$$
$$= \sum_{k=1}^{d_n} |u_k\rangle\langle u_k| \equiv \mathscr{P}_{a_n}.$$

It is also clear that the range of $\mathscr{P}_{a_n}$ is contained in $\ker(A-a_n)$, since

$$\mathscr{P}_{a_n}|\psi\rangle = \sum_{n=1}^{d_n} \langle u_k|\psi\rangle|u_k\rangle \in \operatorname{lin}\{|u_k\rangle : k = 1, \ldots, d_n\} = \ker(A-a_n).$$

Finally, if $|\psi\rangle \in \ker(A - a_n)$ then

$$|\psi\rangle = \sum_{k=1}^{d_n} c_k |u_k\rangle \quad\Longrightarrow\quad \mathscr{P}_{a_n}|\psi\rangle = \sum_{j,k=1}^{d_n} c_k |u_j\rangle\langle u_j| \cdot |u_k\rangle = \sum_{j,k=1}^{d_n} c_k \langle u_j|u_k\rangle |u_j\rangle$$

$$= \sum_{j,k=1}^{d_n} c_k \delta_{jk} |u_j\rangle = \sum_{k=1}^{d_n} c_k |u_k\rangle = |\psi\rangle,$$

so that $|\psi\rangle = \mathscr{P}_{a_n}|\psi\rangle$ is in the range of $\mathscr{P}_{a_n}$. Thus $\ker(A_n - a)$ is also contained in the range of $\mathscr{P}_{a_n}$, which completes the proof.

What happens if the observable A does not possess an orthonormal basis of (genuine) eigenvectors? This is the case, for instance, with important observables like the position and momentum of a particle, and in general with observables part of whose spectrum is continuous. To answer this question, we must introduce the concept of *generalized orthonormal set*. By definition, this is a set $\{|\alpha\rangle : \alpha \in I\}$, where I is an index set (usually an interval $[\alpha_1, \alpha_2]$, or more generally a (connected open) subset of $\mathbb{R}^k$ for an appropriate k) and $|\alpha\rangle$ is a *generalized ket* (a distribution like $\delta(x - \alpha)$, or a non-normalizable ordinary function like $\mathrm{e}^{\mathrm{i}\alpha x}$), satisfying the *Dirac normalization* condition

$$\langle\alpha|\beta\rangle = \delta(\alpha - \beta), \qquad \forall \alpha, \beta \in I.$$

Although $|\alpha\rangle$ is not an ordinary vector, we shall suppose that the formal *scalar product* $\langle\alpha|\psi\rangle$ is defined for all $\alpha \in I$ and any ordinary ket $|\psi\rangle$ in the space of physical states $\mathcal{H}_P$. For instance,

$$\big(\delta(x - \alpha), \psi\big) = \int \mathrm{d}x\, \delta(x - \alpha)\psi(x) = \psi(\alpha), \qquad \big(\mathrm{e}^{\mathrm{i}\alpha x}, \psi\big) = \int \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}\alpha x}\psi(x).$$

This implies that the operator $|\alpha\rangle\langle\alpha|$ —i.e., the formal projector onto the one-dimensional space generated by $|\alpha\rangle$— is well defined (as a generalized ket), since

$$(|\alpha\rangle\langle\alpha|)|\psi\rangle = \langle\alpha|\psi\rangle|\alpha\rangle.$$

A *generalized orthonormal basis* of $\mathcal{H}$ is the union of an orthonormal set $\{|u_n\rangle : n = 1, 2, \dots\} \subset \mathcal{H}$ and a generalized orthonormal set $\{|\alpha\rangle : \alpha \in I\}$ such that

$$\langle\alpha|u_n\rangle = 0, \qquad \forall \alpha \in I, \quad \forall n = 1, 2, \dots,$$

and the following *generalized completeness relation* is verified:

$$\sum_n |u_n\rangle\langle u_n| + \int_I \mathrm{d}\alpha\, |\alpha\rangle\langle\alpha| = \mathbb{1} \tag{4.6}$$

`gencomprel`

(the identity in $\mathcal{H}$). Applying both sides of this relation to an ordinary ket $|\psi\rangle$ we deduce that any such ket can be represented as

$$|\psi\rangle = \sum_n c_n |u_n\rangle + \int_I \mathrm{d}\alpha\, c(\alpha)|\alpha\rangle, \qquad \text{with} \quad c_n = \langle n|\psi\rangle, \quad c(\alpha) = \langle\alpha|\psi\rangle.$$

Example 4.2. *Position and momentum bases.*

The set

$$\left\{|\mathbf{x}\rangle \equiv \delta(\mathbf{r} - \mathbf{x}) : \mathbf{x} \in \mathbb{R}^3\right\} \tag{4.7}$$ `posbasis`

is a generalized orthonormal basis of $\mathcal{H} = L^2(\mathbb{R}^3)$ (here the vector $\mathbf{x}$ plays the role of the parameter α, and the index set I is $\mathbb{R}^3$). Indeed, to begin with

$$\langle \mathbf{x}|\mathbf{x}'\rangle = \int d^3\mathbf{r}\, \delta(\mathbf{r} - \mathbf{x})\delta(\mathbf{r} - \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'),$$

by the defining property of Dirac's delta (cf. Eq. (2.22)). Secondly, if $\psi(\mathbf{r})$ is an ordinary (continuous) function we have

$$\langle \mathbf{x}|\psi\rangle = \int d^3r\, \delta(\mathbf{r} - \mathbf{x})\psi(\mathbf{r}) = \psi(\mathbf{x}), \tag{4.8}$$ `psiposrep`

and therefore

$$\psi(\mathbf{r}) = \int d^3\mathbf{x}\, \delta(\mathbf{r} - \mathbf{x})\psi(\mathbf{x}) \equiv \int d^3\mathbf{x}\, |\mathbf{x}\rangle\langle \mathbf{x}|\psi\rangle = \left(\int d^3\mathbf{x}\, |\mathbf{x}\rangle\langle \mathbf{x}|\right)|\psi\rangle \implies \int d^3\mathbf{x}\, |\mathbf{x}\rangle\langle \mathbf{x}| = \mathbb{1}.$$

Note that $|\mathbf{x}\rangle$ is a formal eigenfunction of the position operator $\mathbf{R}$ with eigenvalue $\mathbf{x}$. For this reason, the basis (4.7) is called the *position basis.*

Likewise, the set

$$\left\{|\phi_{\mathbf{p}}\rangle \equiv (2\pi\hbar)^{-3/2}\mathrm{e}^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} : \mathbf{p} \in \mathbb{R}^3\right\} \tag{4.9}$$ `mombasis`

is another generalized orthonormal basis of $\mathcal{H} = L^2(\mathbb{R}^3)$. This follows immediately from the equalities

$$\langle \phi_{\mathbf{p}}|\phi_{\mathbf{p}'}\rangle = (2\pi\hbar)^{-3}\int d^3r\, \mathrm{e}^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}} = \delta(\mathbf{p} - \mathbf{p}')$$

and

$$\langle \phi_{\mathbf{p}}|\psi\rangle = (2\pi\hbar)^{-3/2}\int d^3r\, \mathrm{e}^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\psi(\mathbf{r}) = \hat{\psi}(\mathbf{p}), \tag{4.10}$$ `psimomrep`

since

$$\psi(\mathbf{r}) = (2\pi\hbar)^{-3/2}\int d^3p\, \mathrm{e}^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\hat{\psi}(\mathbf{p}) \equiv \int d^3p\, |\phi_{\mathbf{p}}\rangle\langle \phi_{\mathbf{p}}|\psi\rangle = \left(\int d^3\mathbf{x}\, |\phi_{\mathbf{p}}\rangle\langle \phi_{\mathbf{p}}|\right)|\psi\rangle$$

$$\implies \int d^3\mathbf{p}\, |\phi_{\mathbf{p}}\rangle\langle \phi_{\mathbf{p}}| = \mathbb{1},$$

where we have used the Fourier transform identities (2.30) and (2.32). The basis (4.9) is called the *momentum basis*, since each $|\phi_{\mathbf{p}}\rangle$ is a formal eigenfunction of the momentum operator $\mathbf{P}$ with eigenvalue $\mathbf{p}$. Note, finally, that from Eqs. (4.8) and (4.10) it follows that the position and momentum wave functions $\psi(\mathbf{r})$ and $\hat{\psi}(\mathbf{p})$ are related to the abstract state vector $|\psi\rangle$ by the formulas

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle, \qquad \hat{\psi}(\mathbf{p}) = \langle \phi_{\mathbf{p}}|\psi\rangle.$$

The following fundamental result is proved in advanced courses in functional analysis[10]:

> Any observable A possesses a generalized orthonormal basis of (genuine and/or formal) eigenfunctions.

Assuming, for the sake of simplicity, that both the point spectrum

$$\sigma_p = \left\{a_n : n = 1, 2, \dots\right\}$$

---

[10]See, e.g., I. M. Gel'fand and N. Ya. Vilenkin, *Generalized Functions, vol. 4. Applications of Harmonic Analysis,* Academic Press, New York (1964).

and the continuous spectrum

$$\sigma_c = \{\alpha : \alpha \in I\}$$

of the observable A are non-empty and non-degenerate, we can write

$$\sum_n |a_n\rangle\langle a_n| + \int_I d\alpha \, |\alpha\rangle\langle \alpha| = \mathbb{1}, \tag{4.11}$$

`Agenbas`

where $|a_n\rangle \in \mathcal{H}$ is a genuine eigenfunction of A with eigenvalue a_n, $|\alpha\rangle$ is a formal eigenfunction of the latter operator with eigenvalue α, and

$$\langle a_n|a_m\rangle = \delta_{nm}, \quad \langle \alpha|\alpha'\rangle = \delta(\alpha - \alpha'), \quad \langle a_n|\alpha\rangle = 0. \tag{4.12}$$

`Aorth`

Applying the operator A to the completeness relation (4.6) and taking into account that by construction

$$A|a_n\rangle = a_n|a_n\rangle, \qquad A|\alpha\rangle = \alpha|\alpha\rangle$$

we immediately obtain the **spectral decomposition** of the self-adjoint operator A:

$$A = \sum_n a_n|a_n\rangle\langle a_n| + \int_I d\alpha \, \alpha|\alpha\rangle\langle \alpha|$$

It also follows from Eq. (4.11) that any ordinary ket $|\psi\rangle$ admits the expansion

$$|\psi\rangle = \sum_n c_n|a_n\rangle + \int_I d\alpha \, c(\alpha)|\alpha\rangle, \qquad \text{with} \quad c_n = \langle a_n|\psi\rangle, \quad c(\alpha) = \langle \alpha|\psi\rangle. \tag{4.13}$$

`Acomprel`

Note that using the completeness relations it is straightforward to show that

$$\|\psi\|^2 = 1 = \sum_n |c_n|^2 + \int_I d\alpha \, |c(\alpha)|^2 \equiv \sum_n |\langle a_n|\psi\rangle|^2 + \int_I d\alpha \, |\langle \alpha|\psi\rangle)|^2.$$

Thus (under the assumption that both the point and the continuous spectrum are non-degenerate) the numbers $|c_n|^2 \equiv |\langle a_n|\psi\rangle|^2$ ($n = 1, 2, \dots$) and $|c(\alpha)|^2 \equiv |\langle \alpha|\psi\rangle)|^2$ ($\alpha \in I$) define a *probability distribution* (in part discrete and in part continuous). We then have the following generalization of Axiom 3:

Axiom 3'. Suppose that an observable A possesses a generalized orthonormal basis of eigenfunctions as in Eqs. (4.11)-(4.13). If we measure the observable A when the system is in a state $|\psi\rangle$, then we can obtain as a result of the measurement either an eigenvalue a_n with probability $|\langle a_n|\psi\rangle|^2$ or a number in the range $[\alpha, \alpha + d\alpha]$ with probability $|\langle \alpha|\psi\rangle|^2 \, d\alpha$, where $\alpha \in I$ is a generalized eigenvalue.

Remarks.

- In particular, when an observable A has only point spectrum (i.e., when $\sigma_c = \emptyset$), the possible results of a measurement of A are *quantized*[11].

---

[11]Recall that the point spectrum of a self-adjoint operator A in a (separable) Hilbert space is a finite or at most *countable* set. Moreover, for the self-adjoint operators normally occurring in quantum mechanics the accumulation points of the point spectrum belong to the continuous spectrum. Under this assumption (which we shall implicitly make in what follows), if $\sigma_c(A) = \emptyset$ the point spectrum is a finite or at most countable set *without accumulation points*. Furthermore, when there is only point spectrum the set of eigenvectors of a self-adjoint operators is *complete*, i.e., its closure is the whole Hilbert space (or, equivalently, there is an orthonormal basis of eigenvectors of A). Hence when $\sigma_c(A) = \emptyset$ and $\dim \mathcal{H} = \infty$ the point spectrum is an infinite set without accumulation points. By the Bolzano–Weierstrass theorem, in this case $\sigma_p(A)$ must be *unbounded* (from above, from below or from both ends).

- From Axiom 3' applied to the position or momentum bases (4.7)-(4.9) it follows that (as we had seen in Chapter 2) $\left|\psi(\mathbf{r})\right|^2 \mathrm{d}^3 r$ and $\left|\hat{\psi}(\mathbf{p})\right|^2 \mathrm{d}^3 p$ are respectively the probabilities of finding the particle in an infinitesimal volume $\mathrm{d}^3 r$ about $\mathbf{r}$ or with momentum lying in an infinitesimal volume $\mathrm{d}^3 p$ about $\mathbf{p}$.

- Axiom 3' is easily generalized to more complex situations in which either the point or the continuous spectrum (or both) are degenerate. For example, if the point spectrum is degenerate the probability to obtain the eigenvalue a_n when measuring A in the state $|\psi\rangle$ is given by Eq. (4.5). ∎

An important consequence of Axiom 3 (or 3'), already anticipated above, is that *the kets $|\psi\rangle$ and $|\psi'\rangle = \mathrm{e}^{i\alpha}|\psi\rangle$, where α is an arbitrary real constant, determine the* same *physical state.* Indeed, the probability distributions of *any* observables are the same for $|\psi\rangle$ as for $|\psi\rangle'$, since for any (genuine or generalized) ket $|\phi\rangle$ we have

$$\left|\langle\phi|\psi'\rangle\right|^2 = \left|\mathrm{e}^{i\alpha}\langle\phi|\psi\rangle\right|^2 = \left|\langle\phi|\psi\rangle\right|^2.$$

Thus we can multiply a given ket by an overall *constant* phase without changing the quantum state. It is important to note, however, that when we take linear combinations of two or more states *relative* phases are relevant, and are in fact essential to explain interference phenomena. This fact is illustrated in the following simple example:

Example 4.3. Given two states $|\psi_1\rangle$ and $|\psi_2\rangle$, consider the linear combination

$$|\psi\rangle := \frac{1}{N}\left(\mathrm{e}^{i\alpha_1}|\psi_1\rangle + \mathrm{e}^{i\alpha_2}|\psi_2\rangle\right),$$

where

$$N = \left\|\mathrm{e}^{i\alpha_1}|\psi_1\rangle + \mathrm{e}^{i\alpha_2}|\psi_2\rangle\right\| = \sqrt{2}\left(1 + \mathrm{Re}\left(\mathrm{e}^{i(\alpha_2-\alpha_1)}\langle\psi_1|\psi_2\rangle\right)\right)^{1/2}$$

(exercise). Since we can write

$$|\psi\rangle = \frac{\mathrm{e}^{i\alpha_1}}{N}\left(|\psi_1\rangle + \mathrm{e}^{i(\alpha_2-\alpha_1)}|\psi_2\rangle\right),$$

$|\psi\rangle$ describes the *same* physical state as

$$|\psi'\rangle = \frac{1}{N}\left(|\psi_1\rangle + \mathrm{e}^{i(\alpha_2-\alpha_1)}|\psi_2\rangle\right).$$

However, the relative phase $\mathrm{e}^{i(\alpha_2-\alpha_1)}$ is obviously essential and hence cannot be dropped. For instance, let us suppose for the sake of simplicity that $|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal, so that

$$|\psi'\rangle = \frac{1}{\sqrt{2}}\left(|\psi_1\rangle + \mathrm{e}^{i(\alpha_2-\alpha_1)}|\psi_2\rangle\right).$$

If $|a\rangle$ is a (normalized) eigenvector of an observable A with non-degenerate eigenvalue a, the probability of obtaining a as the result of a measurement of A when the system is in the state $|\psi\rangle$ —or, equivalently, $|\psi'\rangle$— is

$$p_\psi(a) = \left|\langle a|\psi'\rangle\right|^2 = \frac{1}{2}\left|\langle a|\psi_1\rangle + \mathrm{e}^{i(\alpha_2-\alpha_1)}\langle a|\psi_2\rangle\right|^2$$
$$= \frac{1}{2}\left(\left|\langle a|\psi_1\rangle\right|^2 + \left|\langle a|\psi_2\rangle\right|^2\right) + \mathrm{Re}\left(\mathrm{e}^{i(\alpha_2-\alpha_1)}\langle\psi_1|a\rangle\langle a|\psi_2\rangle\right).$$

This probability is clearly an oscillating function of the relative phase difference $\alpha_2 - \alpha_1$. For instance, if both $\langle a|\psi_1\rangle$ and $\langle a|\psi_2\rangle$ are real we have

$$p_\psi(a) = \frac{1}{2}\left(\langle a|\psi_1\rangle^2 + \langle a|\psi_2\rangle^2\right) + \langle a|\psi_1\rangle\langle a|\psi_2\rangle \cos(\alpha_2 - \alpha_1),$$

which oscillates between the values

$$\frac{1}{2}\left(\langle a|\psi_1\rangle + \langle a|\psi_2\rangle\right)^2$$

for $\alpha_2 - \alpha_1 = 2k\pi$ (with $k \in \mathbb{Z}$) and

$$\frac{1}{2}\left(\langle a|\psi_1\rangle - \langle a|\psi_2\rangle\right)^2$$

for $\alpha_2 - \alpha_1 = (2k+1)\pi$ (with $k \in \mathbb{Z}$). If $\langle a|\psi_1\rangle$ and $\langle a|\psi_2\rangle$ have the same sign the probability is maximum when $\alpha_2 - \alpha_1 = 2k\pi$ and minimum when $\alpha_2 - \alpha_1 = (2k+1)\pi$ (with $k \in \mathbb{Z}$), whereas if they have opposite signs the probability is maximum when $\alpha_2 - \alpha_1 = (2k+1)\pi$ and minimum when $\alpha_2 - \alpha_1 = 2k\pi$. In either case, the probability varies between $\left(\left|\langle a|\psi_1\rangle\right|^2 - \left|\langle a|\psi_2\rangle\right|\right)^2/2$ and $\left(\left|\langle a|\psi_1\rangle\right|^2 + \left|\langle a|\psi_2\rangle\right|\right)^2/2$.

4.3 Measurements

sec.meas

For the case of a single particle, we have already proved in Section 2.11 (cf. result viii)) that the state of the particle immediately after the measurement of an observable A has produced a definite result a (where a is one of the eigenvalues of A) must be an eigenfunction of A with eigenvalue a. We shall admit that this will also be the case for a general quantum system. If (as is the case in many practical problems, especially in one dimension) A has only point spectrum and the eigenvalues of A are *non-degenerate*, the state of the system after a measurement of A yields as a result an eigenvalue $a \in \sigma_p(A)$ is the corresponding eigenstate $|a\rangle$, which is determined up to an irrelevant phase (since by hypothesis $\ker(A - a)$ is one-dimensional). If, on the other hand, the point spectrum of the observable A contains a degenerate eigenvalue a, stating that the state $|\psi\rangle$ of the system is an eigenstate of A with eigenvalue a does not determine $|\psi\rangle$ unambiguously (up to a phase). Since by Axiom 3 the probability of obtaining the value a when measuring the observable A is determined by the orthogonal projection $\mathscr{P}_a|\psi\rangle$ of $|\psi\rangle$ onto the eigenspace $\ker(A - a)$, we shall postulate that if a measurement of A has yielded the value a the (normalized) state of the system immediately after this measurement is $\frac{\mathscr{P}_a|\psi\rangle}{\left\|\mathscr{P}_a|\psi\rangle\right\|}$. In other words:

Axiom 4. The state of the system immediately after a measurement of an observable A has yielded the value $a \in \sigma_p(A)$ is

$$\frac{\mathscr{P}_a|\psi\rangle}{\left\|\mathscr{P}_a|\psi\rangle\right\|} \equiv \frac{\mathscr{P}_a|\psi\rangle}{\sqrt{p_\psi(a)}}. \tag{4.14}$$

cPapsi

Note that the state (4.14) is always an eigenket of A with eigenvalue a, since by construction $\mathscr{P}_a$ projects onto the eigenspace $\ker(A - a)$ of this eigenvalue.

Similar considerations apply if part of the spectrum of an observable A is continuous. For instance, the state of the system immediately after a measurement of the observable A has yielded a value in the interval $[\alpha, \alpha + d\alpha]$, where $\alpha \in \sigma_c(A)$ is a formal non-degenerate eigenvalue of A, is the generalized state $|\alpha\rangle$. Since $|\alpha\rangle$ is not a physical state if $\alpha \in \sigma_c(A)$, what the latter statement actually means is that the state of the system immediately after the measurement of A is a wave packet

$$|\psi\rangle = \int_\alpha^{\alpha+d\alpha} d\alpha\, g(\beta)|\beta\rangle,$$

with $g(\beta)$ narrowly concentrated about α and

$$\int_\alpha^{\alpha+d\alpha} d\beta \, |g(\beta)|^2 = 1.$$

(Note that

$$\|\psi\|^2 = \langle\psi|\psi\rangle = \int_\alpha^{\alpha+d\alpha} d\beta \int_\alpha^{\alpha+d\alpha} d\beta' \, g(\beta)g^*(\beta')|\beta\rangle\langle\beta'|$$

$$= \int_\alpha^{\alpha+d\alpha} d\beta \int_\alpha^{\alpha+d\alpha} d\beta' \, g(\beta)g^*(\beta')\delta(\beta-\beta') = \int_\alpha^{\alpha+d\alpha} d\beta \, |g(\beta)|^2 = 1,$$

so that the state $|\psi\rangle$ is normalized.)

Remark. Axiom 4 implies that when a measurement is performed on a quantum system the state of the system stops evolving continuously (through the time-dependent Schrödinger equation, as we shall see below) and abruptly "jumps" to an eigenstate of the observable that is being measured. This phenomenon, usually called the **collapse of the wave function**[12], is one of the most controversial and least understood features of quantum mechanics. Of course, immediately after this sudden jump caused by the measurement process the quantum state starts evolving continuously again until another measurement is performed, and so on.

Example 4.4. Consider a quantum system whose Hilbert space is the finite-dimensional space $\mathcal{H} = \mathbb{C}^3$. In this case ket vectors can be represented by column vectors

$$|v\rangle = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}, \qquad v_i \in \mathbb{C},$$

which can also be written as

$$|v\rangle = \sum_{i=1}^3 v_i|e_i\rangle$$

in terms of the canonical basis of $\mathbb{C}^3$

$$|e_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |e_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |e_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The bra $\langle v|$ corresponding to the ket $|v\rangle$ is then represented by the *row matrix*

$$\begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}^\dagger = (v_1^* \ v_2^* \ v_3^*) \equiv v_1^*\langle e_1| + v_2^*\langle e_2| + v_3^*\langle e_3|,$$

where

$$\langle e_1| = (1 \ 0 \ 0), \quad \langle e_2| = (0 \ 1 \ 0), \quad \langle e_3| = (0 \ 0 \ 1)$$

---

[12] The reason for this terminology is that in the case of a single particle whose position is being measured the wave function, which is usually a wave packet with a certain spread, collapses to a delta function or, more precisely, a "spike" of unit norm peaked at the point obtained as a result of the position measurement.

© Artemio González López

is the canonical basis of the dual space of $\mathbb{C}^3$. The reason for this is that, if $|u\rangle = u_1|e_1\rangle + u_2|e_2\rangle + u_3|e_3\rangle$ is an arbitrary ket vector, then $\langle v|$ is defined by

$$\langle v|(|u\rangle) = \langle v|u\rangle = \sum_{i=1}^{3} v_i^* u_i = (v_1^* \ v_2^* \ v_3^*)\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} \equiv (v_1^* \ v_2^* \ v_3^*) \cdot |u\rangle,$$

where the last dot denotes matrix multiplication.

Let $A : \mathbb{C}^3 \to \mathbb{C}^3$ be the operator represented by the matrix (in the canonical basis of $\mathbb{C}^3$ and in appropriate units)

$$A = \begin{pmatrix} 3 & i & 0 \\ -i & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix},$$

which, with a slight abuse of notation, we shall also denote by A. Since the matrix elements a_{ij} of a matrix A are given by

$$a_{ij} = (e_i, Ae_j) \equiv \langle e_i|A|e_j\rangle,$$

we have

$$A = \sum_{i,j=1}^{3} a_{ij}|e_i\rangle\langle e_j|,$$

or in this case,

$$A = 3(|e_1\rangle\langle e_1| + |e_2\rangle\langle e_2|) + i(|e_1\rangle\langle e_2| - |e_2\rangle\langle e_1|) + 2|e_3\rangle\langle e_3|.$$

Since A is clearly self-adjoint (i.e., $A^\dagger \equiv (A^{\mathsf{T}})^* = A$), it can be one of the system's observables. The characteristic polynomial of A is

$$\det(A - \lambda) = (2 - \lambda)\begin{vmatrix} 3 - \lambda & i \\ -i & 3 - \lambda \end{vmatrix} = (2 - \lambda)[(3 - \lambda)^2 - 1] = (2 - \lambda)(4 - \lambda)(2 - \lambda) = (2 - \lambda)^2(4 - \lambda).$$

Thus the eigenvalues of A are $a_1 = 2$ (twice degenerate) and $a_2 = 4$ (non-degenerate). In particular, if we measure the observable A the only possible outcomes are 2 and 4. Suppose that at a certain time t the system is in the state

$$|\psi\rangle = \frac{1}{3}(|e_1\rangle + 2i|e_2\rangle + 2|e_3\rangle) = \frac{1}{3}\begin{pmatrix} 1 \\ 2i \\ 2 \end{pmatrix};$$

note that

$$\langle\psi|\psi\rangle = \frac{1}{9}(1 + 4 + 4) = 1,$$

so that $|\psi\rangle$ is properly normalized. To find the probability of obtaining the values 2 and 4 when the observable A is measured at the time t, we note that the eigenspace $\ker(A-4)$ is one-dimensional (since this eigenvalue is simple). Thus the probability of obtaining the value 4 as a result of a measurement of the observable A is simply

$$p_\psi(4) = |\langle 4|\psi\rangle|^2,$$

where $|4\rangle$ is a normalized eigenvector of A with eigenvalue 4. To find this eigenvector we must solve the eigenvalue equation $(A - 4)|v\rangle = 0$, i.e.,

$$\begin{pmatrix} -1 & i & 0 \\ -i & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = 0.$$

Solving this system and normalizing the solution we obtain

$$|4\rangle = \frac{1}{\sqrt{2}}(1 \ -i \ 0)^{\mathsf{T}} \equiv \frac{1}{\sqrt{2}}(|e_1\rangle - i|e_2\rangle),$$

up to an inessential phase. Thus the probability of finding the value 4 when we measure A and the system is in the state $|\psi\rangle$ is

$$p_\psi(4) = \left| \frac{1}{\sqrt{2}}(1, -i, 0) \cdot \frac{1}{3}(1, 2i, 2) \right|^2 = \frac{1}{2} \frac{1}{9} |(1, -i, 0) \cdot (1, 2i, 2)|^2 = \frac{1}{18} \simeq 0.0555556.$$

Consequently, the probability of obtaining the value 2 is

$$p_\psi(2) = 1 - \frac{1}{18} = \frac{17}{18} \simeq 0.944444.$$

It is also instructive to derive the latter result using equation (4.5). To this end, we must first construct the projector $\mathscr{P}_2$ onto the two-dimensional eigenspace $\ker(A - 2)$. This can be done, for instance, by finding two orthogonal normalized eigenvectors $|u_1\rangle$ and $|u_2\rangle$ with eigenvalue 2 and using the formula of Exercise 4.2, namely

$$\mathscr{P}_2 = |u_1\rangle\langle u_1| + |u_2\rangle\langle u_2|.$$

The eigenvalue equation $(A - 2)|v\rangle = 0$ is

$$\begin{pmatrix} 1 & i & 0 \\ -i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = 0 \quad \Longleftrightarrow \quad v_1 + i\,v_2 = 0,$$

and hence

$$(v_1, v_2, v_3) = (a, i\,a, b) \quad \Longrightarrow \quad |v\rangle = a\big(|e_1\rangle + i\,|e_2\rangle\big) + b|e_3\rangle,$$

with a, b arbitrary complex constants. In this case it is straightforward to find an orthonormal basis of $\ker(A - 2)$ by inspection, namely

$$|u_1\rangle = \frac{1}{\sqrt{2}}(|e_1\rangle + i\,|e_2\rangle) \equiv \frac{1}{\sqrt{2}}(1 \ i \ 0)^{\mathsf{T}}, \qquad |u_2\rangle = |e_3\rangle = (0 \ 0 \ 1)^{\mathsf{T}}$$

(in more general situations, one can always use the standard *Gram–Schmidt* orthonormalization procedure taught in linear algebra courses). We thus find

$$\mathscr{P}_2 = \frac{1}{2}\begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}(1 \ -i \ 0) + \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}(0 \ 0 \ 1) = \frac{1}{2}\begin{pmatrix} 1 & -i & 0 \\ i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{i}{2} & 0 \\ \frac{i}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

and therefore

$$\mathscr{P}_2|\psi\rangle = \frac{1}{3}\begin{pmatrix} \frac{1}{2} & -\frac{i}{2} & 0 \\ \frac{i}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 2i \\ 2 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ \frac{i}{2} \\ \frac{2}{3} \end{pmatrix} \implies p_\psi(2) = \|\mathscr{P}_2|\psi\rangle\|^2 = \frac{1}{4} + \frac{1}{4} + \frac{4}{9} = \frac{17}{18}.$$

Since the eigenvalue 4 is simple, if we measure A and obtain 4 as a result the state of the system immediately after this measurement will be simply the eigenket $|4\rangle$ above (up to an inessential phase). If, on the other hand, the result is 2, immediately after the measurement is performed the system will jump to the state

$$\frac{\mathscr{P}_2|\psi\rangle}{\|\mathscr{P}_2|\psi\rangle\|} \equiv \frac{\mathscr{P}_2|\psi\rangle}{\sqrt{p_\psi(2)}} = \sqrt{\frac{18}{17}}\left(\frac{1}{2}|e_1\rangle + \frac{i}{2}|e_2\rangle + \frac{2}{3}|e_3\rangle\right) = \frac{1}{\sqrt{34}}\left(3|e_1\rangle + 3i|e_2\rangle + 4|e_3\rangle\right)$$

(again up to a trivial phase).

4.4 Time evolution. Conserved quantities

sec.timeev

We saw in Chapter 2 that the continuous (i.e., in-between two measurements) time evolution of the wave function of a single particle $\Psi(\mathbf{r}, t)$ is governed by the time-dependent Schrödinger equation (3.1). For a general quantum system, we shall accept that the time evolution of the system's state, which we shall denote by $|\psi(t)\rangle$ to stress its time dependence, is a *linear process.* In other words, *the time evolution must be compatible with the linear superposition of states.* If, for example, initially $|\psi(0)\rangle$ is the sum of two kets $|\psi_1(0)\rangle$ and $|\psi_2(0)\rangle$, then the time-evolved state $|\psi(t)\rangle$ must be the sum of the corresponding time-evolved states $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$ for all subsequent (or previous) times t. This entails that the mapping $|\psi(0)\rangle \mapsto |\psi(t)\rangle$ must be *linear.* In other words, we must have

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle, \tag{4.15}$$

Utpsi

where[13] $U(t) : \mathcal{H} \to \mathcal{H}$ is a linear operator called the system's **time evolution operator.** Since the state's norm must be preserved by the time evolution, if initially $\langle\psi(0)|\psi(0)\rangle = 1$ we must have

$$\langle\psi(t)|\psi(t)\rangle = \langle U(t)\psi(0)|U(t)\psi(0)\rangle = \langle\psi(0)|U^\dagger(t)U(t)|\psi(0)\rangle = 1 = \langle\psi(0)|\psi(0)\rangle.$$

Since $|\psi(0)\rangle$ is an arbitrary state this implies that

$$\langle\phi|U^\dagger(t)U(t)|\phi\rangle = \langle\phi|\phi\rangle$$

for all states $|\phi\rangle \in \mathcal{H}$ of unit norm, and hence for *all* states in $\mathcal{H}$ (just multiply both sides by $|\lambda|^2$, where λ is any complex number). From the previous equality it easily follows that

$$\langle\phi_1|U^\dagger(t)U(t)\phi_2\rangle = \langle\phi_1|\phi_2\rangle = 0, \qquad \forall|\phi_1\rangle, |\phi_2\rangle \in \mathcal{H}$$

(exercise), and hence that

$$U^\dagger(t)U(t) = \mathbb{1}$$

In other words, the time evolution operator $U(t)$ must be a *unitary operator.* Moreover, if (as we shall usually assume to be the case) the system is *invariant under time translations* the time evolution operator must satisfy the identity

$$|\psi(t + s)\rangle = U(t)|\psi(s)\rangle$$

---

[13]In what follows we shall usually simplify matters by assuming that the domains of all operators involved is all of $\mathcal{H}$ even if, as we know, this need not always be the case.

for all $s \in \mathbb{R}$, and therefore

$$U(t+s)\big|\psi(0)\big\rangle = U(t)U(s)\big|\psi(0)\big\rangle$$

for all kets $\big|\psi(0)\big\rangle$ of unit norm, and hence for all kets in $\mathcal{H}$. This shows that

$$U(t+s) = U(t)U(s),$$

i.e., that $\big\{U(t) : t \in \mathbb{R}\big\}$ is a *one-parameter group* of unitary transformations; in particular,

$$U(0) = \mathbb{1}, \qquad U(t)^{-1} = U(-t).$$

By *Stone's theorem* in functional analysis, there is a *self-adjoint* time-independent linear operator $H :$ $\mathcal{H} \to \mathcal{H}$ satisfying

$$U(t) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}tH}, \tag{4.16}$$

`UtH`

where the sign is conventional and the factor $\hbar$ is introduced so that H has dimensions of energy. By analogy with the case of a single particle studied in Chapter 2, the operator H is called the system's **Hamiltonian**. We thus have

$$\big|\psi(t)\big\rangle = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}tH}\big|\psi(0)\big\rangle, \tag{4.17}$$

`psiteitH`

and differentiating both sides of the previous equation we easily obtain the **time-dependent Schrödinger equation**

$$\mathrm{i}\hbar\partial_t\big|\psi(t)\big\rangle = H\big|\psi(t)\big\rangle. \tag{4.18}$$

`Schrgen`

Note that Eqs. (4.16) and (4.18) are actually equivalent, since integrating Eq. (4.18) we get (4.15) with $U(t)$ given by Eq. (4.16). Observe also that from (4.17) we easily obtain the more general equation

$$\big|\psi(t)\big\rangle = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}tH}\big|\psi(0)\big\rangle = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}tH}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}t_0 H}\big|\psi(t_0)\big\rangle = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(t-t_0)H}\big|\psi(t_0)\big\rangle.$$

The above considerations motivate the following axiom:

Axiom 5. In the time interval between two measurements, the time evolution of the state $\big|\psi(t)\big\rangle$ of a quantum system invariant under time translations is governed by the *Schrödinger equation*

$$\mathrm{i}\hbar\partial_t\big|\psi(t)\big\rangle = H\big|\psi(t)\big\rangle,$$

where the *Hamiltonian H* is a self-adjoint and time-independent operator.

Remark. If the system is not invariant under time translations, the evolution of the state vector is still governed by Schrödinger's equation

$$\mathrm{i}\hbar\partial_t\big|\psi(t)\big\rangle = H(t)\big|\psi(t)\big\rangle,$$

where the Hamiltonian H can now depend explicitly on time. ∎

If H has only *point spectrum,* we know that there is an *orthonormal basis* of the Hilbert space $\mathcal{H}$, which we shall denote by

$$\big\{|n\rangle : n = 1, 2, \dots\big\}, \tag{4.19}$$

`enbas`

whose elements are eigenkets of H. We thus can write

$$H|n\rangle = E_n|n\rangle,$$

© *Artemio González López*

where $E_n \in \mathbb{R}$ is the eigenvalue (i.e., energy) of the state $|n\rangle$. Note that E_n is real, as H is self-adjoint, and that we are *not* assuming that the spectrum is non-degenerate, so that E_n might be equal to E_m for $m \neq n$. Expanding the initial state $|\psi(0)\rangle$ in the energy basis (4.19) we obtain

$$|\psi(0)\rangle = \sum_n c_n |n\rangle, \qquad \text{with} \quad c_n = \langle n|\psi\rangle.$$

By Eq. (4.17), if no measurement is performed on the system in the interval $[0, t]$ the state $|\psi(t)\rangle$ at a later time t will be given by

$$|\psi(t)\rangle = \sum_n c_n e^{-\frac{i}{\hbar}tH}|n\rangle = \sum_n c_n e^{-\frac{i}{\hbar}E_n t}|n\rangle.$$

This solution of the Schrödinger equation can be generalized to the case in which the continuous spectrum of H is non-empty. In this case H possesses a generalized orthonormal basis of eigenvectors

$$\{|n\rangle : n = 1, 2, \ldots\} \cup \{|\alpha\rangle : \alpha \in I\},$$

with I a suitable index set and

$$H|n\rangle = E_n|n\rangle, \qquad H|\alpha\rangle = E(\alpha)|\alpha\rangle$$

(again, we are not assuming that $E(\alpha) \neq E(\beta)$ for $\alpha \neq \beta$ to allow for a degenerate continuous spectrum). Multiplying the generalized completeness relation

$$\sum_n |n\rangle\langle n| + \int_I d\alpha\, |\alpha\rangle|\alpha\rangle\langle\alpha| = \mathbb{1}$$

from the right by $|\psi(0)\rangle$ we then obtain the expansion

$$|\psi(0)\rangle = \sum_n c_n|n\rangle + \int_I d\alpha\, c(\alpha)|\alpha\rangle,$$

with

$$c_n = \langle n|\psi(0)\rangle, \qquad c(\alpha) = \langle\alpha|\psi(0)\rangle,$$

from which it follows (if no measurements are performed on the system in the interval $[0, t]$) that

$$|\psi(t)\rangle = \sum_n c_n e^{-\frac{i}{\hbar}E_n t}|n\rangle + \int_I d\alpha\, c(\alpha)e^{-\frac{i}{\hbar}E(\alpha)t}|\alpha\rangle.$$

Ehrenfest's general formula (2.25) for the time derivative of the expectation value (average) of an observable is valid in this more general setting, with the same proof as in Section (2.5). In particular, if an observable A commutes with H its expectation value is time-independent.

Definition 4.5. A (time-independent) observable A is a **constant of motion** (or **conserved quantity**) if it commutes with the Hamiltonian H.

Thus *the expectation value of a constant of motion is time-independent.* This is the quantum analogue of the classical result according to which a dynamical variable whose Poisson bracket with the system's Hamiltonian vanishes is conserved, i.e., does not change with time along a trajectory.

Remark. If an observable A is a constant of motion, the operator $\mathrm{e}^{-\mathrm{i}\varepsilon A}$ is unitary for all real ε, and it commutes with H (since it is a function of A). The unitary mapping

$$|\psi\rangle \in \mathcal{H} \mapsto |\psi_\varepsilon\rangle := \mathrm{e}^{-\mathrm{i}\varepsilon A}|\psi\rangle$$

is then a *symmetry transformation* whose *generator* is the observable A, in the sense that

$$A = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\bigg|_{\varepsilon=0} \mathrm{e}^{-\mathrm{i}\varepsilon A}.$$

For instance, if $|\psi\rangle$ is an eigenket of H with energy E so is $|\psi_\varepsilon\rangle$ for all $\varepsilon \in \mathbb{R}$, since

$$H|\psi_\varepsilon\rangle = H\mathrm{e}^{-\mathrm{i}\varepsilon A}|\psi\rangle = \mathrm{e}^{-\mathrm{i}\varepsilon A}H|\psi\rangle = E\mathrm{e}^{-\mathrm{i}\varepsilon A}|\psi\rangle \equiv E|\psi_\varepsilon\rangle.$$

Conversely, if $R(\varepsilon)$ (with $\varepsilon \in \mathbb{R}$) is a one-parameter group of symmetry transformations, i.e., of unitary operators commuting with the system's Hamiltonian H satisfying

$$R(\varepsilon_1)R(\varepsilon_2) = R(\varepsilon_1 + \varepsilon_2),$$

by Stone's theorem

$$R(\varepsilon) = \mathrm{e}^{-\mathrm{i}\varepsilon A}$$

with A self-adjoint. The operator A is obviously the generator of the symmetry group $\{R(\varepsilon) : \varepsilon \in \mathbb{R}\}$, and it commutes with H, since differentiating the equality

$$R(\varepsilon)H = HR(\varepsilon)$$

with respect to ε and setting $\varepsilon = 0$ we obtain

$$AH = HA.$$

Thus *the generator of a one-parameter group of symmetry transformations is a constant of the motion.* This result can be considered as the quantum-mechanical analogue of *Noether's theorem* in classical Hamiltonian mechanics.

Consider, for instance, the *space translations*

$$\psi(x) \mapsto \psi_\varepsilon(x) = \psi(x - \varepsilon), \qquad \varepsilon \in \mathbb{R},$$

in the Hilbert space $\mathcal{H} = L^2(\mathbb{R})$ of a (spinless) particle moving in one-dimension. In other words, $\psi_\varepsilon(x)$ is the particle's wave function for an observer whose origin is displaced by ε with respect to the original observer. If the motion is *free,* i.e., if

$$H = \frac{P^2}{2m} \equiv -\frac{\hbar^2}{2m}\partial_x^2,$$

this one-parameter group of transformations is a symmetry, since clearly

$$\partial_x^2[\psi(x - \varepsilon)] = (\partial_x^2\psi)(x - \varepsilon), \qquad \forall \varepsilon \in \mathbb{R}.$$

The generator of this one-parameter of transformations is the operator A defined by

$$(A\psi)(x) = \mathrm{i}\partial_\varepsilon\big|_{\varepsilon=0}\psi_\varepsilon(x) = \mathrm{i}\partial_\varepsilon\big|_{\varepsilon=0}\psi(x - \varepsilon) = -\mathrm{i}\psi'(x) \implies A = -\mathrm{i}\partial_x = \frac{P}{\hbar}. \qquad \blacksquare$$

`exe.centpot`

Exercise 4.3. If

$$H = \frac{\mathbf{P}^2}{2m} + V(R), \qquad R := \sqrt{X_1^2 + X_2^2 + X_3^2},$$

show that the *angular momentum* $\mathbf{L} = \mathbf{R} \times \mathbf{P}$ is conserved.

Solution. Using the canonical commutation relations and the properties of the commutator we have

$$[L_k, \mathbf{P}^2] = \sum_{l=1}^{3} [X_i P_j - X_j P_i, P_l^2] = \sum_{l=1}^{3} \left([X_i, P_l^2] P_j - [X_j, P_l^2] P_i \right) = \sum_{l=1}^{3} \left(2\delta_{il} P_l P_j - 2\delta_{jl} P_l P_i \right)$$
$$= 2(P_i P_j - P_j P_i) = 0,$$

where (i, j, k) is a cyclic permutation of $(1, 2, 3)$. In the same way one shows that

$$[L_k, R^2] = 0,$$

and since $V(R)$ is a function of R^2 this implies that $[L_k, V(R)] = 0$.

Alternatively, using the explicit representation of the angular momentum components we have

$$[L_k, V(R)] = -\mathrm{i}\hbar [x_i \partial_{x_j} - x_j \partial_{x_i}, V(r)] = -\mathrm{i}\hbar \left(x_i \frac{\partial V(r)}{\partial x_j} - x_j \frac{\partial V(r)}{\partial x_i} \right)$$
$$= -\mathrm{i}\hbar V'(r) \left(x_i \frac{x_j}{r} - x_j \frac{x_i}{r} \right) = 0.$$

4.5 Canonical quantization

sec.canquant

The final postulate of quantum mechanics deals with the passage from classical dynamical variables (in particular, the system's Hamiltonian) to quantum observables, and is basically a generalization of the canonical quantization procedure outlined in Section 2.2:

Axiom 6. For a physical system with Cartesian coordinates $\mathbf{q} = (q_1, \ldots, q_N)$ and corresponding canonically conjugate momenta $\mathbf{p} = (p_1, \ldots, p_N)$, the quantum observables Q_j and P_j representing respectively the coordinate q_j and its conjugate momentum p_j must satisfy the *canonical commutation relations*

$$[Q_j, Q_k] = [P_j, P_k] = 0, \qquad [Q_j, P_k] = \mathrm{i}\hbar\delta_{jk}, \qquad j, k = 1, \ldots, N. \qquad (4.20)$$

CCRrep

Moreover, the quantum observable representing a classical dynamical variable $f(\mathbf{q}, \mathbf{p})$ is obtained from $f(\mathbf{q}, \mathbf{p})$ through the replacement

$$q_i \to Q_i, \qquad p_i \to P_i,$$

with an appropriate ordering of the products of position and momentum operators involved.

Remark. The standard representation of the canonical commutation relations (CCR) (4.20) is the *position space representation*

$$Q_j = q_j, \qquad P_j = -\mathrm{i}\hbar \frac{\partial}{\partial q_j}, \qquad j = 1, \ldots, N.$$

This representation is certainly *not* unique. For instance, an alternative representation of the CCR is the *momentum space representation*

$$Q_j = \mathrm{i}\hbar \partial_{p_j}, \qquad P_j = p_j, \qquad j = 1, \ldots, N. \qquad \blacksquare$$

Example 4.6. *Hamiltonian of a charged spinless particle in an external electromagnetic field.*

In the classical case, the Hamiltonian (in Cartesian coordinates) of a particle of charge e and mass m moving in an external electromagnetic field with potentials $\phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ is given by

$$H = \frac{1}{2m} \left(\mathbf{p} - e\mathbf{A}(\mathbf{r}, t) \right)^2 + e\phi(\mathbf{r}, t).$$

Hamilton's equation of motion for the Cartesian position vector **r** is

$$\dot{\mathbf{r}} = -\frac{\partial H}{\partial \mathbf{p}} = \frac{1}{m}\big(\mathbf{p} - e\mathbf{A}(\mathbf{r}, t)\big),$$

so that the *canonical momentum*

$$\mathbf{p} = m\dot{\mathbf{r}} + e\mathbf{A}(\mathbf{r}, t)$$

in this case does *not* coincide with the particle's *linear momentum* $m\dot{\mathbf{r}}$. The canonical quantization procedure applied to the classical Hamiltonian yields the quantum operator

$$H = \frac{1}{2m}\big(\mathbf{P} - e\mathbf{A}(\mathbf{R}, t)\big)^2 + e\phi(\mathbf{R}, t),$$

with $\mathbf{R} = (X_1, X_2, X_3)$. Note that in this case no ambiguities arise from the ordering of the operators, since ϕ depends only on position operators (which commute with one another) and $P_i - eA_i(\mathbf{R}, t)$ commutes with itself. It is also clear that H is *self-adjoint* if **R** and **P** are themselves self-adjoint and the potentials ϕ and **A** are real-valued, since

$$\phi(\mathbf{R}, t)^\dagger = \phi^*(\mathbf{R}^\dagger, t), \qquad \mathbf{A}(\mathbf{R}, t)^\dagger = \mathbf{A}^*(\mathbf{R}^\dagger, t)$$

(exercise). Choosing the standard representation of the canonical commutation relations

$$\mathbf{R}\psi(\mathbf{r}, t) = \mathbf{r}\psi(\mathbf{r}, t), \qquad \mathbf{P}\psi(\mathbf{r}, t) = -i\hbar\nabla\psi(\mathbf{r}, t),$$

we obtain the more explicit formula

$$H = \frac{1}{2m}\big(i\hbar\nabla + e\mathbf{A}(\mathbf{r}, t)\big)^2 + e\phi(\mathbf{r}, t).$$

Expanding the square in the first term and using the canonical commutation relations we obtain[a]

$$\big(i\hbar\nabla + e\mathbf{A}\big)^2 \equiv \big(i\hbar\nabla + e\mathbf{A}\big)\cdot\big(i\hbar\nabla + e\mathbf{A}\big) = -\hbar^2\nabla^2 + e^2\mathbf{A}^2 + (i\hbar e\nabla)\cdot\mathbf{A} + i\hbar e\mathbf{A}\cdot\nabla$$
$$= -\hbar^2\nabla^2 + e^2\mathbf{A}^2 + 2i\hbar e\mathbf{A}\cdot\nabla + i\hbar e(\nabla\cdot\mathbf{A}).$$

For example, in a *constant* magnetic field **B** we can take

$$\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{r},$$

and the electric potential ϕ must be time independent by Maxwell's field eeuation for $\nabla\times\mathbf{B}$. Setting $(x, y, z) = (x_1, x_2, x_3)$ we then have

$$2\nabla\cdot\mathbf{A} = \partial_x(B_2 z - B_3 y) + \partial_y(B_3 x - B_1 z) + \partial_z(B_1 y - B_2 x) = 0,$$
$$2\mathbf{A}\cdot\nabla = (B_2 z - B_3 y)\partial_x + (B_3 x - B_1 z)\partial_y + (B_1 y - B_2 x)\partial_z$$
$$= B_1(y\partial_z - z\partial_y) + B_2(z\partial_x - x\partial_z) + B_3(x\partial_y - y\partial_x) \equiv \mathbf{B}\cdot(\mathbf{r}\times\nabla),$$

and therefore

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \mathbf{B}\cdot\frac{e\mathbf{L}}{2m} + \frac{e^2}{8m}\big(B^2 r^2 - (\mathbf{B}\cdot\mathbf{r})^2\big) + e\phi(\mathbf{r}).$$

where

$$\mathbf{L} = \mathbf{R}\times\mathbf{P} = -i\hbar\mathbf{r}\times\nabla$$

is the particle's *angular momentum.* Note that

$$B^2 r^2 - (\mathbf{B} \cdot \mathbf{r})^2 = B^2 r^2 \sin^2 \theta = B^2 r_\perp^2,$$

where θ and $r_\perp$ respectively denote the angle between the vectors $\mathbf{r}$ and $\mathbf{B}$ and the component of $\mathbf{r}$ along the plane perpendicular to $\mathbf{B}$. In the case of a *weak magnetic field* we can drop the term quadratic in $\mathbf{B}$, thus arriving at the simpler expression

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \mathbf{B} \cdot \frac{e\mathbf{L}}{2m} + e\phi(\mathbf{r}).$$

From this formula it follows that in quantum mechanics a spinless charged particle must have a *magnetic moment*

$$\boldsymbol{\mu} = \frac{e\mathbf{L}}{2m}$$

due to its orbital motion. We stress that the above formula is only valid for a spinless particle, since it does not take into account the contribution of the particle's spin angular momentum to the magnetic moment.

---

[a]In the following formula $(\mathrm{i}\hbar e \nabla) \cdot \mathbf{A}$ denotes the composition of the multiplication operator by $\mathbf{A}$ with the operator $\mathrm{i}\hbar e \nabla$, whereas $\mathrm{i}\hbar e(\nabla \cdot \mathbf{A})$ denotes the multiplication operator by $\mathrm{i}\hbar e \nabla \cdot \mathbf{A}$ (where $\nabla \cdot \mathbf{A}$ is the divergence of the function $\mathbf{A}$). In other words, given a wave function $\psi(\mathbf{r}, t)$ we have

$$[(\mathrm{i}\hbar e \nabla) \cdot \mathbf{A}] \psi = \mathrm{i}\hbar e \nabla \cdot (\mathbf{A}\,\psi), \qquad [\mathrm{i}\hbar e(\nabla \cdot \mathbf{A})] \psi = \mathrm{i}\hbar e(\nabla \cdot \mathbf{A})\psi.$$

4.6 Compatible observables. Complete sets of commuting observables

c.compatobs

As mentioned in Section 2.9, two observables A and B are **compatible** if their commutator $[A, B]$ vanishes identically. In fact, the discussion on Section (2.9) is valid without changes in the present, more general, setting. In particular, the general uncertainty relation (2.48) and the time-energy uncertainty relation (2.58)-(2.59), still hold, since they were established using operator methods. In particular, the uncertainty relation (2.48) implies that *in general two incompatible observables cannot be measured simultaneously with unlimited precision.* In this section we shall examine in more detail the properties of compatible observables, and explain how they can be used to label the (basis) states of a quantum system in a convenient way.

In the finite-dimensional case, a self-adjoint operator is always diagonalizable through a real orthogonal transformation. Moreover, if two self-adjoint operators commute it is always possible to find an orthonormal basis of eigenvectors common to both operators. Neither of these two results is true in general in infinite dimension unless we impose some additional requirements. For example, a self-adjoint operator is not diagonalizable unless it has no continuous spectrum. For this reason, in this section *we shall implicitly assume* (unless otherwise stated) *that the (self-adjoint) operators involved have only point spectrum.*

To begin with, let us suppose that two self-adjoint operators A and B commute. It is then easy to show that *the eigenspaces of A are invariant under B* (and vice versa). Indeed, suppose that $|\psi\rangle \in \ker(A - a)$, i.e.,

$$A|\psi\rangle = a|\psi\rangle.$$

Applying the operator B to both sides of this equality and taking into account that $AB = BA$ we obtain

$$a B|\psi\rangle = B(A|\psi\rangle) = A(B|\psi\rangle) \quad \Longrightarrow \quad B|\psi\rangle \in \ker(A - a),$$

as claimed.

Suppose next that two commuting self-adjoint operators A and B have only point spectrum, and let

$$\sigma_p(A) = \{a_n : n = 1, 2, \dots\}.$$

As we have just shown, each eigenspace $\ker(A - a_n)$ of A is invariant under B. The restriction of B to $\ker(A - a_n)$ is then a self-adjoint operator from $\ker(A - a_n)$ into itself with only point spectrum. Thus there exists an orthonormal basis

$$\left\{ |u_n^m\rangle : m = 1, 2, \dots, d_n \right\}$$

of $\ker(A - a_n)$ (where $d_n = \dim \ker(A - a_n)$ can be finite or infinite) whose elements are eigenkets of B, i.e.,

$$B|u_n^m\rangle = b_n^m |u_n^m\rangle, \qquad m = 1, 2, \dots, d_n. \tag{4.21}$$ `Bbasis`

Note that we also have

$$A|u_n^m\rangle = a_n |u_n^m\rangle, \qquad m = 1, 2, \dots, d_n, \tag{4.22}$$ `Abasis`

since by construction $|u_n^m\rangle \in \ker(A - a_n)$ for all m. The set

$$\left\{ |u_n^m\rangle : m = 1, 2, \dots, d_n, \ n = 1, 2, \dots \right\} \tag{4.23}$$ `ABbasis`

is then an orthonormal basis of $\mathcal{H}$. Indeed, this set is complete (since A has only point spectrum). Moreover, two of its elements $|u_n^m\rangle$ and $|u_p^q\rangle$ with $p \neq n$ are automatically orthogonal (since they are eigenvectors of A with different eigenvalues $a_n \neq a_p$), while if $p = n$ we have

$$\langle u_n^m | u_n^q \rangle = \delta_{mq},$$

as $|u_n^m\rangle$ and $|u_n^q\rangle$ belong by construction to an orthonormal basis of $\ker(A - a_n)$. By Eqs. (4.21) and (4.22), each basis vector $|u_n^m\rangle$ is a simultaneous eigenket of both A and B with eigenvalues a_n and b_n^m, respectively. Thus the set (4.23) is an orthonormal basis of $\mathcal{H}$ whose elements are *common eigenvectors* of the commuting operators A and B. We have thus proved the following important result:

> If A and B are two compatible observables having only point spectrum, there is an orthonormal basis of $\mathcal{H}$ whose elements are common eigenvectors of A and B.

Note that we can relabel the elements of the basis (4.23) as

$$|ab; \lambda\rangle \tag{4.24}$$ `anbmk`

where $a \in \sigma_p(A)$, $b \in \sigma_p(B)$,

$$\ker(A - a) \cap \ker(B - b) \neq \{0\}$$

(i.e., there are common eigenkets of A and B with respective eigenvalues a and b) and the additional quantum number λ ranges from 1 to the number of linearly independent simultaneous eigenvectors of A and B with respective eigenvalues a and b.

The above result is easily generalized by induction to any finite number of compatible observables $A_1, \dots, A_N$ (i.e., such that $[A_i, A_j] = 0$ for $i = 1, j = 1, \dots, N$) having only point spectrum. In other words:

> If $A_1, \dots, A_N$ are N compatible observables having only point spectrum, there is an orthonormal basis of $\mathcal{H}$ whose elements are common eigenvectors of the latter operators.

As in the case of two commuting operators, the elements of the orthonormal basis of common eigenvectors of the compatible observables $\{A_1, \dots, A_N\}$ can be labeled as

$$|a_1 \cdots a_N; \lambda\rangle,$$

where

$$A_i |a_1 \ldots a_N; \lambda\rangle = a_i |a_1 \ldots a_N; \lambda\rangle, \qquad i = 1, \ldots, N$$

and the quantum number λ runs from 1 to the dimension of the common eigenspace

$$\ker(A_1 - a_1) \cap \ker(A_2 - a_2) \cap \cdots \cap \ker(A_N - a_n) \equiv \bigcap_{i=1}^{N} \ker(A_i - a_i).$$

The previous considerations motivate the following definition:

Definition 4.7. A **complete set of commuting observables** (or CSCO for short) is a set of N compatible (i.e., mutually commuting) observables having only point spectrum whose common eigenspaces are all *one-dimensional*.

Remark. It is usually understood that a CSCO is actually a *minimal* set $\{A, B, \ldots\}$ of compatible observables satisfying the previous definition, in the sense that if we remove one operator from the set the resulting set is no longer a CSCO. ∎

If $\{A_1, \ldots, A_N\}$ is a CSCO, there is a basis of the Hilbert space $\mathcal{H}$ whose elements are *uniquely determined* (up to a trivial phase factor) by the common eigenvalues $a_1, \ldots, a_N$ of the observables A_i in the set. In other words, the basis elements (4.25) can be labeled simply as

$$|a_1 \cdots a_N\rangle, \tag{4.25}$$

where no degeneracy label λ is needed since the common eigenspaces of the operators $A_1, \ldots, A_N$ in the CSCO are by hypothesis one-dimensional. It is also clear that the converse of this statement is also true (if the given set of compatible observables is also minimal). Recall that the spectrum of a self-adjoint operator is finite or countable, and hence the common eigenvalues $a_1, \ldots, a_n$ labeling the basis states (4.25), usually called **quantum numbers,**, also make up a countable (usually discrete) set. Moreover, by the very definition of a CSCO, these quantum numbers *uniquely determine the basis state*. In other words, if $\{A_1, \ldots, A_N\}$ is a CSCO then there is a *unique* basis (up to trivial phase factors) of common eigenvectors of the latter operators.

Example 4.8. Consider a (spinless) particle moving in one dimension subject to a (smooth) potential $V(x)$ such that

$$\lim_{x \to \pm\infty} V(x) = +\infty,$$

whose Hilbert space is $\mathcal{H} = L^2(\mathbb{R})$. In this case the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \partial_x^2 + V(x)$$

is a self-adjoint operator having no continuous spectrum (see the discussion in Section 3.5). Hence there exists an orthonormal basis of eigenvectors of H, i.e., of energy eigenstates. Since $\mathcal{H}$ is infinite-dimensional, the spectrum of H is an infinite (countable) set. The spectrum is bounded below by $\min V(x)$, and it has no accumulation points (since any such point would belong to the continuous spectrum, which we know to be empty). By the Bolzano–Weierstrass theorem, $\sigma(H)$ cannot be bounded above (since otherwise it would have an accumulation point). Thus $\sigma(H)$ is an infinite increasing succession of energies

$$E_1 < E_2 < \cdots < E_n < \cdots,$$

with $E_1 > \min V(x)$ and

$$\lim_{n \to \infty} E_n = +\infty.$$

Moreover, since the eigenvalues of a one-dimensional Hamiltonian are *non-degenerate,* for each energy E_n there is only one eigenstate $|E_n\rangle$ satisfying

$$H|E_n\rangle = E_n|E_n\rangle, \qquad \langle E_n|E_n\rangle = 1,$$

up to an irrelevant phase factor. Hence the set

$$\big\{|E_n\rangle : n = 0, 1, \dots\big\}$$

is an orthonormal basis of $\mathcal{H}$, and thus $\{H\}$ is in this case a CSCO. Note that if either limit

$$\lim_{x\to\pm\infty} V(x)$$

(or both) is finite the continuous spectrum of H is non-empty, and therefore $\{H\}$ is no longer a CSCO. In fact, in this case even if the point spectrum is also non-empty the set of *genuine* eigenfunctions of H is not *complete* in $\mathcal{H}$, and thus there is no orthonormal basis of $\mathcal{H}$ all of whose elements are genuine eigenfunctions of H.

Remark. It is sometimes convenient to relax the definition of CSCO, allowing for the commuting operators involved to have a non-empty continuous spectrum. In this case, however, it is necessary to use generalized orthonormal bases. For instance, with this more general definition the set $\{P_x, P_y, P_z\}$ is a CSCO for a particle moving in three-dimensional space, since the operators P_x, P_y, P_z commute with one another, and there is a generalized orthonormal basis labeled unambiguously by the common eigenvalues p_x, p_y, p_z of these operators, namely the momentum basis

$$\Big\{|p_x p_y p_z\rangle := (2\pi\hbar)^{-3/2}e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} : \mathbf{p} \equiv (p_x, p_y, p_z) \in \mathbb{R}^3\Big\}. \qquad \blacksquare$$

Exercise 4.4. If $H = \mathbf{P}^2/(2m)$, is the set $\{H, P_x, P_y\}$ a (generalized) CSCO for a particle moving in three-dimensional space?

Solution. To begin with, the three operators H, P_x, P_y commute with one another. Secondly, a state $|\psi\rangle$ is a common (generalized) eigenvector of H, P_x, P_y with eigenvalues E, p_x , and p_y provided that

$$H|\psi\rangle = E|\psi\rangle, \qquad P_x|\psi\rangle = p_x|\psi\rangle, \qquad P_y|\psi\rangle = p_y|\psi\rangle.$$

Solving the last two equations we easily obtain

$$|\psi\rangle = f(z)\, e^{\frac{i}{\hbar}(xp_x+yp_y)},$$

with $f(z)$ an arbitrary (smooth) function of the z variable only. Imposing that $|\psi\rangle$ be an eigenfunction of H with eigenvalue E we obtain

$$H|\psi\rangle = \frac{1}{2m}e^{\frac{i}{\hbar}(xp_x+yp_y)}\big[(p_x^2 + p_y^2)f(z) - \hbar^2 f''(z)\big] = Ef(z)e^{\frac{i}{\hbar}(xp_x+yp_y)},$$

or equivalently

$$f''(z) + \frac{1}{\hbar^2}\big(2mE - p_x^2 - p_y^2\big)f(z) = 0.$$

For this equation to have a bounded solution the factor multiplying $f(z)$ must be a non-negative number $p_z^2/\hbar^2$, with

$$p_z = \sqrt{2mE - p_x^2 - p_y^2},$$

in which case

$$f(z) = ae^{\frac{i}{\hbar}zp_z} + be^{-\frac{i}{\hbar}zp_z}.$$

Thus $|\psi\rangle$ is a linear combination of the two linearly independent functions

$$e^{\frac{i}{\hbar}(xp_x+yp_y\pm zp_z)}.$$

Since the common eigenspaces of H, P_x, and P_y are *two-dimensional*, the set $\{H, P_x, P_y\}$ is *not* a (generalized) CSCO.

Exercise 4.5. Let A be a constant of motion, and suppose that $|\psi(0)\rangle$ is an eigenstate of A. Examine under what conditions $|\psi(t)\rangle = |\psi(0)\rangle$ for all t (up to a trivial phase).

Solution. Since by hypothesis A commutes with the Hamiltonian H, H leaves invariant $\ker(A - a)$, where $A|\psi(0)\rangle = a|\psi(0)\rangle$. We can therefore construct an orthonormal basis of $\ker(A - a)$ with elements

$$|E_n; k\rangle,$$

where $E_n \neq E_m$ if $n \neq m$,

$$H|E_n; k\rangle = E_n|E_n; k\rangle$$

and the index k ranges from 1 to the dimension of the common eigenspace of H and A with respective eigenvalues E_n and a. Since, by hypothesis,

$$|\psi(0)\rangle = \sum_{n,k} c_{nk}|E_n; k\rangle,$$

applying the time evolution operator $e^{-\frac{i}{\hbar}tH}$ to $|\psi(0)\rangle$ we obtain

$$|\psi(t)\rangle = \sum_{n,k} c_{nk}e^{-\frac{i}{\hbar}tE_n}|E_n; k\rangle = \sum_n e^{-\frac{i}{\hbar}tE_n}\sum_k c_{nk}|E_n; k\rangle.$$

Since by construction $E_n \neq E_m$ for $n \neq m$, the state $|\psi(t)\rangle$ will be time dependent unless the above sum contains only a single energy, say E_m, i.e., if $H = E_m$ on $\ker(A - a)$. Indeed, if this is the case

$$|\psi(0)\rangle = \sum_k c_k|E_m; k\rangle \implies |\psi(t)\rangle = e^{-\frac{i}{\hbar}tE_m}\sum_k c_k|E_m; k\rangle = e^{-\frac{i}{\hbar}tE_m}|\psi(0)\rangle,$$

which as we know represents the same quantum state as $|\psi(0)\rangle$. In particular, this will trivially occur if the eigenvalue a of A is *non-degenerate,* since in this case $\ker(A - a)$ is one-dimensional.

Remark. Another useful relaxation of the requirements for a set $\{A_1, \ldots, A_N\}$ of mutually commuting observables to be a CSCO arises if we drop the condition that there be an orthonormal basis of the system's Hilbert space $\mathcal{H}$ of joint eigenvectors of the operators A_i, demanding only that the common eigenspaces to all of these operators be *one-dimensional*. In this way we can still label unambiguously the common eigenvectors of the operators in the set using their eigenvalues (and no additional quantum numbers), as in Eq. (4.25). Moreover, the set of common eigenvectors of the operators $A_1, \ldots, A_N$ is an *orthonormal set*. Indeed, two elements $|a_1 \cdots a_N\rangle$ and $|a'_1 \cdots a'_N\rangle$ of this set differ at least in one of the quantum numbers, say $a_i \neq a'_i$, which implies that

$$\langle a_1 \cdots a_N|a'_1 \cdots a'_N\rangle = 0,$$

as $|a_1 \cdots a_N\rangle$ and $|a'_1 \cdots a'_N\rangle$ are eigenvectors of the self-adjoint operator A_i with different eigenvalues. Thus the set of common eigenvectors $|a_1 \cdots a_N\rangle$ of the compatible observables $\{A_1, \ldots, A_N\}$ is an orthonormal basis of the (closure of) the linear subspace $\mathcal{H}_0$ spanned by the common eigenvectors of the latter operators. Since the elements of this basis are uniquely labeled by the eigenvalues of the operators in the set $\{A_1, \ldots, A_N\}$, this set is a CSCO for the Hilbert space $\mathcal{H}_0$. ∎

exa.Lcomrel

Example 4.9. Consider the Hamiltonian of the hydrogen atom

$$H = \frac{\mathbf{P}^2}{2m} + \frac{q^2}{4\pi\varepsilon_0 R},$$

where $q > 0$ is the proton's charge and m is the electron's mass. As we saw in Exercise 4.3, H commutes with the three components L_i of the angular momentum $\mathbf{L}$. These components, however, do not commute with each other. For instance,

$$[L_1, L_2] = [X_2 P_3 - X_3 P_2, X_3 P_1 - X_1 P_3] = [X_2 P_3, X_3 P_1] + [X_3 P_2, X_1 P_3]$$
$$= X_2[P_3, X_3]P_1 + X_1[X_3, P_3]P_2 = i\hbar(X_1 P_2 - X_2 P_1) = i\hbar L_3,$$

and in general

$$[L_j, L_k] = i\hbar \sum_{n=1}^{3} \varepsilon_{jkn} L_n, \tag{4.26}$$

Lcomm

where ε_{jkn} is the *Levi–Civita* antisymmetric symbol defined by

$$\varepsilon_{ijk} = \begin{cases} 1, & (i, j, k) \text{ even (cyclic) permutation of } (1, 2, 3) \\ -1, & (i, j, k) \text{ odd permutation of } (1, 2, 3) \\ 0, & \text{otherwise.} \end{cases}$$

On the other hand, each component L_i of $\mathbf{L}$ commutes with $\mathbf{L}^2 \equiv L_1^2 + L_2^2 + L_3^2$. For instance,

$$[L_1, \mathbf{L}^2] = [L_1, L_2^2 + L_3^2] = L_2[L_1, L_2] + [L_1, L_2]L_2 + L_3[L_1, L_3] + [L_1, L_3]L_3$$
$$= i\hbar (L_2 L_3 + L_3 L_2 - L_3 L_2 - L_2 L_3) = 0.$$

Thus H, $\mathbf{L}^2$, and any component L_i of $\mathbf{L}$ are a set of mutually commuting observables. We shall show in Section 6.8 that the joint eigenspaces of these operators are one-dimensional. However, the set $\{H, \mathbf{L}^2, L_i\}$ is *not* a CSCO, since the (closure of the) span of the common eigenvectors of the operators H, $\mathbf{L}^2$ and L_i is a *proper* subspace of the whole Hilbert space $\mathcal{H}$. In fact, this subspace is the (closure of the) subspace spanned by the bound states of the Hamiltonian H. It is properly contained in $\mathcal{H}$, since the spectrum of the hydrogen atom has also a *continuous* part $[0, \infty)$.

5 The harmonic oscillator

5.1 Power series solution

Consider a particle of mass m moving in one dimension subject to the potential $V(x)$, and suppose that x_0 is a *stable equilibrium* with $V''(x_0) \neq 0$. Since the equilibrium x_0 is stable it must be a local minimum of the potential, and thus $V''(x_0) > 0$. Assuming, w.l.o.g., that $x_0 = 0$ and $V(0) = 0$, we can the write[1]

$$V(x) = \frac{1}{2} kx^2 + o(x^2), \qquad k := V''(0) > 0.$$

Thus in a sufficiently small neighborhood of the origin the classical Hamiltonian (in Cartesian coordinates) is

$$H = \frac{p^2}{2m} + \frac{1}{2} kx^2, \tag{5.1}$$

and Hamilton's canonical equations read

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \qquad \dot{p} = -\frac{\partial H}{\partial x} = -kx,$$

which yield the following linear homogeneous second-order differential equation for the coordinate x:

$$m\ddot{x} + kx = 0.$$

As is well known, the general solution of this equation is

$$x = a\cos(\omega x) + b\sin(\omega x),$$

with a, b arbitrary constants and

$$\omega := \sqrt{\frac{k}{m}}. \tag{5.2}$$

The motion is thus oscillatory, with circular frequency ω given by the previous equation.

Let us now study the quantum version of the previous problem, i.e., let us determine the energy spectrum of the *one-dimensional quantum harmonic oscillator* Hamiltonian

$$H = \frac{P^2}{2m} + \frac{1}{2} kX^2 \equiv \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2. \tag{5.3}$$

Note that, by the previous discussion, this Hamiltonian will approximately describe the qualitative behavior of a particle subject to a potential with a stable equilibrium position if the particle's energy is close to the value of the potential at the equilibrium.

Since, in the notation of Section 3.5, the harmonic oscillator potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 \tag{5.4}$$

---

[1]By $o(s)$ we mean any function of the variable s such that $o(s)/s$ tends to 0 as $s \to 0$. Intuitively, $|o(s)|$ is "much smaller" than $|s|$ when s tends to zero.

has limits $V_\pm = \infty$ at $\pm\infty$, from Example 3.3 we know that there is only point spectrum. Moreover, $\sigma_p(H)$ is a countably infinite, discrete set strictly bounded below by $\min V(x) = 0$. In other words, we can write

$$\sigma_p(H) = \{E_n : n = 0, 1, \dots\},$$

with

$$0 < E_0 < E_1 < \cdots < E_n < \cdots, \qquad \text{with} \quad \lim_{n\to\infty} E_n = \infty.$$

The allowed energies E_n can be determined from the Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x), \tag{5.5}$$ `HOSch`

which we can also write as

$$-\psi''(x) + \frac{x^2}{\ell^4}\psi(x) = \varepsilon\psi(x), \qquad \varepsilon := \frac{2mE}{\hbar^2}, \tag{5.6}$$ `HOSchep2`

with

$$\ell := \sqrt{\frac{\hbar}{m\omega}}$$

a constant with length dimensions. In order to further simplify Eq. (5.6), it is convenient to introduce the dimensionless variable

$$s := \frac{x}{\ell}$$

and, with a slight abuse of notation, regard ψ as a function of s. Since

$$\partial_x = \frac{1}{\ell}\partial_s,$$

the function $\psi(s)$ satisfies the differential equation

$$\psi''(s) + (\lambda - s^2)\psi(s) = 0, \tag{5.7}$$ `HOSchep`

where the prime now denotes differentiation with respect to s and

$$\lambda := \ell^2\varepsilon = \frac{\hbar}{m\omega}\frac{2m}{\hbar^2}E = \frac{2E}{\hbar\omega} > 0 \tag{5.8}$$ `laeqHO`

a dimensionless parameter. For E to be in the spectrum of H, we need $\psi(s)$ to be square integrable on the real line $\mathbb{R}$ (with respect to s, since x and s are proportional); in particular, we must have

$$\lim_{s\to\pm\infty}\psi(s) = 0. \tag{5.9}$$ `bcHO`

To determine the behavior of the solutions of Eq. (5.7) at $s = \pm\infty$, we note that for $|s| \to \infty$ the term $\lambda\psi$ is negligible compared to $s^2\psi$. Hence for $|s| \to \infty$ we must have

$$\psi''(s) \simeq s^2\psi(s), \tag{5.10}$$ `appSchosc`

which suggests that (up to an irrelevant multiplicative constant)

$$\psi(s) \underset{|s|\to\infty}{\sim} e^{-as^2}$$

for suitable $a \in \mathbb{R}$. Since

$$\partial_s e^{-as^2} = -2as e^{-as^2}, \qquad \partial_s^2 e^{-as^2} = (4a^2 s^2 - 2a) e^{-as^2} \simeq 4a^2 s^2 e^{-as^2},$$

substituting e^{-as^2} into Eq. (5.10) we obtain

$$4a^2 s^2 e^{-as^2} \simeq s^2 e^{-as^2} \quad \Longrightarrow \quad a = \pm \frac{1}{2}.$$

This suggests that for $|s| \to \infty$ the solutions of Eq. (5.7) behave as

$$|\psi(s)| \sim e^{\pm \frac{s^2}{2}},$$

or, more generally, as

$$|\psi(s)| \sim |s|^k e^{\pm \frac{s^2}{2}}$$

with k a nonnegative integer, since $s^k e^{\pm \frac{s^2}{2}}$ is also an approximate solution of Eq. (5.10):

$$\partial_s^2 \left(s^k e^{\pm \frac{s^2}{2}} \right) = \left(s^2 + o(s^2) \right) s^k e^{\pm \frac{s^2}{2}}$$

as $|s| \to \infty$. From the boundary condition (5.9) we deduce that for $\psi(s)$ to be an eigenstate of the harmonic oscillator Hamiltonian it must behave as $s^k e^{-\frac{s^2}{2}}$ for some nonnegative integer k. This suggests performing the change of variable

$$\psi(s) = e^{-\frac{s^2}{2}} u(s), \tag{5.11}$$ `cvH0`

under which Eq. (5.7) transforms into

$$u''(s) - 2s u'(s) + (\lambda - 1) u(s) = 0. \tag{5.12}$$ `ueqH0`

Since the coefficients of this linear differential equation are polynomials, from the theory of such equations it follows that its solutions are analytic functions on the whole real line, i.e., that $u(s)$ admits a power series expansion

$$u(s) = \sum_{k=0}^{\infty} a_k s^k \tag{5.13}$$ `useriesH0`

with an infinite radius of convergence. The coefficients a_n can be computed (up to an overall irrelevant multiplicative constant) by differentiating term by term the previous expansion and substituting into Eq. (5.12). Proceeding in this way we obtain

$$\sum_{k=2}^{\infty} k(k-1) a_k s^{k-2} + \sum_{k=0}^{\infty} (\lambda - 1 - 2k) a_k s^k = \sum_{k=0}^{\infty} \left[(k+1)(k+2) a_{k+2} + (\lambda - 1 - 2k) a_k \right] s^k = 0,$$

which yields the following recursion relation for the coefficients a_k:

$$a_{k+2} = \frac{2k+1-\lambda}{(k+1)(k+2)} a_k, \qquad k = 0, 1, \ldots . \tag{5.14}$$ `rrH0`

Since the latter equation relates a_{k+2} with a_k, the series of the even and odd coefficients

$$u_0(s) = \sum_{k=0}^{\infty} a_{2k} s^{2k}, \qquad u_1(s) = \sum_{k=0}^{\infty} a_{2k+1} s^{2k+1} \tag{5.15}$$ `ueuoH0`

are each of them a solution of the differential equation (5.12), respectively even and odd in s. This is as expected, since the harmonic oscillator potential is an even function of its variable, and thus it has a basis

of solutions with well-defined parity (see Example 3.3). The recursion relations satisfied by the even and odd coefficients can be easily obtained from Eq. (5.14). Indeed, calling

$$b_k^i = a_{2k+i}, \qquad \text{with} \quad i = 0, 1,$$

we have

$$u_i(s) = \sum_{k=0}^{\infty} b_j^i s^{2j+i}$$

and

$$b_{k+1}^i = a_{2k+i+2} = \frac{4k + 2i + 1 - \lambda}{(2k + i + 1)(2k + i + 2)} a_{2k+i} = \frac{4k + 2i + 1 - \lambda}{2(k + 1)(2k + 2i + 1)} b_k^i. \qquad (5.16) \quad \boxed{\text{ueorr}}$$

From Eq. (5.14) (or the previous equation) it also follows that if λ is not an odd positive integer neither series (5.15) terminates. In this case we have

$$\frac{b_{k+1}^i}{b_k^i} = \frac{4k + 2i + 1 - \lambda}{2(k + 1)(2k + 2i + 1)} \underset{k \to \infty}{\sim} \frac{1}{k}. \qquad (5.17) \quad \boxed{\text{bikp1k}}$$

On the other hand, if

$$e^{s^2} = \sum_{k=0}^{\infty} \frac{s^{2k}}{k!} \equiv \sum_{k=0}^{\infty} c_k s^{2k}$$

then

$$\frac{c_{k+1}}{c_k} = \frac{1}{k + 1} \underset{k \to \infty}{\sim} \frac{1}{k}.$$

It is thus to be expected that when λ is *not* an odd positive integer the solutions of Eq. (5.12) behave as

$$|u_i(s)| \underset{|s| \to \infty}{\sim} e^{s^2},$$

and therefore

$$|\psi^{(i)}(s)| \underset{|s| \to \infty}{\sim} e^{\frac{s^2}{2}},$$

where

$$\psi^{(i)}(s) = u_i(s) e^{-\frac{s^2}{2}}$$

is the solution of the Schrödinger equation (5.7) with parity $(-1)^i$. More rigorously, it can be shown that in this case for sufficiently large $|s|$ we have

$$|\psi^{(i)}(s)| > C |s|^i e^{\frac{s^2}{4}}, \qquad i = 0, 1; \qquad (5.18) \quad \boxed{\text{HOest}}$$

see Exercise 5.1 for details. Hence when λ is *not* an odd positive integer neither $\psi^{(0)}$ nor $\psi^{(1)}$ are normalizable. We thus conclude that *when λ is* not *an odd positive integer Eq. (5.5) has no square integrable solutions.*

Suppose, on the other hand, that

$$\lambda = 2n + 1, \qquad \text{with} \quad n = 0, 1, \dots,$$

is a positive odd integer. If $n = 2m$ (with $m = 0, 1, \dots$) is *even*, then $\lambda = 4m + 1$, and the recursion relation (5.16) reads

$$b_{k+1}^i = \frac{2(k - m) + i}{(k + 1)(2k + 2i + 1)} b_k^i, \qquad i = 0, 1.$$

Thus in this case the series for the *odd* solution u_1 does not terminate, whence it follows (reasoning as above) that this solution is not normalizable. On the other hand, the *even* solution u_0 reduces to a polynomial of degree $2m$, since from the recursion relation with $k = m$ we obtain

$$b^0_{m+1} = 0,$$

which in turn implies that $b^0_k = 0$ for all $k \geqslant m + 1$. In this case

$$b^0_{k+1} = -\frac{2(m-k)}{(2k+1)(k+1)} b^0_k,$$

and therefore (taking $b^0_0 = 1$)

$$b^0_j = \frac{m!}{(m-j)!} \frac{(-1)^j 2^j}{(2j-1)!!\, j!} = \frac{m!}{(m-j)!} \frac{(-1)^j 2^{2j}}{(2j)!}, \qquad 0 \leqslant j \leqslant m,$$

whence

$$u_0(s) = \sum_{j=0}^m (-1)^j \frac{m!}{(m-j)!} \frac{(2s)^{2j}}{(2j)!} \equiv P_{2m}(s). \qquad (5.19) \quad \boxed{\text{uosol}}$$

Hence the corresponding solution

$$\psi^{(0)}(s) = u_0(s) \mathrm{e}^{-s^2/2} = P_{2m}(s) \mathrm{e}^{-s^2/2}$$

of the Schrödinger equation (5.7) is normalizable, and $\lambda = 4m + 1$ is therefore an eigenvalue of the latter equation. From Eq. (5.8) we then conclude that the numbers

$$E_{2m} = \left(2m + \frac{1}{2}\right) \hbar\omega, \qquad m = 0, 1, \ldots,$$

are eigenvalues of the original Schrödinger equation (5.5), with corresponding (unnormalized) eigenfunctions

$$\varphi_{2m}(x) = P_{2m}(s) \mathrm{e}^{-s^2/2}, \qquad s = \frac{x}{\ell} = \sqrt{\frac{m\omega}{\hbar}}\, x.$$

Likewise, when $\lambda = 2n + 1$ and $n = 2m + 1$ with $m = 0, 1, \ldots$ is *odd*, we have $\lambda = 4m + 3$ and the recursion relation (5.16) becomes

$$b^i_{k+1} = -\frac{2(m-k)+1-i}{(k+1)(2k+2i+1)} b^i_k, \qquad i = 0, 1.$$

In this case the even solution u_0 is an infinite series, and therefore is not normalizable, while the *odd* one u_1 reduces to a polynomial of degree $2m + 1$. Indeed, since

$$b^1_{k+1} = -\frac{2(m-k)}{(k+1)(2k+3)} b^i_k,$$

we have $b^i_j = 0$ for $j > m$, and (taking $b^1_0 = 1$)

$$b^1_j = \frac{m!}{(m-j)!} \frac{(-1)^j 2^j}{(2j+1)!!\, j!} = \frac{m!}{(m-j)!} \frac{(-1)^j 2^{2j}}{(2j+1)!}, \qquad 0 \leqslant j \leqslant m.$$

Hence

$$u_1(s) = \sum_{j=0}^m (-1)^j \frac{m!}{(m-j)!} \frac{(2s)^{2j+1}}{(2j+1)!} \equiv P_{2m+1}(s), \qquad (5.20) \quad \boxed{\text{uesol}}$$

so that

$$\psi^{(1)}(s) = u_1(s) \mathrm{e}^{-s^2/2} = P_{2m+1}(s) \mathrm{e}^{-s^2/2}$$

is a normalizable solution of the Schrödinger equation (5.7) with eigenvalue $\lambda = 4m + 3$. By Eq. (5.8), the numbers

$$E_{2m+1} = \left(2m + \frac{3}{2}\right)\hbar\omega, \qquad m = 0, 1, \ldots,$$

are eigenvalues of the original Schrödinger equation (5.5), with corresponding (unnormalized) eigenfunctions

$$\varphi_{2m+1}(x) = P_{2m+1}(s)e^{-s^2/2}, \qquad s = \sqrt{\frac{m\omega}{\hbar}}\,x.$$

We have thus established the following important result:

> The eigenvalues of the Schrödinger equation (5.5) are the numbers
>
> $$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, \ldots, \qquad (5.21)$$
>
> with corresponding (unnormalized) eigenfunctions
>
> $$\varphi_n(x) = P_n(s)e^{-s^2/2}, \qquad s = \sqrt{\frac{m\omega}{\hbar}}\,x,$$
>
> where $P_n(s)$ is the n-th degree polynomial defined by Eqs. (5.19)-(5.20).

EnHO

---

exe.HOest

Exercise 5.1. Prove Eq. (5.18).

Solution. Indeed, suppose that λ is not an odd positive integer, so neither solution $u_i(x)$ (with $i = 0, 1$) reduces to a polynomial. From Eq. (5.17) we then deduce that

$$\frac{b^i_{k+1}}{b^i_k} = \frac{c_{k+1}}{c_k}\frac{4k + 2i + 1 - \lambda}{2(2k + 2i + 1)} \neq 0, \qquad \forall k = 0, 1, \ldots. \qquad (5.22)$$

3bs

Since

$$\lim_{k\to\infty}\frac{4k + 2i + 1 - \lambda}{2(2k + 2i + 1)} = 1,$$

if $\alpha \in (0, 1)$ there exists an integer $N > 0$ such that

$$\frac{4k + 2i + 1 - \lambda}{2(2k + 2i + 1)} > \alpha, \qquad \forall k \geqslant N.$$

It follows that

$$\frac{b^i_{k+1}}{b^i_k} > \alpha\frac{c_{k+1}}{c_k} > 0, \qquad \forall k \geqslant N,$$

and since b^i_{k+1}/b^i_k is positive for sufficiently large k we can assume that

$$\frac{b^i_j}{b^i_N} = \frac{b^i_j}{b^i_{j-1}}\cdots\frac{b^i_{N+1}}{b^i_N} > \frac{\alpha c_j}{c_{j-1}}\cdots\frac{\alpha c_{N+1}}{c_N} = \alpha^{j-N}\frac{c_j}{c_N}, \qquad \forall j > N.$$

This implies that

$$\frac{1}{b^i_N}\sum_{j=N+1}^{\infty}b^i_j s^{2j} = \frac{1}{b^i_N}\left(s^{-i}u_i(s) - p_i(s)\right) > \frac{\alpha^{-N}}{c_N}\sum_{j=N+1}^{\infty}c_j(\alpha s^2)^j = \frac{\alpha^{-N}}{c_N}\left(e^{\alpha s^2} - q(s)\right),$$

with $p_i(s)$ and $q(s)$ polynomials of degree up to $2N$ in s. We can rewrite the previous relation as

$$\frac{1}{b_N^i} s^{-i} u_i(s) > \frac{\alpha^{-N}}{c_N} \left(e^{\alpha s^2} - h_i(s) \right),$$

where again h_i is a polynomial of degree up to $2N$ in s. On the other hand, since $\alpha > 0$ for sufficiently large $|s|$ we have

$$|h_i(s)| < \frac{1}{2} e^{\alpha s^2}, \qquad |s| \gg 1,$$

and therefore

$$\frac{1}{b_N^i} s^{-i} u_i(s) > \frac{\alpha^{-N}}{2c_N} e^{\alpha s^2}, \qquad |s| \gg 1,$$

which is easily seen to imply (since the RHS is positive) that

$$\left| u_i(s) \right| > \frac{|b_N^i|}{2\alpha^N c_N} |s|^i e^{\alpha s^2} \equiv C_\alpha |s|^i e^{\alpha s^2},$$

with

$$C_\alpha = \frac{|b_N^i|}{2\alpha^N c_N} > 0.$$

It follows that

$$\left| \psi^{(i)}(s) \right| = |u_i(s)| e^{-\frac{s^2}{2}} > C_\alpha |s|^i e^{(\alpha - \frac{1}{2})s^2},$$

from which Eq. (5.18) follows taking $\alpha = 3/4$.

5.2 Hermite polynomials

The polynomials $P_n(s)$ defined by Eqs. (5.19)-(5.20) are proportional to the classical *Hermite polynomials*[2] $H_n(s)$, defined by

$$H_n(s) = \sum_{k=0}^{\lfloor n/2 \rfloor} \frac{(-1)^k n!}{k!(n-2k)!} (2s)^{n-2k}, \tag{5.23}$$

where $\lfloor x \rfloor$ denotes the integer part of the real number x (i.e., the largest integer less than or equal to x). Indeed, if $n = 2m + i$ with $i = 0, 1$ we have

$$P_n(s) = \sum_{j=0}^{m} (-1)^j \frac{m!}{(m-j)!} \frac{(2s)^{2j+i}}{(2j+i)!} = 2^{-i} \sum_{k=0}^{m} (-1)^{m-k} \frac{m!}{k!(2m+i-2k)!} (2s)^{2m+i-2k}$$

$$= 2^{-i}(-1)^m \sum_{k=0}^{m} (-1)^k \frac{m!}{k!(n-2k)!} (2s)^{n-2k} = 2^{-i}(-1)^m \frac{m!}{n!} H_n(s).$$

Hence for all $n = 0, 1, \ldots$ the unnormalized eigenfunction of the harmonic oscillator Hamiltonian (5.3) with eigenvalue $\left(n + \frac{1}{2}\right)\hbar\omega$ can be taken as

$$\varphi_n(x) = H_n(s) e^{-s^2/2}, \qquad s = \sqrt{\frac{m\omega}{\hbar}} x.$$

The functions $\varphi_n(x)$ with $n = 0, 1, \ldots$ are orthogonal to each other (since they are eigenfunctions with different eigenvalues of the self-adjoint operator H), but they are not normalized. In fact, from Eq. (5.25)

---

[2] See exercises 5.2-5.4 for the main properties of the Hermite polynomials.

in Exercise 5.25 we easily obtain

$$\int_{-\infty}^{\infty} dx \, |\varphi_n(x)|^2 = \int_{-\infty}^{\infty} dx \, e^{-s^2} H_n^2(s) = \ell \int_{-\infty}^{\infty} ds \, e^{-s^2} H_n^2(s) = 2^n n! \sqrt{\pi} \, \ell.$$

It follows that the functions

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} (2^n n!)^{-1/2} H_n(s) e^{-s^2/2}, \qquad s = \sqrt{\frac{m\omega}{\hbar}} \, x. \tag{5.24}$$

`psinHOnorm`

make up an orthonormal set of eigenfunctions of H, with

$$H\psi_n = \left(n + \frac{1}{2}\right)\hbar\omega\psi_n.$$

From the general discussion in Section 3.5 it then follows that the eigenfunctions (5.24) are an *orthonormal basis* of the Hilbert space $L^2(\mathbb{R})$.

The *generating function* of the Hermite polynomials is defined by

$$F(x,t) := \sum_{n=0}^{\infty} H_n(x)\frac{t^n}{n!}.$$

This function can be easily evaluated using the definition (5.23) of the Hermite polynomials. Indeed,

$$F(x,t) = \sum_{n=0}^{\infty} \sum_{k=0}^{\lfloor n/2 \rfloor} \frac{(-1)^k}{k!(n-2k)!}(2x)^{n-2k} \, t^n = \sum_{m=0}^{\infty} \frac{(2tx)^m}{m!} \sum_{k=0}^{\infty} \frac{(-t^2)^k}{k!} = e^{2tx}e^{-t^2},$$

where in the second equality we have changed the summation indices (n,k) to (m,k) with $m = n - 2k$. We thus have

$$F(x,t) = e^{2tx-t^2}.$$

The main properties of Hermite polynomials can be readily established with the help of the generating function, as we shall show in the following exercises.

Exercise 5.2. Show that

$$\int_{-\infty}^{\infty} dx \, e^{-x^2} H_n(x) H_m(x) = 2^n n! \sqrt{\pi} \, \delta_{nm}. \tag{5.25}$$

`normHn`

Solution. Let us compute the integral

$$I(s,t) := \int_{-\infty}^{\infty} dx \, e^{-x^2} F(x,s) F(x,t) = \sum_{m,n=0}^{\infty} \frac{s^n t^m}{n! \, m!} \int_{-\infty}^{\infty} dx \, e^{-x^2} H_n(x) H_m(x)$$

using the previous explicit formula for the generating function:

$$I(s,t) = \int_{-\infty}^{\infty} dx \, e^{-x^2} e^{2sx-s^2} e^{2tx-t^2} = e^{-(s^2+t^2)} \int_{-\infty}^{\infty} dx \, e^{-x^2+2(s+t)x}$$

$$= e^{-(s^2+t^2)} \int_{-\infty}^{\infty} dx \, e^{-(x-s-t)^2} e^{(s+t)^2} = e^{2st} \int_{-\infty}^{\infty} dx \, e^{-(x-s-t)^2}$$

$$= \sqrt{\pi} \, e^{2st} = \sqrt{\pi} \sum_{n=0}^{\infty} \frac{(2st)^n}{n!} \equiv \sum_{m,n=0}^{\infty} \frac{2^n \sqrt{\pi}}{n!} \delta_{nm} s^n t^m.$$

Equating the coefficient of $s^n t^m$ in both expressions for $I(s,t)$ we immediately obtain Eq. (5.25).

Exercise 5.3. Prove *Rodrigues' formula*

$$H_n(x) = (-1)^n e^{x^2} \partial_x^n (e^{-x^2}). \tag{5.26}$$

Solution. From the definition of the generating function it follows that

$$H_n(x) = \partial_t^n F(x,t)\Big|_{t=0} = \partial_t^n e^{2tx-t^2}\Big|_{t=0} = \partial_t^n \left(e^{x^2} e^{-(x-t)^2}\right)\Big|_{t=0} = e^{x^2} \partial_t^n e^{-(x-t)^2}\Big|_{t=0}$$

$$= (-1)^n e^{x^2} \partial_\xi^n e^{-\xi^2}\Big|_{\xi=x} = (-1)^n e^{x^2} \partial_x^n (e^{-x^2}).$$

Exercise 5.4. By differentiating the generating function with respect to x and t, prove the identities

$$H_n'(x) = 2nH_{n-1}, \qquad H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x) \qquad (n = 0, 1, \dots). \tag{5.27}$$

Combine these identities to deduce the second-order differential equation satisfied by $H_n(x)$.

Solution. Differentiating the explicit formula for the generating function with respect to x we obtain

$$\partial_x F(x,t) = \partial_x e^{2xt-t^2} = 2tF(x,t) = 2\sum_{n=0}^\infty \frac{H_n(x)}{n!} t^{n+1} = 2\sum_{n=1}^\infty \frac{H_{n-1}(x)}{(n-1)!} t^n.$$

On the other hand,

$$\partial_x F(x,t) = \sum_{n=0}^\infty \frac{H_n'(x)}{n!} t^n,$$

where the prime denotes differentiation with respect to x. Equating the coefficient of t^n in both expressions for $\partial_x F(x,t)$ we easily obtain the first recursion relation (5.27).

Likewise, differentiating now with respect to t we obtain

$$\partial_t F(x,t) = \partial_t e^{2xt-t^2} = 2(x-t)F(x,t) = 2x\sum_{n=0}^\infty \frac{H_n(x)}{n!} t^n - 2\sum_{n=0}^\infty \frac{H_n(x)}{n!} t^{n+1}$$

$$= \sum_{n=0}^\infty \frac{2}{n!}\Big(xH_n(x) - nH_{n-1}(x)\Big) t^n$$

and

$$\partial_t F(x,t) = \sum_{n=1}^\infty \frac{H_n(x)}{(n-1)!} t^{n-1} = \sum_{n=0}^\infty \frac{H_{n+1}(x)}{n!} t^n.$$

The second recursion relation in Eq. (5.27) follows immediately imposing the equality of the coefficient of t^n in both expressions for $\partial_t F(x,t)$.

Using the second relation (5.27) to express H_{n-1} in terms of H_n and H_{n+1} we obtain

$$H_n'(x) = 2xH_n(x) - H_{n+1}(x)$$
$$\implies H_n''(x) = 2xH_n'(x) + 2H_n(x) - H_{n+1}'(x) = 2xH_n'(x) + 2H_n(x) - 2(n+1)H_n(x)$$
$$= 2xH_n'(x) - 2nH_n(x),$$

where in the penultimate equality we have used the first relation (5.27) with $n + 1$ instead of n. Thus the sought-for differential equation is

$$H_n''(x) - 2x H_n'(x) + 2n H_n(x) = 0.$$

As expected, this is just Eq. (5.12) with $\lambda = 2n + 1$.

5.3 Creation and annihilation operators. Algebraic solution

`sec.algsol`

In this section we shall rederive the spectrum of the harmonic oscillator Hamiltonian (5.3) using an abstract, algebraic method that is in fact of interest in itself as it is applicable in many other important physical problems. To begin with, let us use the dimensionless observables

$$\hat{X} = \frac{X}{\ell} = \sqrt{\frac{m\omega}{\hbar}} X, \qquad \hat{P} = \frac{\ell P}{\hbar} = \frac{P}{\sqrt{\hbar m\omega}},$$ (5.28) `hXPdef`

in terms of which the Hamiltonian reads

$$H = \frac{1}{2}\hbar\omega \left(\hat{X}^2 + \hat{P}^2 \right) \equiv \hbar\omega \hat{H}.$$

The commutator of the operators $\hat{X}$ and $\hat{P}$ follows easily from the canonical commutation relation for X and P:

$$[\hat{X}, \hat{P}] = \frac{1}{\hbar}[X, P] = i.$$ (5.29) `commxp`

With a view of factoring the dimensionless Hamiltonian $\hat{H}$, we next define the operators

$$a = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}), \qquad a^\dagger = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}),$$ (5.30) `Adef`

which obey the commutation relation

$$[a, a^\dagger] = \frac{1}{2}[\hat{X} + i\hat{P}, \hat{X} - i\hat{P}] = \frac{i}{2}\left(-[\hat{X}, \hat{P}] + [\hat{P}, \hat{X}]\right) = -i[\hat{X}, \hat{P}] = 1.$$ (5.31) `commAAdag`

The operators a and $a^\dagger$ are respectively called the harmonic oscillator's **annihilation** and **creation** operators. The dimensionless Hamiltonian $\hat{H}$ is easily expressed in terms of the latter operators. Indeed,

$$a^\dagger a = \frac{1}{2}(\hat{X} - i\hat{P})(\hat{X} + i\hat{P}) = \frac{1}{2}\left(\hat{X}^2 + \hat{P}^2 + i[\hat{X}, \hat{P}]\right) = \frac{1}{2}\left(\hat{X}^2 + \hat{P}^2 - 1\right),$$

and similarly

$$aa^\dagger = a^\dagger a + [a, a^\dagger] = a^\dagger a + 1 = \frac{1}{2}\left(\hat{X}^2 + \hat{P}^2 + 1\right),$$

whence

$$\hat{H} = a^\dagger a + \frac{1}{2} = aa^\dagger - \frac{1}{2}.$$ (5.32) `Haadag`

In particular, since the operator $a^\dagger a$ is positive semidefinite, from the last equation it follows[3] that *the spectrum of $\hat{H}$ is contained in the half line* $[1/2, \infty)$.

The determination of $\sigma(H)$ is based on the commutation relations of this operator —or, equivalently, its dimensionless counterpart $\hat{H}$— with the operators a and $a^\dagger$, namely

$$[a, \hat{H}] = [a, a^\dagger a] = [a, a^\dagger]a = a, \qquad [a^\dagger, \hat{H}] = -[a, \hat{H}]^\dagger = -a^\dagger. \tag{5.33}$$

> AHcomm

Let us further assume that $\hat{H}$ has at least an eigenvalue, since in the present context (i.e., when the operators X and P are defined in the usual way as multiplication by x and $-i\hbar\partial_x$) we know this is indeed the case. Denoting by λ this eigenvalue and by $|\psi\rangle$ any of its corresponding (not necessarily normalized) eigenvectors, from the first commutation relation in Eq. (5.33) we have

$$[a, \hat{H}]|\psi\rangle = a(\hat{H}|\psi\rangle) - \hat{H}(a|\psi\rangle) = (\lambda - \hat{H})a|\psi\rangle = a|\psi\rangle \implies \hat{H}(a|\psi\rangle) = (\lambda - 1)(a|\psi\rangle).$$

Hence either $a|\psi\rangle = 0$, or $a|\psi\rangle$ is an eigenvector of $\hat{H}$ with eigenvalue $\lambda - 1$. In other words:

> Acting with a on an eigenvector of $\hat{H}$ either lowers the eigenvalue by 1 or produces the zero vector.

Note also that

$$\left\| a|\psi\rangle \right\|^2 = \langle a\psi | a\psi \rangle = \langle \psi | a^\dagger a | \psi \rangle = \left\langle \psi \left| \hat{H} - \frac{1}{2} \right| \psi \right\rangle = \left(\lambda - \frac{1}{2} \right) \|\psi\|^2,$$

so that

$$a|\psi\rangle = 0 \iff \lambda = \frac{1}{2}. \tag{5.34}$$

> Apsi0

Thus if λ is *not* a half integer (i.e., one half of an odd integer) then the vectors

$$a^n|\psi\rangle, \qquad n = 0, 1, \ldots,$$

are all eigenvectors of $\hat{H}$ with arbitrarily low eigenvalues $\lambda - n$. Since, as we saw above, the spectrum of $\hat{H}$ is bounded below by $1/2$, this is impossible. We conclude that $\lambda = n + \frac{1}{2}$ for some nonnegative integer n, and that the vector

$$|\psi_0\rangle := a^n|\psi\rangle$$

is an eigenvector of $\hat{H}$ with eigenvalue $1/2$. In particular, the *the only possible eigenvalues of $\hat{H}$ are the positive half integers $n + \frac{1}{2}$* with $n = 0, 1, \ldots$.

Let us next prove that *all* positive half integers are eigenvalues of $\hat{H}$. To this end, consider the action of the operator $a^\dagger$ on an eigenvector $|\psi\rangle$ of $\hat{H}$ with eigenvalue λ. Using now the second equation (5.33) we obtain

$$[a^\dagger, \hat{H}]|\psi\rangle = a^\dagger(\hat{H}|\psi\rangle) - \hat{H}(a^\dagger|\psi\rangle) = (\lambda - \hat{H})a^\dagger|\psi\rangle = -a^\dagger|\psi\rangle \implies \hat{H}(a^\dagger|\psi\rangle) = (\lambda+1)(a^\dagger|\psi\rangle).$$

On the other hand,

$$\left\| a^\dagger|\psi\rangle \right\|^2 = \langle a^\dagger\psi | a^\dagger\psi \rangle = \langle \psi | aa^\dagger | \psi \rangle = \left\langle \psi \left| \hat{H} + \frac{1}{2} \right| \psi \right\rangle = \lambda + \frac{1}{2} \geqslant 1,$$

---

[3]Indeed, if $|\psi\rangle$ is any state then

$$\langle a^\dagger a \rangle_\psi = \left\| a|\psi\rangle \right\|^2 \geqslant 0 \implies \langle \hat{H} \rangle_\psi = \langle a^\dagger a \rangle_\psi + \frac{1}{2} \geqslant \frac{1}{2}.$$

Applying this inequality to an eigenstate $|\psi\rangle$ of $\hat{H}$ with eigenvalue λ we immediately obtain the inequality $\lambda \geqslant 1/2$.

since the spectrum of $\hat{H}$ is bounded below by $1/2$. We conclude that the vector $a^{\dagger}|\psi\rangle$ is an eigenvector of $\hat{H}$ with eigenvalue $\lambda + 1$. In other words,

> Acting with $a^{\dagger}$ on an eigenvector of $\hat{H}$ raises the eigenvalue by 1.

It immediately follows from this statement (applied to the eigenvector $|\psi_0\rangle$) that the vectors

$$|\psi_n\rangle := \left(a^{\dagger}\right)^n |\psi_0\rangle, \qquad n = 0, 1, \dots. \tag{5.35}$$

`psinunn`

are eigenvectors of $\hat{H}$ with corresponding eigenvalues

$$\lambda_n = n + \frac{1}{2}, \qquad n = 0, 1, \dots.$$

Hence *the point spectrum of $\hat{H}$ is the infinite discrete set*

$$\left\{ n + \frac{1}{2} : n = 0, 1, \dots \right\}. \tag{5.36}$$

`specHOA`

Summarizing:

Theorem 5.1. *If the point spectrum $\sigma_p(\hat{H})$ of $\hat{H}$ is nonempty, then*

$$\sigma_p(\hat{H}) = \left\{ n + \frac{1}{2} : n = 0, 1, \dots \right\}.$$

Moreover, if $|\psi_0\rangle$ is a (not necessarily normalized) eigenvector of $\hat{H}$ with eigenvalue $\lambda_0 = 1/2$, then

$$|\psi_n\rangle = \left(a^{\dagger}\right)^n |\psi_0\rangle, \qquad n = 0, 1, \dots,$$

is an eigenvector with eigenvalue $\lambda_n = n + \frac{1}{2}$.

In particular, since the harmonic oscillator Hamiltonian H is equal to $\hbar\omega\hat{H}$, from the latter theorem it immediately follows that the spectrum of H is given by Eq. (5.21).

Remark. In view of the above, it is natural to interpret the spectrum of the harmonic oscillator in the following intuitive way. The eigenstate $|n\rangle$ contains n *quanta* of energy $\hbar\omega$, so that the ground state $|0\rangle$ is regarded as the *vacuum* (i.e., it does not contain any energy quanta, although it has a nonzero *vacuum energy* $\hbar\omega/2$). The annihilation operator then *destroys* (i.e., "annihilates") one of these energy quanta, thus lowering the system's energy by $\hbar\omega$. On the other hand, the creation operator adds an energy quantum to the system, i.e., it "creates" a quantum of energy $\hbar\omega$. In fact, this interpretation of the spectrum of the harmonic oscillator operator is largely adopted in *quantum field theory,* where the energy quanta are regarded as *particles* (that, according to the principles of special relativity, can be created or destroyed). ∎

The sequence of eigenvectors (5.35) generated by an eigenket $|\psi_0\rangle$ of $\hat{H}$ with eigenvalue $1/2$ —i.e., by one of the *ground states* of $\hat{H}$— is not normalized, even if $|\psi_0\rangle$ is. It can be easily normalized by taking into account that if $|\psi\rangle$ is a normalized eigenvector of $\hat{H}$ with eigenvalue $\lambda_{n-1} = n - \frac{1}{2}$ (with $n = 1, 2, \dots$) then

$$\langle a^{\dagger}\psi | a^{\dagger}\psi \rangle = \langle \psi | a a^{\dagger} | \psi \rangle = \left\langle \psi \left| \hat{H} + \frac{1}{2} \right| \psi \right\rangle = \left(\lambda_{n-1} + \frac{1}{2} \right) \langle \psi | \psi \rangle = n \langle \psi | \psi \rangle = n,$$

and thus

$$\frac{1}{\sqrt{n}} a^\dagger |\psi\rangle$$

is a normalized eigenvector with eigenvalue $\lambda_n = n + \frac{1}{2}$. Therefore if $|\psi_0\rangle \equiv |0\rangle$ is normalized so are

$$|1\rangle := a^\dagger |0\rangle, \qquad |2\rangle = \frac{1}{\sqrt{2}} a^\dagger |1\rangle = \frac{1}{\sqrt{2}} (a^\dagger)^2 |0\rangle, \qquad |3\rangle = \frac{1}{\sqrt{3}} a^\dagger |2\rangle = \frac{1}{\sqrt{3!}} (a^\dagger)^3 |0\rangle, \ \ldots,$$

with respective eigenvalues

$$\frac{3}{2}, \qquad \frac{5}{2}, \qquad \frac{7}{2}, \qquad \ldots.$$

It follows that the vectors

$$|n\rangle := \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle, \qquad n = 0, 1, \ldots, \tag{5.37}$$

`ketndef`

where $|0\rangle$ is a normalized eigenvector of $\hat{H}$ with eigenvalue $1/2$, are normalized and satisfy

$$\hat{H} |n\rangle = \left(n + \frac{1}{2}\right) |n\rangle.$$

Although it is not possible to determine the *degeneracy* of the eigenvalues of $\hat{H}$ from the commutation relation (5.31) alone, it is straightforward to prove the following general result:

The degeneracy (finite or infinite) of all the eigenvalues (5.36) of $\hat{H}$ is the same. In other words,

$$\dim \ker(\hat{H} - \lambda_n) = \dim \ker(\hat{H} - \lambda_m), \qquad \forall n, m = 0, 1, \ldots.$$

Proof. Obviously, it suffices to show that

$$\dim \ker(\hat{H} - \lambda_n) = \dim \ker(\hat{H} - \lambda_0), \qquad \forall n \in \mathbb{N}.$$

To this end, note that the operator $(a^\dagger)^n$ maps $\ker(A - \lambda_0)$ injectively into $\ker(A - \lambda_n)$, since applying $a^\dagger$ to an eigenvector $|\psi\rangle$ of $\hat{H}$ with eigenvalue λ produces an eigenvector with eigenvalue $\lambda + 1$ (in particular, a non-zero vector). This shows that

$$\dim \ker(\hat{H} - \lambda_n) \leqslant \dim \ker(\hat{H} - \lambda_n).$$

Likewise, a^n maps $\ker(A - \lambda_n)$ injectively into $\ker(A - \lambda_0)$, since applying a to an eigenvector $|\psi\rangle$ of $\hat{H}$ with eigenvalue $\lambda > 1/2$ produces an eigenvector with eigenvalue $\lambda - 1$. (Recall that if $|\psi\rangle$ is an eigenvector of $\hat{H}$ with eigenvalue λ then $a|\psi\rangle$ cannot vanish unless $\lambda = 1/2$.) Thus

$$\dim \ker(\hat{H} - \lambda_n) \leqslant \dim \ker(\hat{H} - \lambda_0),$$

which together with the previous inequality completes the proof. ∎

The action of the creation and annihilation operators on the normalized eigenvectors $|n\rangle$ is also straightforward to determine. To begin with, we have

$$a^\dagger |n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^{n+1} |0\rangle = \sqrt{n+1} |n+1\rangle, \qquad n = 0, 1, \ldots.$$

To compute $a|n\rangle$, note that applying a to the previous equality we obtain

$$aa^\dagger|n\rangle = \left(\hat{H} + \frac{1}{2}\right)|n\rangle = (n+1)|n\rangle = \sqrt{n+1}\,a|n+1\rangle, \qquad n = 0, 1, \ldots,$$

whence

$$a|n+1\rangle = \sqrt{n+1}\,|n\rangle, \qquad n = 0, 1, \ldots,$$

or equivalently

$$a|n\rangle = \sqrt{n}\,|n-1\rangle, \qquad n = 1, 2, \ldots.$$

We have thus shown that

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle, \qquad a|n\rangle = \sqrt{n}\,|n-1\rangle, \qquad n = 0, 1, \ldots. \tag{5.38}$$

`aadagn`

(Note that, although $|-1\rangle$ is not defined, the term $\sqrt{n/2}\,|n-1\rangle$ in the previous equations vanishes when $n = 0$ due to the factor $\sqrt{n/2}$.) From these equations and the definition (5.30) of the operators a and $a^\dagger$ it is immediate to deduce the action of $\hat{X}$ and $\hat{P}$ on the eigenvector $|n\rangle$:

`XPketn`

$$\hat{X}|n\rangle = \frac{1}{\sqrt{2}}(a + a^\dagger)|n\rangle = \sqrt{\tfrac{n}{2}}\,|n-1\rangle + \sqrt{\tfrac{n+1}{2}}\,|n+1\rangle, \tag{5.39a}$$

`Xketn`

$$\hat{P}|n\rangle = \frac{\mathrm{i}}{\sqrt{2}}(a^\dagger - a)|n\rangle = \mathrm{i}\left(\sqrt{\tfrac{n+1}{2}}\,|n+1\rangle - \sqrt{\tfrac{n}{2}}\,|n-1\rangle\right). \tag{5.39b}$$

`Pketn`

Hence the matrix elements of the position and momentum representation with respect to the orthonormal basis (5.37) are given by

$$X_{jn} \equiv \langle j\,|X\,|n\rangle = \sqrt{\frac{\hbar}{m\omega}}\,\langle j\,|\hat{X}\,|n\rangle = \sqrt{\frac{\hbar}{m\omega}}\left(\sqrt{\frac{n}{2}}\,\delta_{j,n-1} + \sqrt{\frac{n+1}{2}}\,\delta_{j,n+1}\right),$$

$$P_{jn} \equiv \langle j\,|P\,|n\rangle = \sqrt{\hbar m\omega}\,\langle j\,|\hat{P}\,|n\rangle = \mathrm{i}\,\sqrt{\hbar m\omega}\left(-\sqrt{\frac{n}{2}}\,\delta_{j,n-1} + \sqrt{\frac{n+1}{2}}\,\delta_{j,n+1}\right).$$

The previous formulas were at the basis of Heisenberg's early formulation of quantum mechanics known as *matrix mechanics*.

Exercise 5.5. Compute the average value and the uncertainty of the position and momentum of a harmonic oscillator in the energy eigenstate $|n\rangle$.

Solution. To begin with, from Eqs. (5.39) it immediately follows that the average values of $\hat{X}$ and $\hat{P}$ vanish in the state $|n\rangle$:

$$\langle\hat{X}\rangle = \langle n|\hat{X}|n\rangle = 0, \qquad \langle\hat{P}\rangle = \langle n|\hat{P}|n\rangle = 0.$$

Since X and P are respectively proportional to $\hat{X}$ and $\hat{P}$, we also have

$$\langle X\rangle = \langle P\rangle = 0.$$

It follows that

$$(\Delta\hat{X})^2 = \langle\hat{X}^2\rangle = \|\hat{X}|n\rangle\|^2 = \frac{n}{2} + \frac{n+1}{2} = n + \frac{1}{2},$$

since the states $|n-1\rangle$ and $|n+1\rangle$ are orthogonal and of unit norm. Similarly,

$$(\Delta\hat{P})^2 = \langle\hat{P}^2\rangle = \|\hat{P}|n\rangle\|^2 = \frac{n}{2} + \frac{n+1}{2} = n + \frac{1}{2}.$$

From Eq. (5.28) we then obtain

$$\Delta X = \ell \Delta \hat{X} = \sqrt{n + \frac{1}{2}}\, \ell, \qquad \Delta P = \frac{\hbar}{\ell} \Delta \hat{P} = \sqrt{n + \frac{1}{2}}\, \frac{\hbar}{\ell}.$$

In particular, the uncertainty product $\Delta X\, \Delta P$ in the eigenstate $|n\rangle$ is given by

$$\Delta X\, \Delta P = \left(n + \frac{1}{2}\right)\hbar,$$

in agreement with Heisenberg's uncertainty principle. Note also that for $n = 0$ the uncertainty product is exactly $\hbar/2$, and thus the lowest energy eigenstate $|0\rangle$ is a minimum uncertainty wave function.

All the results proved so far in this section did not rely on any particular realization of the annihilation and creation operators, but only on the commutation relation (5.31) and Eq. (5.32) for the Hamiltonian. The results that we shall derive next combine the general algebraic approach outlined above with the standard realization of the operators $\hat{X}$ and $\hat{P}$, namely

$$\hat{X}\psi = \frac{X\psi}{\ell} = \frac{x}{\ell}\psi = s\psi, \qquad \hat{P}\psi = \frac{\ell}{\hbar}P\psi = -i\ell\partial_x\psi = -i\partial_s\psi,$$

where s is again the dimensionless variable x/ℓ and $\psi(s)$ is an arbitrary wave function. In other words, we are dealing with the specific realization

$$\hat{X} = s, \qquad \hat{P} = -i\,\partial_s. \tag{5.40}$$

`hXPreal`

To begin with, let us find all *ground states* of the system, namely all solutions $\psi_0(s)$ of the eigenvalue equation

$$\hat{H}\psi_0(s) = \frac{1}{2}\psi_0(s).$$

From the previous discussion (cf., in particular, Eq. (5.34)), we know that $\psi_0(s)$ must be annihilated by the operator a, i.e., must satisfy the equation

$$a\psi_0(s) = 0.$$

By Eqs. (5.30) and (5.40), this is equivalent to the first-order linear differential equation

$$\psi_0'(s) + s\psi_0(s) = 0,$$

whose general solution is

$$\psi_0(s) = N e^{-\frac{s^2}{2}},$$

where N is a nonzero complex constant. Imposing that ψ_0 be normalized we obtain

$$\int_{-\infty}^{\infty} dx\, \left|\psi_0(s)\right|^2 = \ell \int_{-\infty}^{\infty} ds\, \left|\psi_0(s)\right|^2 = |N|^2 \ell \sqrt{\pi} = 1 \quad \Longrightarrow \quad N = \ell^{-1/2}\pi^{-1/4} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4},$$

up to a trivial global phase. We conclude that the ground state

$$\psi_0(s) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{s^2}{2}},$$

is *non-degenerate*, from which it follows by the previous framed result that *all energy levels are non-degenerate*. This is of course consistent with the result we obtained in Section 3.5 for a general one-dimensional potential with $V_\pm = \infty$.

Once the ground state $\psi_0 = |0\rangle$ is known, the n-th excited state $\psi_n = |n\rangle$ can be computed from Eq. (5.37), which in the representation (5.40) for the position and momentum operators reads:

$$\psi_n(s) = (2^n n!)^{-1/2}(s - \partial_s)^n \psi_0(s) = N(2^n n!)^{-1/2}(s - \partial_s)^n e^{-\frac{s^2}{2}}$$

Taking into account that

$$e^{\frac{s^2}{2}} \partial_s e^{\frac{-s^2}{2}} = \partial_s - s,$$

and hence

$$(\partial_s - s)^n = e^{\frac{s^2}{2}} \partial_s^n e^{\frac{-s^2}{2}},$$

we obtain

$$\psi_n(s) = N(-1)^n (2^n n!)^{-1/2} e^{\frac{s^2}{2}} \partial_s^n \left(e^{-s^2} \right) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(s) e^{-\frac{s^2}{2}},$$

where we have used Rodrigues' formula (5.26) for the n-th Hermite polynomial $H_n(s)$. This is exactly Eq. (5.24) for the n-th normalized eigenstate obtained in the previous section through the power series method.

In fact, one can easily establish most of the identities satisfied by the classical Hermite polynomials proved in the previous section using the operator techniques developed above. For instance, from Eq. (5.38) it easily follows that

$$a\psi_n = \frac{N}{\sqrt{2}}(2^n n!)^{-1/2}(s + \partial_s)\left(H_n e^{-s^2/2}\right) = \frac{N}{\sqrt{2}}(2^n n!)^{-1/2} H_n' e^{-s^2/2}$$

$$= \sqrt{n}\,\psi_{n-1} = \frac{N}{\sqrt{2}}\left(2^{(n-1)}(n-1)!\right)^{-1/2} H_{n-1} e^{-s^2/2} \quad \Longrightarrow \quad H_n' = 2n H_{n-1}.$$

Likewise,

$$a^\dagger \psi_n = \frac{N}{\sqrt{2}}(2^n n!)^{-1/2}(s - \partial_s)\left(H_n e^{-s^2/2}\right) = \frac{N}{\sqrt{2}}(2^n n!)^{-1/2}\left(2s H_n - H_n'\right)e^{-s^2/2}$$

$$= \sqrt{n+1}\,\psi_{n+1} = \frac{N}{\sqrt{2}}\left(2^{(n+1)}(n+1)!\right)^{-1/2} H_{n+1} e^{-s^2} \quad \Longrightarrow \quad -H_n' + 2s H_n = H_{n+1}.$$

Combining both equations we obtain

$$H_{n+1}' = 2(n+1)H_n = -H_n'' + 2s H_n' + 2H_n \quad \Longrightarrow \quad H_n'' - 2s H_n' + 2n H_n = 0,$$

which is the differential equation satisfied by the Hermite polynomials (cf. Exercise 5.4).

6 Three-dimensional problems

The Hamiltonian of a particle of mass m moving in ordinary three-dimensional space $\mathbb{R}^3$ is

$$H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R}),$$ (6.1) `H3D`

where $V(\mathbf{r})$ is the classical potential. In the position representation the position and momentum operators are explicitly given by

$$\mathbf{R} = \mathbf{r}, \qquad \mathbf{P} = -\mathrm{i}\hbar\nabla,$$

and the time-independent Schrödinger equation therefore reads

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}),$$ (6.2) `Schr3D`

where $E \in \mathbb{R}$ is the particle's energy and $\psi(\mathbf{r})$ is its wave function. We seek solutions of the latter equation which are either *square integrable* over $\mathbb{R}^3$ (for *bound states*) or *bounded* but not square integrable (for *scattering states*). The Schrödinger equation (6.2) is a second-order linear homogeneous partial differential equation which can be solved by the standard mathematical technique of *separation of variables* in several coordinate systems, depending on the structure of the potential $V(\mathbf{r})$. In this chapter we shall examine some of the simplest examples of this method, in which the Schrödinger equation separates either in Cartesian or in spherical coordinates.

6.1 Separation of variables in Cartesian coordinates

Suppose, to begin with, that the potential $V(\mathbf{r})$ is the sum of three functions each of which depends on only one of the Cartesian coordinates, i.e.,

$$V(\mathbf{r}) = V_1(x_1) + V_2(x_2) + V_3(x_3).$$ (6.3) `VVxi`

The Hamiltonian H is then itself the sum of three one-dimensional Hamiltonians H_i ($i = 1, 2, 3$), where each H_i depends only on the x_i coordinate:

$$H = H_1 + H_2 + H_3, \qquad H_i := -\frac{\hbar^2}{2m}\partial^2_{x_i} + V_i(x_i).$$ (6.4) `HHi`

Since obviously

$$[H_i, H_j] = 0, \qquad \forall i, j = 1, 2, 3,$$

it follows that there is a (generalized) orthonormal basis made up of common eigenvectors of each Hamiltonian H_i. To see how this works in practice, let us follow the method of separation of variables and seek eigenfunctions of H which factorize as the product of three functions $\psi_i(x_i)$, each of which depends only on the corresponding coordinate x_i:

$$\psi(\mathbf{r}) = \psi_1(x_1)\psi_2(x_2)\psi_3(x_3).$$ (6.5) `psiprod`

Substituting into the Schrödinger equation and dividing by $\psi(\mathbf{r})$ (at points $\mathbf{r}$ where $\psi_i(x_i) \neq 0$ for all i) we obtain the equation

$$\sum_{k=1}^{3} \frac{H_k \psi_k(x_k)}{\psi_k(x_k)} = E.$$

Taking the partial derivative of both sides of the previous equation with respect to a coordinate x_i we obtain

$$\frac{\partial}{\partial x_i} \frac{H_i \psi_i(x_i)}{\psi_i(x_i)} = 0, \qquad i = 1, 2, 3,$$

whence

$$\frac{H_i \psi_i(x_i)}{\psi_i(x_i)} = E_i, \qquad i = 1, 2, 3,$$

or equivalently

$$H_i \psi_i(x_i) = E_i \psi_i(x_i), \qquad i = 1, 2, 3, \tag{6.6}$$

`SchrHi`

where E_i is a constant and

$$E_1 + E_2 + E_3 = E. \tag{6.7}$$

`EEi`

In other words:

> The function (6.5) is a solution of the Schrödinger equation (6.2) with an energy E if and only if each ψ_i is a solution of the one-dimensional Schrödinger equation (6.6), with E equal to the sum of the three energies E_i.

The energies E_i are called in the mathematics literature *separation constants*. Note also that the boundary conditions for the one-dimensional eigenvalue problems (6.6) (an example of what in mathematics is called a *Sturm–Liouville problem*) are similar to the boundary conditions for the three-dimensional problem (6.2), i.e., *each ψ_i must be square integrable* for ψ to be square integrable, or *all the ψ_i must be bounded* (and at least one not square integrable) for the three–dimensional solution ψ to be a scattering state.

Of course, not every solution of Eq. (6.2) is of the form (6.5), since the sum of two or more such solutions with the same energy E is still an eigenfunction with energy E (by linearity) which is not of the form (6.5). Suppose, however, that each one-dimensional problem (6.6) has only point spectrum. In this case, for each of these problems there is an orthonormal basis of $L^2(\mathbb{R})$

$$\{\psi_n^i(x_i) : n \in \mathbb{N}\}, \qquad i = 1, 2, 3,$$

whose elements are eigenfunctions of the corresponding Hamiltonian H_i, i.e.,

$$H_i \psi_n^i(x_i) = E_n^i \psi_n^i(x_i), \qquad n \in \mathbb{N}, \quad i = 1, 2, 3.$$

Here we are denoting the (point) spectrum of H_i by

$$\{E_n^i : n \in \mathbb{N}\},$$

with $E_k^i \neq E_n^i$ for $k \neq n$ (since, as shown in Section (3.5), the point spectrum of one-dimensional potentials is non-degenerate). It can then be shown that the set

$$\{\psi_{kln}(\mathbf{r}) := \psi_k^1(x_1)\psi_l^2(x_2)\psi_n^3(x_3) : k, l, n \in \mathbb{N}\} \tag{6.8}$$

`psilmn`

is an *orthonormal basis* of the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$ of the three-dimensional problem (6.2), with

$$H\psi_{kln} = E_{kln}\psi_{kln}, \qquad E_{kln} := E_k^1 + E_l^2 + E_n^3, \quad k, l, n = 1, 2, \dots. \tag{6.9}$$

`En3DCart`

Thus in this case the (point) spectrum of the three-dimensional Hamiltonian (6.1) is the set

$$\left\{ E_{kln} \equiv E_k^1 + E_l^2 + E_n^3 : k, l, n \in \mathbb{N} \right\}$$

with corresponding eigenfunctions

$$\psi_{kln}(\mathbf{r}) = \psi_k^1(x_1)\psi_l^2(x_2)\psi_n^3(x_3).$$

Note that the orthonormality of the set (6.8) is straightforward to check:

$$\begin{aligned}
(\psi_{kln}, \psi_{k'l'n'}) &= \int \mathrm{d}^3 r \, \psi_{kln}^*(\mathbf{r}) \psi_{k'l'n'}(\mathbf{r}) \\
&= \left(\int \mathrm{d}^3 x_1 [\psi_k^1(x_1)]^* \psi_{k'}^1(x_1) \right) \left(\int \mathrm{d}^3 x_2 [\psi_l^2(x_2)]^* \psi_{l'}^2(x_2) \right) \left(\int \mathrm{d}^3 x_3 [\psi_n^3(x_3)]^* \psi_{n'}^3(x_3) \right) \\
&= (\psi_k^1, \psi_{k'}^1)(\psi_l^2, \psi_{l'}^2)(\psi_n^3, \psi_{n'}^3) = \delta_{kk'}\delta_{ll'}\delta_{nn'}.
\end{aligned}$$

It follows from the discussion in Section 3.1 that the general solution $\Psi(\mathbf{r}, t)$ of the time-dependent Schrödinger equation with initial condition $\Psi(\mathbf{r}, 0) = \psi(\mathbf{r})$ is given by

$$\Psi(\mathbf{r}, t) = \sum_{k,l,n=1}^{\infty} c_{kln} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar} E_{kln} t} \psi_{kln}(\mathbf{r}) \equiv \sum_{k,l,n=1}^{\infty} c_{kln} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(E_k^1 + E_l^2 + E_n^3)t} \psi_k^1(x_1)\psi_l^2(x_2)\psi_n^3(x_3),$$

where the coefficients c_{kln} are computed from the equation

$$c_{kln} = (\psi_{kln}, \psi) = \int \mathrm{d}^3 r \, \psi_{kln}^*(\mathbf{r})\psi(\mathbf{r}).$$

Remarks.

- In the language of Section 4.6, the set $\{H_1, H_2, H_3\}$ is a CSCO for the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$.

- The Hamiltonian H in Eq. (6.4) can be interpreted as describing the motion of three one-dimensional effective particles of the same mass m each of which is subject to its corresponding potential $V_i(x_i)$, but which *do not interact* with each other (since there is no term involving two or more coordinates).

- In general, the spectrum (6.9) is degenerate. The degeneracy of an energy $E \in \sigma_p(H)$ is the cardinal of the set

$$\{(k, l, n) \in \mathbb{N}^3 : E_k^1 + E_l^2 + E_n^3 = E\}. \qquad \blacksquare$$

exe.nondeg

Exercise 6.1. If each of the Hamiltonians H_i has only point spectrum, show that the ground state of the Hamiltonian (6.4) is non-degenerate.

Solution. If the Hamiltonian H_i has only point spectrum, its energy levels are non-degenerate. By Eq. (6.9) for the energy, the minimum energy is obtained by adding the minimum energy of each Hamiltonian H_i. Thus the ground state is the state ψ_{111}, with energy $E_{111} = E_1^1 + E_1^2 + E_1^3$.

6.1.1 The infinite well

As our first example of problem that can be solved separating variables in Cartesian coordinates, consider the infinite potential well

$$V(\mathbf{r}) = \begin{cases} 0, & \mathbf{r} \in (0, L_1) \times (0, L_2) \times (0, L_3) \\ \infty, & \text{otherwise.} \end{cases} \tag{6.10} \quad \boxed{\text{IW3D}}$$

This potential describes the free motion of a quantum particle confined inside a rectangular box with impenetrable walls. Since we can formally write

$$V(\mathbf{r}) = V_1(x_1) + V_2(x_2) + V_3(x_3),$$

where $V_i(x_i)$ is the infinite square well potential

$$V_i(x_i) = \begin{cases} 0, & 0 < x_i < L_i, \\ \infty, & \text{otherwise,} \end{cases}$$

the time-independent Schrödinger equation (6.2) is separable in Cartesian coordinates. As we saw in Section 3.4.1, the potential V_i has only point spectrum, with eigenvalues and corresponding normalized eigenfunctions given by

$$E_n^i = \frac{n^2 \pi^2 \hbar^2}{2m L_i^2}, \qquad n \in \mathbb{N},$$

and

$$\psi_n^i(x_i) = \sqrt{\frac{2}{L_i}} \sin\left(\frac{n \pi x_i}{L_i}\right), \qquad n \in \mathbb{N}, \quad i = 1, 2, 3.$$

From the above discussion it follows that the energies of the three-dimensional infinite well potential (6.10) are

$$E_{kln} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{k^2}{L_1^2} + \frac{l^2}{L_2^2} + \frac{n^2}{L_3^2}\right), \qquad k, l, n \in \mathbb{N},$$

with corresponding (normalized) eigenfunctions

$$\psi_{kln}(\mathbf{r}) = 2\sqrt{\frac{2}{v}} \sin\left(\frac{k \pi x_1}{L_1}\right) \sin\left(\frac{l \pi x_2}{L_2}\right) \sin\left(\frac{n \pi x_3}{L_3}\right),$$

where $v = L_1 L_2 L_3$ is the volume of the box. Note that, in contrast to the one-dimensional case, the spectrum is in general degenerate. For instance, for a cubic well $L_1 = L_2 = L_3 \equiv L$ and hence

$$E_{kln} = \frac{\pi^2 \hbar^2}{2m L^2}\left(k^2 + l^2 + n^2\right).$$

The degeneracy of an energy $E \in \sigma_p(H)$ is in this case the number of triplets $(n_1, n_2, n_3) \in \mathbb{N}^3$ such that

$$n_1^2 + n_2^2 + n_3^2 = \frac{2m E L^2}{\pi^2 \hbar^2}.$$

For instance, the ground state has energy

$$E_{111} = \frac{3\pi^2 \hbar^2}{2m L^2}$$

and (as we know from Exercise 6.1) is non-degenerate, since (for $k, l, n \in \mathbb{N}$)

$$E_{kln} = E_{111} \iff k^2 + l^2 + n^2 = 3 \iff k = l = n = 1.$$

The ground state wave function is therefore

$$\psi_{111}(\mathbf{r}) = \psi_1^1(x_1)\psi_1^2(x_2)\psi_1^3(x_3) = 2\sqrt{\frac{2}{v}}\sin\left(\frac{\pi x_1}{L_1}\right)\sin\left(\frac{\pi x_2}{L_2}\right)\sin\left(\frac{\pi x_3}{L_3}\right),$$

which (as in the one-dimensional case) does not vanish (is strictly positive) inside the box. The first excited state has energy

$$E_{211} = E_{121} = E_{112} = \frac{3\pi^2\hbar^2}{mL^2},$$

and is three times degenerate, etc.

When E is very large compared to $\hbar^2/(mL^2)$, or equivalently $k^2+l^2+n^2 \gg 1$, the energy difference between two consecutive levels is very small (compared to E), and the spectrum is almost continuous. In this limit, it is possible to estimate the number $\rho(E)$ of energy eigenstates with energy less than or equal to a certain energy E (taking into account the degeneracy of each level) by noting that this number is equal to the number of points (n_1, n_2, n_3) with positive integer coordinates such that

$$n_1^2 + n_2^2 + n_3^2 \leqslant \frac{2mL^2 E}{\pi^2\hbar^2}.$$

When E is very large, this number is approximately equal to the volume of an octant of a sphere of radius $\sqrt{2mE}\, L/(\pi\hbar)$, namely

$$\rho(E) \simeq \frac{1}{8}\cdot\frac{4\pi}{3}\frac{v}{\pi^3\hbar^3}(2mE)^{3/2} = (2mE)^{3/2}\frac{v}{6\pi^2\hbar^3}.$$

The the number $\nu(E)\,\mathrm{d}E$ of energy eigenstates with energy between E and $E + \mathrm{d}E$ is therefore given by

$$\nu(E)\,\mathrm{d}E = \rho(E + \mathrm{d}E) - \rho(E) \simeq \rho'(E)\,\mathrm{d}E \simeq \frac{(2m)^{3/2}v}{4\pi^2\hbar^3}E^{1/2}\,\mathrm{d}E.$$

The quantity

$$\nu(E) = \frac{(2m)^{3/2}v}{4\pi^2\hbar^3}E^{1/2}$$

is called the *density of states,* and it plays an important role in statistical mechanics.

6.1.2 The three-dimensional harmonic oscillator

Consider a smooth classical three-dimensional potential $V(\mathbf{r})$ having a *stable equilibrium*, which can be assumed w.l.o.g. to be located at the origin. Thus $\nabla V(0) = 0$, and we can also take w.l.o.g. $V(0) = 0$, since in (non-relativistic) classical mechanics the potential is defined up to a constant. Taylor expanding $V(\mathbf{r})$ about the equilibrium $\mathbf{r} = 0$ we can write

$$V(\mathbf{r}) = \frac{1}{2}\sum_{i,j=1}^{3} a_{ij}x_i x_j + o(r^2),$$

where $A = (a_{ij})_{i,j=1}^{3}$ is a symmetric matrix. If A is assumed to be non-degenerate it must be *positive definite*, as the origin is a *stable* equilibrium by hypothesis. Hence there is an orthogonal transformation (i.e., a rotation of the axes)

$$x_i = \sum_{j=1}^{3} R_{ij}\xi_j, \qquad i = 1, 2, 3,$$

such that

$$\sum_{i,j=1}^{3} a_{ij} x_i x_j = \sum_{i=1}^{3} k_i \xi_i^2,$$

with $k_i > 0$ for all $i = 1, 2, 3$. Hence

$$V(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{3} k_i \xi_i^2 + o(\xi^2). \tag{6.11} \quad \boxed{\text{3DHO}}$$

We thus see that the *three-dimensional harmonic oscillator* (HO) potential

$$V(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{3} k_i x_i^2, \qquad \text{with} \quad k_i > 0, \quad \forall i = 1, 2, 3, \tag{6.12} \quad \boxed{\text{3DHOpot}}$$

approximately describes in appropriate coordinates the *motion of a particle in the neighborhood of a (non-degenerate) stable equilibrium of an arbitrary (smooth) potential.* Evidently V is of the form (6.3), with

$$V_i(x_i) = \frac{1}{2} k_i x_i^2, \qquad i = 1, 2, 3,$$

a one-dimensional HO potential in the variable x_i. Since the latter potential has only point spectrum, from the general discussion of Section (6.1) we conclude that the normalized eigenfunctions of the **three-dimensional harmonic oscillator Hamiltonian**

$$H = \frac{\mathbf{P}^2}{2m} + \frac{1}{2} \sum_{i=1}^{3} k_i X_i^2 \tag{6.13} \quad \boxed{\text{3DHOHam}}$$

are given by

$$\psi_{n_1 n_2 n_3}(\mathbf{r}) = \prod_{i=1}^{3} \left[\pi^{-1/4} \sqrt{\frac{\beta_i}{2^{n_i} n_i!}} \, e^{-\frac{1}{2}\beta_i^2 x_i^2} H_{n_i}(\beta_i x_i) \right] \qquad \left(\beta_i := \sqrt{\frac{m\omega_i}{\hbar}} \right), \tag{6.14} \quad \boxed{\text{3DHoeigf}}$$

with energies

$$E_{n_1 n_2 n_3} = \left(n_1 + \frac{1}{2} \right) \hbar\omega_1 + \left(n_2 + \frac{1}{2} \right) \hbar\omega_2 + \left(n_3 + \frac{1}{2} \right) \hbar\omega_3, \quad n_i = 0, 1, \dots, \tag{6.15} \quad \boxed{\text{3DHOeigv}}$$

where

$$\omega_i = \sqrt{\frac{k_i}{m}}, \qquad i = 1, 2, 3. \tag{6.16} \quad \boxed{\text{omi3D}}$$

Formally, the Hamiltonian (6.13) describes three one-dimensional oscillators with the same mass m and circular frequencies $\omega_1, \omega_2, \omega_3$ which do not interact with each other. The system's energy is thus the sum of the individual energies of each oscillator, and its wave function is the product of each of the one-dimensional oscillators' wave functions.

As in the case of the infinite well potential, the energy levels above the ground state of the three-dimensional HO can be degenerate, depending on the three frequencies ω_i. Indeed, the degeneracy of the energy $E_{n_1 n_2 n_3}$ is the number of solutions $(l_1, l_2, l_3) \in (\mathbb{N} \cup \{0\})^3$ of the equation

$$E_{l_1 l_2 l_3} = E_{n_1 n_2 n_3} \quad \Longleftrightarrow \quad (l_1 - n_1)\omega_1 + (l_2 - n_2)\omega_2 + (l_3 - n_3)\omega_3 = 0.$$

We thus see that when the three frequencies are *rationally independent*, i.e., when

$$\left(k_1\omega_1 + k_2\omega_2 + k_3\omega_3 = 0, \ k_{1,2,3} \in \mathbb{Z}\right) \implies k_1 = k_2 = k_3 = 0,$$

all the energy levels are non-degenerate, while if the three frequencies are rationally dependent (i.e., if one of the frequencies is a linear combination of the other two with rational coefficients; for example, if they are all rational numbers) the energy levels above the ground state may be degenerate.

The degeneracy of the levels can be easily evaluated for the *isotropic* oscillator, whose three frequencies are equal. Calling ω the common value of these frequencies, the Hamiltonian becomes

$$H = \frac{\mathbf{P}^2}{2m} + \frac{1}{2}m\omega^2 R^2.$$

The energies of the three-dimensional isotropic HO are given by

$$E_{n_1 n_2 n_3} = \left(n_1 + n_2 + n_3 + \frac{3}{2}\right)\hbar\omega, \qquad n_i = 0, 1, \dots,$$

and thus the energy spectrum is in this case the set

$$\left\{E_N := \left(N + \frac{3}{2}\right)\hbar\omega : N = 0, 1, \dots\right\}.$$

The degeneracy of the energy E_N is the number of ways in which the non-negative integer N can be written as the sum of three non-negative integers $n_{1,2,3}$. To compute this value, note that given $N = 0, 1, \dots$ the sum $n_1 + n_2$ can take the values $n = 0, 1, \dots, N$, and to each of these values there corresponds a unique value of n_3 ($n_3 = N - n$). Thus the degeneracy of the level E_N is given by

$$d_N = \sum_{n=0}^{N}(n + 1) = \sum_{n=1}^{N+1} n = \frac{1}{2}(N + 1)(N + 2), \tag{6.17}$$

<div style="text-align:right">`dN3DHO`</div>

since $n + 1$ is the number of non-negative integer pairs (n_1, n_2) with $n_1 + n_2 = n$. We thus see that $d_N \simeq N^2/2$ becomes very large when N is large, i.e., for highly excited states.

Exercise 6.2. Compute the density of states for the three-dimensional isotropic harmonic oscillator.

Solution. When N is very large, the number of levels with energy less than or equal to $E = \left(N + \frac{3}{2}\right)\hbar\omega \simeq N\hbar\omega$ is given by

$$\rho(E) = \frac{1}{2}\sum_{n=0}^{N}(n + 1)(n + 2) = \frac{N^3}{2}\cdot\frac{1}{N}\sum_{n=0}^{N}\left(\frac{n}{N} + \frac{1}{N}\right)\left(\frac{n}{N} + \frac{2}{N}\right) \simeq \frac{N^3}{2}\int_0^1 x^2\,\mathrm{d}x = \frac{1}{6}N^3$$

$$\simeq \frac{E^3}{6\hbar^3\omega^3}.$$

The density of states is thus

$$\nu(E) = \rho'(E) = \frac{E^2}{2\hbar^3\omega^3}.$$

Note that for the isotropic HO $\nu(E)$ is proportional to E^2, while for the infinite well it was proportional to $E^{1/2}$.

6.2 Separation of variables in spherical coordinates. Central potentials

Spherical coordinates (r, θ, φ) are defined by the equations

$$x_1 = r\sin\theta\cos\varphi, \qquad x_2 = r\sin\theta\sin\varphi, \qquad x_3 = r\cos\theta,$$

with

$$r \geqslant 0, \qquad 0 \leqslant \theta \leqslant \pi, \qquad 0 \leqslant \varphi < 2\pi.$$

Note that at the origin ($r = 0$) the angles θ and φ are undefined, and that on the x_3 axis the azimuthal angle φ is undefined. In fact, the mapping $(r, \theta, \varphi) \rightarrow (x_1, x_2, x_3)$ is a true change of coordinates (i.e., it is smooth, bijective and with a smooth inverse) only for $r > 0$, $0 < \theta < \pi$ and $0 < \varphi < 2\pi$, i.e., outside the half plane $\{x_2 = 0, x_1 \geqslant 0\}$. The Laplacian in spherical coordinates is given by

$$\nabla^2 = \frac{1}{r^2}\partial_r\left(r^2\partial_r\right) + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\right) + \frac{1}{r^2\sin^2\theta}\partial_\varphi^2, \tag{6.18}$$ `Lapsph`

so that the Schrödinger equation with a potential $V(r, \theta, \varphi)$ reads

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\partial_r\left(r^2\partial_r\psi\right) + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\psi\right) + \frac{1}{r^2\sin^2\theta}\partial_\varphi^2\psi\right] + V\psi = E\psi. \tag{6.19}$$ `Schrspher`

Classically, the kinetic energy in spherical coordinates is given by

$$T = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\varphi}^2\right) = \frac{p_r^2}{2m} + \frac{1}{2}mr^2\left(\dot{\theta}^2 + \sin^2\theta\dot{\varphi}^2\right),$$

since

$$p_r = \frac{\partial T}{\partial \dot{r}} = m\dot{r}.$$

The last term in brackets can be expressed in terms of the angular momentum

$$\mathbf{L} = m\mathbf{r} \times \dot{\mathbf{r}} = mr\mathbf{e}_r \times \left(\dot{r}\,\mathbf{e}_r + r\dot{\theta}\,\mathbf{e}_\theta + r\sin\theta\dot{\varphi}\,\mathbf{e}_\varphi\right) = mr^2\left(\dot{\theta}\,\mathbf{e}_\varphi - \sin\theta\dot{\varphi}\,\mathbf{e}_\theta\right),$$

where

$$\mathbf{e}_r = \frac{\partial\mathbf{r}}{\partial r} = \frac{\mathbf{r}}{r} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta),$$

$$\mathbf{e}_\theta = \frac{1}{r}\frac{\partial\mathbf{r}}{\partial\theta} = (\cos\theta\cos\varphi, \cos\theta\sin\varphi, -\sin\theta),$$

$$\mathbf{e}_\varphi = \frac{1}{r\sin\theta}\frac{\partial\mathbf{r}}{\partial\varphi} = (-\sin\varphi, \cos\varphi, 0)$$

are the *unit coordinate vectors* in spherical coordinates, as

$$\frac{1}{2}mr^2\left(\dot{\theta}^2 + \sin^2\theta\dot{\varphi}^2\right) = \frac{\mathbf{L}^2}{2mr^2}.$$

Thus classically we have

$$T = \frac{p_r^2}{2m} + \frac{\mathbf{L}^2}{2mr^2}. \tag{6.20}$$ `Tclasssph`

Since in quantum mechanics

$$T = \frac{\mathbf{P}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2,$$

comparison with Eq. (6.18) suggests that

$$\mathbf{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\right) + \frac{1}{\sin^2\theta}\partial_\varphi^2\right], \tag{6.21}$$ `L2spher`

where $\mathbf{L}$ is the quantum mechanical *angular momentum*

$$\mathbf{L} = \mathbf{R} \times \mathbf{P} = -i\hbar \mathbf{r} \times \nabla.$$

In fact, it can be proved by direct calculation that Eq. (6.21) is indeed true (see Exercise 6.4). We can thus write the Schrödinger equation in spherical coordinates as

$$-\frac{\hbar^2}{2mr^2} \partial_r \left(r^2 \partial_r \psi \right) + \frac{\mathbf{L}^2}{2mr^2} \psi + V\psi = E\psi. \tag{6.22}$$ `SchrL2`

Note that we can unambiguously write $\mathbf{L}^2/(2mr^2)$, instead of using the more precise notations

$$\frac{1}{2mr^2} \mathbf{L}^2 \quad \text{or} \quad \mathbf{L}^2 \frac{1}{2mr^2},$$

since by Eq. (6.21) the operator $\mathbf{L}^2$ commutes with r.

Exercise 6.3. Show that

$$-\frac{\hbar^2}{2mr^2} \partial_r r^2 = \frac{P_r^2}{2m},$$

where

$$P_r = -i\hbar \frac{1}{r} \partial_r r$$

is the *radial momentum* operator[a]. Thus the kinetic energy operator T can be written in spherical coordinates as

$$T = \frac{P_r^2}{2m} + \frac{\mathbf{L}^2}{2mr^2},$$

which is the quantum analogue of Eq. (6.20).

Solution. Indeed,

$$P_r^2 = -\hbar^2 \frac{1}{r} \partial_r r \cdot \frac{1}{r} \partial_r r = -\hbar^2 \frac{1}{r} \partial_r^2 r = -\hbar^2 \left(\partial_r^2 + \frac{1}{r}[\partial_r^2, r] \right) = -\hbar^2 \left(\partial_r^2 + \frac{1}{r} \partial_r [\partial_r, r] + \frac{1}{r} [\partial_r, r] \partial_r \right)$$

$$= -\hbar^2 \left(\partial_r^2 + \frac{2}{r} \partial_r \right) = -\hbar^2 \frac{1}{r^2} \partial_r r^2.$$

It is also straightforward to show that the operator P_r is *Hermitian* (exercise), and is thus an observable.

---
[a]Do not confuse P_r with the radial component of the momentum operator $\mathbf{P} = -i\hbar \nabla$, namely $\mathbf{e}_r \cdot \mathbf{P} = -i\hbar \partial_r$, which is *not* an observable (i.e., is *not* self-adjoint).

Since the operator $\mathbf{L}^2$ is independent of the r coordinate, we try to separate the variable r from the angular variables (θ, φ) by looking for solutions of the Schrödinger equation (6.22) of the form

$$\psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi). \tag{6.23}$$ `psiRY`

Inserting this solution into Eq. (6.22) and dividing by ψ we obtain

$$\frac{\mathbf{L}^2 Y}{\hbar^2 Y} = \frac{1}{R} \partial_r \left(r^2 \partial_r R \right) + r^2 (\varepsilon - v), \tag{6.24}$$ `L2YR`

where we have used the notation

$$v = \frac{2mV}{\hbar^2}, \qquad \varepsilon = \frac{2mE}{\hbar^2}.$$

Since the LHS of Eq. (6.24) depends only on the angle variables (θ, φ), we conclude that:

© *Artemio González López*

> The Schrödinger equation (6.19) is separable in spherical coordinates if and only if the potential V is **central**, i.e., depends only on the radial coordinate r.

For a central potential $V(r)$, the equation (6.24) separates into the two equations

$$\mathbf{L}^2 Y(\theta, \varphi) = \lambda \hbar^2 Y(\theta, \varphi) \tag{6.25}$$ `Ythvpeq`

and

$$-\frac{1}{r^2} \partial_r \left(r^2 \partial_r R(r) \right) + \frac{\lambda}{r^2} R(r) = \left(\varepsilon - v(r) \right) R(r), \tag{6.26}$$ `radeq`

where $\lambda \geqslant 0$ is a (dimensionless) separation constant[1]. The first of these equations is the eigenvalue equation for the operator $\mathbf{L}^2$, $\lambda \hbar^2$ being the *eigenvalue.* In fact, since

$$\mathbf{L}^2 \psi = \mathbf{L}^2 \big(R(r) Y(\theta, \varphi) \big) = R(r) \mathbf{L}^2 Y(\theta, \varphi) = \lambda \hbar^2 R(r) Y(\theta, \varphi) = \lambda \hbar^2 \psi,$$

the wave function $R(r) Y(\theta, \varphi)$, with R and Y satisfying Eqs. (6.25)-(6.26), is a *common eigenfunction* of the *commuting observables*[2] H and $\mathbf{L}^2$, with respective eigenvalues E and $\lambda \hbar^2$.

`exe.L2Lap`

Exercise 6.4. Derive Eq. (6.21) using the following expression for the gradient in spherical coordinates:

$$\nabla = \mathbf{e}_r \partial_r + \frac{1}{r} \mathbf{e}_\theta \partial_\theta + \frac{1}{r \sin \theta} \mathbf{e}_\varphi \partial_\varphi.$$

Solution. We have

$$\frac{\mathbf{L}}{-i\hbar} = \mathbf{r} \times \nabla = r \mathbf{e}_r \times \left(\mathbf{e}_r \partial_r + \frac{1}{r} \mathbf{e}_\theta \partial_\theta + \frac{\mathbf{e}_\varphi}{r \sin \theta} \partial_\varphi \right) = \mathbf{e}_\varphi \partial_\theta - \frac{1}{\sin \theta} \mathbf{e}_\theta \partial_\varphi.$$

Taking into account the explicit expressions of the unit vectors $\mathbf{e}_\theta$ and $\mathbf{e}_\varphi$ given above we obtain

$$L_1 = i\hbar \left(\sin \varphi \partial_\theta + \cot \theta \cos \varphi \partial_\varphi \right), \quad L_2 = i\hbar \left(- \cos \varphi \partial_\theta + \cot \theta \sin \varphi \partial_\varphi \right), \quad L_3 = -i\hbar \partial_\varphi. \tag{6.27}$$ `Lis`

Hence

$$\begin{aligned}
-\frac{L_1^2 + L_2^2}{\hbar^2} &= \left(\sin \varphi \partial_\theta + \cot \theta \cos \varphi \partial_\varphi \right)^2 + \left(- \cos \varphi \partial_\theta + \cot \theta \sin \varphi \partial_\varphi \right)^2 \\
&= \sin \varphi \partial_\theta \sin \varphi \partial_\theta + \cot \theta \cos \varphi \partial_\varphi \cot \theta \cos \varphi \partial_\varphi \\
&\quad + \cot \theta \cos \varphi \partial_\varphi \sin \varphi \partial_\theta - \cot \theta \sin \varphi \partial_\varphi \cos \varphi \partial_\theta \\
&\quad + \cos \varphi \partial_\theta \cos \varphi \partial_\theta + \cot \theta \sin \varphi \partial_\varphi \cot \theta \sin \varphi \partial_\varphi \\
&= \sin^2 \varphi \, \partial_\theta^2 + \cot^2 \theta \cos \varphi \left(\cos \varphi \, \partial_\varphi^2 - \sin \varphi \partial_\varphi \right) + \cot \theta \cos \varphi \left(\sin \varphi \, \partial_\varphi \partial_\theta + \cos \varphi \, \partial_\theta \right) \\
&\quad - \cot \theta \sin \varphi \left(\cos \varphi \, \partial_\varphi \partial_\theta - \sin \varphi \, \partial_\theta \right) + \cos^2 \varphi \, \partial_\theta^2 + \cot^2 \theta \sin \varphi \left(\sin \varphi \, \partial_\varphi^2 + \cos \varphi \partial_\varphi \right) \\
&= \partial_\theta^2 + \cot \theta \, \partial_\theta + \cot^2 \theta \, \partial_\varphi^2,
\end{aligned}$$

and therefore

$$-\frac{\mathbf{L}^2}{\hbar^2} = \partial_\theta^2 + \cot \theta \, \partial_\theta + (1 + \cot^2 \theta) \partial_\varphi^2 = \partial_\theta^2 + \cot \theta \, \partial_\theta + \frac{1}{\sin^2 \theta} \partial_\varphi^2.$$

---

[1]See Exercise 6.5 for the proof that λ must be non-negative.
[2]In fact, it was shown in Exercise 4.3 that when V is a central potential each component L_i of $\mathbf{L}$ commutes with H.

This is clearly equal to Eq. (6.21), since

$$\frac{1}{\sin\theta}\partial_\theta(\sin\theta\,\partial_\theta) = \partial_\theta^2 + \cot\theta\,\partial_\theta.$$

---

exe.L2sa

Exercise 6.5. Show that $\mathbf{L}^2$, considered as a linear operator acting on the Hilbert space $L^2([0,\pi] \times [0,2\pi]; \mathrm{d}\Omega)$, is positive semidefinite. Deduce from this fact that the separation constant λ in Eq. (6.25) is non-negative.

Solution. Indeed, given a function $f(\theta,\varphi)$ in the domain of $\mathbf{L}^2$ we have

$$
\begin{aligned}
\left(f, -\frac{1}{\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta f\right)\right) &= -\int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta\, f^*\partial_\theta\left(\sin\theta\,\partial_\theta f\right) \\
&= -\int_0^{2\pi} \mathrm{d}\varphi\, \sin\theta\, f^*\partial_\theta f \Big|_{\theta=0}^{\theta=\pi} + \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta\, \sin\theta\,(\partial_\theta f^*)(\partial_\theta f) \\
&= \left\|\partial_\theta f\right\|^2 \geqslant 0.
\end{aligned}
$$

Similarly,

$$
\begin{aligned}
\left(f, -\frac{1}{\sin^2\theta}\partial_\varphi^2 f\right) &= -\int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta\, \frac{f^*}{\sin\theta}\partial_\varphi^2 f \\
&= -\int_0^\pi \mathrm{d}\theta\, \frac{f^*}{\sin\theta}\partial_\varphi f \Big|_{\varphi=0}^{\varphi=2\pi} + \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta\, \frac{1}{\sin\theta}(\partial_\varphi f^*)(\partial_\varphi f) \\
&= \left\|\frac{\partial_\varphi f}{\sin\theta}\right\|^2 \geqslant 0,
\end{aligned}
$$

where we have taken into account that

$$f(\theta, 2\pi) = f(\theta, 0), \qquad \partial_\varphi f(\theta, 2\pi) = \partial_\varphi f(\theta, 0). \tag{6.28}$$

percondvp

From Eq. (6.21) it then follows that

$$(f, \mathbf{L}^2 f) \geqslant 0$$

for any function $f(\theta,\varphi)$, so that $\mathbf{L}^2$ is indeed positive semidefinite. Taking the scalar product of both sides of the equation

$$\mathbf{L}^2 Y(\theta,\varphi) = \lambda\hbar^2 Y(\theta,\varphi)$$

with the function $Y(\theta,\varphi)$ we then obtain

$$\lambda\hbar^2\|Y\|^2 = (Y, \mathbf{L}^2 Y) \geqslant 0 \quad \Longrightarrow \quad \lambda \geqslant 0,$$

as claimed.

Alternative proof. The operators L_i, considered as linear operators from the Hilbert space $L^2([0,\pi] \times [0,2\pi]; \mathrm{d}\Omega)$ into itself, are still self-adjoint. This can be proved by integrating by parts, taking into account the boundary conditions (6.28) above (exercise). Once this fact is established the claim follows immediately, since

$$(f, \mathbf{L}^2 f) = \sum_{i=1}^3 (f, L_i^2 f) = \sum_{i=1}^3 (L_i f, L_i f) = \sum_{i=1}^3 \|L_i f\|^2 \geqslant 0.$$

6.3 Spectrum of $\mathbf{L}^2$

Let us next determine the eigenvalues of the operator $\mathbf{L}^2$, or equivalently the allowed values of the separation constant λ in Eq. (6.25). To this end, we note that a function $Y(\theta, \varphi)$ of the angles θ and φ can be regarded as a function of the components $(\hat{x}_1, \hat{x}_2, \hat{x}_3)$ of the unit vector $\mathbf{r}/r$. Let us Taylor expand Y in powers of the latter variables as

$$Y = \sum_{l \geqslant 0} p_l(\hat{x}_1, \hat{x}_2, \hat{x}_3), \tag{6.29}$$

where $p_l(\hat{x}_1, \hat{x}_2, \hat{x}_3)$ is a homogeneous polynomial[3] in $(\hat{x}_i, \hat{x}_2, \hat{x}_3)$ of degree l (or possibly zero). It follows that

$$r^l p_l(\mathbf{r}/r) = P_l(\mathbf{r}),$$

where $P_l(\mathbf{r})$ is a *homogeneous polynomial* of degree l in $\mathbf{r} = (x_1, x_2, x_3)$ (or possibly zero). Moreover, since the components $x_i \partial_{x_j} - x_j \partial_{x_i}$ of $\mathbf{L}$ applied to a homogeneous polynomial in $\mathbf{r}$ *do not lower the degree,* $\mathbf{L}^2 P_l$ is another homogeneous polynomial in $\mathbf{r}$ of degree l (or possibly zero). Since $\mathbf{L}^2 f(r) = f(r)\mathbf{L}^2$,

$$\mathbf{L}^2 p_l = \mathbf{L}^2(r^{-l} P_l) = r^{-l} \mathbf{L}^2(P_l)$$

is then a homogeneous polynomial in $\mathbf{r}/r$ of degree l (or possibly zero). We thus have

$$\mathbf{L}^2 Y = \sum_{l \geqslant 0} \mathbf{L}^2 p_l = \lambda \hbar^2 Y = \lambda \hbar^2 \sum_{l \geqslant 0} p_l \iff \mathbf{L}^2 p_l = \lambda \hbar^2 p_l, \quad \forall l \geqslant 0.$$

In other words, each non-zero polynomial p_l in the expansion (6.29) is an eigenfunction of $\mathbf{L}^2$ with the same eigenvalue $\lambda \hbar^2$ as Y. We can thus assume w.l.o.g. that $Y(\theta, \varphi)$ *is a homogeneous polynomial in* $\mathbf{r}/r$ *of degree l.*

We next note that from Eqs. (6.18) and (6.21) it follows that

$$\nabla^2 = \frac{1}{r^2} \left(\partial_r r^2 \partial_r - \frac{\mathbf{L}^2}{\hbar^2} \right). \tag{6.30}$$

Applying both sides of this equality to the function $r^l Y(\theta, \varphi)$, which by hypothesis is a homogeneous polynomial in $\mathbf{r}$ of degree l satisfying the eigenvalue equation (6.25), we obtain:

$$\nabla^2(r^l Y) = l(l+1)r^{l-2}Y - \frac{1}{\hbar^2 r^2}\mathbf{L}^2(r^l Y) = l(l+1)r^{l-2}Y - \frac{r^{l-2}}{\hbar^2}\mathbf{L}^2 Y = \left[l(l+1)-\lambda\right]r^{l-2}Y. \tag{6.31}$$

Since ∇^2 lowers the degree by two, the LHS of the previous equation is a homogeneous polynomial of degree $l-2$ in $\mathbf{r}$, including the zero polynomial. Hence either $l(l+1) - \lambda = 0$ or $r^{l-2} p_l$ is a homogeneous polynomial of degree $l-2$ in $\mathbf{r}$. However, the latter possibility cannot occur. Indeed, if $r^{l-2}Y = r^{-2}(r^l Y)$ were a homogeneous polynomial of degree $l-2$ in $\mathbf{r}$ then the polynomial $r^l Y$ would contain the factor r^2. But this is not possible, since in that case Y would contain the factor $\hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2$, which we had agreed to eliminate beforehand (cf. the previous footnote). This shows that the LHS of the previous displayed equation must vanish, i.e., we must have $\lambda = l(l+1)$ and $\nabla^2(r^l Y) = 0$. In other

---

[3]In other words,

$$p_l = \sum_{\substack{n_1, n_2, n_3 \\ n_1+n_2+n_3=l}} c_{n_1 n_2 n_3} \hat{x}_1^{n_1} \hat{x}_2^{n_2} \hat{x}_3^{n_3},$$

with $c_{n_1 n_2 n_3} \in \mathbb{C}$. Since $\hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2 = 1$, it is understood that any factor of $(\hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2)^k$ has been removed from p_l. For example, a homogeneous polynomial of degree zero is a constant, of degree 1 a linear combination of $\hat{x}_1, \hat{x}_2,$ and $\hat{x}_3$, of degree 2 a linear combination of $\hat{x}_i^2$ and $\hat{x}_i \hat{x}_j$ with $1 \leqslant i < j \leqslant 3$, etc.

words, if Y is a (nonzero) homogeneous polynomial of degree l in $\mathbf{r}/r$ then Y is an eigenfunction of $\mathbf{L}^2$ with eigenvalue $l(l+1)\hbar^2$ provided that

$$\nabla^2\big(r^l Y(\theta, \varphi)\big) = 0. \tag{6.32}$$ `LaprlY`

In other words, Y is the restriction to the unit sphere ($r = 1$) of a *harmonic homogeneous polynomial* of degree l in r, namely $r^l Y$. For this reason, the homogeneous polynomials in $\mathbf{r}/r$ solving Eq. (6.25) are called **spherical harmonics.** Since an arbitrary eigenfunction $Y(\theta, \varphi)$ of $\mathbf{L}^2$ must be a sum of homogeneous polynomials in $\mathbf{r}/r$ all having the *same* eigenvalue as Y, i.e., the same *degree*, it follows that the eigenvalues of $\mathbf{L}^2$ are the numbers

$$l(l+1)\hbar^2, \qquad l = 0, 1, \ldots,$$

and its eigenfunctions are the spherical harmonics. We have thus proved the following fundamental result:

> The eigenvalues of the operator $\mathbf{L}^2$ are the numbers $l(l+1)\hbar^2$, with l a non-negative integer. The solutions $Y(\theta, \varphi)$ of Eq. (6.25) with $\lambda = l(l+1)$ are the *spherical harmonics* of degree l, i.e., the *homogeneous polynomials* of degree l in $\mathbf{r}/r$ satisfying Eq. (6.32).

Remark. Since $\mathbf{L}^2$ commutes with $f(r)$, if $Y(\theta, \varphi)$ satisfies Eq. (6.25) with $\lambda = l(l+1)$ then $f(r)Y(\theta, \varphi)$ is also an eigenfunction of $\mathbf{L}^2$ with eigenvalue $l(l+1)\hbar^2$. ∎

We shall next study Eqs. (6.25) and (6.26). Before doing so, note that since the volume element in spherical coordinates is $\mathrm{d}^3 r = r^2 \, \mathrm{d}r \, \mathrm{d}\Omega$, where

$$\mathrm{d}\Omega := \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi$$

is the surface element on the unit sphere $r = 1$, the normalization condition for the product (6.23) reads

$$\|\psi\|^2 = \int \mathrm{d}^3 r \, |\psi|^2 = \left(\int_0^\infty \mathrm{d}r \, r^2 \, |R(r)|^2\right) \left(\int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, |Y(\theta, \varphi)|^2\right) = 1,$$

It is convenient to require that both the radial and the angular parts of the wave function be normalized separately, namely that

$$\int_0^\infty \mathrm{d}r \, r^2 \, |R(r)|^2 = \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, |Y(\theta, \varphi)|^2 = 1. \tag{6.33}$$ `normRY`

We can thus regard $R(r)$ and $Y(\theta, \varphi)$ as unit vectors in the Hilbert spaces $L^2([0, \infty); r^2 \, \mathrm{d}r)$ and $L^2([0, \pi] \times [0, 2\pi]; \mathrm{d}\Omega)$, with respective inner products

$$(R_1, R_2) = \int_0^\infty \mathrm{d}r \, r^2 \, R_1^*(r) R_2(r), \qquad (Y_1, Y_2) = \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^*(\theta, \varphi) Y_2(\theta, \varphi).$$

6.4 The radial equation

`sec.radeq`

We shall next study the radial equation (6.26) with $\lambda = l(l+1)$, where l is a non-negative integer. From the identity

$$\partial_r r = r \partial_r + 1$$

it follows that

$$\frac{1}{r^2} \partial_r r^2 \partial_r = \frac{1}{r^2} \partial_r r \cdot r \partial_r = \frac{1}{r} \partial_r r \partial_r + \frac{1}{r} \partial_r = \frac{1}{r} \partial_r^2 r - \frac{1}{r} \partial_r + \frac{1}{r} \partial_r = \frac{1}{r} \partial_r^2 r. \tag{6.34}$$ `pr2`

Setting

$$u(r) = rR(r), \qquad (6.35) \quad \boxed{\text{udef}}$$

the radial equation (6.26) (multiplied by r) can be written as

$$-u''(r) + \left(\frac{l(l+1)}{r^2} + v(r) \right) u(r) = \varepsilon u(r), \qquad (6.36) \quad \boxed{\text{radequ}}$$

where the prime denotes derivative with respect to r. Multiplying throughout by the factor $\hbar^2/(2m)$ we obtain the equivalent equation

$$-\frac{\hbar^2}{2m} u''(r) + V_l(r)u(r) = E u(r), \qquad (6.37) \quad \boxed{\text{radequunits}}$$

where the *effective potential* $V_l(r)$ (which depends on the angular momentum quantum number l) is given by

$$V_l(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}. \qquad (6.38) \quad \boxed{\text{Urdef}}$$

Since $l(l+1)\hbar^2$ is the eigenvalue of the square of the angular momentum $\mathbf{L}^2$ for the angular part of the wave function, the latter equation is the analogue of the classical formula

$$V_l(r) = V(r) + \frac{\mathbf{L}^2}{2mr^2}.$$

Note that if we are looking for the *bound states* of the central potential $V(r)$ the wave function (6.23) must be normalizable, so that —using the normalization convention in Eq. (6.33)— the radial wave function $u(r)$ must satisfy

$$\int_0^\infty \mathrm{d}r \, |u(r)|^2 = 1. \qquad (6.39) \quad \boxed{\text{normurad}}$$

Thus *the radial equation (6.37) for $u(r)$ is formally the Schrödinger equation for a one-dimensional particle moving on the half-line $[0, \infty)$ under the potential $V_l(r)$.* We must, however, impose an appropriate *boundary condition* to the wave function $u(r)$ at the origin. To find this condition we shall assume that the potential $V(r)$ is either finite at the origin, or diverges there slower than $1/r^2$. In other words,

$$\lim_{r \to 0+} r^2 V(r) = 0. \qquad (6.40) \quad \boxed{\text{Vrorig}}$$

If this condition is satisfied then the radial equation (6.36) implies that

$$l(l+1) - r^2 \frac{u''}{u} = r^2 \big(\varepsilon - v(r) \big) \xrightarrow[r \to 0+]{} 0.$$

If

$$u(r) \underset{r \to 0+}{\sim} r^n \quad \Longrightarrow \quad l(l+1) - r^2 \frac{u''}{u} \sim l(l+1) - n(n-1) = 0,$$

either $n = l + 1$ or $n = -l$. The latter possibility should be ruled out, since $u(r) \sim r^{-l}$ at the origin would imply that $|u(r)|^2 \sim r^{-2l}$ would not be integrable at the origin unless $l = 0$, while for $l = 0$ the condition $u(r) \sim 1$ for $r \to 0+$ would imply that $R(r) \sim 1/r$, which is not acceptable[4].

We thus conclude that the radial equation (6.36) should be supplemented by the boundary condition

$$u(r) \underset{r \to 0+}{\sim} r^{l+1}, \tag{6.41}$$ `bcrad`

or equivalently (since r^{-l} does not tend to zero as $r \to 0+$ for $l = 0, 1, \dots$)

$$\lim_{r \to 0+} u(r) = 0. \tag{6.42}$$ `bcradlim`

Note that in terms of the radial part of the wave function $R(r)$ the previous relation becomes

$$R(r) \underset{r \to 0+}{\sim} r^{l}, \tag{6.43}$$ `Rrorig`

so that the full wave function $\psi(\mathbf{r})$ in Eq. (6.23) satisfies

$$\psi(\mathbf{r}) \underset{r \to 0+}{\sim} r^{l} Y(\theta, \varphi). \tag{6.44}$$ `psiorig`

In other words, $\psi(\mathbf{r})$ approaches a harmonic polynomial of degree l near the origin.

Since we are assuming that the potential $V(r)$ satisfies condition (6.40), for $l > 0$ the effective potential in the Schrödinger equation (6.36) verifies

$$v_l(r) = v(r) + \frac{l(l+1)}{r^2} \underset{r \to 0+}{\simeq} \frac{l(l+1)}{r^2} \to \infty.$$

For $l = 0$ the centrifugal barrier term $l(l+1)/r^2$ disappears, but the boundary condition (6.41) on $u(r)$ is equivalent to placing an infinite potential barrier at $r = 0$. Thus the radial equation (6.37) with the boundary condition (6.41) is equivalent to solving a one-dimensional Schrödinger equation with a potential

$$\begin{cases} \infty, & r < 0 \\ \frac{l(l+1)\hbar^2}{2mr^2} + V(r), & r > 0. \end{cases}$$

Since, in the notation of Section 3.5, $V_- = \infty$, from the discussion in the latter section it then follows that:

> For all $l = 0, 1, \dots$, all the energy levels of the radial Schrödinger equation (6.37) (genuine or generalized) are *non-degenerate*.

If we further assumes that the limit

$$V_\infty := \lim_{r \to \infty} V(r) = \lim_{r \to \infty} V_l(r)$$

exists (or is infinite), for any $l = 0, 1, \dots$ the energy spectrum of the effective Schrödinger equation (6.37)-(6.38) verifies:

---

[4]Indeed, when $l = 0$ the angular part of the wave function $Y(\theta, \varphi)$ is a constant, and hence $\psi(\mathbf{r}) = R(r) \sim 1/r$. However, $1/r$ cannot be a solution of the Schrödinger equation unless the potential $V(r)$ contains a delta function term, since

$$\nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta(\mathbf{r}).$$

1) $V_\infty = -\infty$

In this case there is no point spectrum, and the continuous spectrum is the whole real line. This case is actually unphysical, since the particle would cascade indefinitely to states of increasingly lower energy, radiating in the process an infinite amount of energy.

2) $V_\infty < \infty$

The point spectrum is contained in the interval $(\min V_l(r), V_\infty)$. In particular, there is no point spectrum if $V_l(r) \geqslant V_\infty$ for all r. The point spectrum (when it exists) is either finite, or countably infinite with an accumulation point at V_∞ (and in the latter case V_∞ belongs to the spectrum, usually to its continuous part). The half-line (V_∞, ∞) belongs to the continuous spectrum.

A potential of this form is the *Coulomb potential* $V(r) = \alpha/r$, with continuous spectrum $(0, \infty)$ (with or without the point 0) and no point spectrum in the repulsive case ($\alpha > 0$), while in the attractive case ($\alpha < 0$) there is both point spectrum contained in the interval $\left(-\frac{m\alpha^2}{2l(l+1)\hbar^2}, 0\right)$ as well as continuous spectrum including the half-line $(0, \infty)$. (In fact, we shall see in the sequel that when $\alpha < 0$ the point spectrum is countably infinite and accumulates at zero, which belongs to the continuous spectrum.)

3) $V_\infty = \infty$

In this case there is no continuous spectrum, and the point spectrum is a countably infinite set with no accumulation points, unbounded above and strictly bounded below by $\min V_l(r)$. A potential of this type is the *isotropic harmonic oscillator* potential $V(r) = \frac{1}{2}kr^2$ with $k > 0$.

Notation. As in Section (3.3), we shall denote by

$$E_{1l} < E_{2l} < \cdots < E_{nl} < \cdots$$

the point spectrum of the radial equation (6.37) (i.e., the values of E for which the latter equation admits a square integrable solution) for a given $l = 0, 1, \ldots$. We shall accordingly denote by $u_{nl}(r)$ a (normalized) eigenfunction with energy E_{nl} (usually chosen so that $u_{nl}(r)$ is real for $r > 0$), and set $R_{nl}(r) = r^{-1}u_{nl}(r)$.

Note that the above notation for the eigenfunctions R_{nl} or u_{nl} is unambiguous (up to a trivial constant phase), since by the previous framed remark the spectrum of the radial Schrödinger equation (6.37) is non-degenerate.

The point spectrum of the Hamiltonian

$$H = \frac{\mathbf{P}^2}{2m} + V(R) \tag{6.45} \quad \boxed{\text{Hcentral}}$$

is the union of the point spectra of all the radial Schrödinger equations (6.37), namely (using the previous notation)

$$\sigma_p(H) = \big\{E_{nl} : n = 1, 2, \ldots, \ l = 0, 1, \ldots\big\}.$$

By construction,

$$n < m \quad \Longrightarrow \quad E_{nl} < E_{ml}.$$

It can also be shown [GP90, p. 231] that

$$l < l' \quad \Longrightarrow \quad E_{nl} < E_{nl'}. \tag{6.46} \quad \boxed{\text{Enlnlp}}$$

An immediate consequence of Eq. (6.46) is the following:

The *ground state* of the Hamiltonian H has angular momentum $l = 0$ and energy E_{10}.

6.5 The angular equation. Spherical harmonics

`c.spherharm`

The angular equation

$$\mathbf{L}^2 Y(\theta, \varphi) = l(l+1)\hbar^2 Y(\theta, \varphi) \tag{6.47}$$

`angeq`

is simply the eigenvalue equation for the operator $\mathbf{L}^2$. Since this operator commutes with any of the components L_i of $\mathbf{L}$, without loss of generality we can look for common eigenvalues of $\mathbf{L}^2$ and one of the operators L_i. From Exercise 6.4 we see that in spherical coordinates the simplest of these operators is

$$L_3 = -\mathrm{i}\hbar\partial_\varphi.$$

We thus shall look for solutions of the angular equation (6.47) that satisfy the eigenvalue equation

$$L_3 Y \equiv -\mathrm{i}\hbar\partial_\varphi Y = \mu Y.$$

The solution of the latter equation is immediate:

$$Y(\theta, \varphi) = y(\theta)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\mu\varphi},$$

where $y(\theta)$ is an arbitrary function of θ. However, since the azimuthal angles $\varphi = 0$ and $\varphi = 2\pi$ actually correspond to the same point in space we must require the boundary condition

$$Y(\theta, 0) = Y(\theta, 2\pi), \tag{6.48}$$

`percond`

which implies that μ can only take the values $m\hbar$ with $m \in \mathbb{Z}$. In other words, the spectrum of the operator L_3 (in fact, of any component of the angular momentum or, in general, any operator $\mathbf{n}\cdot\mathbf{L}$ with $\mathbf{n}$ an arbitrary constant unit vector) is the discrete set of numbers

$$\{m\hbar : m \in \mathbb{Z}\}.$$

For historical reasons, the integer m is called the *magnetic quantum number*.

Remark. The condition $Y(\theta, 2\pi) = Y(\theta, 0)$ is also necessary for the operator L_3 to be Hermitian. Indeed,

$$
\begin{aligned}
\left(Y_1, L_3 Y_2\right) &= \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^*(-\mathrm{i}\hbar\partial_\varphi)Y_2 \\
&= -\mathrm{i}\hbar \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^* Y_2 \Big|_{\varphi=0}^{\varphi=2\pi} + \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, (-\mathrm{i}\hbar\partial_\varphi Y_1)^* Y_2 \\
&= -\mathrm{i}\hbar \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^* Y_2 \Big|_{\varphi=0}^{\varphi=2\pi} + (L_3 Y_1, Y_2) \\
&= (L_3 Y_1, Y_2) \iff \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^* Y_2 \Big|_{\varphi=0} = \int_0^\pi \mathrm{d}\theta \, \sin\theta \, Y_1^* Y_2 \Big|_{\varphi=2\pi}.
\end{aligned}
$$

Since Y_1 and Y_2 are arbitrary functions of the variables (θ, φ), the latter condition requires that both functions satisfy the boundary condition (6.48). ∎

Substituting

$$Y(\theta, \varphi) = y(\theta)\mathrm{e}^{\mathrm{i}m\varphi} \qquad (\text{with } m \in \mathbb{Z})$$

into the angular equation (6.47), and taking into account the explicit expression (6.21) for the operator $\mathbf{L}^2$, we easily arrive at the equation

$$\sin\theta \, \partial_\theta\big(\sin\theta \, \partial_\theta y\big) + l(l+1)\sin^2\theta \, y = m^2 y. \tag{6.49}$$

`angeqlm`

Note that

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \, \sin\theta \, |Y(\theta,\varphi)|^2 = 2\pi \int_0^\pi d\theta \, \sin\theta \, |y(\theta)|^2,$$

and hence we seek for solutions $y(\theta)$ of Eq. (6.49) that are square integrable on the interval $[0,\pi]$. The change of independent variable

$$s = \cos\theta \in [-1,1],$$

so that

$$\partial_\theta = \frac{ds}{d\theta}\partial_s = -\sin\theta \, \partial_s \quad \Longrightarrow \quad \sin\theta \, \partial_\theta = -\sin^2\theta \, \partial_s = -(1-s^2)\partial_s$$

transforms Eq. (6.49) into the *associated Legendre equation*

$$\partial_s\left[(1-s^2)\partial_s w\right] + \left(l(l+1) - \frac{m^2}{1-s^2}\right)w = 0,$$

or equivalently

$$(1-s^2)\,\partial_s^2 w - 2s\,\partial_s w + \left(l(l+1) - \frac{m^2}{1-s^2}\right)w = 0 \tag{6.50}$$ `ALeq`

with $w(s) = y(\theta)$. Note that the square integrability of $y(\theta)$ on the interval $[0,\pi]$ with respect to the measure $\sin\theta \, d\theta$ is equivalent to the square integrability of $w(s)$ on $[-1,1]$ with respect to the standard measure ds. It can be shown that equation (6.50) admits a solution square integrable on the interval $[-1,1]$ only for the following values of the magnetic quantum number m:

$$m = -l, -l+1, \ldots, l \,. \tag{6.51}$$ `mcond`

When m takes on one of these values, the square integrable solutions of the associated Legendre equation are proportional to the *associated Legendre functions*

$$P_l^{|m|}(s) = (-1)^{|m|}(1-s^2)^{|m|/2}\partial_s^{|m|}P_l(s), \tag{6.52}$$ `PlmLeg`

where

$$P_l(s) = \frac{1}{2^l l!}\,\partial_s^l\,(s^2-1)^l \tag{6.53}$$ `PlLeg`

is the *Legendre polynomial* of degree l. The latter polynomials are (up to a multiplicative constant) the polynomial solutions of Eq. (6.50) with $m = 0$. In fact, it is convenient to define

$$P_l^{-m}(s) = (-1)^m\frac{(l-m)!}{(l+m)!}\,P_l^m(s), \qquad m > 0, \tag{6.54}$$ `Plmm`

since then we can write

$$P_l^m(s) = \frac{(-1)^m}{2^l l!}(1-s^2)^{m/2}\partial_s^{l+m}(s^2-1)^l \tag{6.55}$$ `Plmall`

for both positive and negative values of m (cf. Exercise 6.6). The admissible (i.e., square integrable on $[0,\pi] \times [0,2\pi]$ with respect to the measure $d\Omega = \sin\theta \, d\theta \, d\varphi$) solutions of equation (6.49) —i.e., for the common eigenfunctions of the operators $\mathbf{L}^2$ and L_3 with respective eigenvalues $l(l+1)\hbar^2$ and $m\hbar$— are then proportional to the spherical harmonics Y_l^m defined by

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi}, \qquad m = -l, -l+1, \ldots, l, \tag{6.56}$$ `SpherHarm`

where the factor multiplying $P_l^{|m|}\mathrm{e}^{\mathrm{i}m\varphi}$ ensures that

$$\left\| Y_l^m \right\| = 1 \tag{6.57}$$

`Ylmnorm`

(see Exercise 6.7 for a proof). The functions Y_l^m with $m = -l, \ldots, l$ are thus a basis of eigenfunctions of L_3 in the eigenspace of $\mathbf{L}^2$ with eigenvalue $l(l+1)\hbar^2$. In other words:

> The square integrable solutions of the angular equation (6.47) are linear combinations of the **spherical harmonics** $Y_l^m(\theta, \varphi)$ in Eq. (6.56) with $m = -l, -l+1, \ldots, l$. The latter functions are normalized on the domain $[0, \pi] \times [0, 2\pi]$ with respect to the measure $\mathrm{d}\Omega = \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi$, and satisfy the eigenvalue equations
> $$\mathbf{L}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m, \qquad L_3 Y_l^m = m\hbar Y_l^m. \tag{6.58}$$

`Ylmeigeqs`

In particular, note that from Eqs. (6.54) and (6.56) it follows that

$$Y_l^{-m}(\theta, \varphi) = (-1)^m \mathrm{e}^{-2\mathrm{i}m\varphi} Y_l^m(\theta, \varphi). \tag{6.59}$$

`Ylpmm`

Remarks.

- If $(l, m) \neq (l', m')$ then Y_{lm} and $Y_{l'm'}$ are *orthogonal*, since they are eigenfunctions of a self-adjoint operator ($\mathbf{L}^2$ or L_3) with different eigenvalues. Since by construction the spherical harmonics are normalized, we conclude that the set

$$\left\{ Y_l^m : m = -l, -l+1, \ldots, l, \ \ l = 0, 1, \ldots \right\} \tag{6.60}$$

`Ylmset`

is an orthonormal set in $L^2([0, \pi] \times [0, 2\pi]; \mathrm{d}\Omega)$. In other words,

$$\left(Y_l^m, Y_{l'}^{m'} \right) \equiv \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, \left[Y_l^m(\theta, \varphi) \right]^* Y_{l'}^{m'}(\theta, \varphi) = \delta_{ll'}\delta_{mm'}. \tag{6.61}$$

`Ylmorth`

In fact, it can be shown that the functions spherical harmonics Y_l^m are also *complete,* i.e, the set (6.60) is an *orthonormal basis* of $L^2([0, \pi] \times [0, 2\pi]; \mathrm{d}\Omega)$. In other words, every function $f(\theta, \varphi) \in L^2([0, \pi] \times [0, 2\pi]; \mathrm{d}\Omega)$ can be expanded as

$$f(\theta, \varphi) = \sum_{l=0}^\infty \sum_{m=-l}^l c_{lm} Y_l^m(\theta, \varphi),$$

with

$$c_{lm} = \left(Y_{lm}, f \right) = \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \, \sin\theta \, \left[Y_l^m(\theta, \varphi) \right]^* f(\theta, \varphi).$$

- From Eqs. (6.52)-(6.53), it follows that $P_l^{|m|}(\cos\theta)$ is a polynomial of degree $l - |m|$ in $\cos\theta$ multiplied by $\sin^{|m|}\theta$. Hence for m even $P_l^{|m|}$ can be expressed as a polynomial of degree l in $\cos\theta$, while when m is odd $P_l^{|m|}$ is the product of $\sin\theta$ times a polynomial of degree $l - 1$ in $\cos\theta$.

- In spherical coordinates, the *parity transformation* $\mathbf{r} \mapsto -\mathbf{r}$ corresponds to[5]

$$(r, \theta, \varphi) \mapsto (r, \pi - \theta, \varphi \pm \pi).$$

Since $\cos(\pi - \theta) = -\cos\theta$ and $P_l^m(s)$ has obviously parity $(-1)^{l+m}$ under $s \mapsto -s$, under a parity transformations the spherical harmonics behave as

$$Y_l^m(\theta, \varphi) \mapsto Y_l^m(\pi - \theta, \varphi \pm \pi) = (-1)^{l+m}(-1)^m Y_l^m(\theta, \varphi) = (-1)^l Y_l^m(\theta, \varphi).$$

In other words, *the spherical harmonics have parity* $(-1)^l$ (independent of m) under the transformation $\mathbf{r} \mapsto -\mathbf{r}$. ∎

---

[5]The $\pm$ in the following formula is the sign of $\pi - \varphi$.

exe.SHnegm

Exercise 6.6. Show that

$$(1-s^2)^{-m/2}\partial_s^{l-m}(s^2-1)^l = (-1)^m \frac{(l-m)!}{(l+m)!}(1-s^2)^{m/2}\partial_s^{l+m}(s^2-1)^l, \qquad m = -l, -l+1, \ldots, l.$$

Solution. Since the identity doesn't change when m goes into $-m$, we can assume w.l.o.g. that $m > 0$. We then have

$$\partial_s^{l-m}(s^2-1)^l = \partial_s^{l-m}\big[(s+1)^l(s-1)^l\big] = \sum_{k=0}^{l-m}\binom{l-m}{k}\frac{(l!)^2}{(l-k)!(k+m)!}(s+1)^{l-k}(s-1)^{k+m}.$$

On the other hand,

$$\partial_s^{l+m}(s^2-1)^l = \partial_s^{l+m}\big[(s+1)^l(s-1)^l\big] = \sum_{k=m}^{l}\binom{l+m}{k}\frac{(l!)^2}{(l-k)!(k-m)!}(s+1)^{l-k}(s-1)^{k-m}$$

$$= \sum_{k=0}^{l-m}\binom{l+m}{k+m}\frac{(l!)^2}{(l-k-m)!k!}(s+1)^{l-k-m}(s-1)^k,$$

and hence

$$(1-s^2)^m\partial_s^{l+m}(s^2-1)^l = (-1)^m \sum_{k=0}^{l-m}\binom{l+m}{k+m}\frac{(l!)^2}{(l-k-m)!k!}(s+1)^{l-k}(s-1)^{k+m}.$$

From the identity

$$\binom{l-m}{k}\binom{l+m}{k+m}^{-1}\frac{(l-k-m)!k!}{(l-k)!(k+m)!} = \frac{(l-m)!}{(l+m)!}$$

it then follows that

$$\partial_s^{l-m}(s^2-1)^l = (-1)^m \frac{(l-m)!}{(l+m)!}(1-s^2)^m\partial_s^{l+m}(s^2-1)^l,$$

from which the proposed identity is obtained multiplying both sides by $(1-s^2)^{-m/2}$.

Note: the previous identity suggests defining the associated Legendre polynomial $P_l^m(s)$ by

$$P_l^m(s) = \frac{(-1)^m}{2^l l!}(1-s^2)^{m/2}\partial_s^{l+m}(s^2-1)^l$$

for both positive and negative values of m between $-l$ and l. This definition obviously coincides with Eqs. (6.52)-(6.53) for $m > 0$, and for $m < 0$ the identity just proved implies that

$$P_l^{-m}(s) = (-1)^m \frac{(l-m)!}{(l+m)!}\, P_l^m(s),$$

which is Eq. (6.54).

pherharmnorm

Exercise 6.7. Using the identity in the previous exercise, show that

$$\int_{-1}^{1} ds\, \big[P_l^m(s)\big]^2 = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}. \tag{6.62}$$

normPlm

Solution. Suppose, to begin with, that $m \geqslant 0$. By the identity in the previous exercise, we have

$$
\int_{-1}^{1} \mathrm{d}s \left[P_l^m(s) \right]^2 = (-1)^m \frac{(l+m)!}{(l-m)!} \int_{-1}^{1} \mathrm{d}s \, P_l^m(s) P_l^{-m}(s)
$$

$$
= \frac{(-1)^m}{2^{2l}(l!)^2} \frac{(l+m)!}{(l-m)!} \int_{-1}^{1} \mathrm{d}s \left[\partial_s^{l+m}(s^2-1)^l \right] \left[\partial_s^{l-m}(s^2-1)^l \right]
$$

$$
= \frac{1}{2^{2l}(l!)^2} \frac{(l+m)!}{(l-m)!} \int_{-1}^{1} \mathrm{d}s \, (1-s^2)^l \partial_s^{2l}(s^2-1)^l = \frac{(2l)!}{2^{2l}(l!)^2} \frac{(l+m)!}{(l-m)!} \int_{-1}^{1} \mathrm{d}s \, (1-s^2)^l,
$$

where we have integrated by parts $l-m$ times taking into account that for $m \geqslant 0$ the term $\partial_s^{l-m-k}(s^2-1)^l$ vanishes at $s = \pm 1$ for $k = 0, \ldots, l-m$ (exercise). Integrating by parts l times we find

$$
\int_{-1}^{1} \mathrm{d}s \, (1-s^2)^l = \int_{-1}^{1} \mathrm{d}s \, (1-s)^l(1+s)^l = \frac{l}{l+1} \int_{-1}^{1} \mathrm{d}s \, (1-s)^{l-1}(1+s)^{l+1}
$$

$$
= \frac{l(l-1)}{(l+1)(l+2)} \int_{-1}^{1} \mathrm{d}s \, (1-s)^{l-2}(1+s)^{l+2} = \cdots
$$

$$
= \frac{(l!)^2}{(2l)!} \int_{-1}^{1} \mathrm{d}s \, (1+s)^{2l} = \frac{(l!)^2}{(2l)!} \frac{2^{2l+1}}{2l+1}.
$$

We thus have

$$
\int_{-1}^{1} \mathrm{d}s \left[P_l^m(s) \right]^2 = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!},
$$

which proves Eq. (6.62) for $m \geqslant 0$. On the other hand, for $m < 0$ Eq. (6.54) implies that

$$
\int_{-1}^{1} \mathrm{d}s \left[P_l^m(s) \right]^2 = \left[\frac{(l+m)!}{(l-m)!} \right]^2 \int_{-1}^{1} \mathrm{d}s \left[P_l^{-m}(s) \right]^2 = \left[\frac{(l+m)!}{(l-m)!} \right]^2 \frac{2}{2l+1} \frac{(l-m)!}{(l+m)!} = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!},
$$

as was to be shown. Note that from Eq. (6.62) it immediately follows that the spherical harmonic $Y_l^m(\theta, \varphi)$ is normalized on the unit sphere:

$$
\int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta \, \sin\theta \left| Y_l^m(\theta, \varphi) \right|^2 = 2\pi \cdot \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \int_0^{\pi} \mathrm{d}\theta \, \sin\theta \left[P_l^m(\cos\theta) \right]^2
$$

$$
= \frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \int_{-1}^{1} \mathrm{d}s \left[P_l^m(s) \right]^2 = 1.
$$

For each $l = 0, 1, \ldots$, the wave functions

$$
\psi_{nlm}(\mathbf{r}) := R_{nl}(r) Y_l^m(\theta, \varphi) = \frac{u_{nl}(r)}{r} Y_l^m(\theta, \varphi)
$$

satisfy the Schrödinger equation[6] (6.22) with an energy E_{nl}, and are eigenfunctions of $\mathbf{L}^2$ and L_3 with respective eigenvalues $l(l+1)\hbar^2$ and $m\hbar$. In other words,

$$
H\psi_{nlm} = E_{nl}\psi_{nlm}, \qquad \mathbf{L}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}, \qquad L_3\psi_{nlm} = m\hbar\psi_{nlm}
$$

In particular, since the eigenvalue E_{nl} of H is independent of the quantum number m, the $2l+1$ eigenfunctions ψ_{nlm} with $m = -l, -l+1, \ldots, l$ have the *same* energy E_{nl}. It follows that *the energy levels of a central potential are* at least $2l+1$ *times degenerate.* For a generic central potential $E_{nl} \neq$

---

[6]The constant m appearing in Eq. (6.22), which denotes the particle's mass, should not be confused with the magnetic quantum number m.

© *Artemio González López*

$E_{n'l'}$ unless $n = n'$ and $l = l'$, so the degeneracy of each level E_{nl} is *exactly* $2l + 1$. We shall show in Section 6.8 that this degeneracy is a consequence of the symmetry (i.e., invariance) of the potential under rotations. On the other hand, if the potential $V(r)$ has some additional symmetry (apart from the symmetry under rotations common to all central potentials), it can happen that $E_{nl} = E_{n'l'}$ for $(n, l) \neq (n', l')$. If this is the case some levels could be more than $2l + 1$ time degenerate, a phenomenon sometimes referred to as **accidental degeneracy.**

The spherical harmonic $Y_l^m(\theta, \varphi)$ has parity $(-1)^l$ under $\mathbf{r} \mapsto -\mathbf{r}$, and $R_{nl}(r)$ is obviously even. It follows that *the wave function ψ_{nlm} has parity $(-1)^l$:*

$$\psi_{nlm}(-\mathbf{r}) = (-1)^l \psi_{nlm}(\mathbf{r}).$$

By construction,

$$\left(\psi_{nlm}, \psi_{n'l'm'}\right) = \left(u_{nl}, u_{n'l'}\right)\left(Y_l^m, Y_{l'}^{m'}\right) = \delta_{ll'}\delta_{mm'}\left(u_{nl}, u_{n'l}\right) = \delta_{nn'}\delta_{ll'}\delta_{mm'},$$

since both u_{nl} and Y_{lm} are normalized, and for $n \neq n'$ the functions $u_{nl}(r)$ and $u_{n'l}(r)$ are solutions of the *same* Schrödinger equation (6.37) with different eigenvalues E_{nl} and $E_{n'l}$. Hence the set

$$\{\psi_{nlm} : n = 1, 2, \ldots, \quad l = 0, 1, \ldots, \quad m = -l, -l + 1, \ldots, l \ \} \tag{6.63}$$

`psinlm`

is *orthonormal*. It can be shown that this set is *complete* in the (closed) linear subspace $\mathcal{H}_{\text{point}}$ of the Hilbert space $\mathcal{H}$ spanned by the genuine eigenfunctions of H. In particular, any eigenfunction of H with energy E is a (finite or infinite) linear combination of eigenfunctions ψ_{nlm} with $E_{nl} = E$.

Remark. Since the quantum numbers (n, l, m) obviously determine the common eigenfunction ψ_{nlm} of the commuting self-adjoint operators H, L^2, and L_3 up to a global phase, the set $\{H, \mathbf{L}^2, L_3\}$ is a CSCO in $\mathcal{H}_{\text{point}}$. If $V_\infty = \infty$ the Hamiltonian H has no continuous spectrum (since $(V_l)_\infty = V_\infty$ for all l), and $\mathcal{H}_{\text{point}}$ is the whole Hilbert space. Thus when $V_\infty = \infty$ the set (6.63) is an *orthonormal basis* of $L^2(\mathbb{R}^3)$, and $\{H, \mathbf{L}^2, L_3\}$ is a CSCO. On the other hand, when V_∞ is finite (like, e.g., for the *Coulomb potential* $-\alpha/r$ with $\alpha > 0$), the half-line (V_∞, ∞) is in the continuous spectrum of H, and the formal eigenfunctions with energy $E > V_\infty$ are therefore needed to construct a generalized orthonormal basis of $L^2(\mathbb{R}^3)$. In particular, when V_∞ is finite the set (6.63) is *not* an orthonormal basis of $L^2(\mathbb{R}^3)$. ∎

Exercise 6.8. Prove condition (6.51) by counting the number of independent harmonic polynomials of degree l. Using the fact that the angular equation (6.47) is equivalent to (6.32), compute the spherical harmonics Y_l^m for $l = 0, 1, 2$ up to normalization. (Cf. [Wei15, pp. 36–37].)

Solution. A homogeneous polynomial p_l of degree l in the variables $(\hat{x}_1, \hat{x}_2, \hat{x}_3)$ can be written as sum of monomials

$$\hat{x}_+^{n_+} \hat{x}_-^{n_-} \hat{x}_3^{n_3}, \tag{6.64}$$

`hxpm3`

with $\hat{x}_\pm = \hat{x}_1 \pm i\hat{x}_2$ and

$$0 \leqslant n_\pm, n_3 \leqslant l, \qquad n_+ + n_- + n_3 = l. \tag{6.65}$$

`hxpm3cond`

Since

$$\hat{x}_1 \pm \hat{x}_2 = \sin\theta\, e^{\pm i\varphi}, \qquad \hat{x}_3 = \cos\theta$$

we have

$$L_3 \hat{x}_+^{n_+} \hat{x}_-^{n_-} \hat{x}_3^{n_3} = (n_+ - n_-)\hbar \hat{x}_+^{n_+} \hat{x}_-^{n_-} \hat{x}_3^{n_3}.$$

For p_l to be an eigenfunction of L_3 with eigenvalue $m\hbar$ we must therefore have

$$n_+ - n_- = m.$$

Since $n_\pm$ range from 0 to l, the difference $n_+ - n_-$ ranges from $-l$ to l, which shows that

$$-l \leqslant m \leqslant l.$$

We must still prove that for all integer values of m between $-l$ and l there is exactly one linearly independent homogeneous polynomial of degree l in $\mathbf{r}/r$ which is a simultaneous eigenfunction of $\mathbf{L}^2$ and L_3 with respective eigenvalues $l(l+1)\hbar^2$ and $m\hbar$. To this end, recall that

$$\mathbf{L}^2 p_l = l(l+1)\hbar^2 p_l \iff \nabla^2(r^l p_l) = 0,$$

where $r^l p_l$ is a homogeneous polynomial in $\mathbf{r}$ of degree l. The number N_l of independent homogeneous polynomials of degree l in $\mathbf{r}$ is equal to the number of monomials $x_1^{n_1} x_2^{n_2} x_3^{n_3}$ such that $n_1 + n_2 + n_3 = l$ and $0 \leqslant n_i \leqslant l$. Thus n_3 can take the values $0, 1, \ldots, l$ without restriction. For each of these values, n_2 can range between 0 and $l - n_3$ and $n_1 = l - n_2 - n_3$ is determined by n_2 and n_3. Thus

$$N_l = \sum_{n_3=0}^{l} (l - n_3 + 1) = \sum_{k=1}^{l+1} k = \frac{1}{2}(l+1)(l+2).$$

On the other hand, since $\nabla^2(r^l p_l)$ is a homogeneous polynomial of degree $l - 2$, the number of independent equations ensuing from the condition $\nabla^2(r^l p_l)$ is N_{l-2}. Thus the number of independent harmonic homogeneous polynomials of degree l is

$$N_l - N_{l-2} = \frac{1}{2}(l+1)(l+2) - \frac{1}{2}l(l-1) = 2l + 1.$$

Since this is also the number of harmonic polynomials $r^l Y_l^m$ with $-l \leqslant m \leqslant l$, we conclude that these polynomials are a basis of the space of harmonic homogeneous polynomials in $\mathbf{r}$ of degree l, and hence $\{Y_l^m : m = -l. -l+1, \ldots, l\}$ is a basis of the space of spherical harmonics of degree l.

As mentioned above, Y_l^m must be a linear combination of monomials (6.64) whose exponents satisfy condition (6.65). The spherical harmonic Y_0^0 must be a constant, since it is of degree 0. For $l = 1$, the condition $n_+ - n_- = m \in \{0, \pm 1\}$ shows that

$$Y_1^{\pm 1} \propto \hat{x}_\pm = \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\varphi}, \qquad Y_1^0 \propto \hat{x}_3 = \cos\theta.$$

For degree $l = 2$, from the condition $n_+ - n_- = m \in \{0, \pm 1, \pm 2\}$ we deduce that

$$Y_2^{\pm 2} \propto \hat{x}_\pm^2 = \sin^2\theta\, \mathrm{e}^{\pm 2\mathrm{i}\varphi}, \qquad Y_2^{\pm 1} \propto \hat{x}_\pm \hat{x}_3 = \sin\theta \cos\theta\, \mathrm{e}^{\pm \mathrm{i}\varphi}.$$

On the other hand, Y_2^0 must be a linear combination of $\hat{x}_+ \hat{x}_-$ and $\hat{x}_3^2$, i.e.,

$$Y_2^0 = a\hat{x}_+ \hat{x}_- + b\hat{x}_3^2 \implies r^2 Y_2^0 = a(x_1^2 + x_2^2) + b x_3^2.$$

Imposing the condition $\nabla^2(r^2 Y_2^0) = 0$ we obtain

$$\nabla^2(r^2 Y_2^0) = 4a + 2b = 0 \implies b = -2a$$
$$\implies Y_2^0 \propto \hat{x}_+ \hat{x}_- - 2\hat{x}_3^2 = \sin^2\theta - 2\cos^2\theta = 1 - 3\cos^2\theta.$$

6.6 Algebraic theory of angular momentum

c.algangmom

As we saw in Example 4.9, the components L_i of the angular momentum operator $\mathbf{L}$ are self-adjoint operators satisfying the commutation relations (4.26). In this section we shall derive some fundamental consequences that follow algebraically from these commutation relations, without making use of the explicit expression of the operators L_i. To underscore this fact, we shall make the following definition:

Definition 6.1. A *general angular momentum operator* is a vector operator $\mathbf{J} = (J_1, J_2, J_3)$ whose components are self-adjoint operators satisfying the commutation relations

$$\left[J_j, J_k \right] = \mathrm{i}\hbar \sum_{l=1}^{3} \varepsilon_{jkl} J_l, \qquad 1 \leqslant j, k \leqslant 3. \tag{6.66}$$

`Jcommrel`

In other words,

$$[J_1, J_2] = \mathrm{i}\hbar J_3, \qquad [J_2, J_3] = \mathrm{i}\hbar J_1, \qquad [J_3, J_1] = \mathrm{i}\hbar J_2,$$

or equivalently

$$\left[J_j, J_k \right] = \mathrm{i}\hbar J_l, \qquad \text{with} \quad (j, k, l) = \text{cyclic permutation of } (1, 2, 3).$$

These commutation relations could also be symbolically expressed as

$$\mathbf{J} \times \mathbf{J} = \mathrm{i}\hbar \mathbf{J}.$$

Note also that from the commutation relations it follows that each operator J_i has the same dimension as $\hbar$, i.e., angular momentum, and that the operator

$$\mathbf{J}^2 := \sum_{i=1}^{3} J_i^2$$

commutes with all the J_i's:

$$\left[\mathbf{J}^2, J_i \right] = 0, \qquad i = 1, 2, 3 \tag{6.67}$$

`J2Jicomm`

(the proof is the same as that given in Example 4.9 for the orbital angular momentum $\mathbf{L}$).

`exa.Pauli`

Example 6.2. Since in finite dimension

$$\mathrm{tr}[A, B] = 0,$$

the components J_i of an angular momentum operator defined in a finite-dimensional Hilbert space must be self-adjoint traceless matrices. In two dimensions, the three **Pauli matrices**

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are a basis of the (real) vector space of 2×2 self-adjoint traceless (complex) matrices. Moreover, from the identities

$$\sigma_j \sigma_k = \mathrm{i} \sum_{l=1}^{3} \varepsilon_{jkl} \sigma_l, \qquad 1 \leqslant j \neq k \leqslant 3,$$

it follows that

$$[\sigma_j, \sigma_k] = 2\mathrm{i} \sum_{l=1}^{3} \varepsilon_{jkl} \sigma_l.$$

The vector operator $\mathbf{J}$ with components

$$J_i = \frac{\hbar}{2} \sigma_i$$

is therefore an angular momentum operator in $\mathcal{H} = \mathbb{C}^2$, since

$$\left[J_j, J_k\right] = \frac{\hbar^2}{4}\left[\sigma_j, \sigma_k\right] = \frac{\mathrm{i}\hbar^2}{2}\sum_{l=1}^{3}\varepsilon_{jkl}\sigma_l = \mathrm{i}\hbar\sum_{l=1}^{3}\varepsilon_{jkl}J_l.$$

This is the simplest non-trivial example of an angular momentum operator, since in one dimension all operators commute. Note also that

$$\sigma_i^2 = \mathbb{1}, \qquad 1 \leqslant i \leqslant 3,$$

and therefore

$$\mathbf{J}^2 = \frac{\hbar^2}{4}\sum_{i=1}^{3}\sigma_i^2 = \frac{3\hbar^2}{4}$$

is proportional to the identity.

Let us next define the **raising** and **lowering** operators $J_\pm$ by

$$J_\pm := J_1 \pm \mathrm{i}J_2;$$

note that, since the operators J_i are self-adjoint by hypothesis, we have

$$J_\pm^\dagger = J_\mp.$$

The commutator of J_+ and J_- is easily computed:

$$[J_+, J_-] = [J_1 + \mathrm{i}J_2, J_1 - \mathrm{i}J_2] = -2\mathrm{i}[J_1, J_2] = 2\hbar J_3.$$

We also have

$$J_\pm J_\mp = (J_1 \pm \mathrm{i}J_2)(J_1 \mp \mathrm{i}J_2) = J_1^2 + J_2^2 \mp \mathrm{i}\,[J_1, J_2] = J_1^2 + J_2^2 \pm \hbar J_3,$$

and therefore

$$\mathbf{J}^2 = J_\pm J_\mp + J_3(J_3 \mp \hbar). \tag{6.68}$$

<div style="text-align:right">J2Jpm</div>

Since $\mathbf{J}^2$ commutes with all the components of $\mathbf{J}$, let us look for common eigenvectors of $\mathbf{J}^2$ and one of the J_i's, for example J_3. Suppose, therefore, that $\left|\psi_\lambda^\mu\right\rangle$ is a nonzero vector (i.e., an element of the Hilbert space on which $\mathbf{J}$ acts) satisfying

$$\mathbf{J}^2\left|\psi_\lambda^\mu\right\rangle = \lambda\hbar^2\left|\psi_\lambda^\mu\right\rangle, \qquad J_3\left|\psi_\lambda^\mu\right\rangle = \mu\hbar\left|\psi_\lambda^\mu\right\rangle, \tag{6.69}$$

<div style="text-align:right">lamudef</div>

with λ and μ two dimensionless *real* numbers (since $\mathbf{J}^2$ and J_3 are both self-adjoint). Note also that $\lambda \geqslant 0$, since $\mathbf{J}^2$ is positive semidefinite:

$$(\psi, \mathbf{J}^2\psi) = \sum_{i=1}^{3}(\psi, J_i^2\psi) = \sum_{i=1}^{3}\left\|J_i\psi\right\|^2 \geqslant 0.$$

Consider next the vector $J_\pm\left|\psi_\lambda^\mu\right\rangle$, whose norm is easily computed:

$$\begin{aligned}\left\|J_\pm\left|\psi_\lambda^\mu\right\rangle\right\|^2 &= \langle\psi_\lambda^\mu|J_\pm^\dagger J_\pm|\psi_\lambda^\mu\rangle = \langle\psi_\lambda^\mu|J_\mp J_\pm|\psi_\lambda^\mu\rangle = \langle\psi_\lambda^\mu|\mathbf{J}^2 - J_3(J_3 \pm \hbar)|\psi_\lambda^\mu\rangle \\ &= \hbar^2\left[\lambda - \mu(\mu \pm 1)\right]\langle\psi_\lambda^\mu|\psi_\lambda^\mu\rangle.\end{aligned} \tag{6.70}$$

<div style="text-align:right">Jpmnorm</div>

Thus

$$J_\pm\left|\psi_\lambda^\mu\right\rangle = 0 \quad\Longleftrightarrow\quad \lambda = \mu(\mu \pm 1). \tag{6.71}$$

<div style="text-align:right">Jpmlamu0</div>

Since $\mathbf{J}^2$ commutes with $J_\pm$, we have

$$\mathbf{J}^2\left(J_\pm\left|\psi_\lambda^\mu\right\rangle\right) = J_\pm\left(\mathbf{J}^2\left|\psi_\lambda^\mu\right\rangle\right) = \lambda\hbar J_\pm\left|\psi_\lambda^\mu\right\rangle,$$

i.e.:

$$J_\pm\big|\psi_\lambda^\mu\big\rangle \text{ is either zero or an eigenvector of } \mathbf{J}^2 \text{ with the same eigenvalue } \lambda\hbar^2 \text{ as } \big|\psi_\lambda^\mu\big\rangle.$$

On the other hand, since

$$[J_3, J_\pm] = [J_3, J_1 \pm iJ_2] = i\hbar J_2 \pm \hbar J_1 = \pm\hbar J_\pm,$$

we have

$$J_3\left(J_\pm\big|\psi_\lambda^\mu\big\rangle\right) = J_\pm\left(J_3\big|\psi_\lambda^\mu\big\rangle\right) \pm \hbar J_\pm\big|\psi_\lambda^\mu\big\rangle = (\mu \pm 1)\hbar\big|\psi_\lambda^\mu\big\rangle.$$

In other words:

$$J_\pm\big|\psi_\lambda^\mu\big\rangle \text{ is either zero or an eigenvector of } J_3 \text{ with eigenvalue } (\mu \pm 1)\hbar.$$

Note that from the equality

$$J_3^2 = \mathbf{J}^2 - (J_1^2 + J_2^2),$$

it follows (since $J_1^2 + J_2^2$ is positive semidefinite) that

$$\mu^2 \leqslant \lambda \iff |\mu| \leqslant \sqrt{\lambda}.$$

Hence there must exist a positive integer p such that

$$J_+^k\big|\psi_\lambda^\mu\big\rangle \neq 0 \quad \text{for} \quad k = 0, \ldots, p-1, \qquad J_+^p\big|\psi_\lambda^\mu\big\rangle = 0.$$

Similarly, there must exist another positive integer q such that

$$J_-^k\big|\psi_\lambda^\mu\big\rangle \neq 0 \quad \text{for} \quad k = 0, \ldots, q-1, \qquad J_-^q\big|\psi_\lambda^\mu\big\rangle = 0.$$

Thus the vectors

$$\big|\psi_\lambda^{\mu+k}\big\rangle := J_+^k\big|\psi_\lambda^\mu\big\rangle, \qquad k = 0, \ldots, p-1,$$

are eigenvectors of $\mathbf{J}^2$ and J_3 with respective eigenvalues $\lambda\hbar^2$ and $(\mu + k)\hbar$, and

$$J_+\big|\psi_\lambda^{\mu+p-1}\big\rangle = J_+^p\big|\psi_\lambda^\mu\big\rangle = 0.$$

From the upper Eq. (6.71) (with μ replaced by $\mu + p - 1$) it then follows that

$$\lambda = (\mu + p - 1)(\mu + p).$$

Likewise, the vectors

$$\big|\psi_\lambda^{\mu-k}\big\rangle := J_-^k\big|\psi_\lambda^\mu\big\rangle, \qquad k = 0, \ldots, q-1,$$

are eigenvectors of $\mathbf{J}^2$ and J_3 with respective eigenvalues $\lambda\hbar^2$ and $(\mu - k)\hbar$, and

$$J_-\big|\psi_\lambda^{\mu-q+1}\big\rangle = J_-^q\big|\psi_\lambda^\mu\big\rangle = 0,$$

whence (from the lower Eq. (6.71) with μ replaced by $\mu - q + 1$)

$$\lambda = (\mu - q)(\mu - q + 1).$$

Equating both expressions for λ we obtain

$$(\mu + p - 1)(\mu + p) = (\mu - q)(\mu - q + 1),$$

from which it follows that[7]

$$\mu + p = \mu - q + 1 \qquad \text{or} \qquad \mu + p = q - \mu.$$

The first of these equations, which is equivalent to $p + q = 1$, is impossible, since both p and q are positive integers. We conclude that

$$\mu = \frac{1}{2}(q - p)$$

is *integer or half-integer*. It then follows from the first equation for λ that

$$\boxed{\lambda = j(j + 1),}$$

where

$$j = \mu + p - 1 = \frac{1}{2}(q - p) + p - 1 = \frac{1}{2}(q + p) - 1$$

is a *non-negative integer or half-integer*. In other words, j can only take the values

$$\boxed{0, \quad \frac{1}{2}, \quad 1, \quad \frac{3}{2}, \quad \ldots.}$$

The vectors

$$\left|\psi_\lambda^{\mu-q+1}\right\rangle, \quad \ldots \quad, \quad \left|\psi_\lambda^{\mu-1}\right\rangle, \quad \left|\psi_\lambda^{\mu}\right\rangle, \quad \left|\psi_\lambda^{\mu+1}\right\rangle, \quad \ldots \quad, \quad \left|\psi_\lambda^{\mu+p-1}\right\rangle \qquad (6.72) \quad \boxed{\texttt{ladder}}$$

form a sequence ("ladder") of eigenvectors of $\mathbf{J}^2/\hbar^2$ with eigenvalue $\lambda = j(j + 1)$ and of $J_3/\hbar$ with respective eigenvalues

$$\mu - q + 1, \quad \ldots \quad, \quad \mu - 1, \quad \mu, \quad \mu + 1, \quad \ldots \quad, \quad \mu + p - 1$$

increasing by 1 from left to right. Taking into account the value of μ found above and the definition of j, we find that the highest and lowest eigenvalues of $J_3/\hbar$ are

$$\frac{1}{2}(q - p) - q + 1 = -\frac{1}{2}(q + p) + 1 = -j, \qquad \mu + p - 1 = j.$$

It follows that the $2j + 1$ vectors $|jm\rangle$ defined by

$$\boxed{|jm\rangle = \frac{\left|\psi_\lambda^m\right\rangle}{\left\langle\psi_\lambda^m\middle|\psi_\lambda^m\right\rangle^{1/2}}, \qquad m = -j, -j + 1, \ldots, j,} \qquad (6.73) \quad \boxed{\texttt{jmdef}}$$

(with $\lambda = j(j + 1)$) satisfy $\langle jm|jm\rangle = 1$ and

$$\boxed{\mathbf{J}^2|jm\rangle = j(j + 1)\hbar^2|jm\rangle, \qquad J_3|jm\rangle = m\hbar|jm\rangle.} \qquad (6.74) \quad \boxed{\texttt{J2J3eigvs}}$$

Note that, by the last two framed remarks, $J_\pm|jm\rangle$ is proportional to $|j, m \pm 1\rangle$ (where $|j, j + 1\rangle$ and $|j, -j - 1\rangle$ should be interpreted as the zero vector). We have thus proved the following fundamental result:

---

[7]Indeed, if $s = \mu + p$ and $t = \mu - q$ we have

$$s(s - 1) - t(t + 1) = s^2 - t^2 - s - t = (s + t)(s - t - 1) = 0 \iff s = t + 1 \text{ or } s = -t.$$

> **thm.J**
>
> **Theorem 6.3.**
>
> 1) *The only possible eigenvalues of the operator $\mathbf{J}^2$ are the numbers $j(j+1)\hbar^2$, with $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ a non-negative integer or half-integer.*
>
> 2) *If $j(j+1)\hbar^2$ is an eigenvalue of $\mathbf{J}^2$, there is as a set of $2j+1$ vectors $|jm\rangle$, with $m = -j, -j+1, \dots, j$, which are common eigenvectors of $\mathbf{J}^2$ and J_3 with respective eigenvalues $j(j+1)\hbar^2$ and $m\hbar$.*
>
> 3) *$J_\pm |jm\rangle$ is proportional to $|j, m \pm 1\rangle$, and $J_\pm |j, \pm j\rangle = 0$.*

Remarks.

- With a slight abuse of language, we shall say that the state $|jm\rangle$ has *angular momentum j*, even if strictly speaking the value of the angular momentum in such a state is $\sqrt{j(j+1)}\,\hbar$.

- Although the square $\mathbf{J}^2$ of a general angular momentum operator $\mathbf{J}$ can have eigenvalues $j(j+1)\hbar^2$ with j a half integer, we showed in Section 6.3 that in the case of the *orbital* angular momentum operator $\mathbf{L}$ the values of j are necessarily (non-negative) integers. This is due to the fact that the 2π-periodicity in φ of the eigenfunctions $Y(\theta, \varphi)$ of L_3 requires that the eigenvalues of the latter operator be *integer* multiples of $\hbar$. This implies that j must itself be an integer, since the allowed values of m for a given j are $-j, -j+1, \dots, j$, which are integers if and only of j is an integer.

- The vectors $|jm\rangle$ satisfy the orthonormalization condition

$$\langle jm | j'm' \rangle = \delta_{mm'}\delta_{jj'},$$

  since they are normalized by construction, and $(j, m) \neq (j', m')$ implies that $|jm\rangle$ and $|j'm'\rangle$ are eigenvectors of the same self-adjoint operator ($\mathbf{J}^2$ or J_3, or both) with different eigenvalues. In particular, the $2j+1$ vectors (6.73) make up an orthonormal basis of their span, which is thus a $(2j+1)$-dimensional subspace of $\mathcal{H}$ that we shall denote by $\mathcal{H}_j$. Note also that, by construction, $\mathcal{H}_j \subset \ker[\mathbf{J}^2 - j(j+1)\hbar^2]$.

- In the case of the *orbital* angular momentum $\mathbf{L}$ no additional quantum number α is needed to label the common eigenstates of $\mathbf{L}^2$ and L_3, since $|lm\rangle = Y_l^m$ is uniquely determined up to a phase.

- Of course, the set $\{\mathbf{J}^2, J_3\}$ need not be a CSCO, and thus there will be in general several (perhaps even an infinite number of) subspaces $\mathcal{H}_j$ with the same j that we shall denote by $\mathcal{H}_j^\alpha$, where α is an extra index labeling different instances of $\mathcal{H}_j$. The corresponding vectors (6.73) will be accordingly denoted by $|\alpha jm\rangle$. In many cases the extra index α is the eigenvalue of a third observable A commuting with both $\mathbf{J}^2$ and J_3, such that $\{A, \mathbf{J}^2, J_3\}$ is a CSCO. If that is the case (and assuming, for simplicity, that the index α is discrete) then

$$\langle \alpha jm | \alpha' j'm' \rangle = \delta_{\alpha\alpha'}\delta_{mm'}\delta_{jj'},$$

  since for $\alpha \neq \alpha'$ the vectors $|\alpha jm\rangle$ and $|\alpha' j'm'\rangle$ are eigenvectors of the observable A with different eigenvalues. ∎

By parts 2) and 3) of Theorem 6.3, each $(2j+1)$-dimensional subspace $\mathcal{H}_j$ generated by the vectors (6.73) is *invariant* under the action of the operators J_3 and $J_\pm$, and hence of the three components of the angular momentum operator $\mathbf{J}$. In other words, the *restriction* of each J_i to $\mathcal{H}_j$ acts as a $(2j+1) \times (2j+1)$ matrix, whose matrix elements we shall determine next. We shall say that these matrices provide an **irreducible[8] representation of spin** j of the commutation relations (6.66), or more formally of the $\mathfrak{so}(3)$ Lie algebra.

---

[8]The term "irreducible" means that there is no proper subspace of $\mathcal{H}_j$ left invariant by all the components J_i of $\mathbf{J}$.

The Lie algebra $\mathfrak{so}(3)$.

The *Lie algebra* $\mathfrak{so}(3)$ of the rotation group SO(3) in three-dimensional space is defined by

$$\mathfrak{so}(3) = \{X \in M_3(\mathbb{R}) : X^\mathsf{T}, \ \operatorname{tr} X = 0\},$$

where $M_3(\mathbb{R})$ denotes the set of 3×3 real matrices. In other words, the elements of $\mathfrak{so}(3)$ are by definition antisymmetric traceless 3×3 (real) matrices. The matrices $X \in \mathfrak{so}(3)$ can be regarded as generators of infinitesimal rotations in three dimensions. For instance, consider the matrix $R_3(\alpha)$ of a rotation around the x_3 axis by an angle α, defined by

$$R_3(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The matrices $R(\alpha)$ (with $\alpha \in \mathbb{R}$) make up a one-parameter group of transformations of $\mathbb{R}^3$, since clearly

$$R(\alpha_1 + \alpha_2) = R(\alpha_1)R(\alpha_2).$$

The generator of rotations around the x_3 axis is the matrix

$$X_3 = \frac{\mathrm{d}}{\mathrm{d}\alpha}\Big|_{\alpha=0} R_3(\alpha) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

which is clearly in $\mathfrak{so}(3)$. By construction

$$R_3(\alpha) = \mathbb{1} + \alpha X_3 + O(\alpha^2),$$

so that $\mathbb{1} + \alpha X_3$ represents a rotation around the x_3 axis by an infinitesimal angle α. Moreover, it can be shown that

$$R_3(\alpha) = \mathrm{e}^{\alpha X_3},$$

and similarly for rotations around the other axes, whose corresponding generators are

$$X_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad X_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}.$$

The set $\mathfrak{so}(3)$ is a Lie algebra under the commutator, by which is meant that the commutator of two $\mathfrak{so}(3)$ matrices is itself an $\mathfrak{so}(3)$ matrix. This is a consequence of the fact that the product of two rotations is a rotation. It can be easily verified that the three generators X_i ($i = 1, 2, 3$) of rotations around the coordinate axes are a basis of $\mathfrak{so}(3)$. Moreover, a direct calculation shows that

$$[X_j, X_k] = \sum_{l=1}^{3} \varepsilon_{jkl} X_l, \qquad 1 \leqslant j, k \leqslant 3.$$

Hence the 3×3 matrices $J_k = \mathrm{i}\hbar X_k$ are self-adjoint and traceless, and satisfy the commutation relations (6.66) characteristic of a general angular momentum operator.

Note: in quantum mechanics, the orbital angular momentum operator $\mathbf{L}$ is the *generator of rotations* (in the case of a *spinless* particle). Indeed, a rotation by an angle α around the x_3 acts on the wave function $\psi(\mathbf{r})$ as

$$\psi(\mathbf{r}) \mapsto \psi_\alpha(\mathbf{r}) = \psi\big(R_3(\alpha)\mathbf{r}\big),$$

which in spherical coordinates reads

$$\psi(r,\theta,\varphi) \mapsto \psi_\alpha(r,\theta,\varphi) = \psi(r,\theta,\varphi+\alpha),$$

where $R_3(\alpha)$ is the rotation matrix defined above. Since

$$L_3 = -i\hbar\partial_\varphi,$$

by Taylor's formula we have

$$e^{\frac{i}{\hbar}\alpha L_3}\psi(r,\theta,\varphi) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i\alpha L_3}{\hbar}\right)^n\psi(r,\theta,\varphi) = \sum_{n=0}^{\infty}\frac{\alpha^n}{n!}\partial_\varphi^n\psi(r,\theta,\varphi) = \psi(r,\theta,\varphi+\alpha)$$
$$\equiv \psi_\alpha(r,\theta,\varphi).$$

More generally, if $R_{\mathbf{n}}(\alpha)$ is a rotation around the axis $\mathbf{n}$ by an angle α, choosing the x_3 axis in the direction of the unit vector $\mathbf{n}$ we deduce that

$$\psi(R_{\mathbf{n}}(\alpha)\mathbf{r}) = e^{\frac{i}{\hbar}\alpha\,\mathbf{n}\cdot\mathbf{L}}\psi(\mathbf{r}).$$

In particular, if α is infinitesimal then

$$\psi(R_{\mathbf{n}}(\alpha)\mathbf{r}) = \psi(\mathbf{r}) + \frac{i\alpha}{\hbar}(\mathbf{n}\cdot\mathbf{L})\,\psi(\mathbf{r}) + O(\alpha^2).$$

We shall next determine the matrix elements in the basis (6.73) of the restriction of the operators J_i or, equivalently, of $J_\pm$ and J_3, to each subspace $\mathcal{H}_j$. Obviously, by the last Eq. (6.74) J_3 is diagonal, with matrix elements

$$\langle jm|J_3|jm'\rangle = m\hbar\delta_{mm'}. \tag{6.75}$$

Likewise, by the first Eq. (6.74) $\mathbf{J}^2$ is proportional to the identity in $\mathcal{H}_j$:

$$\mathbf{J}^2 = j(j+1)\hbar^2\mathbb{1} \quad \text{in} \quad \mathcal{H}_j.$$

Consider next the ladder operators $J_\pm$. By Theorem 6.3, $J_\pm|jm\rangle$ is proportional to $|j, m\pm 1\rangle$. To determine the proportionality constant note that, by Eq. (6.70) with $\mu = m$ and $\lambda = j(j+1)$ we have

$$\left\|J_\pm|jm\rangle\right\|^2 = \hbar^2\left[j(j+1) - m(m\pm 1)\right] = \hbar^2(j\mp m)(j\pm m+1).$$

Hence

$$J_\pm|jm\rangle = \alpha_m^\pm\hbar\sqrt{(j\mp m)(j\pm m+1)}\,|j,m\pm 1\rangle, \tag{6.76}$$

where $\alpha_m^\pm$ is a phase (i.e., a complex number of modulus 1). It can be shown (see Exercise 6.9) that these phases can be eliminated by appropriately redefining the vectors $|jm\rangle$. In other words, we can assume w.l.o.g. that

$$J_\pm|jm\rangle = \hbar\sqrt{(j\mp m)(j\pm m+1)}\,|j,m\pm 1\rangle, \qquad m = -j, -j+1, \ldots, j. \tag{6.77}$$

(Note that, although in the previous equation formally appear the undefined vectors $|j,-j-1\rangle$ and $|j,j+1\rangle$, this is harmless as their respective coefficients vanish.) Thus the matrix elements of the ladder operators $J_\pm$ are

$$\langle jm|J_\pm|jm'\rangle = \hbar\sqrt{(j\pm m)(j\mp m+1)}\,\delta_{m,m'\pm 1}. \tag{6.78}$$

The matrix elements of $J_{1,2}$ are then easily computed from the identities

$$J_1 = \frac{1}{2}(J_+ + J_-), \qquad J_2 = \frac{1}{2i}(J_+ - J_-).$$

In particular, note that in this representation the matrix elements of $\mathbf{J}^2$, J_3, $J_\pm$, and J_1 are all real, while those of J_2 are pure imaginary.

---

exe.phases

Exercise 6.9. Show that the phases $\alpha_m^\pm$ in Eq. (6.76) can be eliminated by appropriately redefining the vectors $|jm\rangle$.

Solution. Indeed, let us set

$$|jm\rangle' = \beta_m |jm\rangle, \qquad m = -j, -j+1, \ldots, j,$$

where β_m is a phase. Obviously the vectors $|jm\rangle'$ still satisfy both equations in (6.74), and they are normalized. We shall next show that we can choose the phases β_m so that

$$J_\pm |jm\rangle' = \hbar\sqrt{(j \mp m)(j \pm m + 1)}\,|j, m \pm 1\rangle'. \tag{6.79}$$

Jpmjmp

Indeed, multiplying both sides of Eq. (6.76) for $J_+|jm\rangle$ by β_m we obtain

$$J_+|jm\rangle' = \frac{\alpha_m^+ \beta_m}{\beta_{m+1}}\hbar\sqrt{(j \mp m)(j \pm m + 1)}\,|j, m \pm 1\rangle', \qquad m = -j, \ldots, j-1.$$

Thus Eq. (6.79) with the upper sign will be satisfied provided that

$$\beta_{m+1} = \alpha_m^+ \beta_m, \qquad m = -j, \ldots, j-1,$$

which is obviously solved by $\beta_{-j} = 1$ and

$$\beta_m = \alpha_{-j}^+ \alpha_{-j+1}^+ \cdots \alpha_{m-1}^+, \qquad m = -j+1, \ldots, j.$$

(Note that β_m is a phase, since it is a product of phases.) With this choice of β_m we have

$$J_+|jm\rangle' = \hbar\sqrt{(j - m)(j + m + 1)}\,|j, m+1\rangle', \qquad m = -j, \ldots, j-1.$$

Applying the operator J_- to both sides of the latter equation and taking into account Eq. (6.68) we obtain

$$\left(\mathbf{J}^2 - J_3(J_3 + \hbar)\right)|jm\rangle' = \hbar^2\left[j(j+1) - m(m+1)\right]|jm\rangle' = \hbar^2(j-m)(j+m+1)|jm\rangle'$$
$$= \hbar\sqrt{(j-m)(j+m+1)}\,J_-|j, m+1\rangle',$$

and therefore

$$J_-|j, m+1\rangle' = \hbar\sqrt{(j-m)(j+m+1)}\,|jm\rangle', \qquad m = -j, \ldots, j-1,$$

or equivalently

$$J_-|j, m\rangle' = \hbar\sqrt{(j+m)(j-m+1)}\,|j, m-1\rangle', \qquad m = -j+1, \ldots, j.$$

Thus the set $\{|jm\rangle' : m = -j, -j+1, \ldots, j\}$ satisfies Eq. (6.79), as was to be shown.

Example 6.4. For $j = 0$, $\mathbf{J}^2 = 0$ and hence the three components J_i vanish on $\mathcal{H}_0 = \mathbb{C}$. This is the trivial (scalar) spin zero representation. The first non-trivial case is that of spin $j = 1/2$, for which

$m = -1/2, 1/2$ and

$$\mathbf{J}^2 = \frac{3}{4}\hbar^2 \mathbb{1}.$$

By Eq. (6.75), ordering (as is customary) the basis $|jm\rangle$ as

$$\left|\tfrac{1}{2}\,\tfrac{1}{2}\right\rangle, \quad \left|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle$$

we have

$$J_3 = \begin{pmatrix} \hbar/2 & 0 \\ 0 & -\hbar/2 \end{pmatrix} = \frac{\hbar}{2}\sigma_3.$$

Moreover, by Eq. (6.78) the only non-vanishing matrix element of J_+ is

$$(J_+)_{12} = \left\langle \tfrac{1}{2}\,\tfrac{1}{2}\left|J_+\right|\tfrac{1}{2}\,-\tfrac{1}{2}\right\rangle = \hbar\sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)} = \hbar,$$

so that

$$J_+ = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix}, \qquad J_- = J_+^\dagger = \begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix},$$

and hence

$$J_1 = \frac{1}{2}\begin{pmatrix} 0 & \hbar \\ \hbar & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_1, \qquad J_2 = \frac{1}{2i}\begin{pmatrix} 0 & \hbar \\ -\hbar & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_2.$$

Thus the spin $1/2$ representation is that of Example 6.2.

Likewise, for spin $j = 1$ we have $m = -1, 0, 1$ and $\mathbf{J}^2 = 2\hbar^2\mathbb{1}$. Ordering the basis vectors in descending order as

$$|1\,1\rangle, \quad |1\,0\rangle, \quad |1\,-1\rangle$$

we then obtain

$$J_3 = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The only non-vanishing matrix elements of J_+ are

$$(J_+)_{12} = \langle 11|J_+|10\rangle = \hbar\sqrt{(1+1)(1-1+1)} = \sqrt{2}\,\hbar,$$
$$(J_+)_{23} = \langle 10|J_+|1\,-1\rangle = \hbar\sqrt{(1+0)(1-0+1)} = \sqrt{2}\,\hbar,$$

so that

$$J_+ = \sqrt{2}\,\hbar\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \qquad J_- = J_+^\dagger = \sqrt{2}\,\hbar\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix},$$

and therefore

$$J_1 = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad J_2 = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}.$$

Exercise 6.10. Show that

$$|jm\rangle = \sqrt{\frac{(j \mp m)!}{(2j)!(j \pm m)!}}\left(\frac{J_\pm}{\hbar}\right)^{j \pm m} |j, \mp j\rangle. \tag{6.80}$$

Solution. By Eq. (6.77), we have

$$\left(\frac{J_-}{\hbar}\right)^{j-m}|jj\rangle = \sqrt{2j}\left(\frac{J_-}{\hbar}\right)^{j-m-1}|j,j-1\rangle = \sqrt{2j(2j-1)\cdot 2!}\left(\frac{J_-}{\hbar}\right)^{j-m-2}|j,j-2\rangle = \dots$$

$$= \sqrt{2j(2j-1)\cdots(j+m+1)\cdot(j-m)!}\,|jm\rangle \equiv \sqrt{\frac{(2j)!(j-m)!}{(j+m)!}}\,|jm\rangle.$$

Likewise,

$$\left(\frac{J_+}{\hbar}\right)^{j+m}|j,-j\rangle = \sqrt{2j}\left(\frac{J_-}{\hbar}\right)^{j+m-1}|j,-j+1\rangle = \sqrt{2j(2j-1)\cdot 2!}\left(\frac{J_-}{\hbar}\right)^{j+m-2}|j,-j+2\rangle = \dots$$

$$= \sqrt{2j(2j-1)\cdots(j-m+1)\cdot(j+m)!}\,|jm\rangle \equiv \sqrt{\frac{(2j)!(j+m)!}{(j-m)!}}\,|jm\rangle.$$

Example 6.5. *Construction of Y_l^m for $m = -l, -l+1, \dots, l-1$ from Y_l^l.*

Equation (6.80) can be used to construct any spherical harmonic Y_l^m from Y_l^l. Indeed, note first of all that from Eq. (6.27) it follows that

$$L_\pm = \hbar e^{\pm i\varphi}\left(\pm\partial_\theta + i\cot\theta\,\partial_\varphi\right).$$

In particular, writing

$$Y_l^l(\theta,\varphi) = f_l(\theta)e^{il\varphi},$$

from the identity $L_+ Y_l^l = 0$ we obtain the following differential equation for the function $f_l(\theta)$:

$$f_l'(\theta) - l\cot\theta\, f(\theta) = 0.$$

The general solution of this equation is

$$f_l(\theta) = c_l \sin^l\theta,$$

where c_l is a complex constant that can be determined up to a phase imposing that Y_l^l ve normalized, i.e., that

$$|c_l|^2 \int_0^{2\pi}\mathrm{d}\varphi\int_0^\pi \mathrm{d}\theta\,\sin\theta\cdot\sin^{2l}\theta = 2\pi|c_l|^2\int_0^\pi\mathrm{d}\theta\,\sin^{2l+1}\theta = 1.$$

Since for $l > 0$ we have

$$I_l \equiv \int_0^\pi \mathrm{d}\theta\,\sin^{2l+1} = -\int_0^\pi \mathrm{d}(\cos\theta)\sin^{2l}\theta = \int_0^\pi \mathrm{d}\theta\,\cos\theta\cdot 2l\sin^{2l-1}\theta\cos\theta = 2l(I_{l-1} - I_l),$$

it follows that

$$I_l = \frac{2l}{2l+1}I_{l-1} = \frac{2l(2l-2)}{(2l+1)(2l-1)}I_{l-2} = \cdots = \frac{(2l)!!}{(2l+1)!!}I_0 = 2\frac{(2l)!!}{(2l+1)!!} = 2\frac{\left[(2l)!!\right]^2}{(2l+1)!}$$

$$= \frac{2^{2l+1}(l!)^2}{(2l+1)!},$$

and hence

$$c_l = \frac{\alpha_l}{2^l l!}\sqrt{\frac{(2l+1)!}{4\pi}},$$

where α_l is a phase. We thus have

$$Y_l^l(\theta, \varphi) = \frac{\alpha_l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \, \mathrm{e}^{il\varphi} \sin^l \theta. \tag{6.81}$$

From the previous equation it is straightforward to obtain an explicit formula for the general spherical harmonic Y_l^m with $m = -l, -l+1, \ldots, l$ using Eq. (6.80). To this end, note first that

$$\frac{L_-}{\hbar} \left[f(\theta) \mathrm{e}^{in\varphi} \right] = -\mathrm{e}^{i(n-1)\varphi} \left(\partial_\theta + n \cot \theta \right) f(\theta) = \mathrm{e}^{i(n-1)\varphi} \sin^{1-n} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right) \left(\sin^n \theta \, f(\theta) \right). \tag{6.82}$$

Calling

$$g(\theta) = \sin^{1-n} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right) \left(\sin^n \theta \, f(\theta) \right)$$

and applying $L_- \hbar$ again we obtain

$$\left(\frac{L_-}{\hbar} \right)^2 \left[f(\theta) \mathrm{e}^{in\varphi} \right] = \frac{L_-}{\hbar} \left[g(\theta) \mathrm{e}^{i(n-1)\varphi} \right] = \mathrm{e}^{i(n-2)\varphi} \sin^{2-n} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right) \left(\sin^{n-1} \theta \, g(\theta) \right)$$

$$= \mathrm{e}^{i(n-2)\varphi} \sin^{2-n} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right)^2 \left(\sin^n \theta \, f(\theta) \right),$$

and in general

$$\left(\frac{L_-}{\hbar} \right)^k \left[f(\theta) \mathrm{e}^{in\varphi} \right] = \mathrm{e}^{i(n-k)\varphi} \sin^{k-n} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right)^k \left(\sin^n \theta \, f(\theta) \right), \qquad k = 1, 2, \ldots .$$

From Eq. (6.81), Eq. (6.80) and the previous equation with $k = l - m$ and $n = l$ we then obtain

$$Y_l^m(\theta, \varphi) = \frac{\alpha_l \mathrm{e}^{im\varphi}}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sqrt{\frac{(l+m)!}{(2l)!(l-m)!}} \sin^{-m} \theta \left(-\frac{1}{\sin\theta} \partial_\theta \right)^{l-m} \left(\sin^{2l} \theta \right)$$

$$= \frac{\alpha_l \mathrm{e}^{im\varphi}}{2^l l!} \sqrt{\frac{2l+1}{4\pi} \frac{(l+m)!}{(l-m)!}} (1-s^2)^{-m/2} \partial_s^{l-m} (1-s^2)^l, \qquad s \equiv \cos\theta.$$

Using Eqs. (6.54) and (6.55) we can rewrite the last equation as

$$Y_l^m(\theta, \varphi) = (-1)^{l+m} \alpha_l \sqrt{\frac{2l+1}{4\pi} \frac{(l+m)!}{(l-m)!}} P_l^{-m}(\cos\theta) \mathrm{e}^{im\varphi}$$

$$= (-1)^l \alpha_l \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) \mathrm{e}^{im\varphi},$$

which indeed coincides with Eq. (6.56) if we take

$$\alpha_l = (-1)^l.$$

   As an example, let us construct the three spherical harmonics with $l = 2$ (and hence $\alpha_2 = 1$) starting from

$$Y_2^2(\theta, \varphi) = \frac{1}{8} \sqrt{\frac{5!}{4\pi}} \, \mathrm{e}^{2i\varphi} \sin^2 \theta = \frac{1}{8} \sqrt{\frac{30}{\pi}} \, \mathrm{e}^{2i\varphi} \sin^2 \theta.$$

In practice, it is better to use Eq. (6.77), i.e.,

$$Y_l^{m-1} = \left[(l+m)(l-m+1)\right]^{-1/2} \left(\frac{L_-}{\hbar}\right) Y_l^m,$$

together with Eq. (6.82). In this way we obtain

$$Y_2^1 = \frac{1}{2}\left(\frac{L_-}{\hbar}\right) Y_2^2 = \frac{1}{16}\sqrt{\frac{30}{\pi}}\, e^{i\varphi} \sin^{-1}\theta \left(-\frac{1}{\sin\theta}\partial_\theta\right)(\sin^4\theta) = -\frac{1}{4}\sqrt{\frac{30}{\pi}}\, e^{i\varphi}\sin\theta\cos\theta,$$

$$Y_2^0 = \frac{1}{\sqrt{6}}\left(\frac{L_-}{\hbar}\right) Y_2^1 = -\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(-\frac{1}{\sin\theta}\partial_\theta\right)(\sin^2\theta\cos\theta) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(2\cos^2\theta - \sin^2\theta)$$

$$= \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3\cos^2\theta - 1).$$

From Eq. (6.59) we then obtain

$$Y_2^{-1} = -Y_2^1 = \frac{1}{4}\sqrt{\frac{30}{\pi}}\, e^{i\varphi}\sin\theta\cos\theta, \qquad Y_2^{-2} = Y_2^2 = \frac{1}{8}\sqrt{\frac{30}{\pi}}\, e^{-2i\varphi}\sin^2\theta.$$

6.7 The infinite spherical well

seq.sphwell

For a quantum particle confined to move inside a sphere of radius $a > 0$ centered at the origin the potential can be taken as

$$V(r) = \begin{cases} 0, & r < a \\ \infty, & r > a. \end{cases} \tag{6.83}$$

spherpot

We must therefore solve Schrödinger's equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

for $r < a$, with the boundary condition that ψ vanishes on the boundary of the well, i.e., for $r = a$ (since ψ must vanish in the region $r \geqslant a$ where the potential is infinite). For zero angular momentum the solution of this problem is straightforward, since the radial equation for $u(r)$ is simply

$$-\frac{\hbar^2}{2m}u''(r) = Eu(r), \qquad 0 \leqslant r \leqslant a,$$

where the prime denotes derivative with respect to r, with the boundary conditions

$$u(0) = u(a) = 0.$$

Thus the solutions of this problem are the eigenfunctions of an infinite one-dimensional well of width a, namely[9]

$$u_{n0}(r) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi r}{a}\right)\chi_{[0,a]}(r), \qquad n \in \mathbb{N},$$

with energies

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

Hence the normalized zero angular momentum (sometimes called s-wave) radial wave functions are given by

$$R_{n0}(r) = \sqrt{\frac{2}{a}}\frac{1}{r}\sin\left(\frac{n\pi r}{a}\right)\chi_{[0,a]}(r), \qquad n \in \mathbb{N}.$$

---

[9]In the following formula $\chi_{[0,a]}(r)$ denotes the *characteristic function* of the interval $[0, a]$, equal to 1 for $0 \leqslant r \leqslant a$ and zero otherwise.

© Artemio González López

Taking into account the angular part $Y_0^0 = (4\pi)^{-1/2}$ we obtain the explicit expression for the full zero angular momentum wave functions:

$$\psi_{n00}(\mathbf{r}) = (2\pi a)^{-1/2} \frac{1}{r} \sin\left(\frac{n\pi r}{a}\right) \chi_{[0,a]}(r), \qquad n \in \mathbb{N}.$$

For nonzero angular momentum l, it is more convenient to work directly with the differential equation (6.26) for the radial function $R(r)$, namely

$$-\frac{1}{r^2}\left(r^2 R'(r)\right)' + \frac{l(l+1)}{r^2} R = k^2 R, \qquad 0 \leqslant r \leqslant a, \quad k := \sqrt{\frac{2mE}{\hbar^2}},$$

or equivalently

$$r^2 R'' + 2rR' + \left(k^2 r^2 - l(l+1)\right)R = 0, \qquad 0 \leqslant r \leqslant a.$$

Setting $s = kr$ we obtain the *spherical Bessel equation*[10]

$$s^2 \partial_s^2 R + 2s \partial_s R + \left(s^2 - l(l+1)\right)R = 0, \qquad 0 \leqslant r \leqslant a, \tag{6.84}$$

`Besselspheq`

A basis of solutions of this equation consists of the *spherical Bessel functions* of order l

$$j_l(s) = (-s)^l \left(s^{-1}\partial_s\right)^l \frac{\sin s}{s}, \qquad y_l(s) = -(-s)^l \left(s^{-1}\partial_s\right)^l \frac{\cos s}{s}.$$

It can be easily shown by induction that

$$y_l(s) = -(2l-1)!!\frac{\cos s}{s^{l+1}} + O(s^{-l}),$$

and thus y_l diverges at the origin for all l. On the other hand, it is also straightforward to show by induction that $j_l(s)$ is finite at the origin for all l. More precisely,

$$j_l(s) = \frac{s^l}{(2l+1)!!} + O(s^{l+1}).$$

From the boundary condition at $r = 0$ we thus conclude that

$$R(r) \propto j_l(s) \equiv j_l(kr).$$

The eigenvalue equation is then obtained from the boundary condition at $r = a$, namely

$$\boxed{j_l(ka) = 0.}$$

It can be shown that the spherical Bessel function $j_l(s)$ is oscillating, with an infinite number of positive zeros z_{nl} ($n \in \mathbb{N}$), which we shall order as follows:

$$z_{1l} < z_{2l} < \cdots < z_{nl} < \cdots.$$

The eigenvalue equation for angular momentum l is thus

$$ka = z_{nl} \quad (n \in \mathbb{N}) \quad \Longrightarrow \quad E_{nl} = \frac{\hbar^2 z_{nl}^2}{2ma^2}.$$

The radial wave functions with angular momentum l are given by

$$\boxed{R_{nl}(r) = N_{nl}\, j_l\left(\frac{z_{nl}r}{a}\right) \chi_{[0,a]}(r),}$$

---

[10]In these notes we shall follow the standard reference `https://dlmf.nist.gov/10.47` for the properties of the spherical Bessel equation and its solutions, the spherical Bessel functions.

where N_{nl} is a normalization constant[11]. Note that the previous formulas are also valid for $l = 0$, since

$$j_0(s) = \frac{\sin s}{s} \quad \implies \quad z_{n0} = n\pi.$$

In Table 6.1 we list the zeros of the spherical Bessel functions $j_l(s)$ with $0 \leqslant l \leqslant 6$ in the interval

l \ n	1	2	3	4	5
0	3.14159	6.28319	9.42478	12.5664	15.708
1	4.49341	7.72525	10.9041	14.0662	17.2208
2	5.76346	9.09501	12.3229	15.5146	18.689
3	6.98793	10.4171	13.698	16.9236	—
4	8.18256	11.7049	15.0397	18.3013	—
5	9.35581	12.9665	16.3547	19.6532	—
6	10.5128	14.2074	17.648	—	—

Table 6.1. Zeros in the interval $0 \leqslant s \leqslant 20$ of the spherical Bessel functions $j_l(s)$ with $0 \leqslant l \leqslant 6$.

$0 \leqslant s \leqslant 20$. Since, as we saw in Section 6.4, $E_{nl} < E_{nl'}$ if $l < l'$ or $n < n'$, we can infer from this table the ten lowest energies of the infinite spherical square well potential (6.83), together with the value of the angular momentum for each of these levels (see Table 6.2).

nl	E_{nl}
$1s$	9.8696
$1p$	20.1907
$1d$	33.2175
$2s$	39.4784
$1f$	48.8312
$2p$	59.6795
$1g$	66.9543
$2d$	82.7192
$1h$	87.5312
$3s$	88.8264

Table 6.2. Lowest ten energy levels of the infinite spherical well potential (6.83). Energies are measured in units of $\hbar^2/(2ma^2)$, and we use the traditional spectroscopic notation s, p, d, f, g, h to denote the values $l = 0, \dots, 5$ of the angular momentum.

6.8 Hydrogen-like atoms

A hydrogen-like atom is an ionized atom whose heavy nucleus is made up of Z protons with charge $q > 0$ (as well as a certain number N of neutrons, which are electrically neutral), around which orbits a single electron of charge $-q < 0$. Since the mass of the nucleus, approximately equal to

$$(Z + N)m_p \simeq (Z + N) \cdot 1.67262192369(51) \cdot 10^{-27} \, \text{kg} \simeq 938.272(Z + N) \, \text{MeV}$$

---

[11]It can be shown that the normalization constant N_{nl} can be taken as

$$N_{nl} = \left(\frac{2}{a^3 z_{nl}}\right)^{1/2} |j_{l\pm1}(z_{nl})|^{-1}.$$
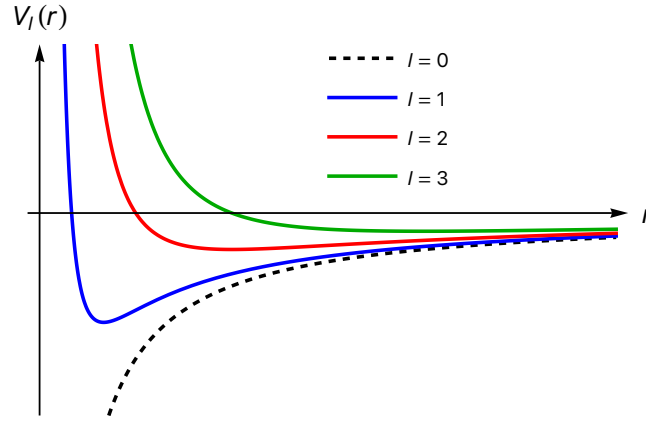
Figure 6.1. Effective potential $V_l(r)$ in Eq. (6.85) for several values of the angular momentum quantum number l.

is much greater than the electron's mass

$$m_e \simeq 9.1093837015(28) \cdot 10^{-31}\,\mathrm{kg} \simeq 0.510999\,\mathrm{MeV}$$

even for $Z + N = 1$, we shall assume that the nucleus is fixed at the origin of coordinates and the electron moves in the electric field created by the nucleus, and is thus subject to a potential

$$V(r) = -\frac{Zq^2}{4\pi\varepsilon_0} \equiv -\frac{Ze^2}{r}, \qquad \text{with} \quad e^2 := \frac{q^2}{4\pi\varepsilon_0}.$$

The effective potential, which in this case is given by

$$V_l(r) = -\frac{Ze^2}{r} + \frac{l(l+1)\hbar^2}{2m_e r^2}, \tag{6.85}$$

is plotted in Fig. 6.1 for several values of the angular momentum l. Since $V_\infty = 0$ for all values of l, the point spectrum is contained in the half-line $(-\infty, 0)$ and the continuous spectrum contains all positive energies. For $l \neq 0$ the effective potential is bounded below by

$$\min V_l = -\frac{m_e Z^2 e^4}{2l(l+1)\hbar^2},$$

so that the point spectrum of V_l is in fact contained in the open interval $(\min V_l, 0)$. For $l = 0$ the effective potential is not bounded from below, but a heuristic argument based on Heisenberg's uncertainty principle shows that the point spectrum must also have a finite lower bound (exercise). Thus for all values of l the point spectrum is a bounded set. We shall see below that the point spectrum is in fact a countably infinite set accumulating at $E = 0$, which being an accumulation point of the point spectrum must itself belong to the spectrum. In fact, we shall see that in this case $E = 0$ belongs to the continuous spectrum, which is therefore the closed half-line $[0, \infty)$.

In what follows we shall only be interested in determining the point spectrum and the corresponding bound states of a hydrogen-like atom of charge Zq. Since $E < 0$, the radial Schrödinger equation is

$$-\partial_r^2 u + \left(\frac{l(l+1)}{r^2} - \frac{2m_e}{\hbar^2}\frac{Ze^2}{r}\right)u = -\frac{2m_e|E|}{\hbar^2}u. \tag{6.86}$$

It is convenient to use the dimensionless length variable

$$\rho = \kappa r,$$

where

$$\kappa = \frac{\sqrt{2m_e|E|}}{\hbar} \tag{6.87}$$ `kaHy`

is an energy-dependent parameter with dimensions of an inverse length. In terms of this variable the radial Schrödinger equation becomes

$$\partial_\rho^2 u = \left(1 - \frac{\lambda}{\rho} + \frac{l(l+1)}{\rho^2}\right) u, \tag{6.88}$$ `radrho`

where

$$\lambda := \frac{\kappa Z e^2}{|E|} = \frac{Z e^2}{\hbar} \sqrt{\frac{2m_e}{|E|}} \tag{6.89}$$ `laHy`

is a dimensionless parameter. Equation (6.88), which can be written as

$$\rho^2 \partial_\rho^2 u + \rho p_1(\rho) \partial_\rho u + p_0(\rho) u = 0$$

with

$$p_1(\rho) = 0, \qquad p_0(\rho) = -\rho^2 + \lambda\rho - l(l+1),$$

has a *singular regular point* at the origin with *indicial equation*

$$s(s-1) + p_1(0)s + p_0(0) = s(s-1) - l(l+1) = 0.$$

Since the roots of the indicial equation are

$$s_1 = l + 1, \qquad s_2 = -l,$$

by *Frobenius theorem* we know that there is a basis of solutions $\{u_1, u_2\}$ of Eq. (6.88) of the form

$$u_1(\rho) = \rho^{l+1} f(\rho), \qquad u_2(\rho) = \rho^{-l} g(\rho) + c \log \rho \, u_1(\rho),$$

where f and g are analytic functions such that $f(0) = g(0) = 1$ and c is a real constant (possibly zero). Since ρ is proportional to r, in view of the boundary condition (6.41) only the first of these solutions is acceptable. Moreover, since for $\rho \gg 1$ Eq. (6.88) reduces to

$$\partial_\rho^2 u - u = 0,$$

whose general solution is

$$u(\rho) = a\mathrm{e}^{-\rho} + b\mathrm{e}^{\rho}$$

with a, b arbitrary complex constants, the solutions of Eq. (6.88) behave as a linear combination $a\mathrm{e}^{-\rho} + b\mathrm{e}^{\rho}$ of the exponentials $\mathrm{e}^{\pm\rho}$ for $\rho \to \infty$. Thus for u to be square integrable it must behave as $\mathrm{e}^{-\rho}$ for $\rho \to \infty$. In other words, we seek for solutions of Eq. (6.88) satisfying the boundary conditions

$$u(\rho) \underset{\rho \to 0+}{\sim} \rho^{l+1}, \qquad u(\rho) \underset{\rho \to \infty}{\sim} \mathrm{e}^{-\rho}.$$

For this reason, it is convenient to look for a new dependent variable $v(\rho)$ defined by

$$u = \rho^{l+1} \mathrm{e}^{-\rho} v.$$

© *Artemio González López*

Since

$$\partial_\rho^2 u = \rho^{l+1} e^{-\rho} \partial_\rho^2 v + 2\partial_\rho \left(\rho^{l+1} e^{-\rho}\right) \partial_\rho v + \partial_\rho^2 (\rho^{l+1} e^{-\rho}) v$$
$$= \rho^l e^{-\rho} \left[\rho \partial_\rho^2 v + 2(l+1-\rho)\partial_\rho v + \left(\frac{l(l+1)}{\rho} - 2(l+1) + \rho\right) v\right],$$

in terms of the variable v the radial Schrödinger equation (6.88) becomes

$$\rho \partial_\rho^2 v + 2(l+1-\rho)\partial_\rho v + \left(\lambda - 2(l+1)\right)v = 0. \qquad (6.90) \quad \boxed{\text{radrhov}}$$

Again $\rho = 0$ is a singular regular point of the latter equation, with indicial equation

$$s(s-1) + 2(l+1)s = 0$$

and roots

$$s_1 = 0, \qquad s_2 = -(2l+1).$$

Thus Frobenius' theorem guarantees the existence of an analytic, non-vanishing solution of Eq. (6.90)

$$v(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \qquad (6.91) \quad \boxed{\text{vseries}}$$

with $a_0 = 1$. The second linearly independent solution of the latter equation is not physically acceptable, since it behaves as ρ^{-2l-1} near the origin and thus $u(\rho) \sim \rho^{-l}$ for $\rho \to 0+$. Since

$$\rho \partial_\rho^2 v = \sum_{k=1}^{\infty} k(k-1)a_k \rho^{k-1} = \sum_{k=0}^{\infty} k(k+1)a_{k+1}\rho^k,$$

$$(l+1-\rho)\partial_\rho v = (l+1)\sum_{k=1}^{\infty} ka_k \rho^{k-1} - \sum_{k=0}^{\infty} ka_k \rho^k = \sum_{k=0}^{\infty}\left[(l+1)(k+1)a_{k+1} - ka_k\right]\rho^k,$$

substituting Eq. (6.91) into (6.90) we obtain

$$\sum_{k=0}^{\infty}\left[(k+1)(k+2l+2)a_{k+1} + \left(\lambda - 2(l+k+1)\right)a_k\right]\rho^k = 0,$$

which is equivalent to the recursion relation

$$a_{k+1} = \frac{2(l+k+1) - \lambda}{(k+1)(2l+k+2)} a_k, \qquad k = 0, 1, \dots. \qquad (6.92) \quad \boxed{\text{rrHy}}$$

Note that the denominator in the RHS never vanishes, since $k, l \geq 0$. It follows from the latter equation that the infinite series (6.91) reduces to a polynomial of degree j if and only if

$$\lambda = 2(l+j+1) \equiv 2(n+l), \qquad \text{with} \quad n \equiv j+1 = 1, 2, \dots, . \qquad (6.93) \quad \boxed{\text{laquant}}$$

On the other hand, when $\lambda \neq 2(n+l)$ with $n = 1, 2, \dots$ (i.e., when λ is *not* an even integer greater than l) the series (6.91) does not terminate, and the function $v(\rho)$ defined by it (with $a_0 = 1$) satisfies

$$|v(\rho)| > C e^{\frac{3}{2}\rho} \qquad (6.94) \quad \boxed{\text{ve2rho}}$$

for some constant $C > 0$ and ρ large enough (cf. Exercise 6.12). It follows that

$$|u(\rho)| > C\rho^{l+1} e^{\rho/2}$$

for large enough ρ, so that u is not normalizable and hence is physically unacceptable. Hence:

The radial equation (6.86) with angular momentum l has normalizable solutions if and only if λ satisfies the quantization condition (6.93). When this is the case, the solution u is of the form

$$u(\rho) = \rho^{l+1} e^{-\rho} P_{n-1}(\rho),$$

where $P_{n-1}(\rho) = \sum\limits_{k=0}^{n-1} a_k \rho^k$ is the polynomial of degree $n-1$ with coefficients a_k satisfying the recursion relation (6.92).

From the definition (6.89) it then follows that the energies of the bound states of the radial Schrödinger equation (6.86) with a given angular momentum $l = 0, 1, \dots$ are the numbers

$$E_{nl} = -\frac{m_e Z^2 e^4}{2\hbar^2} \frac{1}{(n+l)^2}, \qquad n = 1, 2, \dots .$$

(Clearly, for fixed l the energy E_{nl} increases with n, so that E_{nl} is indeed the n-th energy level of the radial Schrödinger equation with angular momentum l.) The number $n \in \mathbb{N}$ is usually called the **radial quantum number.** Note also that when $\lambda = 2(n + l)$ the energy-dependent constant κ in Eq. (6.87) becomes

$$\kappa = \frac{m_e Z e^2}{\hbar^2} \frac{1}{n+l} \equiv \frac{Z}{(n+l)a},$$

where

$$a := \frac{\hbar^2}{m_e e^2} \tag{6.95}$$

`Bohra`

is the Bohr radius of the hydrogen atom. The radial eigenfunction u_{nl} corresponding to the energy E_{nl} is thus proportional to

$$\rho^{l+1} e^{-\rho} P_{n-1}(\rho), \qquad n \in \mathbb{N},$$

where $P_{n-1}(\rho)$ is the polynomial of degree $n-1$ with coefficients determined by Eq. (6.92) with $\lambda = 2(n+l)$. The latter recursion relation is easily solved:

$$\frac{a_k}{a_{k-1}} = \frac{2(l+k) - 2(l+n)}{k(k+2l+1)} = -\frac{2(n-k)}{k(k+2l+1)}$$

$$\implies a_j = \prod_{k=1}^{j} \frac{a_k}{a_{k-1}} = \frac{(-2)^j (n-1)\cdots(n-j)}{j!(2l+2)\cdots(2l+j+1)} = \frac{(-2)^j}{j!} \frac{(n-1)!}{(n-j-1)!} \frac{(2l+1)!}{(2l+j+1)!}$$

$$= \binom{n+2l}{2l+1}^{-1} \frac{(-2)^j}{j!} \binom{n+2l}{2l+j+1},$$

where we have taken into account that $a_0 = 1$. Hence

$$P_n(\rho) = \binom{n+2l+1}{2l+1}^{-1} \sum_{j=0}^{n} \binom{n+2l+1}{j+2l+1} \frac{(-2\rho)^j}{j!} \equiv \binom{n+2l+1}{2l+1}^{-1} L_n^{2l+1}(2\rho),$$

where L_n^k is an *associated Laguerre polynomial* of degree n, defined by

$$L_n^k(z) = \sum_{j=0}^{n} \binom{n+k}{j+k} \frac{(-z)^j}{j!}. \tag{6.96}$$

`ALser`

We can thus write

$$u_{nl}(r) = A_{nl} \rho^{l+1} e^{-\rho} L_{n-1}^{2l+1}(2\rho), \qquad n \in \mathbb{N}. \tag{6.97}$$

`uassLag`

where A_{nl} is a normalization constant. Taking into account the identity

$$\int_0^\infty dx \, x^{k+1} e^{-x} \left[L_n^k(x) \right]^2 = (2n+k+1) \frac{(n+k)!}{n!} \qquad (6.98) \quad \boxed{\text{normRnl}}$$

we easily find

$$\begin{aligned}
\frac{\|u_{nl}^2\|}{|A_{nl}|^2} &= \int_0^\infty dr \, \rho^{2l+2} e^{-2\rho} \left[L_{n-1}^{2l+1}(2\rho) \right]^2 = \frac{1}{\kappa} \int_0^\infty d\rho \, \rho^{2l+2} e^{-2\rho} \left[L_{n-1}^{2l+1}(2\rho) \right]^2 \\
&= \frac{2^{-(2l+3)}}{\kappa} \int_0^\infty dx \, x^{2l+2} e^{-x} \left[L_{n-1}^{2l+1}(x) \right]^2 \\
&= \frac{2^{-(2l+3)}}{\kappa} 2(n+l) \frac{(n+2l)!}{(n-1)!} = 2^{-2(l+1)} \frac{a}{Z} (n+l)^2 \frac{(n+2l)!}{(n-1)!}.
\end{aligned}$$

We can thus take the normalization constant A_{nl} in Eq. (6.97) as

$$A_{nl} = \frac{2^{l+1}}{n+l} \sqrt{\frac{Z(n-1)!}{a(n+2l)!}}. \qquad (6.99) \quad \boxed{\text{Nnhy}}$$

Hence

$$u_{nl}(r) = \frac{1}{n+l} \sqrt{\frac{Z(n-1)!}{a(n+2l)!}} (2\rho)^{l+1} e^{-\rho} L_{n-1}^{2l+1}(2\rho)$$

and

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{\kappa u_{nl}(r)}{\rho} = \frac{2}{(n+l)^2} \left(\frac{Z}{a} \right)^{3/2} \sqrt{\frac{(n-1)!}{(n+2l)!}} (2\rho)^l e^{-\rho} L_{n-1}^{2l+1}(2\rho),$$

with

$$\rho = \kappa r = \frac{Zr}{(n+l)a}.$$

Since the allowed energies of a hydrogen-like atom depend on the radial quantum number n and the angular momentum l only through the combination $n+l$, it is convenient in this case to define the **principal quantum number** N as

$$\boxed{N := n+l.} \qquad (6.100) \quad \boxed{\text{pqn}}$$

With this definition the allowed (bound state) energies are

$$\boxed{E_N = -\frac{m_e Z^2 e^4}{2\hbar^2} \frac{1}{N^2} = -\frac{Z^2 e^2}{2a} \frac{1}{N^2} \simeq -13.6057 \frac{Z^2}{N^2} \text{ eV}, \qquad N = 1, 2, \ldots.} \qquad (6.101) \quad \boxed{\text{Hyspec}}$$

Note that, since $n \geqslant 1$, for each N the angular momentum l can only take the values $l = 0, 1, \ldots, N-1$, and for each of these values of l the radial quantum number n is equal to $N-l$. The corresponding radial wave functions with energy E_N and angular momentum l, that we shall denote by R_N^l to avoid confusion with the general notation R_{nl} adopted in Section 6.4, are given by

$$\boxed{R_N^l(r) = R_{N-l,l}(r) = \frac{2}{N^2} \left(\frac{Z}{a} \right)^{3/2} \sqrt{\frac{(N-l-1)!}{(N+l)!}} (2\rho)^l e^{-\rho} L_{N-l-1}^{2l+1}(2\rho), \qquad \rho = \frac{Zr}{Na}.}$$

Multiplying by the spherical harmonic $Y_l^m(\theta, \varphi)$ we obtain the following expression for the normalized eigenfunctions

$$\psi_N^{lm}(\mathbf{r}) \equiv \psi_{N-l,lm}(\mathbf{r}) = R_N^l(r) Y_{lm}(\theta, \varphi)$$

of a hydrogen-like atom with energy E_N, which are simultaneous eigenfunctions of $\mathbf{L}^2$ and L_3 with respective eigenvalues $l(l+1)\hbar^2$ and $m\hbar$:

$$\psi_N^{lm}(\mathbf{r}) = \left(\frac{Z}{a}\right)^{3/2} \frac{2}{N^2} \sqrt{\frac{(N-l-1)!}{(N+l)!}} \left(\frac{2s}{N}\right)^l e^{-\frac{s}{N}} L_{N-l-1}^{2l+1}\left(\frac{2s}{N}\right) Y_l^m(\theta,\varphi), \qquad s := \frac{Zr}{a},$$

(6.102) $\boxed{\text{Hywfs}}$

where

$$l = 0, 1, \ldots, N-1, \qquad m = -l, -l+1, \ldots, l.$$

Since all of the above wave functions have the same energy E_N, given by Eq. (6.101), the degeneracy of the N-th energy level is given by

$$d_N = \sum_{l=0}^{N-1} (2l+1) = N + 2\sum_{k=1}^{N-1} k = N + N(N-1) = N^2.$$

Note that the subindex N in ψ_N^{lm} denotes the *energy level,* and that the *number of zeros* (usually called *nodes* in the literature) of the radial part $R_N^l = R_{N-l,l}$ of this eigenfunction is therefore $N - l - 1$. Moreover, the parity of ψ_N^{lm} is that of its angular part Y_l^m, namely $(-1)^l$:

$$\psi_N^{lm}(-\mathbf{r}) = (-1)^l \psi_N^{lm}(\mathbf{r}).$$

Remark.

- As remarked in Section 6.5, the energy E_{nl} of a state ψ_{nlm} in an arbitrary central potential is independent of the magnetic quantum number m. This is a direct consequence of the *rotational invariance* of the Hamiltonian (6.45), i.e., of the fact that H commutes with the generators L_i of the *rotation group* SO(3):

$$[H, \mathbf{L}] = 0.$$

To prove this statement, notice that the previous commutation relations obviously imply that

$$[H, L_\pm] = 0.$$

Suppose that a state ψ has energy E and also satisfies

$$\mathbf{L}^2\psi = l(l+1)\hbar^2\psi, \qquad L_3\psi = m\hbar\psi,$$

which is possible since the three operators $\{H, \mathbf{L}^2, L_3\}$ commute. (In other words, ψ is proportional to one of the states ψ_{nlm} defined above.) Applying the operators $L_\pm$ to both sides of the eigenvalue equation

$$H\psi = E\psi,$$

and taking advantage of the commutativity of H and $L_\pm$, we thus find

$$L_\pm(H\psi) = H(L_\pm\psi) = E(L_\pm\psi),$$

and of course (as we saw in Section 6.6)

$$\mathbf{L}^2(L_\pm\psi) = l(l+1)\hbar^2 L_\pm\psi, \qquad L_3(L_\pm\psi) = (m \pm 1)\hbar L_\pm\psi.$$

In other words, the states $L_\pm\psi$ either vanish or are eigenstates of L_3 with eigenvalue $(m \pm 1)\hbar$, and still have energy E and angular momentum l. Proceeding as explained in Section 6.6, by repeatedly

applying the operators $L_{\pm}$ to the original state ψ we can construct a "ladder" of $2l + 1$ states with the same energy E and angular momentum l, which are eigenstates of L_3 with eigenvalues $-l\hbar$, $(-l + 1)\hbar, \ldots, l\hbar$. For a *generic* central potential, $E_{nl} = E_{n'l'}$ if and only if $(n, l) = (n', l')$; hence, as remarked in Section 6.5, the degeneracy of each energy level E_{nl} in a generic central potential is $2l + 1$.

On the other hand, the energy E_{nl} in a hydrogen-like atom depends on n and l only through the sum $n + l$, and thus the N levels $E_{N0}, E_{N-1,1}, \ldots, E_{1,N-1}$ have all the same energy. In other words, the spectrum of a hydrogen-like has an *accidental degeneracy* not accounted for by the rotational — SO(3)— invariance of the Hamiltonian. In fact, it can be shown that this accidental degeneracy is actually a direct consequence of the invariance of the Hamiltonian (6.45) with a $1/r$ potential under the group SO(4), generated by the three components of the orbital angular momentum operator and the *Laplace–Runge–Lenz vector* operator

$$\mathbf{M} = \frac{1}{2m} (\mathbf{P} \times \mathbf{L} - \mathbf{L} \times \mathbf{P}) - \frac{Ze^2}{r};$$

see, e.g., [GP90, Section 6.7]. ∎

Exercise 6.11. Prove that the Laplace–Runge–Lenz vector operator is Hermitian.

Solution. Obviously, it suffices to show that $\mathbf{P} \times \mathbf{L} - \mathbf{L} \times \mathbf{P}$ is Hermitian. To this end note that, since $\mathbf{P}$ and $\mathbf{L}$ are self-adjoint, we have

$$(P_i L_j - P_j L_i)^\dagger = L_j P_i - L_i P_j,$$

or in vector form

$$(\mathbf{P} \times \mathbf{L})^\dagger = -\mathbf{L} \times \mathbf{P}.$$

Hence

$$(\mathbf{P} \times \mathbf{L} - \mathbf{L} \times \mathbf{P})^\dagger = -\mathbf{L} \times \mathbf{P} + \mathbf{P} \times \mathbf{L},$$

as was to be shown.

For instance, the *ground state* ($N = 1$) has energy

$$E_1 = -\frac{m_e Z^2 e^4}{2\hbar^2}$$

and is *non-degenerate.* Its normalized eigenfunction is a *spherically symmetric* state (since $l = m = 0$ implies that the angular part is $Y_0^0 = 1/\sqrt{4\pi}$), given by

$$\psi_1^{00}(\mathbf{r}) = 2 \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} L_0^1 \left(\frac{2Zr}{a}\right) \frac{1}{\sqrt{4\pi}} = \left(\frac{Z}{a}\right)^{3/2} \frac{e^{-Zr/a}}{\sqrt{\pi}}.$$

It is straightforward to check that $\psi_1^{00}(\mathbf{r})$ is indeed normalized:

$$\|\psi_1^{00}\|^2 = 4\pi \int_0^\infty dr\, r^2 \psi_1^{00}(r)^2 = 4 \left(\frac{Z}{a}\right)^3 \int_0^\infty dr\, r^2 e^{-2Zr/a} = \frac{1}{2} \int_0^\infty ds\, s^2 e^{-s} = 1.$$

The next energy level ($N = 2$) has energy $E_2 = E_1/4$, and is four-fold degenerate. The four eigenfunc-

tions with this energy are

$$
\psi_2^{00} = \left(\frac{Z}{a}\right)^{3/2} \frac{e^{-\frac{Zr}{2a}}}{2\sqrt{2}} L_1^1\left(\frac{Zr}{a}\right) \frac{1}{\sqrt{4\pi}} = \left(\frac{Z}{a}\right)^{3/2} \frac{e^{-\frac{Zr}{2a}}}{4\sqrt{2\pi}} \left(2 - \frac{Zr}{a}\right),
$$

$$
\psi_2^{11} = \left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{2\sqrt{6}} L_0^3\left(\frac{Zr}{a}\right) \left(-\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta\, e^{i\varphi}\right) = -\left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{8\sqrt{\pi}} \sin\theta\, e^{i\varphi},
$$

$$
\psi_2^{10} = \left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{2\sqrt{6}} L_0^3\left(\frac{Zr}{a}\right) \cdot \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta = -\left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{4\sqrt{2\pi}} \cos\theta,
$$

$$
\psi_2^{1,-1} = \left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{2\sqrt{6}} L_0^3\left(\frac{Zr}{a}\right) \cdot \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta\, e^{-i\varphi} = \left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \frac{e^{-\frac{Zr}{2a}}}{8\sqrt{\pi}} \sin\theta\, e^{-i\varphi}.
$$

`exe.serieLag`

Exercise 6.12. Prove Eq. (6.94).

Solution. Let

$$
f(\rho) = e^{2\rho} = \sum_{k=0}^{\infty} b_k \rho^k, \qquad \text{with} \quad b_k = \frac{2^k}{k!}.
$$

We then have

$$
\frac{b_{k+1}}{b_k} = \frac{2}{k+1},
$$

and therefore

$$
\frac{a_{k+1}}{a_k} - \frac{b_{k+1}}{b_k} = \frac{1}{k+1}\left(\frac{2(l+k+1)-\lambda}{2l+k+2} - 2\right) = -\frac{1}{k+1}\frac{\lambda+2l+2}{k+2l+2}.
$$

Since

$$
\frac{\lambda+2l+2}{k+2l+2} \xrightarrow[k\to\infty]{} 0,
$$

for any $\varepsilon \in (0,1)$ there exists a sufficiently large integer N such that

$$
k \geqslant N \quad\Longrightarrow\quad \frac{\lambda+2l+2}{k+2l+2} < 2\varepsilon,
$$

and therefore

$$
k \geqslant N \quad\Longrightarrow\quad \frac{a_{k+1}}{a_k} - \frac{b_{k+1}}{b_k} > -\frac{2\varepsilon}{k+1} = -\varepsilon\frac{b_{k+1}}{b_k},
$$

or equivalently (taking into account that $b_{k+1}/b_k > 0$),

$$
k \geqslant N \quad\Longrightarrow\quad \frac{a_{k+1}}{a_k} > (1-\varepsilon)\frac{b_{k+1}}{b_k} > 0.
$$

Thus

$$
j \geqslant N \quad\Longrightarrow\quad \frac{a_{j+1}}{a_N} = \prod_{k=N}^{j} \frac{a_{k+1}}{a_k} > \prod_{k=N}^{j} \frac{(1-\varepsilon)b_{k+1}}{b_k} = (1-\varepsilon)^{j+1-N}\frac{b_{j+1}}{b_N},
$$

and therefore (multiplying throughout by $\rho^{j+1} > 0$ and summing over j from N to ∞)

$$
\frac{1}{a_N}\left(v(\rho) - p_N(\rho)\right) > \frac{(1-\varepsilon)^{-N}}{b_N}\left[f\left((1-\varepsilon)\rho\right) - q_N(\rho)\right] = \frac{(1-\varepsilon)^{-N}}{b_N}\left(e^{2(1-\varepsilon)\rho} - q_N(\rho)\right),
$$

with

$$p_N(\rho) = \sum_{j=0}^{N} a_j \rho^j, \qquad q_N(\rho) = \sum_{j=0}^{N} b_j \big[(1-\varepsilon)\rho\big]^j$$

polynomials of degree at most N in ρ. Rearranging terms in the previous inequality we can rewrite it as

$$v(\rho) > (1-\varepsilon)^{-N} \frac{a_N}{b_N} \left(\mathrm{e}^{2(1-\varepsilon)\rho} + r_N(\rho)\right),$$

where r_N is another polynomial of degree at most N in ρ. Since

$$\mathrm{e}^{-2(1-\varepsilon)\rho} r_N(\rho) \xrightarrow[\rho\to\infty]{} 0,$$

if ρ is large enough so that

$$\mathrm{e}^{-2(1-\varepsilon)\rho} |r_N(\rho)| < \frac{1}{2}$$

we have

$$v(\rho) > (1-\varepsilon)^{-N} \frac{a_N}{2b_N} \, \mathrm{e}^{2(1-\varepsilon)\rho}.$$

As the RHS of the previous inequality is positive so is the LHS, and thus

$$|v(\rho)| = v(\rho) > (1-\varepsilon)^{-N} \frac{a_N}{2b_N} \mathrm{e}^{2(1-\varepsilon)\rho} \quad \Longrightarrow \quad |v(\rho)| > C \mathrm{e}^{2(1-\varepsilon)\rho},$$

with $C = (1-\varepsilon)^{-N} \frac{|a_N|}{2b_N} > 0$. Setting $\varepsilon = 1/4$ we obtain Eq. (6.94).

The associated Laguerre polynomials.

The *associated Laguerre polynomial* $L_n^k(x)$ is defined by

$$L_n^k(x) = (-1)^k \partial_x^k L_{n+k}(x),$$

where $L_n(x)$ denotes the *Laguerre polynomial* of degree n

$$L_n(x) = \frac{\mathrm{e}^x}{n!} \partial_x^n (x^n \mathrm{e}^{-x}) \equiv L_n^0(x).$$

From the operator identity

$$\mathrm{e}^x \partial_x^n \mathrm{e}^{-x} = \left(\mathrm{e}^x \partial_x \mathrm{e}^{-x}\right)^n = (\partial_x - 1)^n,$$

we obtain

$$L_n(x) = \frac{1}{n!}(\partial_x - 1)^n (x^n) = \frac{1}{n!}\sum_{j=0}^{n}\binom{n}{j}(-1)^j \partial_x^{n-j} x^n = \frac{1}{n!}\sum_{j=0}^{n}\binom{n}{j}(-1)^j \frac{n!}{j!}x^j$$

$$= \sum_{j=0}^{n}\binom{n}{j}\frac{(-x)^j}{j!},$$

and therefore

$$L_n^k(x) = (-1)^k \partial_x^k \sum_{j=0}^{n+k}\binom{n+k}{j}\frac{(-x)^j}{j!} = \sum_{j=k}^{n+k}\binom{n+k}{j}\frac{(-1)^{j+k}}{j!}\frac{j!}{(j-k)!}x^{j-k}$$

$$= \sum_{j=0}^{n}\binom{n+k}{j+k}\frac{(-x)^j}{j!},$$

which is Eq. (6.96).

A useful tool for establishing the properties of the associated Laguerre polynomials is their *generating function,* defined by

$$F_k(x, s) = \sum_{n=0}^{\infty} L_n^k(x) s^n.$$

This function can be easily evaluated from Eq. (6.96). Indeed, for $k = 0$ we have

$$F_0(x, s) = \sum_{n=0}^{\infty} L_n(x) s^n = \sum_{n=0}^{\infty} \sum_{j=0}^{n} \binom{n}{j} \frac{(-x)^j}{j!} s^n = \sum_{j=0}^{\infty} \frac{(-x)^j}{j!} \sum_{n=j}^{\infty} \binom{n}{j} s^n$$

$$= \sum_{j=0}^{\infty} \frac{(-sx)^j}{j!} \sum_{n=0}^{\infty} \binom{n+j}{j} s^n.$$

On the other hand, differentiating j times the equality

$$(1-s)^{-1} = \sum_{n=0}^{\infty} s^n$$

we obtain

$$j!(1-s)^{-j-1} = \sum_{n=j}^{\infty} \frac{n!}{(n-j)!} s^{n-j} = \sum_{n=0}^{\infty} \frac{(n+j)!}{n!} s^n \quad \Longrightarrow \quad (1-s)^{-j-1} = \sum_{n=0}^{\infty} \binom{n+j}{j} s^n,$$

and therefore

$$F_0(x, s) = \sum_{j=0}^{\infty} \frac{(-sx)^j}{j!} (1-s)^{-j-1} = (1-s)^{-1} \sum_{j=0}^{\infty} \frac{1}{j!} \left(\frac{-sx}{1-s} \right)^j = \frac{e^{-\frac{sx}{1-s}}}{1-s}.$$

Applying the operator $(-1)^k \partial_x^k$ to both sides of this equality we thus obtain

$$F_k(x, s) = \sum_{n=0}^{\infty} (-1)^k \partial_x^k L_{n+k}(x) s^n = (-1)^k s^{-k} \partial_x^k \sum_{n=k}^{\infty} L_n(x) s^n$$

$$= (-1)^k s^{-k} \partial_x^k F_0(x),$$

where we have taken into account that

$$\partial_x^k L_n(x) = 0, \qquad n = 0, \dots, k-1$$

(since $L_n(x)$ is a polynomial of degree n in x). Using the previous expression for $F_0(x)$ we obtain the explicit formula

$$F_k(x, s) = \frac{e^{-\frac{sx}{1-s}}}{(1-s)^{k+1}}.$$

With the help of the previous formula for the generating function, it is straightforward to establish Eq. (6.98). Indeed, from the definition of the generating function we have

$$\int_0^{\infty} dx \, x^{k+1} e^{-x} F_k(x, s) F_k(x, t) = \sum_{n,m=0}^{\infty} s^n t^m \int_0^{\infty} dx \, x^{k+1} e^{-x} L_n^k(x) L_m^k(x). \tag{6.103}$$

`intgendef`

On the other hand, using the explicit formula for the generating function we obtain

$$\int_0^\infty dx\, x^{k+1} e^{-x} F_k(x,s) F_k(x,t) = (1-s)^{-k-1}(1-t)^{-k-1} \int_0^\infty dx\, x^{k+1} e^{-x} e^{-\frac{sx}{1-s}} e^{-\frac{tx}{1-t}}.$$

Taking into account the identity

$$1 + \frac{s}{1-s} + \frac{t}{1-t} = \frac{(1-s)(1-t) + s(1-t) + t(1-s)}{(1-s)(1-t)} = \frac{1-st}{(1-s)(1-t)}$$

and the value of the integral

$$\int_0^\infty dx\, x^m e^{-ax} = m!\, a^{-m-1}, \qquad m = 0, 1, \ldots, \quad a > 0,$$

we can rewrite the previous formula as

$$\int_0^\infty dx\, x^{k+1} e^{-x} F_k(x,s) F_k(x,t) = (1-s)^{-k-1}(1-t)^{-k-1} \int_0^\infty dx\, x^{k+1} e^{-\frac{1-st}{(1-s)(1-t)}x}$$

$$= (k+1)! \frac{(1-s)(1-t)}{(1-st)^{k+2}} = (1 - s - t + st) \sum_{n=0}^\infty \frac{(n+k+1)!}{n!} s^n t^n.$$

The coefficient of $s^n t^n$ in the RHS of previous expression is

$$\frac{(n+k+1)!}{n!} + \frac{(n+k)!}{(n-1)!} = \frac{(n+k)!}{n!}(n+k+1+n) = (2n+k+1)\frac{(n+k)!}{n!} \qquad (6.104)$$

sntncoeff

for $n > 0$ and

$$\frac{(k+1)!}{0!} = (k+1)!$$

for $n = 0$, which coincides with (6.104) with $n = 0$. Thus Eq. (6.104) is valid for all n. Equating the latter equation to the coefficient of $s^n t^n$ in Eq. (6.103) we obtain Eq. (6.98).

Exercise 6.13. Prove *Rodrigues' formula* for the associated Laguerre polynomials:

$$L_n^k(x) = \frac{x^{-k} e^x}{n!} \partial_x^n \left(x^{n+k} e^{-x} \right).$$

Solution. From the definition of the generating function $F_k(x,s)$ it follows that

$$L_n^k(x) = \frac{1}{n!} \partial_s^n F_k(x,s) \Big|_{s=0} = \frac{1}{2\pi i} \oint \frac{F_k(x,s)}{s^{n+1}} \, ds = \frac{1}{2\pi i} \oint \frac{e^{-\frac{sx}{1-s}}}{s^{n+1}(1-s)^{k+1}} \, ds,$$

where the integral is extended (for instance) along the (positively oriented) circle $|s| = \varepsilon$ with $\varepsilon < 1$. Performing the change of variables

$$\frac{s}{1-s} = t \implies 1 - s = \frac{1}{1+t}, \quad s = \frac{t}{1+t}, \quad ds = \frac{dt}{(1+t)^2}$$

we obtain

$$L_n^k(x) = \frac{1}{2\pi i} \oint t^{-n-1}(1+t)^{n+k} e^{-tx} \, dt,$$

where for small enough ε the integral is extended along a positively oriented simple closed curve encircling the origin (indeed, $s = \varepsilon e^{i\varphi}$ implies that $t = \varepsilon e^{i\varphi} + O(\varepsilon^2)$). The last integral can be easily

computed with the help of the residue theorem, namely

$$L_n^k(x) = \frac{1}{n!}\,\partial_t^n\Big|_{t=0}\left((1+t)^{n+k}\mathrm{e}^{-tx}\right) = \frac{1}{n!}\,\partial_u^n\Big|_{u=1}\left(u^{n+k}\mathrm{e}^{(1-u)x}\right) = \frac{\mathrm{e}^x}{n!}\,\partial_u^n\Big|_{u=1}\left(u^{n+k}\mathrm{e}^{-ux}\right).$$

Performing the change of variable

$$\xi = xu \quad \Longrightarrow \quad \partial_u = x\partial_\xi$$

we finally obtain

$$L_n^k(x) = \frac{\mathrm{e}^x}{n!}\,x^n\partial_\xi^n\Big|_{\xi=x}\left(x^{-n-k}\xi^{n+k}\mathrm{e}^{-\xi}\right) = \frac{x^{-k}\mathrm{e}^x}{n!}\,\partial_\xi^n\Big|_{\xi=x}\left(\xi^{n+k}\mathrm{e}^{-\xi}\right) \equiv \frac{x^{-k}\mathrm{e}^x}{n!}\,\partial_x^n\!\left(x^{n+k}\mathrm{e}^{-x}\right).$$

Exercise 6.14.

i) Determine the probability density of finding the electron in a hydrogen-like atom at a distance r from the origin when it is in the energy eigenstate ψ_N^{lm}.

ii) Find the most likely and the mean distance of the electron to the origin when $l = N - 1$ (which in Bohr's atomic model corresponds to a *circular* orbit).

iii) Again for $l = N - 1$, find the uncertainty in the electron's distance to the origin, and comment on the result obtained.

Solution.

i) The probability of finding the electron at a distance in the range $[r, r + \mathrm{d}r]$ from the origin is found integrating the probability density

$$\left|\psi_N^{lm}(r, \theta, \varphi)\right|^2 \mathrm{d}^3 r \equiv \left|R_N^l(r)Y_l^m(\theta, \varphi)\right|^2 r^2\, \mathrm{d}r\, \mathrm{d}\Omega$$

over $\theta \in [0, \pi]$ and $\varphi \in [0, 2\pi]$, namely

$$\left|R_N^l(r)\right|^2 r^2\, \mathrm{d}r \int_{[0,\pi]\times[0,2\pi]} \left|Y_l^m(\theta, \varphi)\right|^2 = \left|R_N^l(r)\right|^2 r^2\, \mathrm{d}r,$$

since the spherical harmonics are normalized over the unit sphere (cf. Eq. (6.57)). Thus the sought-for probability density is

$$p_N^l(r) := \left|R_N^l(r)\right|^2 r^2.$$

which is obviously independent of the magnetic quantum number m.

ii) When $l = N - 1$ we have

$$p_N^{N-1}(r) = \frac{4}{N^4}\left(\frac{Z}{a}\right)^3 r^2 \frac{(2\rho)^{2(N-1)}\mathrm{e}^{-2\rho}}{(2N-1)!} = \frac{Z}{N^2 a}\frac{(2\rho)^{2N}\mathrm{e}^{-2\rho}}{(2N-1)!}, \qquad \rho = \frac{Zr}{Na},$$

as $L_0^k(s) = 1$. Since p_N^{N-1} is proportional to $\rho^{2N}\mathrm{e}^{-2\rho}$, the most likely distance of the electron to the origin is found setting the derivative of the latter function equal to zero, namely

$$0 = \partial_\rho\left(\rho^{2N}\mathrm{e}^{-2\rho}\right) = (2N - 2\rho)\rho^{2N-1}\mathrm{e}^{-2\rho} \iff \rho = 0, N.$$

Clearly $\rho = 0$ is a minimum of $\rho^{2N}\mathrm{e}^{-2\rho}$ and $\rho = N$ is a maximum. Thus the most likely distance of the electron to the origin is obtained when $\rho = N$, i.e.,

$$\frac{Zr}{Na} = N \iff r = \frac{N^2 a}{Z}.$$

(This is, coincidentally, the radius of the N-th electron orbit in Bohr's atomic model.) To determine the average value of the distance of the electron to the origin we must evaluate the integral

$$\langle r \rangle = \int_0^\infty \mathrm{d}r \, r p_N^{N-1}(r) = \frac{1}{(2N-1)!} \frac{Z}{N^2 a} \int_0^\infty \mathrm{d}r \, r (2\rho)^{2N} \mathrm{e}^{-2\rho}$$

$$= \frac{1}{(2N-1)!} \frac{Z}{N^2 a} \left(\frac{Na}{2Z} \right)^2 \int_0^\infty \mathrm{d}s \, s^{2N+1} \mathrm{e}^{-s} = \frac{a}{4Z} \frac{(2N+1)!}{(2N-1)!} = N \left(N + \frac{1}{2} \right) \frac{a}{Z}.$$

In particular, notice that the mean distance to the origin is slightly larger than the most probable distance.

iii) The expectation value of r^2 in an orbital with $l = N - 1$ is computed similarly:

$$\langle r^2 \rangle = \int_0^\infty \mathrm{d}r \, r^2 p_N^{N-1}(r) = \frac{1}{(2N-1)!} \frac{Z}{N^2 a} \int_0^\infty \mathrm{d}r \, r^2 (2\rho)^{2N} \mathrm{e}^{-2\rho}$$

$$= \frac{1}{(2N-1)!} \frac{Z}{N^2 a} \left(\frac{Na}{2Z} \right)^3 \int_0^\infty \mathrm{d}s \, s^{2N+2} \mathrm{e}^{-s} = \frac{Na^2}{8Z^2} \frac{(2N+2)!}{(2N-1)!} = N^2(N+1) \left(N + \frac{1}{2} \right) \frac{a^2}{Z^2}.$$

Thus the square of the uncertainty in the electron's distance to the origin is given by

$$\Delta r^2 = \langle r^2 \rangle - \langle r \rangle^2 = \frac{a^2}{2Z^2} N^2 \left(N + \frac{1}{2} \right).$$

In particular, the relative uncertainty

$$\frac{\Delta r}{\langle r \rangle} = (2N+1)^{-1/2} \xrightarrow[N \to \infty]{} 0,$$

in agreement with Bohr's *correspondence principle.*

6.9 The three-dimensional isotropic oscillator

In Section 6.1.2 we solved the Schrödinger equation for the three-dimensional harmonic oscillator potential (6.12) by separation of variables in Cartesian coordinates. In the *isotropic case,* i.e., when the three constants k_i are equal:

$$k_1 = k_2 = k_3 \equiv k = \frac{1}{2} m\omega^2,$$

the oscillator potential reduces to the *central* potential

$$V(r) = \frac{1}{2} m\omega^2 r^2. \tag{6.105}$$

`IsoHOpot`

Thus the Schrödinger equation for the isotropic harmonic oscillator can also be solved by separating variables in *spherical coordinates,* using the method outlined in Section 6.2.

Remark. The fact that the Schrödinger equation for a potential $V(\mathbf{r})$ can be solved by separating variables in more than one coordinate system always indicates that the potential in question possesses a certain symmetry. In the case of the isotropic harmonic oscillator, this symmetry is known to be related to the U(3) group. Likewise, the Schrödinger equation for the Coulomb potential can be solved by separating variables both in spherical and parabolic coordinates. In this case, the corresponding symmetry group is SO(4). ∎

The radial equation for the isotropic three-dimensional oscillator is

$$-\frac{\hbar^2}{2m} \partial_r^2 u + \left(\frac{1}{2} m\omega^2 r^2 + \frac{l(l+1)}{r^2} - E \right) u(r) = 0.$$
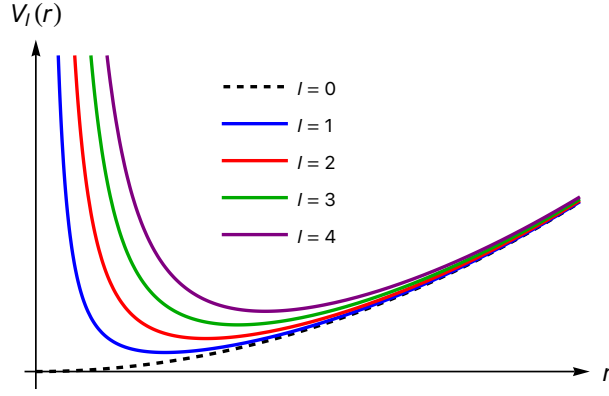
Figure 6.2. Effective potential $V_l(r)$ for the three-dimensional isotropic harmonic oscillator for several values of the angular momentum quantum number l.

fig.VlHO

It is convenient to use the dimensionless length variable

$$s = \alpha r, \qquad \alpha := \sqrt{m\omega\hbar},$$

in terms of which the radial equation becomes

$$u''(s) - \left(s^2 + \frac{l(l+1)}{s^2}\right)u + 2\lambda u = 0, \qquad \lambda := \frac{E}{\hbar\omega}, \tag{6.106}$$

ueq3DHO

where the prime denotes differentiation with respect to s. We seek for square integrable solutions $u(s)$ of the latter equation satisfying the boundary condition at the origin

$$u(s) \underset{s\to 0+}{\sim} s^{l+1}.$$

Moreover, for $s \to \infty$ we have

$$u''(s) \underset{s\to\infty}{\sim} s^2 u(s),$$

an approximate solution of which is

$$u(s) = e^{\pm\frac{s^2}{2}}.$$

Thus for $|s| \to \infty$ the solutions of Eq. (6.106) should behave as $e^{\pm s^2/2}$. Since $e^{s^2/2}$ is not square integrable, we conclude that the square-integrable solutions of Eq. (6.106) must behave as $e^{-s^2/2}$ at infinity. The asymptotic behavior of the normalizable solutions of the latter equation suggests the change of dependent variable

$$u(s) = s^{l+1}e^{-s^2/2}v(s).$$

The differential equation satisfied by the function $v(s)$ is easily found:

$$u'(s) = s^l e^{-s^2/2}\big[(l+1-s^2)v(s) + sv'(s)\big],$$
$$u''(s) = s^{l-1}e^{-s^2/2}\Big\{(l-s^2)\big[(l+1-s^2)v(s) + sv'(s)\big] + s^2v''(s) + (l+2-s^2)sv'(s) - 2s^2v(s)\Big\}$$
$$= s^{l-1}e^{-s^2/2}\Big\{s^2v''(s) + 2s(l+1-s^2)v'(s) + \big[l(l+1) - (2l+3)s^2 + s^4\big]v(s)\Big\},$$

and thus

$$s^2u''(s) + \big(2\lambda s^2 - s^4 - l(l+1)\big)u(s) = s^{l+2}e^{-s^2/2}\Big[sv''(s) + 2(l+1-s^2)v'(s) + (2\lambda - 2l - 3)sv(s)\Big],$$

whence

$$sv''(s) + 2(l+1-s^2)v'(s) + (2\lambda - 2l - 3)sv(s) = 0. \tag{6.107}$$

veq3DHO

The latter equation has a *singular regular point* at the origin, with indicial equation

$$\sigma(\sigma - 1) + 2(l + 1)\sigma = 0$$

and roots

$$\sigma_1 = 0, \qquad \sigma_2 = -2l - 1.$$

By Frobenius's theorem, Eq. (6.107) has a fundamental systems of solutions of the form

$$v_1(s) = \sum_{n=0}^{\infty} a_n s^n, \qquad v_2(s) = s^{-2l-1} \sum_{n=0}^{\infty} b_n s^n + c \log s \, v_1(s),$$

with $a_0, b_0 \neq 0$ and c a (possibly vanishing) constant. However, for $u(s)$ to behave as s^{l+1} for $s \to 0+$ we need $v(s)$ to tend to a non-zero constant in this limit. It follows that the only acceptable solutions of Eq. (6.107) are proportional to the power series v_1. Substituting this series into the latter equation we obtain

$$\sum_{n=0}^{\infty} [n(n-1) + 2n(l+1)] a_n s^{n-1} + \sum_{n=0}^{\infty} (2\lambda - 2l - 3 - 2n) a_n s^{n+1}$$

$$= 2(l+1)a_1 + \sum_{n=2}^{\infty} n(n + 2l + 1)a_n s^{n-1} + \sum_{n=0}^{\infty} (2\lambda - 2l - 3 - 2n) a_n s^{n+1}$$

$$= 2(l+1)a_1 + \sum_{n=0}^{\infty} [(n+2)(n+2l+3)a_{n+2} + (2\lambda - 2l - 3 - 2n)a_n] s^{n+1} = 0.$$

Equating to zero the coefficients of the powers of s in the previous equation we obtain

$$a_1 = 0$$

and

$$a_{n+2} = \frac{2n + 2l + 3 - 2\lambda}{(n+2)(n+2l+3)} a_n, \qquad n = 0, 1, \dots.$$

From the recursion relation and the vanishing of a_1 we deduce that the odd coefficients vanish:

$$a_{2k+1} = 0, \qquad \forall k = 0, 1, \dots.$$

Calling $b_k = a_{2k}$, we can write the recursion relation for the even coefficients a_{2k} as

$$b_{k+1} = \frac{2k + l + 3/2 - \lambda}{(k+1)(2k+2l+3)} b_k, \qquad k = 0, 1, \dots.$$

Moreover, since the quotient

$$\frac{b_{k+1}}{b_k} \underset{k \to \infty}{\simeq} \frac{1}{k}$$

is asymptotically the same as for the series of e^{s^2}, reasoning as in Sections 5.1 and 6.8 we conclude that the if the power series $v_1(s)$ does not terminate then $v_1(s) \sim e^{s^2}$ for $s \to \infty$. But this is unacceptable, since it implies that $u(s) = s^{l+1}e^{-s^2/2}v_1(s) \sim e^{s^2/2}$ is not square integrable. Hence the series for $v_1(s)$ must terminate. In view of the recursion relation, this is only possible if

$$\boxed{\lambda = 2n_r + l + \frac{3}{2}} \qquad (6.108)$$

for some nonnegative integer n_r. From the latter equation we obtain the following formula for the energies of the bound states of the three-dimensional isotropic harmonic oscillator:

$$\boxed{E_{n_r l} = \left(2n_r + l + \frac{3}{2}\right) \hbar\omega, \qquad l, n_r = 0, 1, 2, \dots.}$$

The nonnegative integer n_r appearing in the latter formula is called the *radial quantum number*. It is apparent that the energy depends on n_r and l through the combination $N := 2n_r + l$. It follows that, for a given N, the angular momentum quantum number l must have the same parity as N. We can therefore label the energy levels as

$$E_N^l \equiv E_{(N-l)/2,l} = \left(N + \frac{3}{2}\right)\hbar\omega, \qquad l = \pi(N), \pi(N) + 2, \ldots, N,$$

where $\pi(N)$ denotes the parity of N (i.e., $\pi(N) = 0$ for even N, $\pi(N) = 1$ for odd N). Note that we obtain the same numerical value of the energies of the bound states that we derived in Section 6.1.2 solving the Schrödinger equation in Cartesian coordinates, as expected. As to the degeneracy of the energy levels, for N even we have

$$l = 0, 2, \ldots, N \quad \Longrightarrow \quad l = 2p, \quad p = 0, 1, \ldots, \frac{N}{2}.$$

Since the energy is independent of the azimuthal quantum number m, which for a given l can take $2l + 1 = 4p + 1$ values, the degeneracy d_N of the energy $(N + \frac{3}{2})\hbar\omega$ is in this case

$$d_N = \sum_{p=0}^{N/2}(4p + 1) = 2\frac{N}{2}\left(\frac{N}{2} + 1\right) + \frac{N}{2} + 1 = \frac{1}{2}(N + 1)(N + 2).$$

Likewise, for odd N we have

$$l = 1, 3, \ldots, N \quad \Longrightarrow \quad l = 2p + 1, \quad p = 0, 1, \ldots, \frac{N - 1}{2},$$

and

$$d_N = \sum_{p=0}^{(N-1)/2}(4p + 3) = 2\frac{N - 1}{2}\frac{N + 1}{2} + \frac{3}{2}(N + 1) = \frac{1}{2}(N + 1)(N + 2).$$

We thus see that the degeneracy of the energy $(N + \frac{3}{2})\hbar\omega$ is in all cases

$$d_N = \frac{1}{2}(N + 1)(N + 2),$$

again in agreement with the result obtained in Section 6.1.2 (cf. Eq. (6.17)).

Bibliography

`CDL20` [CDL20] Charles Cohen-Tannoudji, Bernard Diu, and Franck Laloë. *Quantum Mechanics*. 2nd ed. Vol. I. Weinheim (Germany): Wiley-VCH, 2020.

`GP90` [GP90] A. Galindo and P. Pascual. *Quantum Mechanics I*. Berlin: Springer-Verlag, 1990.

`Gr18` [GS18] David J. Griffiths and Darrell F. Schroeter. *Introduction to Quantum Mechanics*. 3rd ed. Cambridge (UK): Cambridge University Press, 2018.

`Me99` [Mes99] Albert Messiah. *Quantum Mechanics*. New York: Dover, 1999.

`We15` [Wei15] S. Weinberg. *Lectures on Quantum Mechanics,* 2nd ed. Cambridge (UK): Cambridge University Press, 2015.

A Some useful integrals

Euler's gamma function $\Gamma(z)$ is defined by

$$\Gamma(z) := \int_0^\infty t^{z-1} \mathrm{e}^{-t} \, \mathrm{d}t, \qquad \mathrm{Re}\, z > 0. \tag{A.1}$$ `Gadef`

Note that the integral is indeed convergent for all complex z with $\mathrm{Re}\, z > 0$. Integrating by parts we obtain

$$\Gamma(z+1) = \int_0^\infty t^z \mathrm{e}^{-t} \, \mathrm{d}t = -t^z \mathrm{e}^{-t}\Big|_{t=0}^{t=\infty} + z \int_0^\infty t^{z-1} \mathrm{e}^{-t} \, \mathrm{d}t = z\Gamma(z),$$

so that

$$\Gamma(z+1) = z\Gamma(z). \tag{A.2}$$ `Gaid`

When $n \in \mathbb{N}$, applying the previous identity n times we obtain

$$\Gamma(n+1) = n!. \tag{A.3}$$ `Gafact`

Note that this equality is obviously valid for $n = 0$. From Eq. (A.3) we easily obtain

$$\int_0^\infty x^n \mathrm{e}^{-ax} \, \mathrm{d}x = a^{-n-1} \Gamma(n+1) = \frac{n!}{a^{n+1}}, \qquad a > 0. \tag{A.4}$$ `Gapar`

This identity can be more directly proved differentiating the integral for $n = 0$ with respect to the parameter a:

$$\int_0^\infty x^n \mathrm{e}^{-ax} \, \mathrm{d}x = \left(-\frac{\partial}{\partial a}\right)^n \int_0^\infty \mathrm{e}^{-ax} \, \mathrm{d}x = \left(-\frac{\partial}{\partial a}\right)^n a^{-1} = 1 \cdot 2 \cdot \dots \cdot n\, a^{-n-1} = \frac{n!}{a^{n+1}}.$$

Consider next the Gaussian integral

$$\int_{-\infty}^\infty \mathrm{e}^{-ax^2} \, \mathrm{d}x.$$

The integral is obviously convergent when $\mathrm{Re}\, a > 0$, and it can be shown to be also convergent for all nonzero a with $\mathrm{Re}\, a = 0$. By suitably deforming the integration contour, it is shown that

$$\int_{-\infty}^\infty \mathrm{e}^{-ax^2} \, \mathrm{d}x = \sqrt{\frac{\pi}{a}}, \qquad a \neq 0 \quad \text{and} \quad \mathrm{Re}\, a \geqslant 0, \tag{A.5}$$ `Gaussint`

with the following choice of square root:

$$\sqrt{a} := |a|^{1/2} \mathrm{e}^{\frac{\mathrm{i}}{2} \mathrm{Arg}\, a},$$

where $\mathrm{Arg}\, a \in (-\pi, \pi]$ is the principal value of the argument of a. For instance,

$$\int_{-\infty}^\infty \mathrm{e}^{\mathrm{i}x^2} \, \mathrm{d}x = \sqrt{\pi}\, \mathrm{e}^{\frac{\mathrm{i}\pi}{4}},$$

or equivalently

$$\int_{-\infty}^\infty \cos(x^2) \, \mathrm{d}x = \int_{-\infty}^\infty \sin(x^2) \, \mathrm{d}x = \sqrt{\frac{\pi}{2}}. \tag{A.6}$$ `sincosint`

SOME USEFUL INTEGRALS

The more general integral

$$\int_{-\infty}^{\infty} e^{-(ax^2+bx+c)}\, dx,$$

where b, c are arbitrary complex constants, is computed completing the square:

$$ax^2 + bx + c = a\left(x + \frac{b}{2a}\right)^2 + c - \frac{b^2}{4a} \quad\Longrightarrow\quad \boxed{\int_{-\infty}^{\infty} e^{-(ax^2+bx+c)}\, dx = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2-4ac}{4a}},} \quad \text{(A.7)} \quad \boxed{\texttt{Gaussintgen}}$$

where we have used the fact (easily proved by deforming the integration contour) that

$$\int_{-\infty}^{\infty} e^{-a(x-z_0)^2}\, dx = \int_{-\infty}^{\infty} e^{-ax^2}\, dx$$

for arbitrary complex z_0. Equation (A.7) admits a straightforward three-dimensional generalization that is often used in quantum mechanics, namely

$$\boxed{\int d^3r\, e^{-(ar^2+\mathbf{b}\cdot\mathbf{r}+c)} = \left(\frac{\pi}{a}\right)^{3/2} e^{\frac{b^2-4ac}{4a}},}$$

where a and c are as above and $\mathbf{b} \in \mathbb{C}^3$ is a constant vector. Indeed, completing the square we obtain

$$ar^2 + \mathbf{b}\cdot\mathbf{r} + c = a\left(\mathbf{r} + \frac{\mathbf{b}}{2a}\right)^2 + c - \frac{b^2}{4a}$$

and therefore

$$\int d^3r\, e^{-(ar^2+\mathbf{b}\cdot\mathbf{r}+c)} = e^{\frac{b^2-4ac}{4a}}\int d^3r\, e^{-a\left(\mathbf{r}+\frac{\mathbf{b}}{2a}\right)^2} = e^{\frac{b^2-4ac}{4a}}\prod_{i=1}^{3}\int_{-\infty}^{\infty} dx_i\, e^{-a\left(x_i+\frac{b_i}{2a}\right)^2} = \left(\frac{\pi}{a}\right)^{3/2} e^{\frac{b^2-4ac}{4a}}.$$

A related integral that frequently appears in quantum mechanics is

$$I_n(a) := \int_{-\infty}^{\infty} x^{2n} e^{-ax^2}\, dx = a^{-\left(n+\frac{1}{2}\right)} I_n(1),$$

where $a > 0$ and $n = 0, 1, \ldots$. This integral can be easily evaluated by differentiating

$$I_0(a) = \int_{-\infty}^{\infty} e^{-ax^2}\, dx = \sqrt{\frac{\pi}{a}}$$

with respect to the parameter a:

$$I_n(a) = \left(-\frac{\partial}{\partial a}\right)^n \int_0^{\infty} e^{-ax^2}\, dx = \sqrt{\pi}\left(-\frac{\partial}{\partial a}\right)^n a^{-1/2} = \sqrt{\pi}\,\frac{1}{2}\cdot\frac{3}{2}\cdot\;\cdots\;\cdot\frac{2n-1}{2}\, a^{-\frac{1}{2}-n},$$

whence

$$\boxed{\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} = \frac{(2n-1)!!}{2^n}\sqrt{\pi}\, a^{-\left(n+\frac{1}{2}\right)}, \qquad a > 0 \quad\text{and}\quad n = 0, 1, 2, \ldots.} \quad \text{(A.8)} \quad \boxed{\texttt{Gaussxint}}$$

In fact. the integral $I_n(1)$ could also have been evaluated through the change of variable $x^2 = s$:

$$I_n(1) = 2\int_0^{\infty} x^{2n} e^{-x^2}\, dx = \int_0^{\infty} s^{n-\frac{1}{2}} e^{-s}\, ds = \Gamma\left(n + \tfrac{1}{2}\right)$$

using the fundamental identity (A.2) for the gamma function:

$$\Gamma\left(n + \tfrac{1}{2}\right) = \left(n - \tfrac{1}{2}\right)\Gamma\left(n - \tfrac{1}{2}\right) = \left(n - \tfrac{1}{2}\right)\left(n - \tfrac{3}{2}\right)\Gamma\left(n - \tfrac{3}{2}\right) = \cdots = \left(n - \tfrac{1}{2}\right)\left(n - \tfrac{3}{2}\right)\cdots\tfrac{1}{2}\Gamma\left(\tfrac{1}{2}\right)$$
$$= \frac{(2n-1)!!}{2^n}\Gamma\left(\tfrac{1}{2}\right),$$

which coincides with the previous result since

$$\boxed{\Gamma\left(\tfrac{1}{2}\right) = I_0(1) = \sqrt{\pi}.} \quad \text{(A.9)} \quad \boxed{\texttt{Ga1half}}$$

Index