

Quantum Mechanics I

Lecture Notes

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1. History and Background

Quantum mechanics constitutes a huge departure from classical physics and completely alters the view we have of how the universe functions. In order to understand where quantum mechanics came from, and why it was necessary to replace classical physics by it, in this first section we briefly describe some of the key phenomena that arose, roughly around the turn of the last century, that classical physics was simply unable to give a satisfactory explanation of. The list here will be neither comprehensive nor in chronological order, but is meant just to provide a short account of the main difficulties faced by classical physics, for which a new physical theory was ultimately necessary. We will also discuss at the same time some of the early ideas and insights which would eventually develop into the theory that we now call quantum mechanics. The goal of this section is to set the scene and provide the a small amount of context for the following sections, where we will begin our exploration of quantum mechanics.

1.1 The photoelectric effect

A key effect that classical physics was unable to explain is the **photoelectric effect**. It is observed that if light is shone on a piece of metal, then electrons are emitted. This effect can be studied carefully by forming a capacitor out of two metal plates in vacuum, placing this in a circuit, and applying a voltage (potential difference) across the plates.

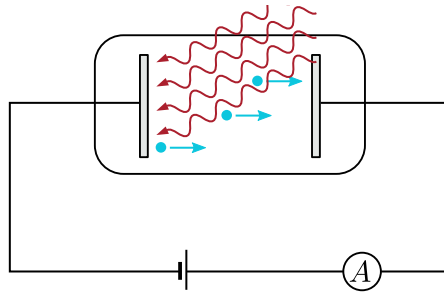


Figure 1.1: **The photoelectric effect**. Schematic diagram of the photoelectric effect. Light of a fixed frequency f is shone on one of the metal plates of a capacitor (which is in a vacuum). This causes electrons to be emitted. Some of these arrive at the other plate, and a current is generated. By placing a potential across the plates the maximum kinetic energy of the emitted electrons can be measured.

When light is shone on one of the plates, it causes a current to flow, which is how we know that electrons are being emitted. Varying the potential difference between the plates allows us to study the **kinetic energy** of the emitted electrons. It is observed that if light of a **fixed wavelength** λ , and therefore frequency $f = c/\lambda$, is shone, then for all metals the maximum kinetic energy E_{\max} of the electrons emitted follows a simple rule

$$E_{\max} = hf - \phi, \quad (1.1)$$

where h is a constant of nature known as Planck's constant (since it was discovered by Planck, while exploring blackbody radiation), and equal to

$$h = 6.626 \times 10^{-34} \text{ Js}, \quad (1.2)$$

and ϕ is known as the **workfunction**, and is in general different for different metals. This maximum energy is determined by shining the light on the plate at the lower potential, and measuring the potential difference that needs to be put between the plates in order to **just stop** the current, since in order to reach the other plate (and generate a current) the electron needs enough kinetic energy to overcome this potential difference.

There are some particularly surprising aspects about what is observed:

- As the **intensity** of light is increased, the **rate** at which electrons are emitted increases – producing a bigger current – but does **not** affect the maximum energy of the emitted photons, as measured by varying the potential.
- Even for extremely weak light, a small current is observed to begin flowing **immediately** when the light is shone on the metal. That is, there is no delay after shining the light before some current starts flowing.
- Low frequency/long wavelength light, for example red light, for certain metals is **unable** to generate any current, no matter how intense the light, while very weak light of higher frequency/shorter wavelength, for example violet light, is able to generate a weak current.

All of these aspects of the photoelectric effect seem impossible to explain within classical physics. In classical physics, the energy density of the light is proportional to the amplitude squared, and does not depend upon the wavelength. Moreover, the energy arrives at a constant rate, and so if the light is very weak, it should take a long time before enough energy is supplied in order to account for the kinetic energy of the emitted electron, so there should be a long delay before the current begins to flow. Finally, why it should be that long wavelength light is simply unable to free any electrons was a mystery.

1.1.1 The photon

Einstein was able to provide an explanation for the photoelectric effect by postulating that classical electromagnetism does not in fact completely describe the properties of light. He said that we need to assume moreover that light is **quantized** in small ‘packets’ known as **photons**. Einstein postulated that a photon of wavelength λ and frequency f has energy

$$E = hf, \quad (1.3)$$

which we will refer to as the **Einstein relation**. With this postulate, the maximum energy that an electron can gain is the energy of the photon $E = hf$. Part of this energy will be used in order to liberate the electron from the surface – this is precisely the workfunction ϕ . The remaining energy is then converted into the kinetic energy of the freed electron.

This model of the photon also accounts for the two surprising aspects of the photoelectric effect. As the intensity is increased, the **number of photons** increases, accounting for the larger current. It also explains why a current is observed immediately even for very weak light – since now the rate at which photons arrive will be very slow, but whenever a photon does arrive, it arrives with all of its energy, and there is a chance of emitting an electron.

1.2 Atoms

Atoms also provided big challenges for classical physics, from two completely different perspectives: The observation of spectral lines, and their stability.

1.2.1 Spectral lines

It is observed that if a gas of atoms (all of the same element) is ‘excited’ – for example by making an electrical spark – then light is emitted. If this light is analysed spectroscopically, then the light is found to contain only certain very precise wavelengths, and none others. These are known as **spectral lines**. These lines were moreover found to have intricate structure. For example, for Hydrogen, it was found that all the observed wavelengths fitted the formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (1.4)$$

for integers m and n , and where R_H is a constant known as Rydberg’s constant.

In order to explain the existence of spectral lines from the perspective of classical physics, the small number of allowed frequencies of the emitted light must arise from some characteristic vibrations within



Figure 1.2: **Spectral lines**. Example diagram of the emission spectrum of Hydrogen (showing only lines in the visible part of the spectrum).

the atom. But what could these characteristic vibrations be? Moreover, where does the intricate relation between the allowed wavelengths come from? Classical physics seems to provide no satisfactory answer to these questions, and therefore the existence of spectral lines was a mystery.

1.2.2 The stability of the atom

A second problem concerns the stability of the atom. Once the nucleus and the electron had been discovered, one possible model for an atom was the ‘solar system’ model, of a positively charged nucleus at the centre, around which the electron orbits.

Classical electromagnetism says however that **accelerating charges emit radiation**, and that this radiation carries away with it energy. The electron, which is undergoing circular motion, is accelerating constantly, and should therefore emit radiation and lose energy. Ultimately the electron should therefore spiral into the nucleus as it loses its energy and slows down. Atoms in vacuum are however observed to be very stable, surviving almost indefinitely – much longer than the timescale over which the electron should lose all its energy and spiral into the nucleus. No satisfactory way of accounting for the stability of atoms from such a classical model was ever found.

1.2.3 Quantisation of angular momentum and the Bohr atom

Bohr was able to provide partial answers to both of these problems by postulating that **angular momentum of the electron is quantised**. In particular, Bohr postulated that much like the energy of a photon is quantised, so too is the angular momentum L of an electron in orbit around a nucleus. Bohr postulated that an elementary **quanta** of orbital angular momentum is the **Reduced Plank constant**

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} \text{ Js} \quad (1.5)$$

This constant is commonly referred to simply as “**h-bar**”. Bohr postulated that the angular momentum of electrons is only ever an integer multiple of \hbar , and no other value, $L = n\hbar$.

Under this assumption, Bohr was able to give a **stable** model for an atom. In particular, electrons do not radiate continuously as classical electromagnetism predicts, but lose angular momentum and energy in finite, quantised amounts, by emitting photons. This radiation continues until the electron has reached the minimum angular momentum of \hbar , after which it no longer radiates, and orbits the nucleus in a stable fashion. Bohr found that the radii and energies of the allowed orbits are

$$r_n = \frac{\epsilon_0 \hbar^2}{\pi M_e e^2} n^2, \quad E_n = -\frac{M_e e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2}, \quad (1.6)$$

where ϵ_0 is the permittivity of free space, M_e is the mass of the electron, e is the electron charge, and n is an arbitrary positive integer.

Exercise 1.1 — Bohr Atom. In this exercise we will derive the allowed radii and associated energies of the Bohr atom. We will assume that the electron is orbiting the nucleus at radius r and speed v , and is performing uniform circular motion about the nucleus, which comprises a single proton.

- Write down the Coulomb force experienced by the electron, and the corresponding Coulomb potential.
- Write down the acceleration of the electron, given that it is performing circular motion.

- (c) Write down the angular momentum of the electron, in terms of the radius and velocity.
- (d) By using Newton's second law, find the relationship that must hold between the radius and angular momentum of the electron.
- (e) Find expressions for the kinetic energy of the electron in terms of the angular momentum and radius, and for the potential energy. Use these to find an expression for the total energy.
- (f) Finally, using the Bohr formula $L = n\hbar$, find the allowed radii and energies of the Bohr atom (note that in order to reproduce (1.6) you will need to change from \hbar to h).

The spectral lines are also explained by this model. When an electron 'jumps' from one orbit to another, its energy changes, and the photon carries away this energy. In particular, if it jumps from the orbit with energy E_n to the one with energy E_m , then the photon must carry away the energy $\Delta E = E_m - E_n$. However, Einstein already told us that a photon with energy ΔE has frequency $f = \Delta E/h$ and wavelength $\lambda = hc/\Delta E$. Thus

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{E_m - E_n}{hc} = \frac{M_e e^4}{8\epsilon_0^2 h^3 c} \left(\frac{1}{n^2} - \frac{1}{m^2} \right). \quad (1.7)$$

The constant out the front exactly matches the experimentally observed Rydberg constant, and thus reproduced the spectral lines of Hydrogen. In fact, this prediction of the Bohr model led to the search, and subsequent discovery of new lines outside the visible part of the electromagnetic spectrum, which had previously not been observed.

1.3 Matter waves

Einstein postulated that electromagnetic radiation was in fact comprised of 'packets' which he called photons, which can roughly be thought of as particles. De Broglie postulated that **matter might conversely behave like a wave**. When electromagnetic radiation has energy E , its momentum is $p = E/c$. Using the Einstein formula for the energy of the photon, $E = hf = hc/\lambda$, we see that

$$p = \frac{E}{c} = \frac{hc}{\lambda c} = \frac{h}{\lambda}. \quad (1.8)$$

De Broglie postulated that this formula **holds universally** for both radiation and matter, and prescribed that if a particle has momentum p then it will behave like a wave of wavelength

$$p = \frac{h}{\lambda} \quad (1.9)$$

At first sight this seems strange, but it can be readily seen that the wavelengths for "everyday" objects are so small that they would be imperceptible. However, for elementary particles, in conditions which could be formed in the laboratory at that time, in principle this wavelength should have been observable. Two-slit experiments were subsequently carried out, and interference effects, at the wavelength predicted by de Broglie, were observed, indicating that indeed matter can exhibit wave-like properties too.

However, this raised a huge number of questions. Were particles really waves? How does this fit with the conclusion of the photoelectric effect, that waves are in fact particles? There were numerous other phenomena that couldn't be explained – subtle aspects of black-body radiation, the way x-rays scatter off solids, the so-called Compton effect. Everything pointed towards the need for a radical re-thinking of the physical world. Quantum mechanics was invented to answer these questions, and in the next section we will start of exploration of the basic aspects of this new theory.

2. Basics of Quantum Mechanics

In the previous section some of the shortcomings of classical physics were seen, along with the initial attempts for how to resolve them. These attempts collectively are now known as the *old quantum theory*, since they contained some of the right ideas, but did not constitute the complete theory that is now known as **quantum theory**. In reality, the necessary departure from classical physics is much larger, and it was only a couple of decades later that quantum theory proper was discovered, which allowed for all of the shortcomings of classical physics, and the old quantum theory, to be addressed.

In this section we introduce the basic aspects of quantum theory, as applied to the motion of single particles in space. This thus concerns the **mechanics** of particles, and hence why this branch of quantum theory is known as **quantum mechanics**.

As the first part of the first formal course on quantum theory, this course is just an introduction, and there is much more to quantum theory than is taught here. As you will see in later courses, there is some powerful mathematical machinery in the background of quantum theory that we will not delve into at this introductory stage. In quantum theory the process of **measurement** also becomes much more fundamental compared to classical physics, but again we will largely skim over this subtle issue here, leaving it for Quantum Mechanics II.

The goal of this half of the course is to **introduce the basic concepts of quantum theory**, to gain some familiarity with the **picture of nature according to quantum theory**, and finally to gain practice in **solving problems** in quantum mechanics.

2.1 The mechanics of a particle

For the majority of this course we will consider the mechanics of a particle in one-dimension. All of the basic concepts of quantum mechanics can be introduced in this simple setting, without loss of generality. At the end of the course we will discuss the mechanics of a particle in three-dimensions, necessary for fully describing the physics of the world around us.

The basic setting of interest is that of a particle of mass M and co-ordinate x . The particle will be acted on by a force $F(x)$ which in general will change in space, for example, a particle attached to a spring, or a particle moving vertically in a gravitational field. We will restrict our attention here to **conservative forces**, ones to which we can associate a **potential energy** $V(x)$ such that

$$F(x) = -\frac{dV(x)}{dx}. \quad (2.1)$$

In classical mechanics, a **complete description** of the **state** of a particle at a given time $t = t_0$ is to specify both the **position** $x(t_0) = x_0$ and **momentum** $p(t_0) = p_0$. If the position and momentum of the particle are known, then all other physical properties are also determined. For example, the velocity of the particle is

$$v(t_0) = \frac{p_0}{M}, \quad (2.2)$$

and the kinetic energy is

$$K(t_0) = \frac{p_0^2}{2M} = \frac{1}{2}Mv_0^2. \quad (2.3)$$

! *An alternative choice would be to specify the position $x(t_0) = x_0$ and the velocity $v(t_0) = v_0$. The reason for choosing to specify the momentum $p(t_0) = p_0$ over the velocity comes from other branches of physics, such as Electromagnetism and General Relativity, where momentum is found to play a more fundamental role than velocity. We will also see that momentum plays a fundamental role in quantum mechanics, whereas the velocity does not.*

In general, we have a lot of **freedom** in specifying the state of the particle – we can consider a particle at an arbitrary position x_0 with an arbitrary momentum p_0 . Of course, if the particle is meant to be confined to some region of space, then we must specify the particle to be in that region, and to avoid having to use special relativity, we should only consider momentum small enough so that the particle is not moving close to the speed of light. Apart from these reasonable requirements, we are otherwise free to specify the state of the particle arbitrarily.

The basic problem of classical mechanics is to determine the state of the particle at all times, given knowledge of the state at one instant of time, t_0 . That is, the goal is to solve the **equation of motion**, given the initial conditions, which specify the state of the system. The equation of motion is Newton's second law, which states that

$$\frac{dp}{dt} = F(x), \quad \frac{dx}{dt} = \frac{p(t)}{M}. \quad (2.4)$$

Solving the equation of motion, subject to the initial conditions $x(t_0) = x_0, p(t_0) = p_0$, provides us with solutions $x(t)$ and $p(t)$ which then completely specify the state **at all times** t .

! Note that the more familiar form of Newton's second law, $M \frac{d^2 x(t)}{dt^2} = F(x)$, is obtained by combining these two equations together. This is not done here, as it is important to stress that the equation of motion allows us to find the **state** of the system (i.e. both the position and the momentum) at later times, something which is not as explicit in the familiar form, which concerns only $x(t)$.

Quantum theory provides a completely new description of the mechanics of a particle, which we will now begin to explore. Nevertheless, the basic structure is the same as in classical mechanics: quantum mechanics provides a **complete description** of the **state** of a system, and an **equation of motion** that must be solved in order to determine how the state changes in time.

2.2 The wavefunction

In quantum mechanics, a **complete description** of the **state** of a particle **at time** t_0 is specified by the quantum mechanical **wavefunction** $\Psi(x, t_0)$. This is the basic object of quantum mechanics.

Mathematically, it is a **complex-valued** function of space (and time), meaning that $\Psi(x, t_0)$ is of the form $\Psi(x, t_0) = \Psi_R(x, t_0) + i\Psi_I(x, t_0)$, where $\Psi_R(x, t_0)$ and $\Psi_I(x, t_0)$ are real functions, which are respectively the real and imaginary parts of the wavefunction.

Once the wavefunction is known at time $t = t_0$, it is possible to calculate all physical properties at t_0 , such as position, momentum and kinetic energy at that time. Precisely **how** this is done for each physical property will take up a large part of this course, and will be the topic of many later sections. The simplest property, which we start with now, is the position of the particle.

2.2.1 The Statistical Interpretation

According to quantum mechanics, in general, particles **do not have well-defined properties such as position, momentum or energy**.

Quantum mechanics says that if at time $t = t_0$ a particle has a wavefunction $\Psi(x, t_0)$ then the **probability** to find the particle between $x = x_a$ and $x = x_b$ is

$$P(x_a \leq x \leq x_b, t_0) = \int_{x_a}^{x_b} |\Psi(x, t_0)|^2 dx. \quad (2.5)$$

That is, the **modulus square** of the wavefunction specifies, in the form of probabilities, where the particle is at time t_0 . We will return later to related questions, about the momentum and energy of the particle, and how these too are specified by the wavefunction.

Recall that for a complex number $c = a + ib$ (where $i = \sqrt{-1}$), the complex conjugate is denoted c^* and is equal to $c^* = a - ib$ and the modulus square is $|c|^2 = c^*c = a^2 + b^2$, which is a real, positive

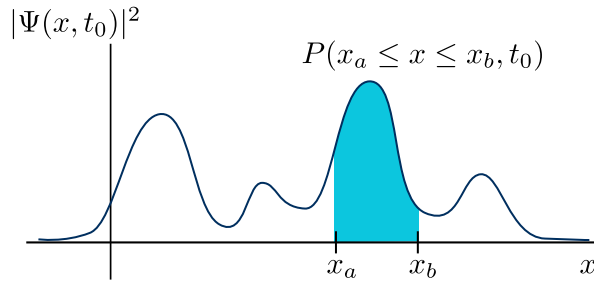


Figure 2.1: **Probability.** The probability to find the particle between x_a and x_b is the integral of the modulus square of the wavefunction between these two values. This is the shaded area under the curve in the above figure.

number. Thus

$$|\Psi(x, t_0)|^2 = |\Psi_R(x, t_0)|^2 + |\Psi_I(x, t_0)|^2 \quad (2.6)$$

is always real and positive.

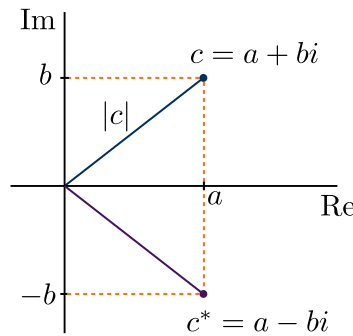


Figure 2.2: **Complex numbers.** A diagram of the complex plane, with the real and imaginary parts of a complex number plotted along the x and y axes respectively. Here, we plot the real and imaginary parts of the complex number $c = a + ib$, and its complex conjugate $c^* = a - ib$, which is seen to be mirrored in the x -axis compared to c . The absolute value $|c|$ is geometrically the length of the line connecting the origin to either the point c or c^* in the complex plane.

We can interpret $|\Psi(x, t_0)|^2$ as the **probability density** $P(x, t_0)$ to find the particle at position x at time $t = t_0$. That is,

$$P(x, t_0)dx = |\Psi(x, t_0)|^2 dx \quad (2.7)$$

is the probability to find the particle between x and $x + dx$ at time t_0 , for dx infinitesimally small. We can think of this as being the probability to find the particle **in the vicinity** of x at time t_0 .

It is important to note that probabilities enter quantum mechanics in a **fundamental** way: Even if the most careful and ideal experiment were to be carried out in order to measure the position of a particle, then it would still be found in different places in different runs of the experiment. This means that in quantum mechanics, identical experiments lead to non-identical outcomes.

The probabilities that arise in quantum mechanics have nothing to do with **imperfections** or **experimental limitations**. This is contrary to classical mechanics, where in principle all experiments can be made perfectly repeatable, such that identical experiments lead to identical outcomes if sufficient care is taken (this is true even for chaotic systems, which are very sensitive to changes in conditions).

The probabilistic nature of quantum mechanics is arguably the **biggest departure** from classical mechanics, from which many of its counter-intuitive predictions arise.

2.2.2 Probability amplitudes and superposition

With the above statistical interpretation in place, it is useful to introduce some terminology.

We will say that $\Psi(x, t_0)$ is the **probability amplitude** for the particle to be at position x at time t_0 . When there is no loss of confusion, we will also simply use **amplitude** in place of probability amplitude. Probability amplitudes are thus complex numbers, whose modulus squares are probabilities.

We also say that the particle is in a **superposition** of different locations, with the probability amplitude to be at x at time t_0 given by the value of the wavefunction $\Psi(x, t_0)$.

2.3 Normalisation

In order for the statistical interpretation of the wavefunction to be possible, $\Psi(x, t_0)$ is required to satisfy a **normalisation condition** which ensures that the total probability for the particle to be found somewhere is one. Mathematically, because $|\Psi(x, t_0)|^2$ is the probability density $P(x, t_0)$, this condition is given by

$$\int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = 1. \quad (2.8)$$

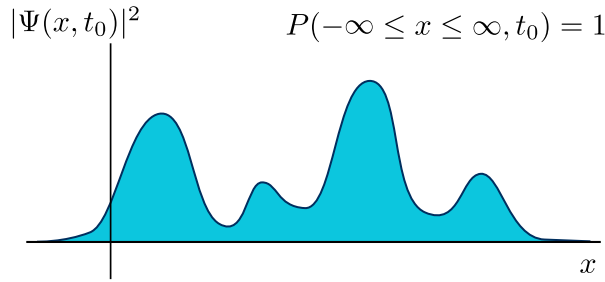


Figure 2.3: **Normalisation**. The total probability to find the particle somewhere must be one. This means that the total area shaded under the curve must be unity.

Normalisation is not a very restrictive property, since we can **normalise** functions to turn them into valid wavefunctions. In particular, if we have some unnormalised function $\Psi(x, t_0)$ that satisfies

$$\int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = N, \quad (2.9)$$

where $N < \infty$, that is, if this integral is **finite**, then

$$\Psi'(x, t_0) = \frac{1}{\sqrt{N}} \Psi(x, t_0) \quad (2.10)$$

will be a normalised wavefunction, since

$$\int_{-\infty}^{\infty} |\Psi'(x, t_0)|^2 dx = \frac{1}{N} \int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = \frac{1}{N} \times N = 1, \quad (2.11)$$

If N would have been infinite then it would not have been possible to divide by \sqrt{N} in order to obtain a normalised wavefunction, as dividing by infinity would have left us with a wavefunction that vanishes everywhere, which doesn't make sense physically.

The condition (2.9) is known as being **square-integrable**. It simply says that the integral of the modulus squared of the function should be a finite number, i.e. that the total area under the curve is not infinite.

Exercise 2.1 — Arbitrary phase factor. Show that $\Psi''(x, t) = \frac{e^{i\theta}}{\sqrt{N}} \Psi(x, t_0)$ will be a normalised wavefunction for all θ whenever $\int_{-\infty}^{\infty} |\Psi(x, t_0)|^2 dx = N$, and that $|\Psi''(x, t_0)|^2$ is independent of θ .

*This shows that there is **freedom** in choosing how to normalise a wavefunction, since no matter how we normalise it we end up with the **same** probability density. A standard choice is to pick $\theta = 0$, such that $e^{i\theta} = 1$. That is, the standard choice is to normalise by a real and positive number (even though a negative, or complex number would also be an equally valid choice).*

2.3.1 Behaviour at infinity

The requirement that the wavefunction be normalised imposes constraints on the behaviour of particles at $x = \pm\infty$. Physically, the integral (2.8) says that the probability to find the particle *somewhere* must be one. If there is a non-zero probability to find the particle at infinity, then such a wavefunction necessarily cannot be normalised, as the area under the curve will be infinite.

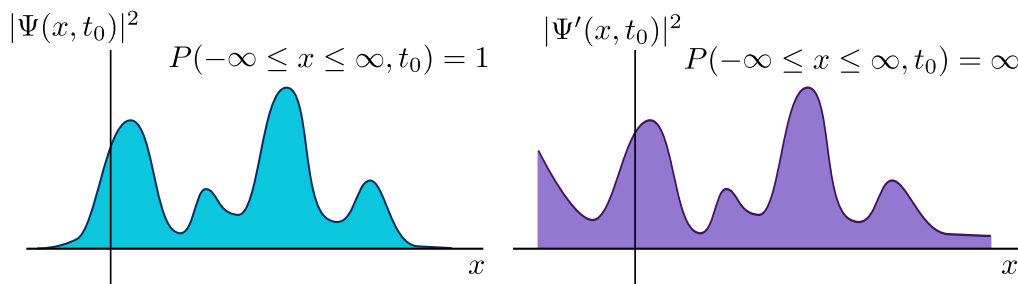


Figure 2.4: **Normalised vs. unnormalisable wavefunctions.** Left: Example of a wavefunction that is normalised, since it has the correct behaviour for large positive and negative x . Right: Example of a wavefunction that is not normalised: the wavefunction grows as $x \rightarrow -\infty$, leading to infinite area on this side. Also, the wavefunction does not decay rapidly enough for $x \rightarrow \infty$, again leading to infinite area.

This statement can be made more precise, as we can show that the wavefunction **must decay to zero sufficiently fast** in order to be normalised. In particular, in Exercise 2.2 it is shown that $\Psi(x, t_0)$ must decay **faster than**

$$\frac{1}{\sqrt{|x|}} \quad (2.12)$$

in order that the probability to find the particle at large x does not diverge.

Exercise 2.2 — Decay of wavefunctions at infinity. In this exercise we will see why the wavefunction must decay sufficiently fast for large values of x in order for it to be normalised.

Assume that for $x \geq x_0$, the wavefunction has the form $\Psi(x, t_0) = \frac{a}{\sqrt{x}}$, where a is a constant. Show that the total area under the curve of $|\Psi(x, t_0)|^2$ in the region $x \geq x_0$ is infinite.

This shows that this function is not square integrable, and we cannot form a valid wavefunction from it.

Assume now that for $x \geq x_0$, the wavefunction has the form $\Psi'(x, t_0) = \frac{b}{x^{(1/2+\alpha)}}$, where b is another constant, and $\alpha > 0$. Show now that the total area under the curve of $|\Psi'(x, t_0)|^2$ in the region $x \geq x_0$ is finite.

This shows that this function is potentially square integrable (it is only potentially so since we don't know how it behaves in other regions).

2.4 Freedom in specifying the initial state of a particle

As we discussed briefly above, in classical mechanics we have a lot of freedom in specifying the state of the particle at some time t_0 . In quantum mechanics, we have **even more freedom**. In general, within reason, **any normalised wavefunction $\Psi(x, t_0)$ is a valid state for a particle**. This is rather remarkable, as the wavefunction specifies a complex number at every point in space. There is thus significantly more freedom than just specifying the initial position x_0 and initial momentum p_0 in classical mechanics. Understanding this additional freedom, what it means, and how it specifies physical properties such as momentum and energy will be a large part of this course.

2.5 The equation of motion: the Schrödinger Equation

In order to determine how the state of a particle changes in time from some initial time t_0 to later times t , we need an **equation of motion**. In quantum mechanics the equation of motion for a particle is given by the **Schrödinger equation**,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi(x, t), \quad (2.13)$$

where $V(x)$ is the potential, which encodes the forces acting on the particle, M is the mass, and \hbar is the “**h-bar**” (i.e. the **reduced Planck constant**) from (1.5).

The Schrödinger equation is a complex, second-order linear partial differential equation. It replaces Newton’s second law as the basic equation governing the **dynamics** in quantum mechanics.

By solving the Schrödinger equation, given the **initial condition** $\Psi(x, t_0)$, (i.e. a complete specification of the **state** of the particle at time t_0), we find the state of the system for all times t , $\Psi(x, t)$.

2.5.1 The Superposition Principle

Because of the fact that the Schrödinger equation is **linear**, it has an extremely important property known as the **superposition principle**: If $\Psi_1(x, t)$ and $\Psi_2(x, t)$ are both solutions of the Schrödinger equation, then

$$\Psi'(x, t) = \alpha\Psi_1(x, t) + \beta\Psi_2(x, t) \quad (2.14)$$

is also a solution of the Schrödinger equation for all complex numbers α and β .

Derivation To show this, we start by writing out explicitly what it means for $\Psi_1(x, t)$ and $\Psi_2(x, t)$ to be solutions to the Schrödinger equation (2.13). It means that they satisfy

$$i\hbar \frac{\partial \Psi_1}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi_1}{\partial x^2} + V(x)\Psi_1(x, t), \quad (2.15a)$$

$$i\hbar \frac{\partial \Psi_2}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi_2}{\partial x^2} + V(x)\Psi_2(x, t), \quad (2.15b)$$

Multiplying (2.15a) by α and (2.15b) by β , and adding together, the following equation is satisfied:

$$i\alpha\hbar \frac{\partial \Psi_1}{\partial t} + i\beta\hbar \frac{\partial \Psi_2}{\partial t} = -\frac{\alpha\hbar^2}{2M} \frac{\partial^2 \Psi_1}{\partial x^2} + \alpha V(x)\Psi_1(x, t) - \frac{\beta\hbar^2}{2M} \frac{\partial^2 \Psi_2}{\partial x^2} + \beta V(x)\Psi_2(x, t). \quad (2.16)$$

Since α and β are constants, meaning that they do not depend upon x or t , we can move them through the derivatives, and factorise the above, to arrive at

$$i\hbar \frac{\partial}{\partial t} (\alpha\Psi_1(x, t) + \beta\Psi_2(x, t)) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} (\alpha\Psi_1(x, t) + \beta\Psi_2(x, t)) + V(x)(\alpha\Psi_1(x, t) + \beta\Psi_2(x, t)). \quad (2.17)$$

Finally, given the definition of $\Psi'(x, t)$ in (2.14), this is equivalent to

$$i\hbar \frac{\partial \Psi'}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi'}{\partial x^2} + V(x) \Psi'(x, t). \quad (2.18)$$

This is precisely the Schrödinger equation (2.13) for $\Psi'(x, t)$. Thus $\alpha\Psi_1(x, t) + \beta\Psi_2(x, t)$ satisfies the Schrödinger equation whenever $\Psi_1(x, t)$ and $\Psi_2(x, t)$ do.

The above shows that knowing two solutions to the Schrödinger equation, infinitely many more solutions can be found, by simply adding together the known solutions with arbitrary complex factors.

The fact that the Schrödinger equation satisfies the superposition principle will play a central role in all of quantum mechanics. It shows, in particular, that **the evolution of a superposition of wavefunctions is equal to the superposition of the evolutions**. This is **conceptually** important, but will also provide us with our general **strategy** for solving the Schrödinger equation: We will look for **special** wavefunctions whose evolution is **simple**. Once we have found these, we will then figure out how to write a general wavefunction as a superposition of these special wavefunctions. Remarkably, we will then be able to simply **write down** the evolution of a particle.

It is useful to again introduce some terminology. We say that solutions of the Schrödinger equation can be **superposed** in order to obtain new solutions.

In the previous subsection we also introduced the terminology of superposition for wavefunctions and amplitudes, stating that when a particle has a wavefunction $\Psi(x, t)$, the particle is in a superposition of locations, and that $\Psi(x, t)$ is the probability amplitude to be at x at time t .

We use the **same terminology** here as it leads to the same phenomena: By superposing the wavefunctions $\Psi_1(x, t)$ and $\Psi_2(x, t)$ we alter the probability amplitude at x to be $\alpha\Psi_1(x, t) + \beta\Psi_2(x, t)$. Nevertheless, the particle is still in superposition of different positions, just now the probability amplitudes are given by $\Psi'(x, t)$.

2.5.2 Conservation of normalisation

A second important physical property of the Schrödinger equation is that **the wavefunction remains normalised in time**. That is, if $\Psi(x, t_0)$ is normalised at t_0 , then after solving the Schrödinger equation for $\Psi(x, t)$, we also find that $\Psi(x, t)$ is normalised, for all time,

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1 \quad \text{for all } t. \quad (2.19)$$

As such, the probability to find the particle *somewhere* is always one.

Mathematically, one way to show that the normalisation of the wavefunction is constant in time is to show that

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 0. \quad (2.20)$$

Therefore, if we understand the behaviour of $\frac{\partial}{\partial t} |\Psi(x, t)|^2$, we will be able to compute the above integral, and check that the normalisation is constant. We will therefore try to understand how the probability density $P(x, t) = |\Psi(x, t)|^2$ changes in time, given that the wavefunction $\Psi(x, t)$ satisfies the Schrödinger equation.

In the derivation below (which you are encouraged to work through yourself, but can be skipped over and will not be presented in the lectures), we show that the following equation holds:

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0, \quad (2.21)$$

where

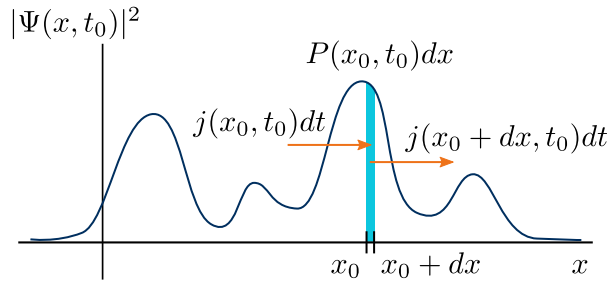


Figure 2.5: **Visualising the current.** At t_0 the probability to find the particle between x_0 and $x_0 + dx$ is $P(x_0, t_0)dx$. During a time dt the probability current that flows into this region from the left is $j(x_0, t_0)dt$. During the same time, a probability current $j(x_0 + dx, t_0)dt$ flows out from the right. The continuity equation says that the change in probability in the vicinity of x_0 during the time dt must be equal to the net current flowing into that region.

$$j(x, t) = \frac{i\hbar}{2M} \left(\frac{\partial \Psi^*}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi}{\partial x} \right), \quad (2.22)$$

You have encountered equations of the form (2.21) before, for example in Electromagnetism. It is in the form of a **continuity equation**. It says that the rate of change of probability at a location x at time t is equal to the net **probability current** flowing into that point. That is, $j(x, t)$ **can be seen as the probability current associated to the wavefunction $\Psi(x, t)$** . In quantum mechanics, it thus appears that probability is much like other physical ‘substances’, such as water, or electrical charge: probabilities **flow** in and out of regions. The continuity equation captures the idea of a **local conservation**: Changes in the probability density at x are completely determined by the probability current that is flowing in to or out of it.

Derivation By applying the product rule it is seen that

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi(x, t)|^2 &= \frac{\partial}{\partial t} (\Psi^*(x, t) \Psi(x, t)) \\ &= \frac{\partial \Psi^*}{\partial t} \Psi(x, t) + \Psi^*(x, t) \frac{\partial \Psi}{\partial t}. \end{aligned} \quad (2.23)$$

The Schrödinger equation can now be used to substitute for $\partial \Psi / \partial t$, and by taking the complex conjugate, for $\partial \Psi^* / \partial t$. Namely, by taking the complex conjugate of the Schrödinger equation, we have

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi^*}{\partial x^2} + V(x) \Psi^*(x, t), \quad (2.24)$$

Substituting both the Schrödinger equation and its conjugate, it is found that

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi(x, t)|^2 &= \left(-\frac{i\hbar}{2M} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V(x) \Psi^*(x, t) \right) \Psi(x, t) \\ &\quad + \Psi^*(x, t) \left(\frac{i\hbar}{2M} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V(x) \Psi(x, t) \right). \end{aligned} \quad (2.25)$$

The second terms in each bracket cancel each other out, and it can be noticed furthermore that

$$\frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi}{\partial x} \right) = \frac{\partial^2 \Psi^*}{\partial x^2} \Psi(x, t) - \Psi^*(x, t) \frac{\partial^2 \Psi}{\partial x^2} \quad (2.26)$$

to arrive at

$$\frac{\partial}{\partial t} |\Psi(x, t)|^2 = -\frac{\partial}{\partial x} \left[\frac{i\hbar}{2M} \left(\frac{\partial \Psi^*}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi}{\partial x} \right) \right]. \quad (2.27)$$

If we now define

$$j(x, t) = \frac{i\hbar}{2M} \left(\frac{\partial \Psi^*}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi}{\partial x} \right), \quad (2.28)$$

then, recalling that $P(x, t) = |\Psi(x, t)|^2$, (2.27) can be re-expressed as

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0, \quad (2.29)$$

which is what we wanted to show.

Returning to the problem we started with, the conservation of normalisation, we now see that, by integrating (2.21),

$$\begin{aligned} \frac{\partial}{\partial t} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx &= - \int_{-\infty}^{\infty} \frac{\partial j}{\partial x} dx, \\ &= - [j(x, t)]_{-\infty}^{\infty}, \\ &= j(-\infty, t) - j(\infty, t). \end{aligned} \quad (2.30)$$

This says that the change in total probability is equal to the difference between the probability current flowing at $x = +\infty$ and $x = -\infty$. Physically, we see that the probability to find the particle somewhere will remain unity if there is no probability current at infinity,

$$j(+\infty, t) = j(-\infty, t) = 0. \quad (2.31)$$

Physically, we are interested in situations where the particle is somewhere at time t_0 , (i.e. it is **not** infinitely far away), and we already saw that we need the wavefunction to vanish at infinity. It is then natural that it will not be able to reach infinity in finite time either, since in order to do so it would have to travel infinitely fast. This intuitive idea is captured by saying that there is no probability current at $x = \pm\infty$.

This intuition can be shown to be correct, and in fact normalised wavefunctions have the property that

$$j(+\infty, t) = j(-\infty, t) = 0 \quad (2.32)$$

This shows that probability is conserved, and the particle is always somewhere (with probability one) at all times.

The point of the above, from a practical perspective, is that **if we have a proper, normalised wavefunction at t_0 , then it will remain normalised thereafter** – we don't have to worry about the normalisation changing in time.

3. Separation of Variables & the Time-Independent Schrödinger Equation

The equation of motion of a quantum particle is the Schrödinger equation. Much of this course will be concerned with solving the Schrödinger equation, in order to study how quantum particles evolve in time, starting from some initial wavefunction $\Psi(x, t_0)$.

The main technique that will be used is a standard technique used to solve many partial differential equations. It is known as **separation of variables**. This will lead to two **ordinary** differential equations, one involving only time, which can be solved easily, and the second involving only the position of the particle, known as the **Time-Independent Schrödinger Equation (TISE)**. The latter, although still challenging to solve in general, is more tractable than the Schrödinger equation itself, and thus this method gives us a simpler method for solving the Schrödinger equation.

In this section, we will carry out separation of variables for the Schrödinger equation. We will see that the solutions we obtain are very special solutions, known as **stationary states**, since all of their physical properties are constant in time.

3.1 Separation of Variables

The starting point of the technique of separation of variables is to **make an assumption** about the form of the wavefunction $\Psi(x, t)$: we assume that it **factorises** into two functions, $f(t)$ and $u(x)$, one depending only upon time, and the other only upon position,

$$\Psi(x, t) = f(t)u(x). \quad (3.1)$$

It must be emphasised that this is a **strong assumption** – most functions definitely do not factorise in this way. Nevertheless, for reasons that will only become clear later, we will make this assumption, and study its consequences. Using the facts that

$$\frac{\partial}{\partial t}(f(t)u(x)) = \frac{df}{dt}u(x), \quad \frac{\partial^2}{\partial x^2}(f(t)u(x)) = f(t)\frac{d^2u}{dx^2}, \quad (3.2)$$

i.e. the fact that partial derivatives equal ordinary derivatives for functions of a single variable, substituting (3.1) into the Schrödinger equation (2.13) leads to

$$i\hbar \frac{df}{dt}u(x) = -\frac{\hbar^2}{2M}f(t)\frac{d^2u}{dx^2} + V(x)f(t)u(x). \quad (3.3)$$

Dividing both sides by $f(t)u(x)$ leads to

$$i\hbar \frac{1}{f(t)} \frac{df}{dt} = -\frac{\hbar^2}{2M} \frac{1}{u(x)} \frac{d^2u}{dx^2} + V(x). \quad (3.4)$$

This equation has an important form. The left-hand side is a function **only** of t and is independent of x . On the other hand, the right-hand side is a function **only** of x and is independent of t . The only way that this equation can be true for all values of x and t is if **both sides are in fact constant and independent of x and t** .

This is a central point of the argument and important to stop and think about. Consider two times t_0 and t_1 , and a single point x_0 . In general, the left-hand side will be different at t_0 and t_1 . But, if we only consider the single point x_0 , the right-hand-side is constant. Thus the left-hand side must be the same at t_0 and t_1 . Playing around with this type of reasoning, it should become clear that both sides indeed must be constant.

The standard choice is to call the constant which both sides must necessarily equal E . That is, we arrive at the **pair** of equations

$$i\hbar \frac{1}{f(t)} \frac{df}{dt} = E, \quad (3.5a)$$

$$-\frac{\hbar^2}{2M} \frac{1}{u(x)} \frac{d^2u}{dx^2} + V(x) = E. \quad (3.5b)$$

These equations are completely equivalent to the Schrödinger equation under the assumption that the wavefunction factorises as $\Psi(x, t) = f(t)u(x)$.

The reason for calling the constant that appears in these equations E will become clear later in the course. We will see that it has an important physical meaning as the **energy** of the particle.

3.1.1 Time equation

The first of the above two equations, (3.5a), which involves only the time, is straightforward to solve. Multiplying both sides by $-if(t)/\hbar$ the equation becomes

$$\frac{df}{dt} = -\frac{iE}{\hbar} f(t). \quad (3.6)$$

By inspection, it can be seen that the solution of this equation will be of exponential form (since the derivative of the function is proportional to the function itself) and given by

$$f(t) = Ae^{-iEt/\hbar}, \quad (3.7)$$

where A is an integration constant. This is a particularly simple function, which amounts to **circular motion** in the complex plane.

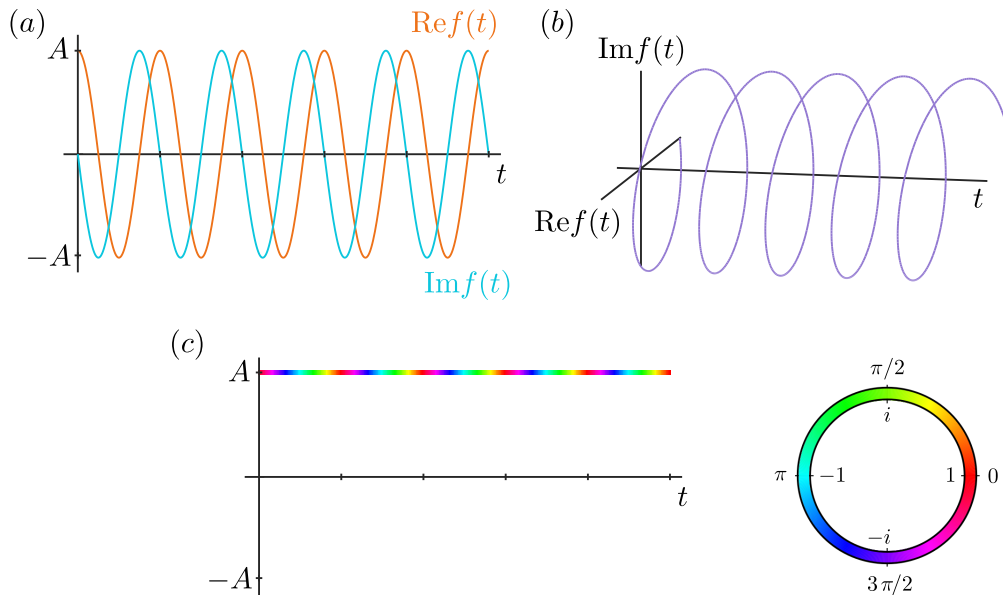


Figure 3.1: **Circular motion**. The function $f(t) = Ae^{-iEt/\hbar}$ represents circular motion in the complex plane. (a) 2D plot: The real and imaginary parts plotted on the same pair of axes. Each part oscillates sinusoidally. (b) 3-D plot: The y -axis and z -axis are the real and imaginary parts of $f(t)$. In this representation, the function looks like a corkscrew. (c) Colour plot: The y -axis is the absolute value $|f(t)|$, which is constant, $|f(t)| = 1$. The colour of the line represents the phase of $f(t)$. This is the angle on the corkscrew in (b). The legend shows how the colour varies with phase as you move around in a circle.

It is instructive to look at the **angular frequency** ω of this circular motion. Recall that the angular frequency is defined as $\omega = 2\pi/T$, where T is the period. For (3.7) the period is seen to be $T = 2\pi\hbar/E$, since

$$f(t+T) = Ae^{-iE(t+2\pi\hbar/E)/\hbar} = Ae^{-iEt/\hbar - 2\pi i} = Ae^{-iEt/\hbar} = f(t). \quad (3.8)$$

Therefore, we find that

$$\omega = \frac{E}{\hbar}, \quad (3.9)$$

i.e. $E = \hbar\omega$. This is very suggestive, as a little thought shows that it is in fact of exactly the same form as the relation Einstein used in the photoelectric effect, (1.3), if E is indeed the energy. In particular, we should recall that $\hbar = h/2\pi$, and the frequency f of an oscillation is related to the angular frequency ω via $\omega = 2\pi f$. Putting this together, we see that

$$E = \hbar\omega = \frac{h}{2\pi} 2\pi f = hf, \quad (3.10)$$

which is now exactly the Einstein relation (1.3). This is a first indication for why E is related to the energy. We will make this connection much stronger later.

3.2 The Time-Independent Schrödinger Equation

The second equation from above, (3.5b), that only depends upon the position x is known as the **Time-Independent Schrödinger Equation** (TISE). It is customary to write it in a form where both sides have been multiplied by $u(x)$, namely

$$-\frac{\hbar^2}{2M} \frac{d^2u}{dx^2} + V(x)u(x) = Eu(x). \quad (3.11)$$

Unlike the time equation (3.5a), it is not so straightforward to solve the TISE. In particular, whereas the time equation was **independent of the forces acting on the particle**, the TISE depends upon them, through the potential energy $V(x)$. Thus, depending upon the situation of interest, the equation that needs to be solved changes. We will explicitly solve this equation in a number of simple instances in this course, starting in the next section.

3.3 Separable solutions to the Schrödinger equation

Putting the above results together, it is seen that all **separable** solutions (i.e. those that factorise) of the Schrödinger Equation have the form

$$\Psi(x, t) = Ae^{-iEt/\hbar}u(x) \quad (3.12)$$

where E and A are constants, and $u(x)$ satisfies the TISE (3.11) with the same constant E as appearing in the exponential.

Exercise 3.1 By substituting a wavefunction of the form $\Psi(x, t) = Ae^{-iEt/\hbar}u(x)$ into the Schrödinger equation (2.13), confirm that it is a solution as long as $u(x)$ satisfies the TISE (3.11).

3.3.1 Stationary States

Separable solutions have a number of interesting and important properties. First, note that the time evolution of separable solutions is particularly simple. Whatever the function $u(x)$ is, then in time this whole function **undergoes circular motion** in the complex plane, at the angular frequency $\omega = E/\hbar$.

Furthermore, **the probability to find the particle somewhere is constant in time**. In particular, looking at the probability density we see that

$$P(x, t) = |\Psi(x, t)|^2 = |A|^2 |u(x)|^2, \quad (3.13)$$

which is manifestly independent of time.

We will also show later on, when we consider other physical properties of the particle, such as momentum and energy, that they too are **constant in time for separable solutions**.

For this reason, separable solutions are known as **stationary states**. We use this terminology since all physical properties are constant in time for stationary states. However, it is very important that the **wavefunction itself is definitely *not* stationary**. As we noted above, it has a non-trivial time-dependence, which corresponds to circular motion in the complex plane. What is constant is the spatial **form** of the wavefunction, i.e. the ‘shape’, which merely rotates without changing form.

4. The Free Particle

In this section we will solve the Schrödinger equation fully for the first time, in order to learn about the quantum mechanics of a “free particle” – one where there are no forces acting, such that $V(x) = 0$.

Before solving the Schrödinger equation, it is instructive to briefly recall how free particles behave in classical mechanics. When there are no forces, the equation of motion (2.4) becomes

$$\frac{dp}{dt} = 0, \quad \frac{dx}{dt} = \frac{p(t)}{M}, \quad (4.1)$$

with the arbitrary initial condition $x(t_0) = x_0, p(t_0) = p_0$. The solution is

$$x(t) = x_0 + \frac{p_0}{M}(t - t_0), \quad p(t) = p_0. \quad (4.2)$$

That is, the momentum of the particle is **constant in time**, and the particle travels with constant momentum, and therefore constant velocity. We would like to understand now the similarities and differences that arise with this in quantum mechanics.

4.1 Solving the Time-Independent Schrödinger Equation

In the previous section, we saw that under the assumption of a separable solution, we can reduce the problem of solving the Schrödinger equation (2.13), to that of solving the TISE (3.11). We will make this assumption here, and study the consequences.

In the case of a free particle, the TISE becomes

$$-\frac{\hbar^2}{2M} \frac{d^2 u}{dx^2} = Eu(x). \quad (4.3)$$

It will be useful to rearrange this equation and introduce a new constants in order to better understand it. Multiplying both sides by $-\frac{2M}{\hbar^2}$ leads to

$$\frac{d^2 u}{dx^2} = -\frac{2ME}{\hbar^2} u(x). \quad (4.4)$$

This form suggests that we can introduce a constant k ,

$$k = \frac{\sqrt{2ME}}{\hbar}. \quad (4.5)$$

If the constant E is **real** and **positive**, $E > 0$, then k too will be real and positive. Since E was introduced arbitrarily before, let us tentatively assume that it is indeed real and positive (we will come back to this assumption later, but it will be justified once we have confirmed that E is the energy of the particle). With this substitution, (4.4) now becomes

$$\frac{d^2 u}{dx^2} = -k^2 u(x). \quad (4.6)$$

We now see that the TISE for a free particle is in fact an equation that we have encountered before in the context of **simple harmonic motion** in classical mechanics. Two functions that are readily seen to solve this equation are e^{ikx} and e^{-ikx} . In particular,

$$\frac{d^2}{dx^2} e^{\pm ikx} = \frac{d}{dx} [\pm ik e^{\pm ikx}] = (\pm ik)^2 e^{\pm ikx} = -k^2 e^{\pm ikx}. \quad (4.7)$$

Therefore, the general solution of the TISE (4.6) is any superposition of these two solutions, namely

$$u(x) = B e^{ikx} + C e^{-ikx} \quad (4.8)$$

where B and C are arbitrary complex constants.

ⓘ Previously you may have found $\cos(kx)$ and $\sin(kx)$ to be the solutions to (4.6). Using the complex exponential solutions, instead of the trigonometric solutions is merely a matter of preference, as both are equivalent. In particular, since $\cos \theta = \frac{1}{2}(e^{i\theta} + e^{-i\theta})$ and $\sin \theta = \frac{1}{2i}(e^{i\theta} - e^{-i\theta})$, a general superposition of complex exponentials is equivalent to a general superposition of cosines and sines. As an exercise, you should confirm that this is true.

Having solved the TISE, we can now use (3.12) to **write down** a solution to the Schrödinger equation. In particular, we obtain a solution to the Schrödinger equation by multiplying by $f(t) = Ae^{-iEt/\hbar}$,

$$\begin{aligned}\Psi(x, t) &= f(t)u(x), \\ &= Ae^{-iEt/\hbar}(Be^{ikx} + Ce^{-ikx}), \\ &= e^{-i\hbar k^2 t/2M}(A'e^{ikx} + B'e^{-ikx})\end{aligned}\quad (4.9)$$

This is a separable solution to the free-particle Schrödinger equation, and in the third line we have used (4.5) to write $E = \hbar^2 k^2/2M$, and have combined the constants together, i.e. $A' = AB$ and $B' = AC$. This is a solution for all values of A' and B' , and all values of $k > 0$.

Exercise 4.1 By substituting the wavefunction (3.12) into the Schrödinger equation (2.13), confirm that it is a solution.

It might appear that we are thus done, as we have managed to solve the Schrödinger equation, and thus have found how a free particle evolves in time. There are however a number of obstacles that we still need to overcome.

First, as discussed in Sec. 2.4, we can specify an **arbitrary** initial state of the particle, i.e. an arbitrary wavefunction $\Psi(x, t_0)$ at $t = t_0$. For stationary states of the form (4.9), at $t = t_0$, we only have two complex numbers A' and B' to specify, and hence this definitely does not amount to an arbitrary wavefunction. We therefore seem to have much less generality than we need.

More worryingly, as we will see next, the solutions found don't appear to be permissible at all, due to their normalisation. We will see below that both of these problems can be overcome, by using the **superposition principle** from Sec. 2.5.1.

4.2 Using the Superposition Principle to Find Normalised Solutions

4.2.1 Separable solutions are unnormalisable for a free particle

Wavefunctions must be normalised in order that the probability to find the particle somewhere is one, as discussed in Sec. 2.3. Let us therefore attempt to normalise the wavefunction (4.9):

$$\begin{aligned}\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx &= \int_{-\infty}^{\infty} |(A'e^{ikx} + B'e^{-ikx})|^2 dx \\ &= \int_{-\infty}^{\infty} |A'|^2 + |B'|^2 + A'B'^*e^{2ikx} + A'^*B'e^{-2ikx} dx, \\ &= \infty\end{aligned}\quad (4.10)$$

unless $A' = B' = 0$. Indeed, when $A' \neq 0$ and $B' \neq 0$, the first two terms are positive and constant, and hence contribute an infinite amount to the integral. Moreover, the wavefunction **does not decay** for large x , as we already showed was necessary for normalised wavefunctions in Sec. 2.3.1. On the other hand, $A' = B' = 0$ leads to the solution $\Psi(x, t) = 0$, which also cannot be normalised, and is inadmissible.

At first sight, this appears like a major problem with the separation of variables method. Assuming a separable form, we found the most general solution to the Schrödinger equation, of the form (3.12). This form is not normalisable for a free particle, hence it implies that our initial assumption, that the wavefunction was separable is inconsistent, and there are no stationary states for a free particle.

It is true that our assumption that the wavefunction is separable, for a free particle, is in fact inconsistent, and free particles cannot be in stationary states. However, it does not mean that the method of separation

of variables is a bad one, but only that we have to **use it in a smarter way**. We must further make use of the **superposition principle** in order to turn it into a powerful technique for solving the Schrödinger equation.

4.2.2 Normalisation of superposed wavefunctions

Consider two distinct separable solutions to the Schrödinger equation, $\Psi_1(x, t)$ and $\Psi_2(x, t)$, each with a corresponding constant $E_1 > 0$ and $E_2 > 0$, such that $E_1 \neq E_2$. That is, consider

$$\Psi_1(x, t) = e^{-i\hbar k_1^2 t/2M} (A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}), \quad (4.11a)$$

$$\Psi_2(x, t) = e^{-i\hbar k_2^2 t/2M} (A_2 e^{ik_2 x} + B_2 e^{-ik_2 x}), \quad (4.11b)$$

where $k_1 = \sqrt{2ME_1}/\hbar$ and $k_2 = \sqrt{2ME_2}/\hbar$, and A_1, B_1, A_2 and B_2 are arbitrary complex constants. Both of these wavefunctions solve the Schrödinger equation separately. Now, because of the superposition principle from Sec. 2.5.1, we know that

$$\begin{aligned} \Psi'(x, t) &= \alpha \Psi_1(x, t) + \beta \Psi_2(x, t) \\ &= \alpha e^{-i\hbar k_1^2 t/2M} (A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}) + \beta e^{-i\hbar k_2^2 t/2M} (A_2 e^{ik_2 x} + B_2 e^{-ik_2 x}) \end{aligned} \quad (4.12)$$

is also a solution to the Schrödinger equation, for arbitrary complex numbers α and β .

This new superposed wavefunction has an interesting form. First, it is **no longer separable**. That is, $\Psi'(x, t)$ is not of the form $\Psi'(x, t) = f'(t)u'(x)$, for some functions $f'(t)$ and $u'(x)$. Second, the normalisation of $\Psi'(x, t)$ is not directly related to the normalisation of $\Psi_1(x, t)$ or $\Psi_2(x, t)$. We will not calculate the normalisation of $\Psi'(x, t)$ just yet, but will show next that we can in fact **form normalised wavefunctions by carefully superposing separable solutions**.

Before doing so, it will turn out to be important to first ask ourselves what form the **most general** superposition of separable solutions can take. In particular, whereas we superposed two solutions in the above, more generally we can in fact superpose as many solutions as we wish.

In the above example (4.12) it is instructive to realise that although we superposed two solutions, it is more natural to view it as a superposition of **four wavefunctions** all of the form

$$\Psi_k(x, t) = \frac{1}{\sqrt{2\pi}} e^{-i\hbar k^2 t/2M} e^{ikx}, \quad (4.13)$$

where $k = k_1, -k_1, k_2$ and $-k_2$. These all correspond to separable solutions, with $f(t)$ of the form $f(t) = e^{-i\hbar k^2 t/2M}$ and $u(x)$ of the form $u(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$.

❗ I have introduced the constant $\frac{1}{\sqrt{2\pi}}$ in $\Psi_k(x, t)$ as it turns out to be the ‘**correct**’ normalisation. It is much easier to introduce it at this stage, even if this appears somewhat arbitrary and unjustified, rather than to wait and fix the normalisation later.

With this in mind, we could in fact superpose **infinitely many** separable solutions, one for every value of k – positive or negative. Such a wavefunction can be written

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) e^{-i\hbar k^2 t/2M} e^{ikx} dk, \quad (4.14)$$

where $c(k)$ is a complex function which collects together all of the constants that multiply each function $\Psi_k(x, t)$. We have written this as an **integral** as k can vary continuously. This should not alarm you. Although this form may appear at first sight more complicated than the superposition in (4.12), which is just a sum, it is really of the same form.

We will now show that by choosing the function $c(k)$ appropriately – i.e. by carefully superposing separable solutions – we can obtain a normalised solution to the Schrödinger equation. This is in spite of the fact that the separable solutions themselves cannot be normalised.

We can also use the insight from Sec. 2.5.2, that **normalisation is conserved in time**, in order to simplify our calculation. In particular, we need only calculate the normalisation of $\Psi(x, 0)$, which has a simpler form than $\Psi(x, t)$. If $\Psi(x, 0)$ is normalised, we know that $\Psi(x, t)$ will also be normalised, so we should carry out the simplest calculation we can. We see that

$$\begin{aligned} \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 dx &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dk c^*(k) e^{-ikx} \int_{-\infty}^{\infty} dk' c(k') e^{ik'x}, \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' c^*(k) c(k') \int_{-\infty}^{\infty} dx e^{i(k' - k)x}, \end{aligned} \quad (4.15)$$

where we introduced a new variable k' for the second integration (which is just a dummy variable that we are integrating over).

This expression looks formidable, but it can in fact be substantially simplified, by using some of the mathematics from your Mathematical Physics 202 course. In particular, there you learnt about the **Dirac Delta function**:

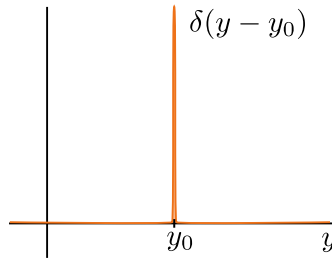
Definition 4.1 — Dirac Delta Function. The Dirac Delta function $\delta(y)$ is defined such that

$$\int_{-\infty}^{\infty} f(y) \delta(y - y_0) dy = f(y_0). \quad (4.16)$$

One representation of the Dirac Delta function is

$$\delta(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iay} da. \quad (4.17)$$

The delta function is an infinitely thin, infinitely tall ‘spike’, as depicted below:



Two key properties of the delta function are that it is an **even** function,

$$\delta(-y) = \delta(y). \quad (4.18)$$

and that under a **change of scale**

$$\delta(by) = \frac{1}{|b|} \delta(y), \quad (4.19)$$

We therefore see, using (4.17), that the final integral in (4.15) is in fact $2\pi\delta(k' - k)$, and so

$$\begin{aligned} \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 dx &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' c^*(k') c(k) 2\pi \delta(k' - k) \\ &= \int_{-\infty}^{\infty} |c(k)|^2 dk. \end{aligned} \quad (4.20)$$

❗ Note that the $\frac{1}{\sqrt{2\pi}}$ that was introduced ‘arbitrarily’ into the definition of $\Psi_k(x, t)$, has ended up being squared, and has exactly cancelled the 2π which arises from the definition of the Dirac Delta function. This is the first way of seeing why this was the ‘correct’ normalisation.

Therefore the wavefunction $\Psi(x, 0)$ will be normalised if

$$\int_{-\infty}^{\infty} |c(k)|^2 dk = 1 \quad (4.21)$$

This has exactly the form of a **normalisation condition** for the function $c(k)$, just like (2.8). In the next section we will study further this function and the significance of this normalisation condition.

To summarise, a wavefunction of the form (4.14) is a **normalised solution** to the Schrödinger equation whenever (4.21) is satisfied. We thus see that the superposition principle allows us to go from the unnormalised separable solutions (4.9) to normalised inseparable ones.

We now have enough machinery in place to actually study concrete examples, in order to start building some intuition for how particles behave in quantum mechanics.

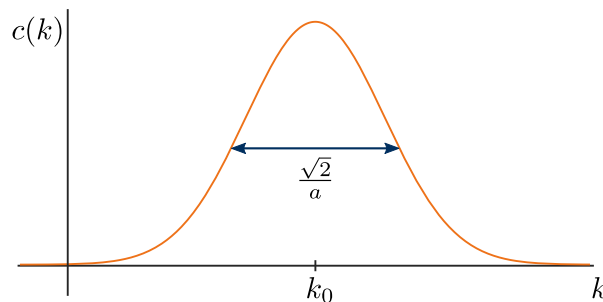
4.3 Gaussian wavepackets

We are going to study a solution to the Schrödinger equation known as a **Gaussian wavepacket**. This is a very special solution, whereby the particle is seen to be roughly **localised** in a **packet**, which evolves in time in a rather simple way, maintaining the same general form for all time.

Example 4.1 — Gaussian wavepacket. Consider a superposition specified by

$$c(k) = \left(\frac{2a^2}{\pi} \right)^{1/4} e^{-a^2(k-k_0)^2}. \quad (4.22)$$

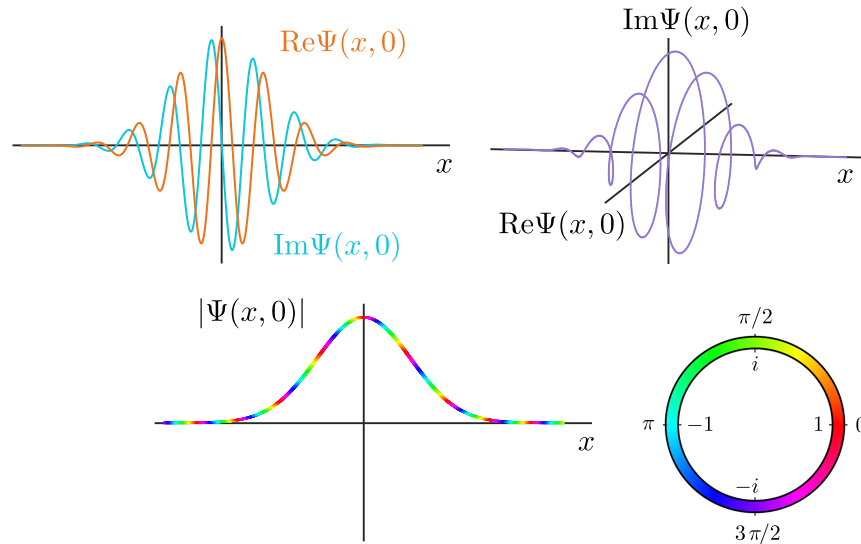
which is a Gaussian function, centred at $k = k_0$, with width $\sqrt{2}/a$ (distance between inflection points).



The integral (4.14) can be evaluated explicitly in this case, and this is carried out as an Problem in Problem Sheet 1. At $t = 0$, the wavefunction is found to be

$$\Psi(x, 0) = \left(\frac{1}{a\sqrt{2\pi}} \right)^{1/2} e^{-x^2/4a^2} e^{ik_0x} \quad (4.23)$$

This is also a Gaussian function, now centred at the origin, $x = 0$, and multiplied by a **phase factor** e^{ik_0x} . This is depicted below:



The probability density to find the particle at position x is

$$P(x, 0) = \frac{1}{a\sqrt{2\pi}} e^{-x^2/2a^2}, \quad (4.24)$$

which is a **normal distribution** (see figure below) with mean and standard deviation

$$\langle x \rangle = 0, \quad (4.25)$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = a. \quad (4.26)$$

The particle is therefore localised close to the origin, and the smaller a is, the smaller the standard deviation is, and hence the particle is more tightly localised.

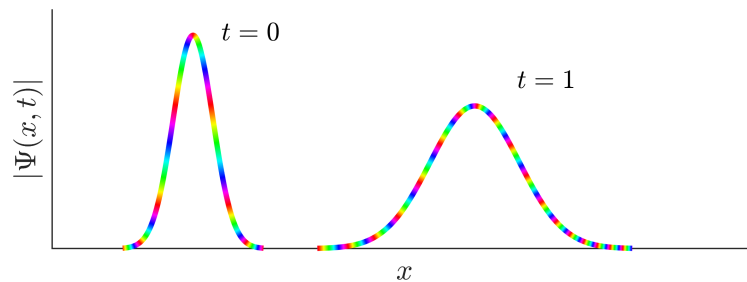
For other times t the integral (4.14) can again be carried out, although the calculation is significantly more lengthy. It is found that the wavefunction is given by

$$\Psi(x, t) = \left(\frac{1}{a(1 + i\gamma t)\sqrt{2\pi}} \right)^{1/2} \exp \left(\frac{-(x - \hbar k_0 t/M)^2}{4a^2(1 + i\gamma t)} \right) \exp(i k_0(x - \hbar k_0 t/2M)) \quad (4.27)$$

where

$$\gamma = \frac{\hbar}{2Ma^2}. \quad (4.28)$$

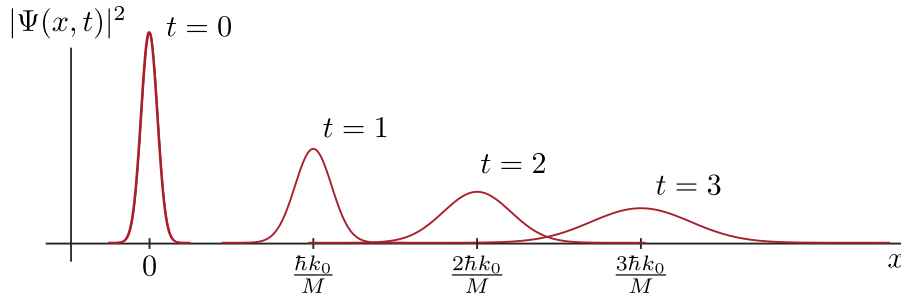
Although this formula looks much more complicated, the wavefunction looks very similar in form at later times:



The probability density to find the particle at a position x at time t is

$$P(x, t) = \frac{1}{a\sqrt{2\pi(1 + \gamma^2 t^2)}} \exp\left(\frac{-(x - \hbar k_0 t/M)^2}{2a^2(1 + \gamma^2 t^2)}\right) \quad (4.29)$$

This is plotted for a number of times below (with a reduced scale for the x -axis, in order to fit everything into one plot):



The probability distribution is a normal distribution (Gaussian) for all times, with mean and standard deviation given by

$$\langle x(t) \rangle = \frac{\hbar k_0 t}{M}, \quad (4.30)$$

$$\Delta x(t) = a\sqrt{1 + \gamma^2 t^2}. \quad (4.31)$$

Thus, the centre of the wavepacket is moving with a constant **speed** equal to $v = \hbar k_0 t/M$. This is somewhat analogous to a classical free particle, that moves with constant speed.

At the same time, the wavepacket of a quantum particle is also seen to **spread** – its width (which is what the standard deviation is measuring) increases in time from the initial width of a at $t = 0$, to $a\sqrt{1 + \gamma^2 t^2}$ at time t . The parameter γ therefore dictates the **rate** of spreading: when γ is large the packet spreads faster, whereas when γ is small, the packet spreads more slowly. We see from (4.28) that if we have a **heavier** particle, with a larger mass, γ is smaller, and the wavefunction spreads more slowly in time compared to a lighter particle. More interestingly, we see that the particle **spreads faster if it has a smaller width initially**. In particular, γ is inversely proportional to a^2 , which is precisely the variance (standard deviation squared) of the wavepacket at $t = 0$. We will come back to this phenomenon in the next section.

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4.4 Arbitrary initial wavefunction

In the above example we specified the function $c(k)$ and then used this to determine the wavefunction at all times $\Psi(x, t)$. This fixed the wavefunction at the initial time $t = 0$ also, and hence specifying $c(k)$ can be seen to be equivalent to specifying an initial condition $\Psi(x, 0)$.

What we really want to be able to do however is to specify an initial condition $\Psi(x, 0)$ (i.e. a complete description of the particle at a time $t = 0$), and to determine how the wavefunction evolves in time from this initial condition. It is also possible to do this, as we now see.

The problem that we need to solve is the **reverse** problem to the one we already solved: In the example we saw how to determine $\Psi(x, 0)$ from $c(k)$, now we want to determine the function $c(k)$ from an initial wavefunction $\Psi(x, 0)$. That is, we want to find the the function $c(k)$ that satisfies

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) e^{ikx} dk. \quad (4.32)$$

To do so, we consider multiplying both sides of (4.32) by $e^{-ik'x}$ and integrating over x , to obtain

$$\begin{aligned}\int_{-\infty}^{\infty} \Psi(x, 0) e^{-ik'x} dx &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dk c(k) e^{ikx} e^{-ik'x}, \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk c(k) \int_{-\infty}^{\infty} dx e^{i(k-k')x}.\end{aligned}\quad (4.33)$$

The inner integral is equal to $2\pi\delta(k - k')$, as can be seen from (4.17), thus we arrive at

$$\begin{aligned}\int_{-\infty}^{\infty} \Psi(x, 0) e^{-ik'x} dx &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) 2\pi\delta(k - k') dk, \\ &= \sqrt{2\pi} c(k').\end{aligned}\quad (4.34)$$

We therefore find (changing from k' to k), that

$$c(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{-ikx} dx. \quad (4.35)$$

There is a wonderful symmetry between this result and (4.32). In fact, what we have just shown is that $c(k)$ is the **inverse Fourier transform** of $\Psi(x, 0)$, and $\Psi(x, 0)$ is the **Fourier transform** of $c(k)$, which you learnt about in Mathematical Physics 202.

Importantly, this shows that for a free particle, we now have the **general solution for an arbitrary initial condition** $\Psi(x, 0)$. It is worth pausing to take in the implications of this. In principle, you now have the ability to specify an arbitrary initial wavefunction for the particle $\Psi(x, t_0)$ (which of course must be normalised), and from this determine the wavefunction of the particle at all other times, $\Psi(x, t)$. Combining (4.35) with (4.14) (and taking care to introduce a number dummy variable x' for the integration), we arrive at the – rather formidable looking – general solution

$$\Psi(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx' \Psi(x', 0) e^{-ikx'} e^{-i\hbar k^2 t/2M} e^{ikx} \quad (4.36)$$

It is indeed difficult in general to **evaluate** the right-hand side, that is to carry out the two integrations, but that is a calculational issue, not a conceptual one. Eq. (4.36) really is the completely general solution, the equivalent to (4.2) – which provides the analogous general solution in classical mechanics (and is remarkably simpler).

There is nevertheless more to understand about free particles, and otherwise. In particular, we can use the free particle stationary states (4.13) in order begin understanding **momentum** in quantum mechanics, which we start in the next section.

5. Momentum in Quantum Mechanics

In the previous section we determined how free particles behave according to quantum mechanics. We saw that the stationary states of a free particle are unnormalisable, but by carefully constructing superpositions of stationary states it is possible to find normalised wavefunctions. In this section we will take a closer look at the significance of these superpositions, which will provide a way to define **momentum** in quantum mechanics.

Much like a particle doesn't have a well-defined position, but is rather in a superposition of locations, in quantum mechanics **particles do not have well-defined momenta**, but rather have a **superposition** of momenta. We will see below that we can define **probability amplitudes** for a particle to have a momentum p , and that this amplitude is specified by a **momentum wavefunction**.

5.1 Plane waves and De Broglie

In the previous section, we found that the separable solutions to the Schrödinger equation for a free particle were given by (4.13), i.e.

$$\Psi_k(x, t) = \frac{1}{\sqrt{2\pi}} e^{-i\hbar k^2 t/2M} e^{ikx}, \quad (5.1)$$

where $E = \hbar^2 k^2/2M$ was the constant which appeared in the TISE. Our starting point will be to take a closer look at these solutions, to better understand what they represent.

Similarly to how it was instructive to look at the angular frequency of the temporal part of a stationary state (see Sec. 3.1.1) it will also be instructive to look at the **wavelength** of the spatial part of these wavefunctions. In particular, for the function e^{ikx} we immediately see that the wavelength is $\lambda = 2\pi/k$ since

$$e^{ik(x+\lambda)} = e^{i(kx+2\pi)} = e^{ikx} \quad (5.2)$$

which means that k is in fact the **wave number** of the wave (which is the reason why we chose to call it k in the first place). Such functions are in fact **complex plane waves**. The real and imaginary parts of such functions oscillate sinusoidally with wavelength $\lambda = 2\pi/k$.

We can now invoke de Broglie's hypothesis (1.9), but **in reverse**. Whereas de Broglie's hypothesis is that if a particle has a definite momentum p , then it has definite wavelength $\lambda = h/p$ and therefore definite wavenumber $k = 2\pi/\lambda = p/\hbar$, we can go in reverse, and say that **if a wavefunction has a definite wavenumber k , then it has a definite momentum $p = \hbar k$** .

We thus tentatively view the stationary wavefunctions $\Psi_k(x, t)$ in (4.13) as **corresponding to particles with momentum $p = \hbar k$** , since they are states with a definite wavelength $\lambda = 2\pi/k$.

A first indication that this is a good idea is to recall the relation between E and k from (4.5). We see that, in conjunction with the de Broglie relation $p = \hbar k$, we obtain

$$E = \frac{\hbar^2 k^2}{2M} = \frac{p^2}{2M}, \quad (5.3)$$

which shows that the identification of $\hbar k$ with the momentum fits together nicely with the identification of E in the TISE with the energy. In particular, if E is the energy, and p is the momentum, this equation is precisely the equation defining the **kinetic** energy of a particle.

5.2 Superpositions of momenta

In the previous section we saw that the wavefunctions $\Psi_k(x, t)$ for a free particle are unnormalisable, and hence are inadmissible states for a particle. Now that these wavefunctions are seen to correspond to

states of definite momentum, we arrive at the absolutely fundamental conclusion that **it is impossible for a particle to have a definite momentum in quantum mechanics**.

In order to get around this problem, we realised that a superposition of the states $\Psi_k(x, t)$ could in fact form a normalised wavefunction. We now see that such superpositions correspond to **superpositions of momenta**. In particular, when we introduced the superposition principle, we stressed that if the different wavefunctions being superposed have **different physical properties**, then it is natural to say that in the superposed wavefunction this **property is in superposition**. This is exactly what we are doing here, but now for the momentum of a particle.

5.3 The momentum wavefunction

We will now show how to go one step further, and describe the superposition of momentum **quantitatively** by introducing the idea of a **probability density** for momentum and an associated **probability amplitude**, in direct analogy to the way we defined these quantities for the position of the particle. In particular, previously we said that a particle with wavefunction $\Psi(x, t_0)$ is in a superposition of locations, with the probability amplitude at the position x at time t_0 given by $\Psi(x, t_0)$, and the probability density given by $P(x, t_0) = |\Psi(x, t_0)|^2$.

Our goal is to determine analogous quantities for momentum, namely a **momentum wavefunction** $\tilde{\Psi}(p, t_0)$ such that the probability amplitude for the particle to have momentum p at time t_0 is $\tilde{\Psi}(p, t_0)$, and the probability density for momentum is $|\tilde{\Psi}(p, t_0)|^2$.

To guide us, let us look once again at the expression (4.32) from the previous section, for a free particle at $t = 0$, namely

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) e^{ikx} dk, \quad (5.4)$$

which we showed was a normalised wavefunction as long as

$$\int_{-\infty}^{\infty} |c(k)|^2 dk = 1. \quad (5.5)$$

If we substitute the de Broglie relation $p = \hbar k$ into this condition, taking care that $dp = \hbar dk$, we obtain

$$\int_{-\infty}^{\infty} \frac{1}{\hbar} |c(p/\hbar)|^2 dp = 1. \quad (5.6)$$

This suggests that we should identify the integrand $\frac{1}{\hbar} |c(p/\hbar)|^2$ with $P(p, 0)$, the **probability density for momentum** at $t = 0$. Going one step further, it also suggests that we identify $\frac{1}{\sqrt{\hbar}} c(p/\hbar)$ with $\tilde{\Psi}(p, 0)$, the **momentum wavefunction** at $t = 0$, since the modulus square of this function is precisely $P(p, 0)$.

Having the momentum wavefunction and probability density defined in terms of $c(p/\hbar)$ is however not fully satisfactory, and hides the final message, since ultimately we would like to have them expressed in terms of the wavefunction $\Psi(x, 0)$ itself, which, after all, is a complete description of the state of the particle at $t = 0$. We can achieve this by using the relation (4.35) from the previous section. In particular, we find

$$\tilde{\Psi}(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{-ipx/\hbar} dx. \quad (5.7)$$

This form also suggests how to extend the definition from $t = 0$ to all times t : We simply replace $\Psi(x, 0)$ on the right-hand side, with $\Psi(x, t)$, arriving at

$$\tilde{\Psi}(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-ipx/\hbar} dx. \quad (5.8)$$

This is the **momentum wavefunction** of a particle. We see that at any given time t_0 it is **completely specified** by the wavefunction $\Psi(x, t_0)$ at the same time. That is, the momentum wavefunction is not

independent of the wavefunction, but is a function of it. This was to be expected, since the wavefunction is a **complete specification** of the state of the particle at any given time. What we see is that a (rather complicated) function of the wavefunction specifies the **probability amplitude** and the corresponding probability density for the particle to have momentum p .

We have thus achieved a **very important goal** – we now understand, in full generality, **how momentum is specified in quantum mechanics**.

5.3.1 The momentum wavefunction as a different representation of the state

Interestingly, **the momentum wavefunction is also a complete specification of the state of a particle**. To see this, consider, just as we did in Sec. 4.4, multiplying both sides of (5.8) by $e^{ipx'/\hbar}$ and integrating over p , to obtain

$$\begin{aligned}\int_{-\infty}^{\infty} \tilde{\Psi}(p, t) e^{ipx'/\hbar} dp &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \Psi(x, t) e^{-ipx/\hbar} e^{ipx'/\hbar}, \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) 2\pi \delta\left(\frac{x'-x}{\hbar}\right) dx, \\ &= \sqrt{2\pi\hbar} \Psi(x', t),\end{aligned}\tag{5.9}$$

where we used the definition of the Dirac Delta function (4.17) to arrive at the second line, and the change of scale property (4.19), i.e. that $\delta\left(\frac{x'-x}{\hbar}\right) = \hbar\delta(x' - x)$, to arrive at the third line. This shows that, after replacing everywhere x' with x , that

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \tilde{\Psi}(p, t) e^{ipx/\hbar} dp.\tag{5.10}$$

Thus, if the momentum wavefunction is known at a time t_0 , then it is possible to recover the spatial wavefunction $\Psi(x, t_0)$ at that time. **Both wavefunctions are complete specifications of the state of a particle**. We say that they constitute two different **representations** of the state.

In many problems we are interested primarily in the position of the particle, hence the wavefunction $\Psi(x, t)$ is a more **useful** representation. If however we care more about the momentum of the particle, which happens for instance often in **scattering experiments in particle physics**, or often in **condensed matter physics**, then it is more useful to work with the momentum wavefunction $\tilde{\Psi}(p, t)$. You will see this later in your physics education.

5.4 Gaussian wavepacket

We end this section by returning to our example of the Gaussian wavepacket of a free particle from Sec. 4.3, to look at it's momentum.

Example 5.1 — Gaussian wavepacket of a free particle. Recall that in Example 4.1 we considered the following superposition

$$c(k) = \left(\frac{2a^2}{\pi}\right)^{1/4} e^{-a^2(k-k_0)^2}.\tag{5.11}$$

which was a Gaussian function, centred at $k = k_0$. We saw that it lead to the wavefunction

$$\Psi(x, 0) = \left(\frac{1}{a\sqrt{2\pi}}\right)^{1/2} e^{-x^2/4a^2} e^{ik_0x}.\tag{5.12}$$

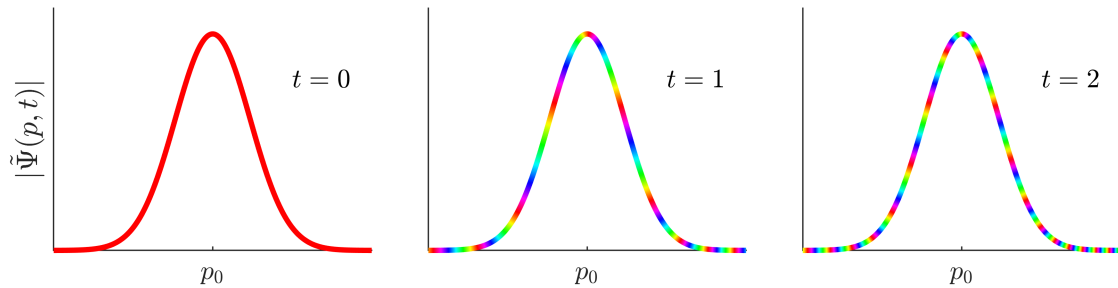
Using the identity $\tilde{\Psi}(p, 0) = \frac{1}{\sqrt{\hbar}} c(p/\hbar)$, we see that the corresponding momentum wavefunction is

$$\tilde{\Psi}(p, 0) = \left(\frac{2a^2}{\pi\hbar^2} \right)^{1/4} e^{-a^2(p-p_0)^2/\hbar^2}, \quad (5.13)$$

where we have defined $p_0 = \hbar k_0$. In Exercise 5.1 below, we show that at later times the momentum wavefunction is

$$\tilde{\Psi}(p, t) = \left(\frac{2a^2}{\pi\hbar^2} \right)^{1/4} e^{-a^2(p-p_0)^2/\hbar^2} e^{-ip^2 t/2M\hbar}, \quad (5.14)$$

i.e. the wavefunction at later times is multiplied by the **phase factor** $e^{-ip^2 t/2M\hbar}$. We say that it **accumulates a phase in time**. In a figure:



The probability density for momentum at time t , $P(p, t) = |\tilde{\Psi}(p, t)|^2$, is therefore

$$P(p, t) = \left(\frac{2a^2}{\pi\hbar^2} \right)^{1/2} e^{-2a^2(p-p_0)^2/\hbar^2}. \quad (5.15)$$

Notably this is **independent of time** – the probability density of the momentum of the particle does not change in time for a free particle. This is the quantum mechanical manifestation of **conservation of momentum** that we expect to hold for a free particle from classical physics.

Moreover, we see that, just like the probability density in space $P(x, t)$, the probability density for momentum is also a **normal distribution**, with mean and standard deviation

$$\langle p(t) \rangle = p_0, \quad (5.16)$$

$$\Delta p(t) = \frac{\hbar}{2a}. \quad (5.17)$$

This now **explains** why the wavepacket **spreads** in time. The particle has a **superposition of momenta** at all times. The evolution of the particle is the **superposition** of the different evolutions, one for each momentum. If the particle has larger momentum, then it travels further in a given time, and if it has small momentum, it travels less. It is the superposition of the initial wavepacket travelling all of the different distances that leads to a wider Gaussian wavepacket at later times.

Exercise 5.1 — Momentum wavefunction of a Gaussian wavepacket at time t . In this exercise, we will derive the momentum wavefunction $\tilde{\Psi}(p, t)$ of a free particle at time t , and apply it to the Gaussian wavepacket from Example 4.1.

- (a) By making the substitution $k = p/\hbar$, show that expression for the wavefunction $\Psi(x, t)$ at time t for a free particle, as given in (4.14), can be rewritten as

$$\Psi(x, t) = \frac{1}{\hbar\sqrt{2\pi}} \int_{-\infty}^{\infty} c(p/\hbar) e^{-ip^2 t/2M\hbar} e^{ipx/\hbar} dp.$$

- (b) By appealing to the relationship between $\Psi(x, t)$ and $\tilde{\Psi}(p, t)$ given in (5.10), show that the above implies that the momentum wavefunction $\tilde{\Psi}(p, t)$ for a free particle is

$$\tilde{\Psi}(p, t) = \frac{1}{\sqrt{\hbar}} c(p/\hbar) e^{-ip^2 t / 2M\hbar}$$

- (c) Substitute $c(k)$ for a Gaussian wavepacket, given in (5.11), into this expression, to reproduce (5.14).

6. Operators

In this section we will introduce another basic ingredient of quantum mechanics, the fact that **physical quantities are represented by mathematical operators**. Such operators are sometimes referred to as **observables**, as they correspond to observable quantities, such as position and momentum. This will allow us to understand the true meaning of the time-independent Schrödinger equation, and why E corresponds to energy. Finally, it will show that stationary states correspond to states with **definite** energy.

In order to arrive at quantum mechanical operators we will look at **averages** of physical quantities, and how they are expressed in quantum mechanics, and see that this naturally leads us somewhere interesting.

In this section we will be interested exclusively in the properties of a quantum particle **at a given time** t_0 , and not the dynamics in time. In order to avoid clutter, instead of writing $\Psi(x, t_0)$ all of the time, we will **simplify the notation and write simply $\Psi(x)$** . Similarly, we will write $\tilde{\Psi}(p)$ in place of $\tilde{\Psi}(p, t_0)$ to refer to the momentum wavefunction at t_0 . Whenever we need to talk about the dynamics, we will revert back to the full notation.

6.1 Average values of position and momentum

The wavefunction $\Psi(x)$ specifies the probability density for a particle to be found at position x , according to $P(x) = |\Psi(x)|^2$. It can often be useful to study **properties** of this probability density, for example the **average position** of the particle,

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x)|^2 dx, \quad (6.1)$$

or more generally the average of some function of position $f(x)$,

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) |\Psi(x)|^2 dx, \quad (6.2)$$

for example the squared position $f(x) = x^2$, or the squared distance from the average, $f(x) = (x - \langle x \rangle)^2$.

❗ Such average values are often referred to as **expectation (or expected) values**. This terminology can however be misleading. For example, it can give the impression that you ‘expect’ to find the particle at $\langle x \rangle$, i.e. that the expectation value is equal to the most likely value of x . **This is most definitely not the case in general.** In fact, the expectation value is rather fictitious, and can be a position where there is zero probability density to find the particle. One should always think about what the probability density **looks like** before asking oneself whether the average value is a meaningful quantity to calculate or not.

Equivalently, $\tilde{\Psi}(p)$ specifies the probability density for the momentum of the particle. It is also often useful to study properties such as the **average momentum** of the particle,

$$\langle p \rangle = \int_{-\infty}^{\infty} p |\tilde{\Psi}(p)|^2 dp, \quad (6.3)$$

or other functions of momentum $g(p)$,

$$\langle g(p) \rangle = \int_{-\infty}^{\infty} g(p) |\tilde{\Psi}(p)|^2 dp. \quad (6.4)$$

6.1.1 Average of momentum from the wavefunction

In (6.3) the average momentum of the particle is calculated from the momentum wavefunction $\tilde{\Psi}(p)$. However, it is customary to have the state of the particle specified not in terms of the momentum wavefunction, but in terms of the (spatial) wavefunction $\Psi(x)$.

It thus appears that in order to calculate the average momentum (or function of momentum) a rather complicated procedure needs to be carried out: first the momentum wavefunction must be obtained, by carrying out the integration in (5.8). Then the expectation value must be calculated, by carrying out the integration in (6.3). In the derivation below we will show that there is **a much more direct method** for calculating the average momentum directly from the wavefunction, by introducing the notion of a **momentum operator**.

As our starting point, we first show below that the average momentum can equivalently be expressed as

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} dx \Psi^*(x) \frac{\partial \Psi}{\partial x}. \quad (6.5)$$

Derivation Let us start by substituting the explicit expressions for the momentum wavefunction (5.8), and its complex conjugate, into (6.3),

$$\begin{aligned} \langle p \rangle &= \int_{-\infty}^{\infty} p \tilde{\Psi}^*(p) \tilde{\Psi}(p) dp, \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp p \int_{-\infty}^{\infty} dx' \Psi^*(x') e^{ipx'/\hbar} \int_{-\infty}^{\infty} dx \Psi(x) e^{-ipx/\hbar}, \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx' \Psi^*(x') \int_{-\infty}^{\infty} dx \Psi(x) \int_{-\infty}^{\infty} dp p e^{ip(x'-x)/\hbar}, \end{aligned} \quad (6.6)$$

which is another formidable looking expression. The inner integral can be written in a different form by noting that

$$p e^{ip(x'-x)/\hbar} = i\hbar \frac{\partial}{\partial x} e^{ip(x'-x)/\hbar}. \quad (6.7)$$

This means that (6.6) can be written as

$$\begin{aligned} \langle p \rangle &= \frac{i}{2\pi} \int_{-\infty}^{\infty} dx' \Psi^*(x') \int_{-\infty}^{\infty} dx \Psi(x) \frac{\partial}{\partial x} \int_{-\infty}^{\infty} dp e^{ip(x'-x)/\hbar}, \\ &= i\hbar \int_{-\infty}^{\infty} dx' \Psi^*(x') \int_{-\infty}^{\infty} dx \Psi(x) \frac{\partial}{\partial x} \delta(x' - x), \end{aligned} \quad (6.8)$$

where in the first line we pulled $\frac{\partial}{\partial x}$ outside the integral over p , and in the second line we used the definition of the Dirac delta function (4.17), and the scaling property (4.19). We can now integrate by parts on the inner integral, to move the partial derivative from the delta function $\delta(x' - x)$ onto the wavefunction $\Psi(x)$,

$$\langle p \rangle = i\hbar \int_{-\infty}^{\infty} dx' \Psi^*(x') \left([\Psi(x) \delta(x' - x)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \frac{\partial \Psi(x)}{\partial x} \delta(x' - x) \right). \quad (6.9)$$

The term $[\Psi(x) \delta(x' - x)]_{-\infty}^{\infty}$ vanishes, since the wavefunction goes to zero at infinity (in order to be normalised). Finally, the relation (4.19) can be used, to arrive at

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} dx \Psi^*(x) \frac{\partial \Psi(x)}{\partial x}, \quad (6.10)$$

This is the final form, which should be compared to (6.6) to appreciate how significant of a simplification it is.

6.2 The momentum operator

We are now going to make an important realisation. We can in fact express the average momentum in a slightly different form, which will ultimately suggest the correct way to understand it. We can write it as

$$\langle p \rangle = \int_{-\infty}^{\infty} dx \Psi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x), \quad (6.11)$$

that is, we can bring the $-i\hbar$ into the middle, and “pull-out” the partial derivative. This new expression for the average momentum in terms of the wavefunction (6.5) suggests that we associate to momentum a **momentum operator** \hat{P}

$$\hat{P} = -i\hbar \frac{\partial}{\partial x}. \quad (6.12)$$

This is an operator since its **acts on functions to create new functions**. In particular, it is a **partial differential operator**.

This allows us to write the expectation of momentum as

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \hat{P} \Psi(x) dx, \quad (6.13)$$

in which the momentum operator is **“sandwiched”** between $\Psi^*(x)$ and $\Psi(x)$ and integrated over all space.

This formula is the quantum mechanical formula for the average (or expectation value of) momentum. It is important to stress that the left-hand side is **purely statistical** – it is the average value of momentum, as calculated from the probability density $P(p)$ (which we have denoted $P(p, t_0)$ up until now, when we explicitly want to talk about the time). This represents what will be measured in an experiment. The right-hand side gives the quantum mechanical **prediction** for this average momentum, in terms of a simple function of the wavefunction.

❗ *In some places (e.g. in textbooks, or other lecture notes), you will find that once the momentum operator has been introduced, the expectation value of momentum as denoted by $\langle \hat{P} \rangle$, i.e. making explicit reference to the momentum operator \hat{P} . We will not use this notation here, as I think it is more important to emphasise that the average momentum is a physical quantity (which makes sense outside of the context of quantum mechanics), and to recall the quantum mechanical prediction of average momentum. The latter is equally given by the right-hand side of (6.13), in terms of the momentum operator \hat{P} , as well as the right-hand side of (6.3), in terms of the momentum wavefunction $\tilde{\Psi}(p)$. These two choices for notation for expectation values occur for all physical quantities, and in all cases we will here use the notation which does not make reference to the operator.*

6.2.1 Functions of momentum

We could carry out similar calculations to determine expressions for other functions of momentum. For example, if we were to look at the average square momentum $\langle p^2 \rangle$, starting with the definition

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} p^2 |\tilde{\Psi}(p)|^2 dp, \quad (6.14)$$

by following a similar route, we would find an equivalent expression

$$\begin{aligned}
\langle p^2 \rangle &= -\hbar^2 \int_{-\infty}^{\infty} \Psi^*(x) \frac{\partial^2 \Psi}{\partial x^2} dx, \\
&= \int_{-\infty}^{\infty} \Psi^*(x) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x) dx, \\
&= \int_{-\infty}^{\infty} \Psi^*(x) \hat{P}^2 \Psi(x) dx
\end{aligned} \tag{6.15}$$

where

$$\hat{P}^2 \Psi(x) = \hat{P} \hat{P} \Psi(x) = -i\hbar \frac{\partial}{\partial x} \left(-i\hbar \frac{\partial}{\partial x} \Psi(x) \right) = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}. \tag{6.16}$$

In general we find that

$$\langle g(p) \rangle = \int_{-\infty}^{\infty} g(p) |\tilde{\Psi}(p)|^2 dp = \int_{-\infty}^{\infty} \Psi^*(x) g(\hat{P}) \Psi(x) dx, \tag{6.17}$$

and hence the operator associated to $g(p)$, which we denote $\hat{g}(p)$, is

$$\hat{g}(p) = g(\hat{P}), \tag{6.18}$$

i.e. in the function, p is replaced everywhere by $-i\hbar \frac{\partial}{\partial x}$.

! *Strictly speaking, the above works **only** when the function $g(p)$ has a Taylor series, i.e. when it can be expanded in a power series of the form $g(p) = \sum_n a_n p^n$, in which case every p^n in the series is replaced by \hat{P}^n to obtain $\hat{g}(p)$. Any function we will meet in this course will have this form. You will learn in *Quantum Mechanics II* much more about operators, and that will allow you to furthermore understand how to associate operators to functions more generally.*

6.3 The position operator

Inspired by the momentum operator, it is also possible to introduce a position operator. In particular, the average position of the particle (6.1) can be written in a form similar to (6.13), using the fact that $|\Psi(x)|^2 = \Psi^*(x)\Psi(x)$,

$$\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} x |\Psi(x)|^2 dx, \\
&= \int_{-\infty}^{\infty} \Psi^*(x) x \Psi(x) dx.
\end{aligned} \tag{6.19}$$

So too can any function of position be written in a form similar to (6.17),

$$\begin{aligned}
\langle f(x) \rangle &= \int_{-\infty}^{\infty} f(x) |\Psi(x)|^2 dx, \\
&= \int_{-\infty}^{\infty} \Psi^*(x) f(x) \Psi(x) dx.
\end{aligned} \tag{6.20}$$

Both of these suggest that the **position operator** \hat{X} is given by

$$\hat{X} = x, \tag{6.21}$$

i.e. the position operator is just the co-ordinate x . This is still an **operator**, since when we act on the function $\Psi(x)$ with the operator \hat{X} it creates the function $\hat{X}\Psi(x) = x\Psi(x)$, i.e. the function $\Phi(x) = x\Psi(x)$ from the function $\Psi(x)$.

As with momentum, the operator $\hat{f}(x)$ corresponding to $f(x)$ is

$$\hat{f}(x) = f(\hat{X}). \quad (6.22)$$

In this case, since $\hat{X} = x$, we in fact have $\hat{f}(x) = f(x)$, which is to say that $\hat{f}(x)\Psi(x) = f(x)\Psi(x)$, i.e. the wavefunction is just multiplied by the number $f(x)$ at every position x .

6.4 The time-independent Schrödinger equation

Having introduced the notion of an operator, now is the time to return to the time-independent Schrödinger equation (3.11) and take a closer look at its physical significance. The TISE is

$$Eu(x) = -\frac{\hbar^2}{2M} \frac{d^2u}{dx^2} + V(x)u(x). \quad (6.23)$$

Recalling that for functions of a single variable, such as $u(x)$, differentiation and partial differentiation coincide, then from (6.16) we see that the first term on the right-hand side can be written as

$$\begin{aligned} -\frac{\hbar^2}{2M} \frac{d^2u}{dx^2} &= -\frac{\hbar^2}{2M} \frac{\partial^2 u}{\partial x^2} \\ &= \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} \right) u(x), \\ &= \frac{\hat{P}^2}{2M} u(x). \end{aligned} \quad (6.24)$$

For the second term, from (6.22), we have that $V(x) = \hat{V}(x)$, and so altogether the time-independent Schrödinger equation becomes

$$Eu(x) = \left(\frac{\hat{P}^2}{2M} + \hat{V}(x) \right) u(x). \quad (6.25)$$

We have thus re-expressed the right-hand side of the equation as a sum of two operators acting on $u(x)$. This pair of operators has a special importance, as we see next.

6.4.1 The Hamiltonian Operator

The operator appearing on the right-hand side is known as the **Hamiltonian operator** \hat{H} ,

$$\hat{H} = \frac{\hat{P}^2}{2M} + \hat{V}(x). \quad (6.26)$$

In classical mechanics, $p^2/2M$ is the **kinetic energy** of the particle and $V(x)$ is the **potential energy**. The sum of the two is thus the **total energy of the particle**. In classical mechanics the total energy function is known as the **Hamiltonian**, since it is the central object used in the formalism discovered by Hamilton, known as **Hamiltonian mechanics**. This is a powerful formalism which generalises Newton's laws to more general situations, and which is taught in the Analytical Mechanics course.

6.4.2 Eigenvalue equation

Using the definition (6.26), and interchanging the left-hand and right-hand side, the time-independent Schrödinger equation can be written

$$\hat{H}u(x) = Eu(x). \quad (6.27)$$

Written this way, the time-independent Schrödinger equation is seen to have a form that is very important and prevalent in physics and mathematics. It has the form of an **eigenvalue equation**: the solutions $u(x)$ are precisely those functions that are only **scaled** when operated on by \hat{H} . We say that the solutions to this equation are **eigenfunctions** of the Hamiltonian operator \hat{H} , and that the scaling factor E is the corresponding **eigenvalue**.

6.4.3 Stationary states are states of definite energy

The realisation that the time-independent Schrödinger equation is an eigenvalue equation is **extremely important** as it shows that stationary states are states of definite energy.

Recall that a stationary state is of the form $\Psi(x, t) = Ae^{-iEt/\hbar}u(x)$, where $u(x)$ is a solution to the time-independent Schrödinger equation, which we now see is equivalent to saying that $u(x)$ is an eigenfunction of the Hamiltonian operator \hat{H} with eigenvalue E . First, it is important to realise that **stationary states are also eigenfunctions of the Hamiltonian operator**. In particular,

$$\begin{aligned}\hat{H} \left(Ae^{-iEt/\hbar}u(x) \right) &= \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right) Ae^{-iEt/\hbar}u(x), \\ &= Ae^{-iEt/\hbar} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right) u(x), \\ &= Ae^{-iEt/\hbar} Eu(x), \\ &= E \left(Ae^{-iEt/\hbar}u(x) \right),\end{aligned}\tag{6.28}$$

where in the first line we wrote out the Hamiltonian operator in full, and in the second line we pulled $Ae^{-iEt/\hbar}$ to the front, which is allowed since it is not a function of x . The third line uses the fact that $u(x)$ is a solution to the time-independent Schrödinger equation (6.27) with eigenvalue E , and the last is just a rearrangement.

Let us now ask what is the **average total energy** of a stationary state? We now have the ability to answer this question given what we have learnt above. First, since the Hamiltonian is synonymous with total energy, we are interested in the average of the Hamiltonian $\langle H \rangle$. Although the Hamiltonian is a function of both momentum and position, we can still **use the same rule** as for position or momentum for the expectation value of **any** physical quantity in terms of the quantum mechanical operator associated with that quantity. In particular, quantum mechanics predicts that the average total energy of the particle is given by

$$\langle H \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{H} \Psi(x, t) dx,\tag{6.29}$$

When we consider stationary states, we can furthermore use (6.28) to arrive at

$$\begin{aligned}\langle H \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{H} \Psi(x, t) dx, \\ &= \int_{-\infty}^{\infty} \Psi^*(x, t) E \Psi(x, t) dx, \\ &= E \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx, \\ &= E,\end{aligned}\tag{6.30}$$

where to obtain the second line we used (6.28), the fact that stationary states are eigenfunctions of the Hamiltonian operator. The average is thus seen to be equal to E . This already shows that **E is in fact the average energy of the particle in the state $\Psi(x, t) = Ae^{-iEt/\hbar}u(x)$** .

We can go further by first noticing that for the operator \hat{H}^2 the stationary state is still an eigenfunction, but now with eigenvalue E^2 ,

$$\begin{aligned}\hat{H}^2 \Psi(x, t) &= \hat{H} \left(\hat{H} \Psi(x, t) \right), \\ &= \hat{H} (E \Psi(x, t)), \\ &= E \hat{H} \Psi(x, t), \\ &= E^2 \Psi(x, t).\end{aligned}\tag{6.31}$$

Thus, looking at the average square total energy, $\langle H^2 \rangle$, we see that

$$\begin{aligned}
 \langle H^2 \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{H}^2 \Psi(x, t) dx, \\
 &= \int_{-\infty}^{\infty} \Psi^*(x, t) E^2 \Psi(x, t) dx, \\
 &= E^2 \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx, \\
 &= E^2.
 \end{aligned} \tag{6.32}$$

Finally, if we look at the standard deviation of the total energy in a stationary state, we see that

$$\begin{aligned}
 \Delta H &= \sqrt{\langle H^2 \rangle - \langle H \rangle^2}, \\
 &= \sqrt{E^2 - E^2}, \\
 &= 0.
 \end{aligned} \tag{6.33}$$

The fact that the standard deviation vanishes implies that **the energy of the particle is E with certainty**. This is because the standard deviation tells us the **width** of the probability distribution of energy. The only way for the width of a probability distribution to be zero is if the energy takes on a certain value with certainty, in this case E .

We have arrived at the very important conclusion that **stationary states are states of definite energy E** . This is why we chose to call the constant E all along.

Note that we have implicitly assumed in the above that we are **not** talking about a **free** particle. For free particles we saw that the stationary states cannot be normalised. This is however **only** the case for free particles – in general there is no problem with normalising stationary states, as we will see in later sections. The above in fact teaches us an important new lesson about the free particle. We previously saw that stationary states of a free particle were states of definite **momentum**. We now realise that this is specific to free particles, and occurs **only** because a free particle only has kinetic energy (and no potential energy): For a free particle, having definite energy is **equivalent** to having definite momentum. More generally, when there are forces acting on the particle, the total energy is the sum of both kinetic and potential energies. In this case, stationary states remain states of definite energy, but fail to be states of definite momentum.

6.4.4 Conservation of Energy

Finally, the above leads us to another extremely important conclusion: **energy is conserved in quantum mechanics**. Indeed, we have just seen that stationary states, $\Psi(x, t) = Ae^{-iEt/\hbar}u(x)$, are eigenfunctions of the Hamiltonian operator and have energy E **independent of time**. Thus if a particle has a definite energy at $t = 0$, it will have the same definite energy for all time.

Later on we will furthermore see that energy is conserved even when a particle does not have a definite energy, but has a superposition of energies.

6.5 Eigenfunctions of operators

We introduced the notion of an operator above in order to calculate average values more directly from the wavefunction. There are however numerous important reasons for introducing operators. We have already begun to see one of these when looking at the time-independent Schrödinger equation. One of the most important features of operators is that they allow us to understand **how definite physical properties arise in quantum mechanics**.

The wavefunction $\Psi(x, t_0)$ is a complete specification of the physical state of a particle at time t_0 . However, just knowing this isn't yet very satisfactory, since one would like to know what form $\Psi(x, t_0)$ has in order to have some physical property. We now have the ability to answer this question: **the**

eigenfunctions of an operator associated to a physical property correspond to states where that property is well defined/definite.

It is easiest to illustrate this with examples. First, in section 6.4.3 we saw that the eigenfunctions of the Hamiltonian operator are wavefunctions which have definite energy E . Thus, if $\Psi(x, t_0) = u(x)$, an eigenfunction of the Hamiltonian operator with eigenvalue E , then the particle has definite energy equal to E .

Consider now the momentum operator \hat{P} . We can consider the **momentum eigenvalue equation**

$$\hat{P}v(x) = p_0v(x), \quad (6.34)$$

That is, we can ask **what are the functions $v(x)$ that are eigenfunctions of the momentum operator, with eigenvalue p_0 ?** Given the definition of the momentum operator (6.12), they are solutions to the differential equation

$$-i\hbar \frac{\partial}{\partial x} v(x) = p_0v(x). \quad (6.35)$$

This equation is readily solved by inspection, the solutions are

$$v(x) = Ae^{ip_0x/\hbar}. \quad (6.36)$$

This is precisely as to be expected, given Sec. 5.1. In particular, we saw that de Broglie told us that wavefunctions with definitive wavelengths λ – i.e. plane waves, correspond to states of definite momentum $p = h/\lambda$. We have just arrived at the same result in a completely independent manner.

What is important is that this is **fully general**: although for momentum we already had some understanding of what form a wavefunction $\Psi(x)$ needed to have in order to have definite momentum, for other physical quantities, such as energy, this is no longer true. We now see how to answer this question, by solving the corresponding eigenvalue equation.

More generally, this provides the general answer to the question of just **how** all the physical information is contained in the wavefunction $\Psi(x, t_0)$. It is precisely in the **form** of the complex function – how it varies in space.

Exercise 6.1 — Eigenfunctions of position. In this exercise, we will try to gain some understanding of what the eigenfunctions of the position operator \hat{X} are. Since eigenfunctions have definite properties, these should correspond to states of a particle where the particle has a definite position.

- Write down the eigenvalue equation for the position operator $\hat{X} = x$. That is, write down what it would mean for a function $v(x)$ to be an eigenfunction of the operator \hat{X} with eigenvalue x_0 .
- Show that this implies that $v(x)$ must vanish at all positions x except $x = x_0$.
- (Tricky) Try to normalise this wavefunction. Is there a problem?

7. Commutation and the Uncertainty Principle

In the previous section we introduced the notion of an operator and saw that to each physical quantity in quantum mechanics we associate an operator. This operator is useful for calculating average values, and the eigenfunctions of the operator are precisely those wavefunctions where the property becomes definite.

In this section we will now move on to looking at **multiple quantities** in quantum mechanics. This will lead us to the notion of **incompatible** observables, which are **physical properties that cannot be simultaneously well defined or measured**. This leads to one of the most famous results in quantum mechanics, namely **Heisenberg's uncertainty principle**, which states, roughly, that the more *certain* the position of a particle, the more *uncertain* the momentum, and vice versa.

7.1 Commutation

Operators act on functions to generate new functions. The net effect of acting on a function with multiple operators in general **depends upon the order in which the operators are applied**. This shouldn't be too surprising, since it is common from everyday life: for example, cracking an egg open before placing it in boiling water makes a poached egg, while placing it in boiling water before cracking it upon makes a boiled egg. The order in which we act on the egg matters. So too does the order in which we act on wavefunctions.

Let us consider the action of the position and momentum operators applied to a wavefunction $\Psi(x)$, in the two different orders:

$$\begin{aligned}\hat{X}\hat{P}\Psi(x) &= \hat{X}\left(\hat{P}\Psi(x)\right), \\ &= \hat{X}\left(-i\hbar\frac{\partial\Psi(x)}{\partial x}\right), \\ &= -i\hbar x\frac{\partial\Psi(x)}{\partial x},\end{aligned}\tag{7.1}$$

while

$$\begin{aligned}\hat{P}\hat{X}\Psi(x) &= \hat{P}\left(\hat{X}\Psi(x)\right), \\ &= -i\hbar\frac{\partial}{\partial x}\left(x\Psi(x)\right), \\ &= -i\hbar\left(\Psi(x) + x\frac{\partial\Psi(x)}{\partial x}\right), \\ &= -i\hbar\Psi(x) - i\hbar x\frac{\partial\Psi(x)}{\partial x}\end{aligned}\tag{7.2}$$

where we have used the product rule for differentiation to obtain the two terms.

The two resulting functions are clearly different from each other, and hence applying the operators in the two different orders is not equivalent.

Whenever this happens, we say that the operators **do not commute**. If on the other hand it would have been the case that the two different orders lead to the *same* final function, then we would have said that the operators **commute**.

It is useful to consider the **difference** between the two orders. That is, it is useful to look at

$$\hat{X}\hat{P}\Psi(x) - \hat{P}\hat{X}\Psi(x)\tag{7.3}$$

In this case, we see that

$$\begin{aligned}\hat{X}\hat{P}\Psi(x) - \hat{P}\hat{X}\Psi(x) &= -i\hbar x \frac{\partial \Psi(x)}{\partial x} - \left(-i\hbar \Psi(x) - i\hbar x \frac{\partial \Psi(x)}{\partial x} \right), \\ &= i\hbar \Psi(x).\end{aligned}\tag{7.4}$$

That is, the difference between the action of \hat{X} followed by \hat{P} and the action of \hat{P} followed by \hat{X} is **proportional** to the original function $\Psi(x)$, with the constant of proportionality being the imaginary number $i\hbar$.

The difference between the action of operators is such an important concept that we will use a special notation and terminology for it. We define **the commutator** of the operators \hat{X} and \hat{P} to be

$$[\hat{X}, \hat{P}] = \hat{X}\hat{P} - \hat{P}\hat{X}.\tag{7.5}$$

With this notation we can re-express (7.4) as

$$[\hat{X}, \hat{P}]\Psi(x) = i\hbar \Psi(x).\tag{7.6}$$

Since this holds for all wavefunctions $\Psi(x)$, it is common to write, **as an abuse of notation**,

$$[\hat{X}, \hat{P}] = i\hbar,\tag{7.7}$$

that is, **to omit the function $\Psi(x)$** that the operators are acting upon. One of the most common mistakes that students make is to forget that (7.7) is an abuse of notation. Indeed, to arrive at (7.7) we had to use the product rule for differentiation, which required \hat{P} to act on $x\Psi(x)$, hence there is no way to derive or make sense of this equation without the wavefunction present.

Equation (7.7) is known as the **canonical commutation relation**. It shows that operators corresponding to the two fundamental properties of a particle – the position and the momentum – do not commute with each other.

7.2 Incompatible observables

The fact that the operators corresponding to position and momentum do not commute is a signature that these physical properties are **incompatible** in quantum mechanics. By this we mean that in quantum mechanics **it is impossible for a particle to have at the same time a definite position and a definite momentum**. Said another way, states that correspond to definite position do not correspond to definite momenta, and vice versa.

More generally, when you come to look at other physical quantities, such as energy, or angular momentum, if the quantum mechanical operators associated to these quantities do not commute, it signifies, just as for position and momentum, that it is impossible in quantum mechanics for a particle to have at the same time a definite value for both quantities simultaneously, and they cannot be measured simultaneously.

Importantly the opposite is also true: If the operators corresponding to two quantities in fact **commute**, then a particle can have at the same time definite values for both quantities, and both can be measured simultaneously.

7.3 The uncertainty principle

We can in fact make the above statements about incompatible observables more quantitative through the notion of **the uncertainty principle**. In this part of the course we will only present the uncertainty principle for **position and momentum**, known as the **Heisenberg Uncertainty Principle**. It is possible to write down uncertainty relations for any pair of observables, but this will only be covered later on in the degree.

The uncertainty principle states that for any wavefunction $\Psi(x)$, the following relationship holds between the **standard deviation** of position and momentum,

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \quad (7.8)$$

where

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}, \quad \Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}. \quad (7.9)$$

The uncertainty principle states that the **product** of the standard deviations of position and momentum are lower bounded by a constant, equal to $\hbar/2$. We will **not prove** the uncertainty principle in this course – for that you will have to wait until Quantum Physics 301 next year. Nevertheless, the uncertainty principle arises precisely because of the fact that the operators for position and momentum **do not commute**. In fact, any pair of observables that don't commute satisfy an uncertainty principle, as you will also see next year.

The standard deviation of position tells us how well defined the position of the particle is. If the standard deviation is small, this means that all of the probability amplitude $\Psi(x)$ to find the particle somewhere must be concentrated around some particular point. On the other hand, if the standard deviation is large, it means that the probability amplitude must be spread out, and the particle can be found in a wide range of places. The situation is completely analogous for momentum.

Therefore, the uncertainty principle says that if the uncertainty in position Δx is **small**, then necessarily the uncertainty in the momentum of the particle is **large**,

$$\Delta p \geq \frac{\hbar}{2\Delta x}. \quad (7.10)$$

Therefore, the particle must be in a superposition of a wide range of momentum. Conversely, if the uncertainty in momentum is small, then the uncertainty in position must be high, signifying that the particle is in a superposition of being in a wide range of places.

Example 7.1 — Gaussian wavepacket. Consider again the Gaussian wavepacket from Examples 4.1 and 5.1. At $t = 0$, the wavefunction is

$$\Psi(x, 0) = \left(\frac{1}{2\pi a^2} \right)^{1/4} e^{-x^2/4a^2} e^{ik_0 x}. \quad (7.11)$$

The standard deviations in position and momentum of this wavefunction were previously shown to be

$$\Delta x = a, \quad \Delta p = \frac{\hbar}{2a} \quad (7.12)$$

Therefore,

$$\Delta x \Delta p = \frac{\hbar}{2}. \quad (7.13)$$

The Gaussian wavepacket at $t = 0$ therefore **saturates** the uncertainty principle: the product of the uncertainty in position and momentum is as small as allowed by quantum mechanics. This is very special, and it can in fact be shown that **only** the Gaussian wavepacket has this property.

8. The Infinite Square Well: Energy Eigenstates

In this section we now move onto how quantum mechanics describes the behaviour of particles that are acted on by forces. Previously in Section 4 we analysed the case of a free particle – one where there are no forces acting. Now we would like to begin our study of situations with a non-vanishing potential energy term $V(x)$ in the Schrödinger equation, signifying that there are external forces acting on the particle.

We will be interested in situations where there is a **potential well** of some type, i.e. such that in order for the particle to leave a certain region of space it would need to have a significant amount of energy. That is, there is some kind of **attractive force** between the particle and its surroundings. Such situations occur almost universally in physics – from planets in orbit around stars, to electrons inside atoms, to masses on springs and pendulums. In all of these cases, and many many more, the potential energy associated to the (conservative) force forms a potential well. Our general goal is therefore to understand how quantum mechanics describes particles trapped in potential wells, which will then explain a vast range of physical situations.

Crucially, we will see that when studying potential wells, one of the most distinctive features of quantum mechanics arises – **quantisation of energies**, also known as **discrete energy levels**.

Our general approach, as will be the case in almost all problems, will be to start off by solving the time-independent Schrödinger equation, to find the stationary states. We now know that the stationary states are also states of definite energy. It is customary to refer to them as **energy eigenstates** – which is just a fancy way of signalling that they are states of definite energy, and reminds us that the time-independent Schrödinger equation is an eigenvalue equation for the Hamiltonian \hat{H} .

We will analyse the properties of energy eigenstates in detail in this section. In the next section we will move on to studying the **dynamics** of a particle trapped inside the infinite square well.

8.1 General properties of energy eigenstates

Recall that the time-independent Schrödinger equation is

$$Eu(x) = -\frac{\hbar^2}{2M} \frac{d^2u}{dx^2} + V(x)u(x). \quad (8.1)$$

We now know that this is also the eigenvalue equation for the Hamiltonian operator \hat{H} , with E being the energy eigenvalue.

This shows that physically **E must be a real number**, since the energy of a particle is real, physical and measurable quantity. Before this realisation, in principle E was an arbitrary constant, which could well have been a complex number. Now we see that this is not the case.

This has an important implication: **we can always find real solutions $u(x)$ to the TISE**. This is proven in the next exercise:

Exercise 8.1 — Real solutions to the TISE. In this exercise we will show we can always find real solutions to the TISE.

- Assume first that $u(x)$ is a general, complex function that satisfies the time-independent Schrödinger equation. By taking the complex conjugate of each term in the TISE, show that $u^*(x)$ is also a solution, with the same energy E .
- Consider the function $u'(x) = (u(x) + u^*(x))/2$. Show that it too is a solution to the TISE.
- Confirm that $u'(x)$ is a real function.
- Consider also the function $u''(x) = (u(x) - u^*(x))/2i$. Show that it too is a solution of the TISE.
- Confirm that $u''(x)$ is a real function.

This shows that as soon as we find any (complex) solution $u(x)$ to the TISE, we can always find two real solutions $u'(x)$ and $u''(x)$, which are just the real and imaginary parts of the complex solution.

The next important property is that $u(x)$ and du/dx are **continuous functions**. That is, there are no ‘jumps’ (or discontinuities) in either $u(x)$ or du/dx . Examples of functions ‘bad’ functions are shown in Fig. 8.1. This is again proven in Exercise 8.2 below.

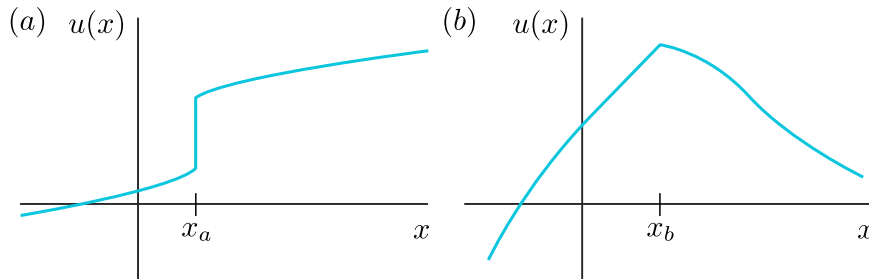


Figure 8.1: **Examples of ‘bad’ functions.** (a) An example of a function which has a discontinuity, i.e. a jump, at $x = x_a$. (b) An example of a function which has a discontinuous first derivative, i.e. a kink, at $x = x_b$. If we were to plot the function du/dx , then this would be a discontinuous function at $x = x_b$, similar to (a). Energy eigenstates cannot have jumps, and can only have kinks at locations where the potential energy $V(x)$ is infinite.

Like every good rule, there is an **exception** to the previous one, that occurs when **the potential energy is infinite**. Although this is a rather unphysical situation, it is one we will encounter as an idealisation in this section.

At points where the potential is infinite, $V(x) = \infty$, then **the first derivative du/dx can be discontinuous**. At these points $u(x)$ however must remain continuous. We will not prove these conditions in the course, but we see how they arise later when we look at a particle trapped in a finite potential well.

With these general considerations in place, we are now ready to study our first example in full.

Exercise 8.2 — $u(x)$ must be a continuous function. In this exercise we will outline an argument showing that $u(x)$ must be a continuous function. A similar argument works to show that du/dx must also be continuous.

We want to show that if $u(x)$ has a discontinuity, then it cannot be a solution to the TISE. That is, we want to assume that $u(x)$ changes abruptly from some value a to some other value b at a point x_0 , and to show that such a function cannot satisfy the TISE. It is difficult to work with such a discontinuity directly, but we can understand it by considering it as the **limit** of something nicer.

(a) Consider the function $v(x)$ defined as follows:

$$v(x) = \frac{a+b}{2} + \frac{b-a}{2} \tanh(c(x-x_0)),$$

where c is a positive constant. Make sketches of this function for various values of c , to demonstrate that when c becomes large, it approaches a function that changes abruptly from a to b at x_0 .

(b) Find $\frac{dv}{dx}$ and $\frac{d^2v}{dx^2}$. By making sketches, demonstrate that when c becomes large, $\frac{dv}{dx}$ and $\frac{d^2v}{dx^2}$ both become large in the vicinity of x_0 .

(c) Rearrange the TISE to show that it can be written as

$$\frac{1}{u(x)} \frac{d^2u}{dx^2} = \frac{2M(V(x) - E)}{\hbar^2}.$$

Physically, we want to consider only finite energies, $E < \infty$. Furthermore, let us consider that

$V(x) \neq \infty$, i.e. that the potential energy is finite. This means that the right-hand side of the TISE above is a finite number for all x .

(d) Assume that $u(x)$ is approximated by $v(x)$ in the vicinity of x_0 . Using part (b), argue that for large values of c the left-hand side of the TISE becomes large for values of x close to x_0 .

Since the right-hand side of the TISE in the above doesn't depend upon c , while the left does, we can always find a c large enough such that the left-hand side is bigger than the right-hand side, and hence the equation is not satisfied. Hence, solutions to the TISE cannot change arbitrarily abruptly at a point. Note that this argument fails at any point where the potential energy $V(x)$ is infinite.

8.2 The infinite square well potential

We are going to consider a situation where a particle is trapped inside an **infinite square well**. That is, we are going to take the potential energy of the particle to be

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a, \\ \infty & \text{if } x < 0 \text{ or } x > a. \end{cases} \quad (8.2)$$

which is depicted in Fig. 8.2.

This models a situation where a particle is confined to the region $0 \leq x \leq a$, as it would need to have infinite potential energy to be outside this region. We can think that there are infinitely rigid and perfectly impenetrable walls at $x = 0$ and $x = a$, and that the particle is bouncing between them. Inside the well, there are no forces acting on the particle, and the potential energy is constant, here taken to be $V(x) = 0$. In reality there is no such thing as an infinite square well, as there are no perfectly rigid walls, however this is an idealisation similar to a 'light inextensible string', that is very useful to study.

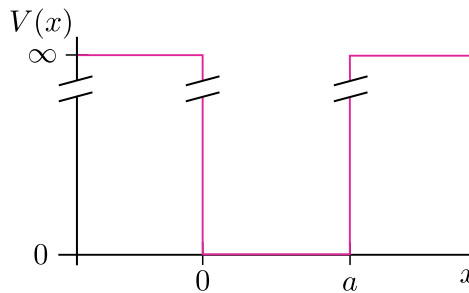


Figure 8.2: **Infinite square well**. The potential energy of the infinite square well. The potential vanishes for $0 \leq x \leq a$, and is infinite otherwise. This well is an idealisation for a situation where a particle is trapped between two perfectly impenetrable walls.

8.3 Energy eigenstates

Our first goal is to solve the time-independent Schrödinger equation to find the stationary states of infinite square well – i.e. the energy eigenstates.

To do so, we will need to consider the 3 regions – to the left of the well, $x < 0$, inside the well $0 \leq x \leq a$ and to the right of the well, $x > a$ – separately. We will call these regions I, II and III respectively, and denote the solution in these regions by $u_I(x)$, $u_{II}(x)$, and $u_{III}(x)$ respectively.

In the region to the left of the well, where $V(x) = \infty$, we do not expect to find the particle. We thus should expect that $u_I(x) = 0$ in this region. This is indeed a solution to the TISE, and it is also the **only** solution.

To see this, we can consider each term in the TISE separately. If $u_I(x)$ would not vanish at some point or in some subregion, then the potential energy term $V(x)u_I(x)$ would be infinite at those points or subregions. However the energy term $Eu_I(x)$ is not infinite, as we only want to consider particles with

finite energy E , and d^2u_I/dx^2 cannot be infinite either, hence there is no way to ‘compensate’ for the infinite potential energy term. Thus, we must have that $u_I(x) = 0$ everywhere in this region.

Similarly, in region III to the right of the well, where the potential is again infinite, we must have $u_{III}(x) = 0$ everywhere.

Finally, inside the well we have $V(x) = 0$, and thus the TISE becomes

$$Eu_{II}(x) = -\frac{\hbar^2}{2M} \frac{d^2u_{II}}{dx^2}. \quad (8.3)$$

This is the same equation that we had to solve for the **free particle** in Section 4. We found previously that the solutions were of the form

$$u_{II}(x) = Ae^{ikx} + Be^{-ikx}, \quad (8.4)$$

where

$$k = \frac{\sqrt{2ME}}{\hbar}. \quad (8.5)$$

This is a complex solution, but as we saw above, we can always find real solutions. We can arrive at these rather quickly by recalling the Euler identity $e^{i\theta} = \cos \theta + i \sin \theta$, from which we see that a real solution is of the form

$$u_{II}(x) = C \cos kx + D \sin kx \quad (8.6)$$

where C and D are real constants.

It is at this point that we must make use of the continuity conditions from above. In particular, we must now ensure that $u(x)$ **is continuous**, and therefore must ‘**stitch**’ together the solutions found in the 3 regions to make one continuous function for all x . Note that the places where we need to stitch together the solutions, at $x = 0$ and $x = a$, have $V(x) = \infty$, and therefore fall into the ‘exceptional’ case. As such, we **do not** require du/dx to be continuous at these points.

Starting at $x = 0$, from the left we have $u_I(0) = 0$, while on the right we have $u_{II}(0) = C$. Thus, in order to obtain a continuous solution at $x = 0$ we **must set** $C = 0$. Inside the well the solutions therefore must be of the form

$$u_{II}(x) = D \sin kx. \quad (8.7)$$

If we consider now the right-hand wall of the potential at $x = a$, we again have $u_{III}(a) = 0$, while $u_{II}(a) = D \sin ka$. We therefore must have

$$D \sin ka = 0 \quad (8.8)$$

in order to have a continuous solution at $x = a$.

One potential possibility is to choose $D = 0$. However, then $u_{II}(x) = 0$. This means that the wavefunction vanishes **everywhere**, which is **not a normalisable solution** since the particle is nowhere to be found. Thus we have to discount $D = 0$.

On the other hand, we know that $\sin \theta = 0$ whenever θ is a multiple of π , that is if $\theta = n\pi$, for n an integer. Thus, we will have a continuous solution at $x = a$ if we choose the wavenumber k such that

$$ka = n\pi, \quad (8.9)$$

which is to say that

$$k = \frac{n\pi}{a}. \quad (8.10)$$

Recalling that k is positive, since the energy E must be positive, we therefore see that n is a positive integer. This shows that the solutions in region II are given by

$$u_{II}(x) = D \sin \frac{n\pi x}{a}. \quad (8.11)$$

8.3.1 Discrete energy levels

In the above we have just seen one of the most important and iconic aspects of quantum mechanics, namely **quantisation** or **discrete energy levels**.

In order to find a solution to the time-independent Schrödinger equation that is continuous everywhere, including at the walls of the potential, we have just seen that only certain **special** values of the wavenumber k are allowed. For any other value of k the solution would not be continuous at $x = a$.

The significance of this is that **the allowed energies for a particle in the infinite square well are quantised**. In particular, from (8.5) and (8.10),

$$\begin{aligned} E &= \frac{\hbar^2 k^2}{2M}, \\ &= \frac{\hbar^2 \pi^2 n^2}{2Ma^2}. \end{aligned} \quad (8.12)$$

Thus, the particle cannot have any energy, but must have one of the **quantised** or **discrete** energies

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2Ma^2}, \quad (8.13)$$

where we use the notation E_n to distinguish between the different allowed energies. It is common to refer to these as the **energy levels** of the infinite square well, and n as a **quantum number**. A particle in the infinite square well can have a superposition of **only these energies**.

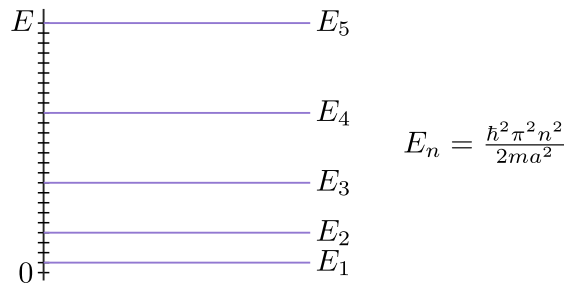


Figure 8.3: **Energy levels of the infinite square well**. The allowed energies of the infinite square well are quantised. The allowed energies are denoted by E_n , and they increase quadratically, proportional to n^2 .

This is in fact the **origin** of discrete energy levels in quantum mechanics: it is precisely the requirement that solutions to the time-independent Schrödinger equation (and in general their first derivative) must be continuous, normalisable functions. These requirements **can only be met for certain special values of energy**.

8.3.2 Normalisation

The above shows that for the infinite square well there are an infinite number of energy eigenstates, labelled by the quantum number n , given by

$$u_n(x) = D_n \sin\left(\frac{n\pi x}{a}\right) \quad (8.14)$$

for $0 \leq x \leq a$ and $u_n(x) = 0$ otherwise (outside the well), with the energy eigenvalues E_n given by (8.13). The constant D_n must be fixed by demanding that the wavefunction is **normalised**, i.e. by

requiring that for every energy eigenstate the probability to find the particle somewhere is one:

$$\begin{aligned}
 \int_{-\infty}^{\infty} |u_n(x)|^2 dx &= |D_n|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx, \\
 &= \frac{|D_n|^2}{2} \int_0^a 1 - \cos\left(\frac{2n\pi x}{a}\right) dx, \\
 &= \frac{|D_n|^2}{2} \left[x - \frac{a}{2n\pi} \sin\left(\frac{2n\pi x}{a}\right) \right]_0^a, \\
 &= \frac{|D_n|^2}{2} \left[a - \frac{a}{2n\pi} \sin(2n\pi) - 0 + \frac{a}{2n\pi} \sin(0) \right], \\
 &= \frac{|D_n|^2 a}{2},
 \end{aligned} \tag{8.15}$$

where in the first line we used the fact that $u(x) = 0$ for $x < 0$ and $x > a$ to restrict the limits of integration to 0 and a and in the second line we used the trigonometric identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$. Thus the wavefunction will be normalised if

$$|D_n|^2 = \frac{2}{a}. \tag{8.16}$$

The simplest solution to this equation that we can take (i.e. making D_n real and positive), is to choose

$$D_n = \sqrt{\frac{2}{a}}. \tag{8.17}$$

Notably this has a very special property – it is in fact independent of n . Thus, we finally arrive at the **normalised energy eigenstates**

$$u_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \tag{8.18}$$

for $0 \leq x \leq a$, and $u_n(x) = 0$ otherwise.

The first few energy eigenstates are depicted in Fig. 8.4. Note that the wavefunctions are continuous everywhere (i.e. have no jumps) but do not have continuous derivatives at the walls (i.e. have kinks there).

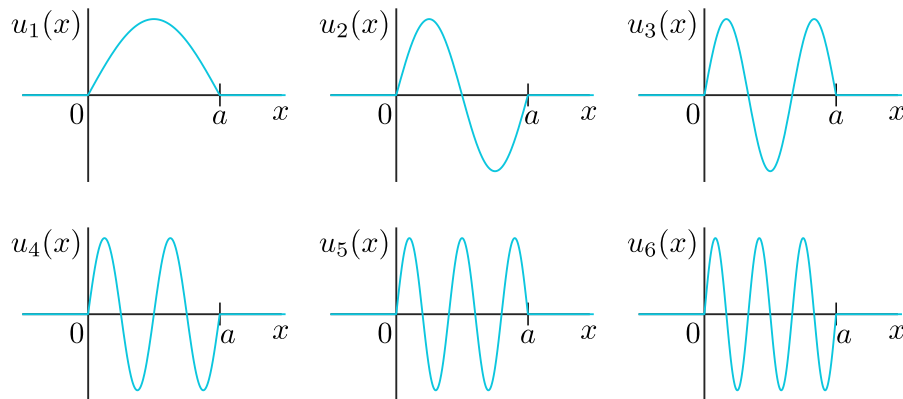


Figure 8.4: **Wavefunctions of energy eigenstates of the infinite square well.** The first six energy eigenstates $u_n(x)$ of the infinite square well. The number of nodes (places where the wavefunction vanishes, except at the boundaries) is equal to $n - 1$.

8.3.3 Further properties of energy eigenstates

We will now outline some of the important properties of energy eigenstates. **All of the properties we discuss below are true for the energy eigenstates of any potential well $V(x)$,** and not just the infinite

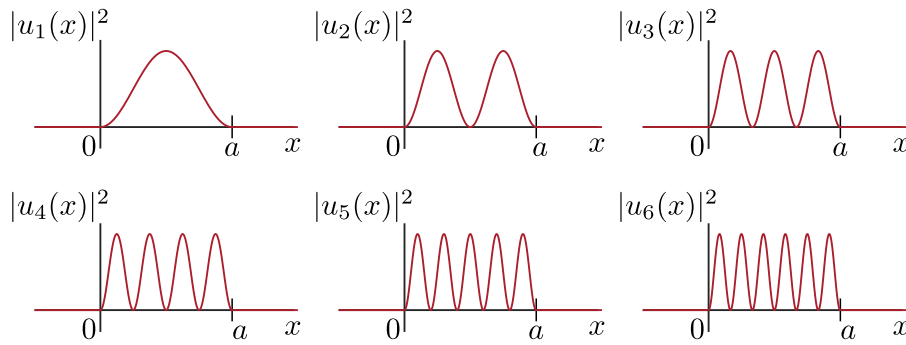


Figure 8.5: **Probability densities of the infinite square well.** The probability densities for finding the particle at x for the first six energy eigenstates of the infinite square well.

square well. That is, although we are highlighting them here, in the context of the infinite square well, everything below is generic, and we will come back to these properties later in the course when we study other potential wells.

Zero-point energy

The first important property is that the lowest energy that the particle can have is **greater than the minimal potential energy**. The state of lowest energy of a particle is typically called the **ground state**. In this case the ground state is

$$u_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right). \quad (8.19)$$

and the **ground state energy** is

$$E_1 = \frac{\hbar^2 \pi^2}{2Ma^2} \quad (8.20)$$

which is greater than the minimal potential energy, which is zero. Thus the particle **must have some energy in quantum mechanics** inside a potential well.

The reason for this is the **uncertainty principle**. Because the particle is completely confined inside the well, its standard deviation is definitely not larger than the width of the well, $\Delta x \leq a$. This implies that the uncertainty in momentum cannot be too small, in fact

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{\hbar}{2a}. \quad (8.21)$$

This means that the particle does not have zero momentum with certainty, but rather **must have a range of momenta**, and so is in fact **not at rest** even in the ground state. As such, its kinetic energy also cannot vanish, but the particle has a range of kinetic energies. This is precisely the **zero-point energy** of the particle.

Higher energies for more tightly confined particles

In the same direction as above, it is also generally true that **the more tightly confined the particle is, the larger all the allowed energies become**.

For the infinite square well we confine the particle more tightly by making a smaller. In this instance, we see that all of the energy eigenvalues increase, since $E_n \propto 1/a^2$.

The reason for this, just as in the above, is the uncertainty principle. If the particle is more tightly constrained in position it must have a larger uncertainty in momentum – i.e. must be in a superposition of a larger range of momenta – and therefore a larger uncertainty in kinetic energy. This leads to higher energy levels.

Lower energies for more massive particles

In the opposite direction, we also see that **the allowed energies decrease** for particles that are more massive, i.e. have a larger mass M .

For the infinite square well we see that the energies scale as $E_n \propto 1/M$, and therefore as the mass increases the energies all become lower.

This is also general, and makes sense due to the fact that the kinetic energy is $p^2/2M$, hence for a given momentum, if the mass increases, the kinetic energy decreases.

Number of nodes increase as the energy increases

The next general property is a geometrical property of the wavefunctions of energy eigenstates. Looking at Fig. 8.4 we see that apart from at the walls, the ground states has no ‘**nodes**’ – points where the wavefunction vanishes, $u(x) = 0$. The next wavefunction, the so-called **first excited state**, has exactly one node, in the centre of the well. The next state has two nodes, at $x = a/3$ and $x = 2a/3$. As we increase the energy we find that **the n th energy eigenstate has $n - 1$ nodes**.

This is also a general feature for all potential wells. Although the form of the wavefunction for the energy eigenstates will change as the potential changes, the fact that the n th energy eigenstate has $n - 1$ nodes remains completely general. This provides a very quick way to identify energy eigenstates, or more generally to ‘see’ if a wavefunction corresponds to a state of high or low energy.

Even/odd about the centre of the well

Related to the above, if the potential energy has a **symmetry**, then the eigenstates also inherit symmetries of their own. In particular, if the potential well is **symmetric** around a point, then the eigenstates are either **symmetric or anti-symmetric** about that point.

For the infinite square well, the well is symmetric around the point $x = a/2$, i.e. **the middle of the well**: if we mirror the left-half of the well in the line $x = a/2$, we reproduce the right-half. The energy eigenstates have the property that the right-half is either the mirror of the left half, when n is odd, or is equal to minus the mirror of the right-half, when n is even (it is really best to spend some time looking at Fig. 8.4 to convince yourself of this fact). That is to say, they are alternatively **even or odd about the centre of the well**. This is a general property of energy eigenstates, which will always be alternatively even and odd about the centre of the well whenever the potential energy is symmetric about the centre, as can often be the case.

Orthogonality

The next property is an extremely important one that is known as **orthogonality**. In Mathematical Physics 202 you saw that for functions we can define a notion of a **scalar product** and as a consequence the notion of orthonormal functions **as those for which the scalar product is zero**:

Definition 8.1 — Scalar Products, Orthogonality and Orthonormal functions. The **scalar product** between two functions $f(x)$ and $g(x)$, which we denote here by $\langle f, g \rangle$, is defined by

$$\langle f, g \rangle = \int_{-\infty}^{\infty} f^*(x)g(x)dx. \quad (8.22)$$

Two functions are **orthogonal** if the scalar product between them is zero, i.e.

$$f(x) \text{ and } g(x) \text{ are orthogonal} \leftrightarrow \langle f, g \rangle = 0. \quad (8.23)$$

Finally, a set of functions $f_i(x)$, for $i = 1, 2, \dots$, forms an **orthonormal set of functions** if

$$\langle f_i, f_j \rangle = \delta_{i,j} \quad (8.24)$$

where δ_{ij} is the **Kronecker delta function**, such that

$$\delta_{i,j} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{if } i \neq j. \end{cases} \quad (8.25)$$

Note that the condition of orthonormality also contains within it a **normalisation** condition for the functions $f_i(x)$. In particular, setting $i = j$, it says that

$$\langle f_i, f_i \rangle = \int_{-\infty}^{\infty} |f_i(x)|^2 dx = 1. \quad (8.26)$$

We can apply this notion to energy eigenstates to show that they constitute an orthonormal set of functions. In particular,

$$\langle u_m, u_n \rangle = \int_{-\infty}^{\infty} u_m^*(x) u_n(x) dx = \delta_{n,m} \quad (8.27)$$

Derivation We will prove (8.27) explicitly for the eigenstates of the infinite square well below. When $m = n$, we have already carried out this integral, which corresponds to the normalisation of the wavefunction, and we already fixed the constant D_n such that $\int_{-\infty}^{\infty} |u_n(x)|^2 dx = 1$. This shows that the functions are correctly normalised.

Let us consider therefore the case $m \neq n$. Substituting the explicit form of $u_n(x)$, and using the trigonometric identity

$$\sin \theta \sin \phi = \frac{1}{2} (\cos(\theta - \phi) - \cos(\theta + \phi)), \quad (8.28)$$

we see that

$$\begin{aligned} \langle u_m, u_n \rangle &= \int_{-\infty}^{\infty} u_m^*(x) u_n(x) dx, \\ &= \int_0^a \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx \\ &= \frac{1}{2} \int_0^a \cos\left(\frac{(n-m)\pi x}{a}\right) - \cos\left(\frac{(n+m)\pi x}{a}\right) dx, \\ &= \frac{1}{2} \left[\frac{a}{(n-m)\pi} \sin\left(\frac{(n-m)\pi x}{a}\right) - \frac{a}{(n+m)\pi} \sin\left(\frac{(n+m)\pi x}{a}\right) \right]_0^a, \\ &= \frac{1}{2} \left[\frac{a}{(n-m)\pi} \sin((n-m)\pi) - \frac{a}{(n+m)\pi} \sin((n+m)\pi) \right], \\ &= 0 \end{aligned} \quad (8.29)$$

where we used the fact that $\sin(0) = 0$ for the lower limit in the second to last line, and the fact that $\sin(\ell\pi) = 0$ for ℓ an integer, in the last line. This shows that when $m = n$ the energy eigenstates are orthogonal.

The meaning of **orthogonality**, as you will see in more detail later on in your quantum mechanics education, is that these are states of a particle that can be **perfectly distinguished**. In particular, if you knew (somehow) that the particle was in an energy eigenstate, but not which one, then since each one corresponds to a state of different energy, by measuring the energy of the particle, it is possible to figure out which state you really have. If two quantum states are not orthogonal, then it turns out that there is no way to perfectly distinguish them.

Completeness

Finally, energy eigenstates have a second extremely important property known as **completeness**. This says that **any valid wavefunction can be expressed as a superposition of energy eigenstates**. In particular,

any valid, normalised wavefunction can be written as

$$\begin{aligned}\Psi(x) &= \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \\ &= \sum_{n=1}^{\infty} c_n u_n(x).\end{aligned}\tag{8.30}$$

Note that here ‘valid’ depends upon **the particular context** – for the infinite square we know the particle cannot be found outside the well. Therefore any wavefunction where the particle is confined inside the well, which are the only permissible ones, can be written as a superposition of energy eigenstates. If we were to try to decompose a wavefunction where the particle is **not** confined to the well into energy eigenstates, we would not be able to do so. However, this is a physically impermissible situation, and hence there is no problem or lack of generality here.

Completeness is in many respects **rather natural**: As we will discuss further below, it says that the most general state of a particle is to have a superposition of energies. This is completely in line with what we saw previously – that the most general state of a particle is to be in a superposition of locations, and to have a superposition of momenta. Here we are seeing exactly the same thing once again, but now for the energy of the particle.

8.3.4 Determining c_n

Given that every wavefunction can be expressed as a superposition of energy eigenstates, it is also important to be able to determine the coefficients c_n for a given wavefunction $\Psi(x)$. In order to do this we assume that the wavefunction $\Psi(x)$ can be written as in (8.30), and consider multiplying both sides by $u_m^*(x)$ and integrating over x , to obtain

$$\begin{aligned}\int_{-\infty}^{\infty} u_m^*(x) \Psi(x) dx &= \int_{-\infty}^{\infty} u_m^*(x) \sum_{n=1}^{\infty} c_n u_n(x) dx, \\ &= \sum_{n=1}^{\infty} c_n \int_{-\infty}^{\infty} u_m^*(x) u_n(x) dx, \\ &= \sum_{n=1}^{\infty} c_n \delta_{n,m}, \\ &= c_m,\end{aligned}\tag{8.31}$$

where to obtain the third line we use the orthonormality of the energy eigenstates. We thus have the nice result that

$$c_m = \int_{-\infty}^{\infty} u_m^*(x) \Psi(x) dx,\tag{8.32}$$

We can also write this using the notation of the scalar product, in which case it takes the form

$$c_m = \langle u_m, \Psi \rangle.\tag{8.33}$$

8.3.5 The energy representation

In section 5.3 we saw that we can define a **momentum wavefunction** as an **alternative representation** of the state of a particle in quantum mechanics. We saw that we have a function $\tilde{\Psi}(p)$ that gives the **probability amplitude** for a particle to have momentum p , and that knowledge of the probability amplitude for all momenta was a complete description of the state of a particle. Finally, the probability density $P(p)$ for the particle to have momentum p was given by $P(p) = |\tilde{\psi}(p)|^2$.

With this in mind, we now will do exactly the same for energy. In particular, c_n is the probability amplitude for a particle to have energy E_n , and $|c_n|^2$ is the probability $P(E_n)$ for the particle to have energy E_n .

Note that since the energy is **quantised**, there are only **discrete** energies that the particle can have. This is in contrast to position or momentum, which are not quantised, and both can vary continuously. This leads to two significant changes for the energy representation compared to the position and momentum representations.

First of all, due to the fact that position and momentum vary continuously, we have to specify probability amplitudes continuously, which is to say as **functions**, $\Psi(x)$ and $\tilde{\Psi}(p)$. In contrast, since the allowed energies are **discrete**, we no longer need to use functions, but just need to specify a probability amplitude for each value of the energy. That is to say, we now just have **coefficients** c_n , one for each allowed energy E_n . We have thus replaced x and p by the quantum number n . We write it as a subscript in order to help emphasise that it only takes on integer values, and does not change continuously.

Second, for position and momentum the wavefunctions specify **probability densities**, since again x and p vary continuously. For example, we know that the **probability** to find the particle between x_0 and $x_0 + dx$ is $|\Psi(x_0)|^2 dx$. For energy, since the allowed energies are discrete, we do not have to deal with probability densities at all, but have directly **probabilities**. For example, the probability for the particle to have energy E_1 is $P(E_1) = |c_1|^2$.

It is good to check that $P(E_n) = |c_n|^2$ is indeed a valid probability distribution. In order for this to be the case, we require that the **total probability** for the particle to have an energy is one. This is indeed the case for a normalised wavefunction, as we can easily show:

$$\begin{aligned}
 1 &= \int_{-\infty}^{\infty} |\Psi(x)|^2 dx, \\
 &= \int_{-\infty}^{\infty} \sum_{m=1}^{\infty} c_m^* u_m(x) \sum_{n=1}^{\infty} c_n u_n(x) dx, \\
 &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \int_{-\infty}^{\infty} u_m(x) u_n(x) dx, \\
 &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_m^* c_n \delta_{n,m}, \\
 &= \sum_{n=1}^{\infty} |c_n|^2
 \end{aligned} \tag{8.34}$$

where we used (8.30) to write the wavefunction $\Psi(x)$ as a superposition of energy eigenstates $u_n(x)$ in the second line, and in order to arrive at the fourth line we use the orthonormality of the energy eigenstates (8.27). This shows that the energy amplitudes c_n are **square-normalised**, meaning that the sum of the modulus squared amplitudes is one. This is consistent with the interpretation of them as the probabilities for the particle to have energy E_n .

Finally, it is useful to realise that the energy amplitudes c_n constitute a third **complete specification** of the state of a particle. In particular, we see from (8.30) that if we know all of the amplitudes c_n then we can recover the wavefunction $\Psi(x)$. We call this representation of the state of a particle the **energy representation**.

Just like the momentum wavefunction $\tilde{\Psi}(p)$ can be the most useful representation of the state of the particle in certain circumstances, so too can the energy representation be a particularly useful representation of the state of a particle. As we will see in the next section in more detail, **whenever** we wish to look at the **dynamics** of a particle, it turns out that the energy representation is absolutely indispensable.

9. The Infinite Square Well: Dynamics

In the previous section we started our exploration of the infinite square well potential. We found the energy eigenstates of the well, which are the stationary states, and explored some of their properties, which hold for arbitrary potential wells.

We would now like to move onto studying the **dynamics** of a particle trapped inside an infinite square well. In particular, given an arbitrary initial wavefunction $\Psi(x, 0)$ at $t = 0$ – i.e. a complete specification of the state of the particle – we would like to solve for the wavefunction $\Psi(x, t)$ at later times t . Having found the energy eigenstates, this is in fact a relatively easy task, as we will now show.

9.1 Dynamics of an energy eigenstate

We will start our exploration not with an arbitrary initial state $\Psi(x, 0)$, but with a single energy eigenstate. That is, let us first recap how the state

$$\Psi(x, 0) = u_n(x) \quad (9.1)$$

evolves in time, for n an arbitrary integer, i.e. an arbitrary energy eigenstate.

Recall from Sec. 3 that energy eigenstates are solutions to the time-independent Schrödinger equation, which we arrived at by postulating a **separable** solution to the Schrödinger equation. We know that such states constitute **stationary states**, and evolve in time in a very simple manner, in particular

$$\Psi(x, t) = e^{-iE_n t/\hbar} u_n(x), \quad (9.2)$$

where

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2Ma^2} \quad (9.3)$$

is the corresponding energy eigenvalue. That is, stationary states **only accumulate a phase $e^{-iE_n t/\hbar}$ in time**. Recall that these are called stationary states since **all physical properties are constant in time** for stationary states.

9.2 Dynamics of an arbitrary state

Moving on to an arbitrary initial state $\Psi(x, 0)$, we saw in the previous section that we can always express this as a superposition of energy eigenstates. In particular, it is always possible to write

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n u_n(x), \quad (9.4)$$

where the **amplitude** to have energy E_n is

$$c_n = \int_{-\infty}^{\infty} u_n^*(x) \Psi(x, 0) dx. \quad (9.5)$$

It is now that we once again apply the **superposition principle**: Since we know how each energy eigenstate evolves, **the evolution of the superposition is precisely the superposition of the evolution**, that is

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n e^{-iE_n t/\hbar} u_n(x). \quad (9.6)$$

As we have stressed before, remarkably we **are simply able to write down the solution** once we have expressed the wavefunction at $t = 0$ as a superposition of energy eigenstates. This is precisely the reason why the energy eigenstates are so important. The above formula shows that all of the hard calculational work that needs to be done in quantum mechanics is in **finding the energy eigenstates and energy eigenvalues** for a given potential $V(x)$. Once this has been done, by writing an arbitrary initial state as a superposition of energy eigenstates, writing down how this state evolves in time is immediate.

We can express the above in a slightly different way, which makes the analogy between the energy amplitudes c_n , the spatial amplitudes $\Psi(x, t)$ and the momentum amplitudes $\tilde{\Psi}(p, t)$ clearer. To do so, we write $c_n = c_n(0)$ as the energy amplitudes at $t = 0$, and realise that we can write

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n(t) u_n(x), \quad (9.7)$$

where

$$c_n(t) = c_n(0) e^{-iE_n t/\hbar} \quad (9.8)$$

Written in this form, it emphasises that at all times $c_n(t)$ is the amplitude for the particle to have energy E_n , and that the amplitudes evolve in a very simple fashion: they accumulate the phase $e^{-iE_n t/\hbar}$ over time. This should be contrasted to both $\Psi(x, t)$, which in general has a (very) complicated relation with $\Psi(x, 0)$, (as given by (4.36) for a free particle), and $\tilde{\Psi}(p, t)$, which also in general has a complicated relationship with $\tilde{\Psi}(p, 0)$.

The reason why the time evolution in terms of the energy amplitudes is much simpler than position and momentum amplitudes is precisely because of the fact that **energy is a constant of motion, whereas the position of the particle is most definitely not a constant of motion, and in general neither is the momentum.**

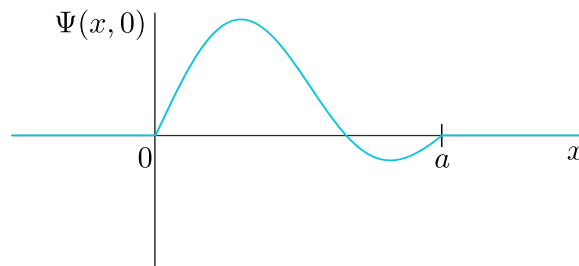
It is most insightful to put the above into context in a simple example.

Example 9.1 — Simple bouncing particle. It is instructive to consider a very simple example, of a particle bouncing back and forth, in order to see how simple superpositions of energy eigenstates evolve in time, and lead to interesting, and in some respects recognisable, dynamics.

Consider the following wavefunction at time $t = 0$,

$$\begin{aligned} \Psi(x, 0) &= \frac{1}{\sqrt{2}} (u_1(x) + u_2(x)), \\ &= \sqrt{\frac{1}{a}} \sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{1}{a}} \sin\left(\frac{2\pi x}{a}\right), \end{aligned} \quad (9.9)$$

for $0 \leq x \leq a$, and $\Psi(x, 0) = 0$ otherwise (i.e. the particle is inside the well, as expected). This wavefunction is a **superposition** of the ground state $u_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$ and the first excited state $u_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$ with equal **real** amplitudes $c_1 = c_2 = \frac{1}{\sqrt{2}}$. The form of the wavefunction is the following:



We see that most of the probability amplitude is on the left-hand side of the well, with a much smaller amount on the right-hand side. We can write down the wavefunction of the particle at time t immediately, since we have already written it as a superposition of energy eigenstates. In particular, the wavefunction is

$$\Psi(x, t) = \sqrt{\frac{1}{a}} e^{-i\hbar\pi^2 t/2Ma^2} \sin\left(\frac{\pi x}{a}\right) + \sqrt{\frac{1}{a}} e^{-2i\hbar\pi^2 t/Ma^2} \sin\left(\frac{2\pi x}{a}\right). \quad (9.10)$$

That is, the first term is simply multiplied by $e^{-iE_1 t/\hbar} = e^{-i\hbar\pi^2 t/2Ma^2}$ and the second term is multiplied by $e^{-iE_2 t/\hbar} = e^{-2i\hbar\pi^2 t/Ma^2}$.

It is most illuminating to look at the **probability density** to find the particle at x at time t , i.e. to look at $P(x, t) = |\Psi(x, t)|^2$. After simplification, we find

$$P(x, t) = \frac{1}{a} \left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{2\pi x}{a}\right) + 2 \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right) \cos\left(\frac{3\hbar\pi^2 t}{2Ma^2}\right) \right] \quad (9.11)$$

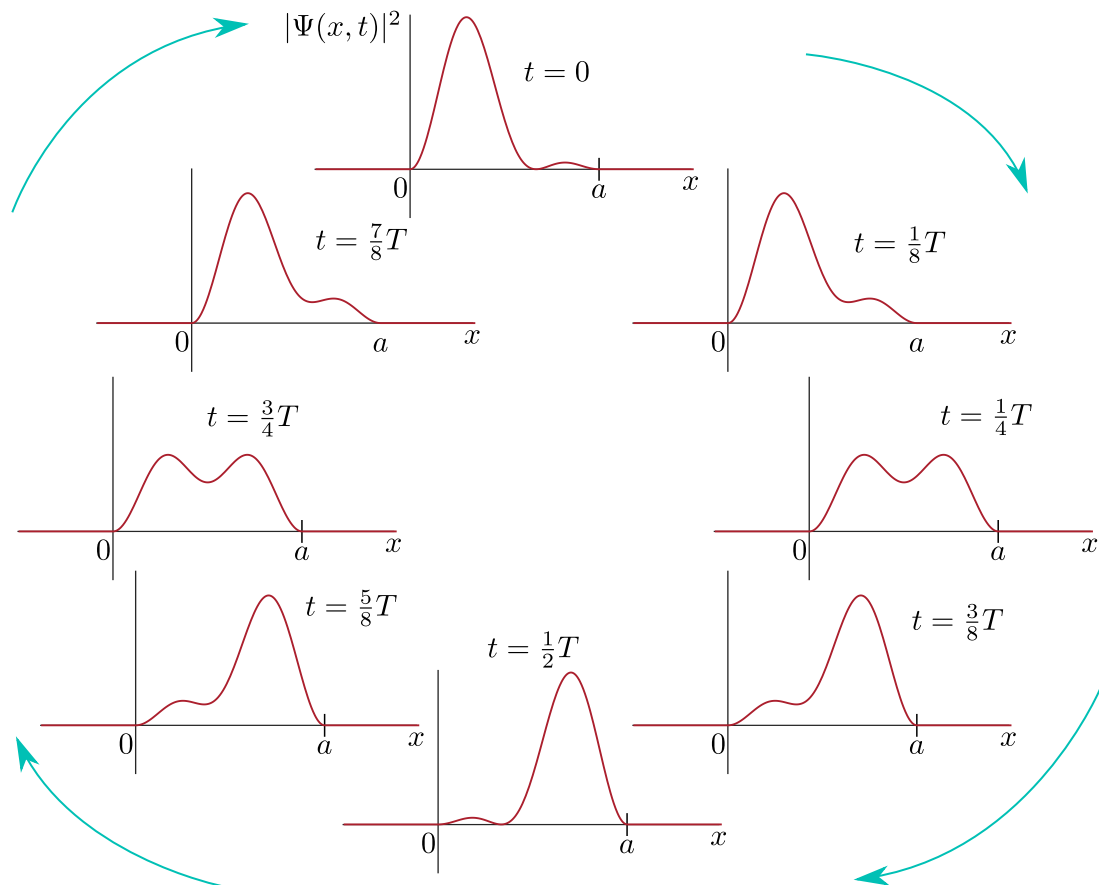
where the final cosine term is $\cos((E_2 - E_1)t/\hbar)$.

The first term is just the probability density for a particle in the ground state, while the second term is just the probability density for a particle in first excited state. Both of these terms are independent of time. What is interesting is the final term, which we call the **interference term**, and is where all the time dependence occurs.

We see furthermore that this interference term has an interesting structure: The spatial profile is constant, and equal to $2 \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi x}{a}\right)$. This is multiplied by a term which depends **only** upon time, and **oscillates** sinusoidally with period

$$T = \frac{2\pi\hbar}{E_2 - E_1} = \frac{4Ma^2}{3\hbar\pi}. \quad (9.12)$$

The motion of the particle is thus oscillatory, and we can sketch the probability density at a number of times within a period to get a feeling for how the particle evolves:



We see that the particle roughly ‘**bounces**’ back and forth between the two walls of the well. Remarkably, this is all generated by the simple interference term.

More general initial states, which are superpositions of more than two energy eigenstates will in general have more intricate dynamics. However, the underlying **mechanism** is the same: there is interference between the different energy eigenstates, and this is what leads to the probability density evolving in time.

10. The Finite Square Well

In the previous two sections we studied a particle confined in an infinite square well potential. This is a highly idealised well, which does not occur in real life. The merit of studying it, however, is that it is relatively simple to analyse, and allowed us to see how discrete energy levels arises. It however missed some crucial general aspects of quantum mechanics.

In this section, we will study a second potential well, which is the **finite square well**. It is still a highly idealised well, but a better physical approximation to the types of forces that can occur in nature. Our focus will be on finding the energy eigenstates and eigenvalues of this well. These are the only aspect that differs compared to the previous section. Once we know the energy eigenstates and eigenvalues, the dynamics of a particle confined to the well are solved in exactly the same way as previously.

We will see here that, unlike for the infinite square well, it is not possible to find exact **analytic** formulas for the energy eigenvalues. Nevertheless, we will see how we can approximately find them graphically, and understand their structure nevertheless. This is in itself an important lesson – almost all real problems in physics cannot be solved exactly. It is important to realise that we can obtain good approximations, and make use of sensible methods, such as graphical ones, to essentially solve the problem to the desired level of detail.

Studying the finite square well will also allow us to see a new and absolutely fundamental feature of quantum mechanics that is not present in the infinite square well: **tunnelling** or **barrier penetration**. In quantum mechanics particles can pass through regions or can be found in places where classically they should never be found or never have been able to reach, as they shouldn't have sufficient energy to be or get there. The importance of tunnelling cannot be understated – it is fundamental to the functioning of transistors, one of the most important inventions of the last century.

10.1 The finite square well potential

We are going to consider a situation where a particle is trapped inside a **finite square well**. That is, we are going to take the potential energy of the particle to be

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a, \\ V_0 & \text{if } x < 0 \text{ or } x > a. \end{cases} \quad (10.1)$$

which is depicted in Fig. 10.1. As you can see, this is closely related to the infinite square well, the only difference now is that outside the well the potential energy is no longer infinite, but takes some value $V_0 > 0$, which is positive, but otherwise arbitrary.

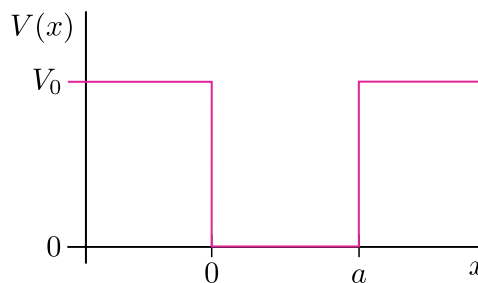


Figure 10.1: **Finite square well**. The potential energy of the finite square well. The potential vanishes for $0 \leq x \leq a$, and is equal to V_0 otherwise.

10.2 Energy eigenstates: bound states

In this section we are going to find the energy eigenstates and eigenvalues of the finite square well. We are however not going to consider **all** eigenstates, but only a subset of them. In particular, we are only going to be interested in solving the time-independent Schrödinger equation for particles that have energies E between 0 and V_0 – that is, only those particles which are **bound inside the well**. We will return in Sec. 12 to study the energy eigenstates when $E > V_0$. Since such particles have more energy than the well, these are **free states**, much like the free particle we studied in Sec. 4, that are not trapped inside the well. As such, their behaviour is fundamentally different to bound states, and this is the reason why we will treat these two situations separately.

Just as for the infinite square well, we consider three distinct regions: to the left of the well; inside the well; and to the right of the well. In each region we need to solve the time-independent Schrödinger equation. We will then use the continuity of the eigenstates and their first derivatives at the boundary between the regions to determine the integration constants, and to find the quantisation condition on the energy. Note that for the infinite square well we only had to use the continuity of the wavefunction, and not the first derivative, since the potential was infinite at the boundary. That is no longer the case here, and we will need to enforce **both** continuity conditions.

In region I, where $x < 0$, the time-independent Schrödinger equation is

$$Eu_I(x) = -\frac{\hbar^2}{2M} \frac{d^2 u_I}{dx^2} + V_0 u_I(x). \quad (10.2)$$

Re-arranging, this is equivalent to

$$\frac{2M(V_0 - E)}{\hbar^2} u_I(x) = \frac{d^2 u_I}{dx^2}. \quad (10.3)$$

At this stage, it is useful to make three new definitions:

$$k^2 = \frac{2ME}{\hbar^2}, \quad k_0^2 = \frac{2MV_0}{\hbar^2}, \quad (10.4)$$

and

$$\zeta^2 = \frac{2M(V_0 - E)}{\hbar^2} = k_0^2 - k^2 \quad (10.5)$$

The definition of k is exactly the same definition we have used previously (in (4.5) in the context of a free particle, and in (8.5) in the context of the infinite square well), and we recognise it as the wavenumber associated to the energy E . k_0 is similar – it is the wavenumber associated with the energy V_0 that characterises the height of the potential well.

Note that since in this section we are only interested in the situation where $E \leq V_0$, such that the particle is bound to the well, we have that $k^2 \leq k_0^2$, and hence $\zeta^2 \geq 0$.

With these definitions, the time-independent Schrödinger equation becomes

$$\zeta^2 u_I(x) = \frac{d^2 u_I}{dx^2}. \quad (10.6)$$

The general solution to this can be written down straightforwardly. It is

$$u_I(x) = Ae^{\zeta x} + Be^{-\zeta x}, \quad (10.7)$$

where A and B are arbitrary constants. This can readily be verified to be a solution.

We saw in Sec. 2.3.1 that the wavefunction must decay at $x = -\infty$ in order to be a normalisable. For this reason, we see that **B must vanish**, otherwise the term in $e^{-\zeta x}$ would diverge to infinity as x tends to $-\infty$. The permissible solution in region I is therefore

$$u_I(x) = Ae^{\zeta x}. \quad (10.8)$$

In Region II, where $0 \leq x \leq a$, the situation is **identical** to the infinite square well: the potential vanishes, and we already solved the time-independent Schrödinger equation in Sec. 8.3. The solution, from (8.6) is

$$u_{II}(x) = C \cos kx + D \sin kx, \quad (10.9)$$

where C and D are two more integration constants.

Finally, region III, where $x > a$, is identical to region I, with constant potential $V = V_0$. The general solution to the time-independent Schrödinger equation is thus identical to before,

$$u_{III}(x) = F e^{\zeta x} + G e^{-\zeta x}, \quad (10.10)$$

with F and G two final constants.

Similarly to region I, we know that the wavefunction must decay to zero at $x = +\infty$ in order to be normalised. This now means that we must take $F = 0$, since $e^{\zeta x}$ diverges as x tends towards infinity. The permissible solution in region III is thus

$$u_{III}(x) = G e^{-\zeta x}. \quad (10.11)$$

10.2.1 Continuity between region I and region II

We now use the fact that energy eigenstates must be continuous and have continuous first derivatives whenever the potential is not infinite, in order to determine the constants A , C , D and G that have appeared in the above solutions. We will start at $x = 0$, i.e. the boundary between region I and region II. We see that

$$u_I(0) = A, \quad u_{II}(0) = C. \quad (10.12)$$

Therefore, in order for the wavefunction to be continuous, **we must set $C = A$** .

Considering the first derivative, we see that

$$\frac{du_I}{dx} = \zeta A e^{\zeta x}, \quad \frac{du_{II}}{dx} = -kA \sin kx + kD \cos kx, \quad (10.13)$$

where we have substituted $C = A$ into the expression for region II. Therefore, at the boundary $x = 0$ we have

$$\left. \frac{du_I}{dx} \right|_{x=0} = \zeta A, \quad \left. \frac{du_{II}}{dx} \right|_{x=0} = kD. \quad (10.14)$$

Therefore, in order to have a continuous first derivative at $x = 0$ we must take

$$D = \frac{\zeta}{k} A. \quad (10.15)$$

We have therefore found that the wavefunction in region II must be given by

$$u_{II}(x) = A \left(\cos kx + \frac{\zeta}{k} \sin kx \right), \quad (10.16)$$

where A is still undetermined.

10.2.2 Continuity between region II and region III

We now use the continuity of energy eigenstates and their first derivative at the boundary between regions II and III at $x = a$, in order to further fix the constants. As before, for the wavefunction we find

$$u_{II}(a) = A \left(\cos ka + \frac{\zeta}{k} \sin ka \right), \quad u_{III}(a) = G e^{-\zeta a}. \quad (10.17)$$

Therefore, to be continuous at $x = a$, we obtain (the more cumbersome) expression

$$G = A \left(\cos ka + \frac{\zeta}{k} \sin ka \right) e^{\zeta a} \quad (10.18)$$

The first derivative in region III is

$$\frac{du_{\text{III}}}{dx} = -\zeta A \left(\cos ka + \frac{\zeta}{k} \sin ka \right) e^{\zeta a} e^{-\zeta x}. \quad (10.19)$$

At the boundary we therefore have

$$\left. \frac{du_{\text{II}}}{dx} \right|_{x=a} = -kA \sin ka + \zeta A \cos ka, \quad \left. \frac{du_{\text{III}}}{dx} \right|_{x=a} = -\zeta A \left(\cos ka + \frac{\zeta}{k} \sin ka \right), \quad (10.20)$$

and so to have continuity we must satisfy the equation

$$-kA \sin ka + \zeta A \cos ka = -\zeta A \left(\cos ka + \frac{\zeta}{k} \sin ka \right). \quad (10.21)$$

The constant A appears in each term. We can cancel it out, as long as it does not vanish. It is straightforward to see that this must in fact be the case, due to normalisation: We have just seen above that in all 3 regions, the wavefunction is proportional to A . If it were to vanish, the wavefunction would therefore vanish everywhere, and we would have the trivial, but unphysical solution $u(x) = 0$ everywhere. We are therefore only interested in situations where $A \neq 0$, and hence can safely cancel it. A is fixed when we want to **normalise** the energy eigenstates, just as for the infinite square well.

After a small amount of re-arrangement, we see that (10.21) can be transformed to

$$\tan ka = \frac{2k\zeta}{k^2 - \zeta^2} \quad (10.22)$$

Finally, we can recall that k and ζ are not independent. In fact, in (10.5) we see that $\zeta^2 = k_0^2 - k^2$, where $k_0^2 = 2MV_0/\hbar^2$ is a constant, determined by the depth of the well and the mass of the particle. We therefore arrive at an equation, solely in terms of a single unknown k ,

$$\tan ka = \frac{2k\sqrt{k_0^2 - k^2}}{2k^2 - k_0^2}. \quad (10.23)$$

Only those values of k that satisfy this equation are allowed values of k : for any other value of k the first derivative of the wavefunction will not be continuous at $x = a$. **This is our quantisation condition for the finite square well.** Just as for the infinite square well, once the allowed values of k are determined, so too are the allowed energies – the energy eigenvalues – since $E = \hbar^2 k^2 / 2M$, as in all previous cases.

10.2.3 Graphically solving the quantisation condition

Unfortunately it is not possible to solve analytically (10.23) for the allowed values of k . This type of equation is known as a **transcendental equation**, and is known not to admit closed form expressions for the solutions. However, this definitely doesn't mean we should stop here, it just means we have to change our expectations for what we can learn. There are now essentially two ways to proceed: the first is to numerically solve (10.23), after fixing specific values for a , m and V_0 ; the second is to look at the solutions **graphically** to obtain a **qualitative** understanding of the solutions. In practice, both methods are often useful in combination. Here we will focus on the latter, since for our purposes all we really want to do is to understand qualitatively the allowed energies, and how they relate to the allowed energies of the infinite square well.

The easiest way to solve (10.23) graphically is to plot the left-hand side and the right-hand side separately, and look for the places where their curves **intersect**. These are precisely the values of k such that the equation is satisfied. This is plotted below:

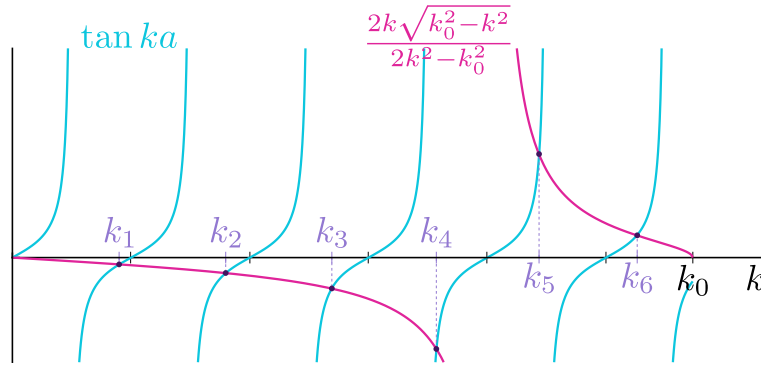


Figure 10.2: **Graphically solving for the allowed values of k .** To solve graphically for the allowed values of k , we plot separately the left-hand and right-hand side of (10.23), and look at the *intersection points*. The values of k at which this happens – which we denote by k_n , are the allowed values of k . In this example, we see that there are 6 intersection points, indicating that the finite square well has 6 allowed energy eigenvalues (equal to $E_n = \hbar^2 k_n^2 / 2M$) less than V_0 (which corresponds to k_0 on the k axis), and accordingly only 6 bound energy eigenstates.

We see that the curves intersect a number of times, and these are the allowed values of k . We will call these intersection points k_n , for $n = 1$ to N , where N is the total number of intersections. We see that there are thus N energy eigenvalues, equal to

$$E_n = \frac{\hbar^2 k_n^2}{2M}. \quad (10.24)$$

The energy levels are plotted in Fig. 10.3, alongside the corresponding levels for the infinite square well, for comparison.

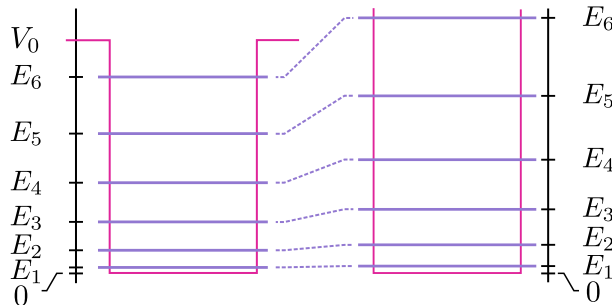


Figure 10.3: **Energy levels of the finite square well.** On the left are the 6 energy levels for the finite square well from Fig. 10.2. On the right are the 6 lowest energy levels of the infinite square well of the same width. In both cases, we plot the well in the background for illustrative purposes. We can see that for the low lying levels (the ground state, and first couple of excited states) there is little change in the energy eigenvalues. However, for higher levels, there is a significant change in the energy levels.

What can we say about the values of k_n ? By being careful, we will see that we can say a fair amount:

- The allowed values k_n are not regularly spaced. However, they still have some regularity about them. If we look carefully at Fig. 10.2, we see that there is **exactly one intersection** between $k = 0$ and $k = \pi/a$ (where $\tan ka = 0$ for the second time), one intersection between $k = \pi/a$ and $k = 2\pi/a$, and so on, up until the value k_0 . The largest allowed value of k for a particle confined to the well cannot be larger than k_0 , which corresponds to an energy $E = V_0$.
- The values $k = n\pi/a$ are exactly the allowed values of k for the infinite square well. We thus see that **all of the allowed energies have decreased** compared to the infinite square well.
- In order to increase the depth of the well we need to increase k_0 . Since the left-hand side (the tangent function) is independent of k_0 , this only has the effect of **stretching** the pink curve, while

leaving the blue curve untouched. We will thus have **more** intersections, and therefore more allowed energies, for a deeper well. This shows that as the well gets deeper, there are more allowed energies, which is reasonable.

- Since the pink curve starts off slightly negative, but close to zero, as we increase k , the first few intersections – i.e. the ground state energy, and energies of the low lying excited states – start to get closer to the values where $\tan ka = 0$. These are the values $n\pi/a$, i.e. the energies of the infinite square well. Therefore, as the well becomes deeper, **the low lying energy levels start to approach the energy levels of the infinite square well**.
- However, for the higher levels, where the pink curve is not close to zero, the intersection points are different. This means that the energy levels close to the top of the potential barrier differ significantly more than the low lying energy levels.

10.2.4 Comparing the eigenstates with those of the infinite square well

Having solved for the allowed energy eigenvalues, it is useful to return to the energy eigenstates $u_n(x)$, and to see what they look like. Before doing so, we should put everything together from Secs. 10.2.1 and 10.2.2, in order to write down a final expression for $u_n(x)$. Collecting everything, the final expression is

$$u_n(x) = \begin{cases} A_n e^{\zeta_n x} & \text{if } x < 0, \\ A_n \left(\cos(k_n x) + \frac{\zeta_n}{k_n} \sin(k_n x) \right) & \text{if } 0 \leq x \leq a, \\ A_n \left(\cos(k_n a) + \frac{\zeta_n}{k_n} \sin(k_n a) \right) e^{\zeta_n (a-x)} & \text{if } x > a, \end{cases} \quad (10.25)$$

where $\zeta_n = \sqrt{k_0^2 - k_n^2}$, and where A_n is the **normalisation constant** that needs to be calculated, and is in general complicated. Written in this form, the energy eigenstates appear complicated, however, this hides the fact that they are in fact **very similar** to the eigenstates of the infinite square well. This is best demonstrated by plotting the solutions. We do this below in Fig. 10.4 and Fig. 10.5 for V_0 finite, as well as for the infinite square well ($V_0 = \infty$) eigenstates. As we can see, the eigenstates are **qualitatively very similar** to the eigenstates of the infinite square well.

The main difference is that while for the infinite square well for all energy eigenstates the wavefunction vanishes at the edge of the well at $x = 0$ and $x = a$, and is zero everywhere outside the well, that is no longer the case for the finite square well. Now we find that the wavefunction does not vanish at $x = 0$ and $x = a$, but **decays exponentially** as we move into the barrier in either direction. This is in fact an extremely surprising and important aspect of quantum mechanics, as we discuss below.

10.3 Tunnelling and barrier penetration

The fact that the wavefunction does not vanish outside the well means that there is non-zero probability density to find the particle at positions $x < 0$ or $x > a$. This probability density decays exponentially with distance as we move away from the well.

This is surprising, since if the particle is at any position $x < 0$ or $x > a$, then its potential energy is $V(x) = V_0$. However, we only looked for solutions to the time-independent Schrödinger equation when the total energy of the particle is $E_n \leq V_0$. That is, **the total energy of the particle is less than the potential energy!** In classical physics in order for the particle to be in this region it would need to have negative kinetic energy, which is impossible, and hence this region is “**forbidden**”. How then can it be that the particle is in this forbidden region? This is indeed one of the mysteries of quantum mechanics – particles can **penetrate** or **tunnel** into regions that they should not be allowed to be in from the perspective of energy conservation.

! Some texts like to make a distinction between **tunnelling** and **barrier penetration**. They use the former to refer to situations where a particle passes through a forbidden region, i.e. passes through a potential ‘wall’ and escapes to the other side, and use the latter to refer to situations where the particle can be found in the forbidden region, i.e. within the wall itself. In truth, these are one and

the same effect, and merely two different aspects of it. For that reason, I will use the terminology ‘tunneling’ in both situations – i.e. to also refer to situations where a particle penetrates into a wall, since I want it to be clear that this is the same effect.

For the infinite square well we did not see tunnelling, because the well was so deep that the decay of the wavefunction was infinitely fast. It is important to stress that **tunnelling is a completely generic feature of quantum mechanics** and it is only for the infinite square well where this effect is completely suppressed.

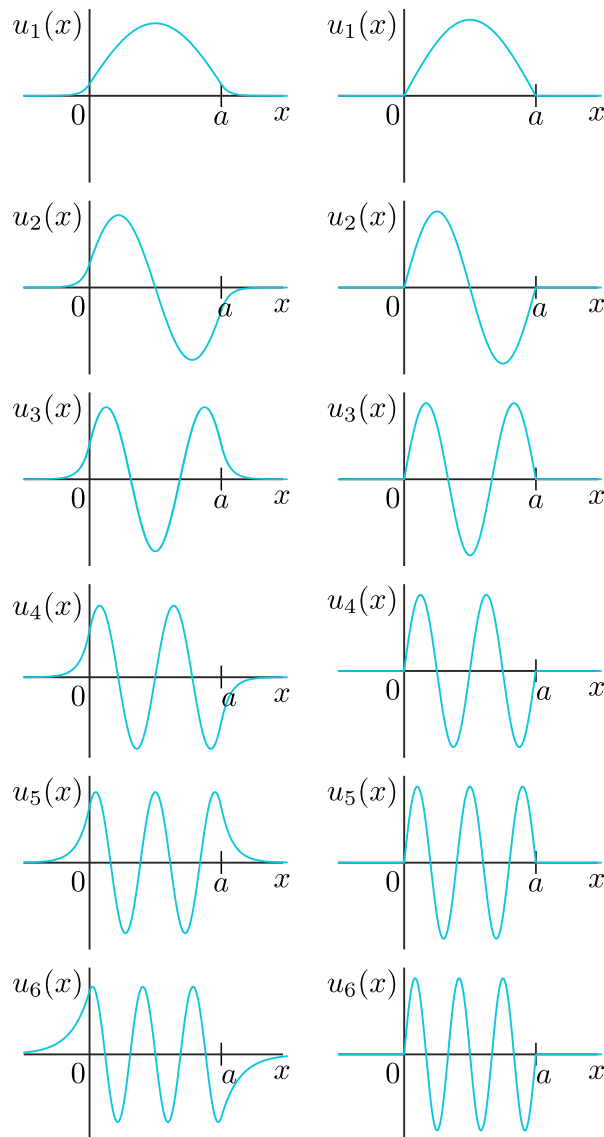


Figure 10.4: **Wavefunctions of energy eigenstates for the finite square well.** On the left are the wavefunctions for the 6 energy levels for the finite square well from Fig. 10.2. On the right are the 6 corresponding wavefunctions for the infinite square well of the same width. We can see that for the low lying levels (the ground state, and first couple of excited states) there is a small amount of tunneling into the classically-forbidden region, while for larger energy levels the amount of tunneling becomes significant, and hence the difference with the infinite square well is more noticeable.

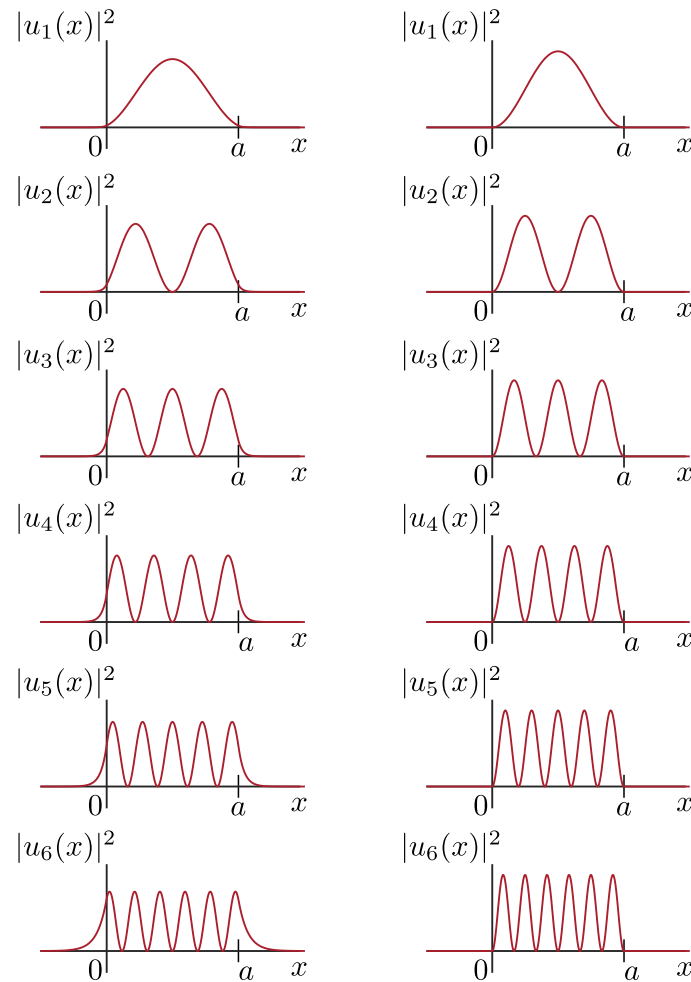


Figure 10.5: **Probability densities for the finite square well.** On the left are the probability densities for the 6 energy levels for the finite square well from Fig. 10.2. On the right are the 6 corresponding probability densities for the infinite square well of the same width. We can see that for the low lying levels (the ground state, and first couple of excited states) there is a small amount of tunneling into the classically-forbidden region, while for larger energy levels the amount of tunneling becomes significant, and hence the difference with the infinite square well is more noticeable.

11. The Quantum Harmonic Oscillator

We now turn our attention to arguably the most important system in all of quantum mechanics – the quantum harmonic oscillator. Here we will study the quantum mechanics of a particle whose force is of the form $F(x) = -kx$. That is, a restorative force proportional to the displacement from the origin. We know that in classical mechanics systems with such forces lead to simple harmonic motion. Our goal now is to understand the quantum mechanics of such systems.

Why is this one of the most important systems to study? The first reason is that it provides an approximation to the behaviour of **almost all** potential wells, as we outline briefly below. Second, you will see later in your degree that the quantum harmonic oscillator pops up in a huge range of situations, from describing light in quantum field theory, to describing phonons in condensed matter physics and far beyond.

In this section we will also learn a couple of general lessons about solving physics problems. First, we will use **dimensionless co-ordinates**, which is a useful way of simplifying equations, and also helps to bring out their underlying structure. We will then study the behaviour of the quantum harmonic oscillator **far from the centre of force**, to see how a particle behaves approximately when the force has become very large. Finally, instead of solving head on, we will use a bit of **trial and error** and see that it can lead us to a complete solution.

11.1 Approximation of an arbitrary potential well

Imagine a situation where a particle is acted on by a conservative force $F(x)$, with associated potential energy $V(x)$. Let us assume that this force wants to push the particle back to a position x_0 . An example is depicted in Fig. 11.1.

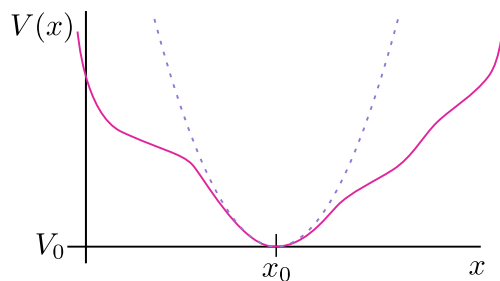


Figure 11.1: **Harmonic approximation for the bottom of an arbitrary potential well.** The solid curve depicts the potential energy of an arbitrary potential well. The dotted curve depicts the leading approximation to the well, which is seen to be accurate for small displacements about the bottom (i.e. for x close to x_0). This leading approximation is a harmonic oscillator, of the form $V(x) \approx \frac{1}{2}kx^2$.

We would like to look at **the form of the potential when the particle is close to the bottom of the well**. In order to do so, we can **expand** the potential energy around the bottom, to obtain

$$V(x) \approx V_0 + \left. \frac{dV}{dx} \right|_{x_0} (x - x_0) + \frac{1}{2} \left. \frac{d^2V}{dx^2} \right|_{x_0} (x - x_0)^2 \quad (11.1)$$

where $V_0 = V(x_0)$.

At $x = x_0$, the bottom of the well, the first derivative of the potential vanishes, $\left. \frac{dV}{dx} \right|_{x_0} = 0$, since the bottom is, by definition, a **turning point**. Thus, to leading order, the potential will be approximately

$$V(x) \approx V_0 + \frac{1}{2} \left. \frac{d^2V}{dx^2} \right|_{x_0} (x - x_0)^2. \quad (11.2)$$

We can finally make two simplifications without loss of generality: First, we can **redefine the zero of the energy scale**, so that $V_0 = V(x_0) = 0$. Second, we can change our co-ordinate so that the bottom of the well corresponds to $x_0 = 0$. With these two simplifications, we arrive at

$$V(x) \approx \frac{1}{2} \frac{d^2V}{dx^2} \Big|_0 x^2 \quad (11.3)$$

If we call $k = \frac{d^2V(x)}{dx^2} \Big|_0$, then we arrive precisely at the potential energy $V(x) = \frac{1}{2}kx^2$ associated to the force $F(x) = -kx$, through $F(x) = -dV/dx$.

This shows that the harmonic oscillator is the leading-order approximation to any potential well in the vicinity of the bottom of the well. It means that if the particle is not too far from $x_0 = 0$, then the force it experiences (and the potential energy it will have) will be essentially indistinguishable from the linear force of simple harmonic motion.

This region of small x is precisely the region that is explored classically by a particle with low energy. It is thus reasonable to assume that for low energies, all systems behave roughly like the harmonic oscillator, and that this is also true in quantum mechanics. Hence, by solving the quantum mechanics of a harmonic oscillator, we hope to obtain an approximation to the quantum mechanics of any particle trapped in a potential well.

❗ *The only caveat to the above is when d^2V/dx^2 vanishes. In this case, we need to go to higher-order derivatives in order to find the leading-order approximation to the potential well, and the behaviour will not be well approximated by the harmonic oscillator. The square well is precisely a potential of this kind – at the bottom of the well **all derivatives d^nV/dx^n vanish**. However, this indicates that there is no force on the particle whatsoever, which is a very special situation. In general, it will be the case that d^2V/dx^2 does not vanish, and that the leading-order behaviour is well approximated by the harmonic oscillator.*

11.2 The quantum harmonic oscillator potential

For the classical harmonic oscillator, the relation between the **spring-constant** k , the **mass** M and **angular frequency** ω is $\omega = \sqrt{k/M}$. For this reason, it is customary to write $k = M\omega^2$ and take the definition of the harmonic oscillator potential to be

$$V(x) = \frac{1}{2}M\omega^2x^2. \quad (11.4)$$

This is depicted below in Fig. 11.2.

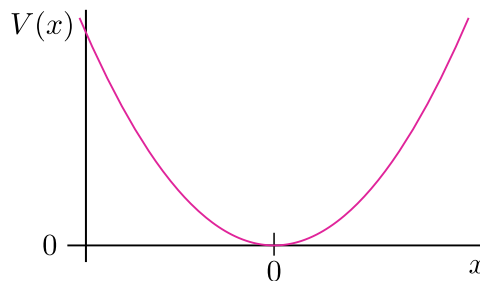


Figure 11.2: **Harmonic oscillator potential.** The potential energy of the harmonic oscillator.

11.3 Dimensionless co-ordinates

The time-independent Schrödinger equation for the quantum harmonic oscillator is

$$Eu(x) = -\frac{\hbar^2}{2M} \frac{d^2u}{dx^2} + \frac{1}{2}M\omega^2 x^2 u(x). \quad (11.5)$$

There are a lot of constants floating around in this equation, which can easily get confused, and to some extent obscure the form of the equation. A general method to deal with this is to **define new dimensionless co-ordinates**, which generally help to ‘clean-up’ the equation.

We would therefore like to find a new co-ordinate y , that is dimensionless. In order to do so, we need to find a combination of physical quantities that together have the units of length, which we will call a . If we can do so, then a will define a **natural length scale** for the system, and we can measure the physical distance x in multiples of this length scale a .

The dimensionful quantities that we have, and their dimensions, are

$$\text{mass of the particle : } M \quad [M] = \text{M}, \quad (11.6a)$$

$$\text{angular frequency : } \omega \quad [\omega] = \text{T}^{-1}, \quad (11.6b)$$

$$\text{Reduced Planck constant : } \hbar \quad [\hbar] = \text{ML}^2\text{T}^{-1}. \quad (11.6c)$$

In the problem sheet, you will show that

$$a = \sqrt{\frac{\hbar}{M\omega}} \text{ has the units of length, i.e. } [a] = \text{L}. \quad (11.7)$$

Therefore, we will introduce a dimensionless co-ordinate

$$y = \frac{x}{a} = \sqrt{\frac{M\omega}{\hbar}} x. \quad (11.8)$$

We can then re-write the time-independent Schrödinger equation in the variable y instead of x , which gives

$$\frac{d^2u}{dy^2} = (y^2 - \mathcal{E})u(y), \quad (11.9)$$

where

$$\mathcal{E} = \frac{2E}{\hbar\omega} \quad (11.10)$$

is a dimensionless energy, measuring energy in multiples of $\hbar\omega/2$, which has units of energy, as does E . All of the above is carried out as an exercise in the Problem sheet 3.

11.4 Behaviour far from the force centre

The time-independent Schrödinger equation for the harmonic oscillator potential is not as straightforward to solve as in the previous examples. Whereas for the finite square well solutions in the three regions could be readily written down, we are going to have to work a little harder to get to a position where we can find solutions now.

In order to make progress, the first step we can take is to **try and find a solution which is valid for large values of y** . That is, we are going to try and find the form of the energy eigenstates **far from the bottom of the well**. Classically, if the total energy of the particle is fixed at E , then there is a maximum distance that the particle can be from the origin: It can only make it to the point where all of its energy is potential energy, and therefore its kinetic energy becomes zero. Such as points are known as the **classical turning-points**.

We saw in the previous section that in quantum mechanics particles can **tunnel** into this forbidden region. Therefore, if we go far enough away from the centre of force for a fixed energy E , then we expect

that the wavefunction should decay towards zero, just like the decay in the forbidden region of the finite square well.

Mathematically, when $y \gg 1$, we see that an **approximate** form of the time-independent Schrödinger equation is

$$\frac{d^2 u}{dy^2} = y^2 u(y). \quad (11.11)$$

That is, we neglect \mathcal{E} compared to y^2 , since the latter is very large, while \mathcal{E} is constant. On the right-hand side, if the y^2 that multiplies $u(y)$ would have been a constant c^2 (and not the dimensionless position), then this equation would have been easy to solve: the solutions would have been e^{cy} and e^{-cy} . Maybe we can try to get some intuition, and set $c = y$ in these solutions, and guess that a solution could be of the form e^{y^2} or e^{-y^2} . Let us tentatively proceed, and calculate the derivatives:

$$\begin{aligned} \frac{d}{dy} e^{y^2} &= 2y e^{y^2}, & \frac{d}{dy} e^{-y^2} &= -2y e^{-y^2}, \\ \frac{d^2}{dy^2} e^{y^2} &= 2e^{y^2} + 4y^2 e^{y^2}, & \frac{d^2}{dy^2} e^{-y^2} &= -2e^{-y^2} + 4y^2 e^{-y^2}. \end{aligned} \quad (11.12)$$

Remember that we are interested in solutions **for large values of y** . Therefore, just as we approximated the time-independent Schrödinger equation, we should also approximate the second derivatives of e^{y^2} and e^{-y^2} . In particular,

$$\frac{d^2}{dy^2} e^{y^2} \approx 4y^2 e^{y^2}, \quad \frac{d^2}{dy^2} e^{-y^2} \approx 4y^2 e^{-y^2}. \quad (11.13)$$

We are very close to obtaining what we want: for this to be an approximate solution, we need that $\frac{d^2 u}{dy^2} \approx y^2 u(y)$, however what we have obtained is $\frac{d^2 u}{dy^2} \approx 4y^2 u(y)$. We can however easily take care of this unwanted factor of 4, by considering instead $e^{\frac{1}{2}y^2}$ and $e^{-\frac{1}{2}y^2}$. Then we find

$$\frac{d^2}{dy^2} e^{\frac{1}{2}y^2} \approx y^2 e^{\frac{1}{2}y^2}, \quad \frac{d^2}{dy^2} e^{-\frac{1}{2}y^2} \approx y^2 e^{-\frac{1}{2}y^2}, \quad (11.14)$$

just as we want. Therefore, what we have shown is that the two functions $e^{\frac{1}{2}y^2}$ and $e^{-\frac{1}{2}y^2}$ are **approximate solutions** to the time-independent Schrödinger equation when $y \gg 1$.

Since physically permissible solutions must decay towards zero as $y \rightarrow \infty$, we see that $e^{\frac{1}{2}y^2}$ is impermissible, and thus the form of the wavefunction of energy eigenstates for large values of y must be

$$u(y) = A e^{-\frac{1}{2}y^2}. \quad (11.15)$$

This is precisely a **Gaussian**-type decay. Whereas for the infinite square well, where the potential energy was constant and equal to V_0 outside the well, and where the wavefunctions of the energy eigenstates decayed exponentially as $e^{-\zeta x}$, now for the harmonic oscillator, where the potential energy increases as we move further away from the origin, the decay is even faster, now like $e^{-\frac{1}{2}y^2}$.

What have we learnt: We now know that no matter the energy E , and no matter the form of the wavefunction close to the origin, for large values of y , the wavefunction must be like a Gaussian function. This means that we are going to search for wavefunctions of the form

$$u(y) = v(y) e^{-\frac{1}{2}y^2}, \quad (11.16)$$

where $v(y)$ is some function which we don't know much about. All we know is that for large values of y we want it not to vary quickly compared to $e^{-\frac{1}{2}y^2}$, such that altogether $u(x)$ has the correct behaviour.

11.5 The ground state

After solving the infinite square well, we covered some of the general properties of energy eigenstates in Section 8.3.3. One of these properties was that the **number of nodes increases as the energy increases** and that **the ground state wavefunction has no nodes**.

Although in the above we were only looking for the form of the wavefunction at large y , since it has no nodes, it is advantageous to check whether it might in fact solve the time-independent Schrödinger equation **for all** y , and not just for large y . We see that if $u(y) = Ae^{-\frac{1}{2}y^2}$, then

$$\frac{d^2u}{dy^2} = (y^2 - 1)u(y), \quad (11.17)$$

and so it indeed solves the time-independent Schrödinger equation (11.9) with

$$\mathcal{E} = 1. \quad (11.18)$$

Since this is a solution, and since it has no nodes, we know immediately that **we have just found the ground-state of the quantum harmonic oscillator**. If we go back to the physical co-ordinate $x = ay$ and energy $E = \hbar\omega\mathcal{E}/2$, we see that the ground state wavefunction, which we will denote by $u_0(x)$ is

$$u_0(x) = Ae^{-x^2/2a^2} = Ae^{-M\omega x^2/2\hbar}, \quad (11.19)$$

with energy eigenvalue

$$E_0 = \frac{1}{2}\hbar\omega. \quad (11.20)$$

! Somewhat confusingly, for the harmonic oscillator we are going to count the energy levels starting from $n = 0$ instead of from $n = 1$. I am not making this choice in order to confuse you – I am making this choice since it is in line with all of the major textbooks, just as all of the major textbooks take $n = 1$ for the ground state of the infinite and finite square wells. I can only apologise for this strange inconsistency, which is used solely so that the formulas in each case are ‘nice’.

The constant A is the normalisation constant, fixed as always by requiring that the total probability to find the particle somewhere is one. In the problem sheet you will show that the normalised wavefunction is

$$u_0(x) = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} e^{-x^2/2a^2}. \quad (11.21)$$

11.6 The first excited state

We just saw that the Gaussian solves the time-independent Schrödinger equation, and was a good **guess** for a solution. Looking at the form (11.16), we see that the Gaussian corresponds to $v(y) = 1$, i.e. the constant function. This is arguably the **simplest** function we could have thought of for $v(y)$.

We are therefore going to try and make further progress by asking ourselves what is the **next simplest** choice of function $v(y)$. Before doing so, we are going to recall one further general property of energy eigenstates that we saw in Section 8.3.3: The wavefunctions of the energy eigenstates are **alternatively odd and even about the centre of the well whenever the potential is symmetric**. In our case, the centre of the well is at $x = 0$, and indeed it is symmetric about the line $x = 0$. The ground state $u_0(x)$ is an even function (around the centre), as expected, and so for the first excited state we are now looking to form an **odd** function.

If we remember that the product of an odd function and an even function is odd, this shows that we are looking for **the simplest odd function** $v(y)$ that we can multiply the Gaussian by, in order to create an

overall odd wavefunction $u(y) = v(y)e^{-\frac{1}{2}y^2}$. The simplest choice we can take is $v(y) = Ay$. Let us see if this could indeed form a solution:

$$\frac{d}{dy} \left(Aye^{-\frac{1}{2}y^2} \right) = Ae^{-\frac{1}{2}y^2} - Ay^2e^{-\frac{1}{2}y^2}, \quad (11.22a)$$

$$\begin{aligned} \frac{d^2}{dy^2} \left(Aye^{-\frac{1}{2}y^2} \right) &= -Aye^{-\frac{1}{2}y^2} - 2Aye^{-\frac{1}{2}y^2} + Ay^3e^{-\frac{1}{2}y^2}, \\ &= (y^2 - 3)Aye^{-\frac{1}{2}y^2}. \end{aligned} \quad (11.22b)$$

Looking at the time-independent Schrödinger equations (11.9), we see that we have again obtained a solution, now with $\mathcal{E} = 3$. Moreover, this function has exactly one node at $y = 0$. This shows that it **must be the first excited state**. After normalising the wavefunction (i.e. finding A), which you will do as an exercise in the problem sheet, and expressed in terms of the physical co-ordinate x , we have just shown that the first excited state of the harmonic oscillator is

$$u_1(x) = \left(\frac{2}{a\sqrt{\pi}} \right)^{1/2} \left(\frac{x}{a} \right) e^{-x^2/2a^2}. \quad (11.23)$$

with energy

$$E_1 = \frac{3}{2}\hbar\omega. \quad (11.24)$$

11.7 The second excited state

We will consider one more case explicitly, before drawing some general conclusions. Let us now see if we can find the second excited state. Just as previously, we would like to make an educated guess for a function $v(y)$. We now need this to be an **even** function, so that the wavefunction $u(y) = v(y)e^{-\frac{1}{2}y^2}$ is even. We also need it to have precisely two nodes to be the second excited state.

In order to be even, and have only two nodes, a guess at a function would be

$$\begin{aligned} v(y) &= A(y - b)(y + b), \\ &= A(y^2 - b^2), \end{aligned} \quad (11.25)$$

where A and b are unknown constants. This function has nodes at $y = b$ and $y = -b$, and is even. Let us see if this may also give us a solution:

$$\begin{aligned} \frac{d}{dy} \left(A(y^2 - b^2)e^{-\frac{1}{2}y^2} \right) &= 2Aye^{-\frac{1}{2}y^2} - Ay(y^2 - b^2)e^{-\frac{1}{2}y^2}, \\ &= A[(2 + b^2)y - y^3]e^{-\frac{1}{2}y^2} \end{aligned} \quad (11.26a)$$

$$\begin{aligned} \frac{d^2}{dy^2} \left(A(y^2 - b^2)e^{-\frac{1}{2}y^2} \right) &= A[(2 + b^2) - 3y^2]e^{-\frac{1}{2}y^2} - A[(2 + b^2)y - y^3]ye^{-\frac{1}{2}y^2} \\ &= A[(2 + b^2) - (5 + b^2)y^2 + y^4]e^{-\frac{1}{2}y^2}. \end{aligned} \quad (11.26b)$$

In order for this to be a solution, we need it to be equal to

$$(y^2 - \mathcal{E})A(y^2 - b^2)e^{-\frac{1}{2}y^2} \quad (11.27)$$

for some constants \mathcal{E} , A , and b . We see that both sides are again proportional to A , as we should expect by now, since A will again be the normalisation constant, and that both sides are proportional to $e^{-\frac{1}{2}y^2}$. Therefore, cancelling these terms on both sides, we need to try and see if we can solve the equation

$$(2 + b^2) - (5 + b^2)y^2 + y^4 = (y^2 - \mathcal{E})(y^2 - b^2) \quad (11.28)$$

Expanding out the right-hand side, we have

$$(2 + b^2) - (5 + b^2)y^2 + y^4 = y^4 - (\mathcal{E} + b^2)y^2 + \mathcal{E}b^2 \quad (11.29)$$

Since we want this equation to hold **for all values of y** , we can equate the coefficients of the different powers of y . We therefore obtain the equations

$$2 + b^2 = \mathcal{E}b^2, \quad (11.30a)$$

$$5 + b^2 = \mathcal{E} + b^2, \quad (11.30b)$$

The second equation shows immediately that

$$\mathcal{E} = 5,$$

and substituting this into the first, that

$$b^2 = \frac{1}{2}.$$

Therefore, once again we have found a solution to the time-independent Schrödinger equation. This solution has 2 nodes, and thus corresponds to the second excited state (third energy level). After normalising the wavefunction, and writing it in terms of the physical co-ordinate, the second excited state is

$$u_2(x) = \left(\frac{2}{a\sqrt{\pi}}\right)^{1/2} \left(\frac{x^2}{a^2} - \frac{1}{2}\right) e^{-x^2/2a^2}, \quad (11.31)$$

corresponding to energy

$$E_2 = \frac{5}{2}\hbar\omega. \quad (11.32)$$

The procedure for the second excited state was a little more involved than for the first excited state, since now we had an unknown parameter b that we needed to find. Nevertheless, we saw that we were able to do so, and find a solution.

As a final exercise, in Problem Sheet 3 you will find $u_3(x)$, the third excited state, which will follow the same procedure as for the second excited state. In particular, you will show that a sensible guess is $v(y) = Ay(y - c)(y + c)$, which is an odd function with 3 nodes. You will solve for c , to obtain the third excited state, and show that the corresponding energy eigenvalue is $E_3 = \frac{7}{2}\hbar\omega$.

11.8 General energy eigenstates and eigenvalues

The above construction can be carried on indefinitely, and in fact leads to **all energy eigenstates of the quantum harmonic oscillator**. The wavefunctions of all energy eigenstates take the form

$$u_n(x) = A_n v_n\left(\frac{x}{a}\right) e^{-x^2/2a^2}, \quad (11.33)$$

where A_n is the normalisation constant, which ensures that the total probability density to find the particle somewhere is one, and $v_n(y)$ is a **degree- n polynomial** which are alternatively **even** and **odd**, meaning that they only contain even powers of y or odd powers of y .

These polynomials are known as the **Hermite polynomials** and were in fact discovered long before quantum mechanics. You can find a complete treatment of Hermite polynomials in almost all textbooks on quantum mechanics, and in almost all textbooks on mathematical methods for physicists. As far as this course is concerned, it is useful for you to know that these polynomials have a name, so that you recognise them when you see them in other contexts, however we will not delve further into their properties.

In Table 11.1 we list the first few Hermite polynomials for reference, and the associated wavefunctions.

The wavefunctions and corresponding probability densities of the first few energy eigenstates are plotted in Fig. 11.3 and Fig. 11.4 respectively.

The energy levels of the quantum harmonic oscillator are

n	Hermite polynomial $v_n(y)$	Wavefunction $u_n(x)$
0	1	$\left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} e^{-x^2/2a^2}$
1	$2y$	$\left(\frac{2}{a\sqrt{\pi}}\right)^{1/2} \left(\frac{x}{a}\right) e^{-x^2/2a^2}$
2	$4y^2 - 2$	$\left(\frac{2}{a\sqrt{\pi}}\right)^{1/2} \left(\frac{x^2}{a^2} - \frac{1}{2}\right) e^{-x^2/2a^2}$
3	$8y^3 - 12y$	$2\left(\frac{1}{3a\sqrt{\pi}}\right)^{1/2} \frac{x}{a} \left(\frac{x^2}{a^2} - \frac{3}{2}\right) e^{-x^2/2a^2}$

Table 11.1: **Hermite polynomials and normalised energy eigenstates of the harmonic oscillator.** We give here the first 4 Hermite polynomials, and the corresponding normalised wavefunctions of the energy eigenstates of the quantum harmonic oscillator.

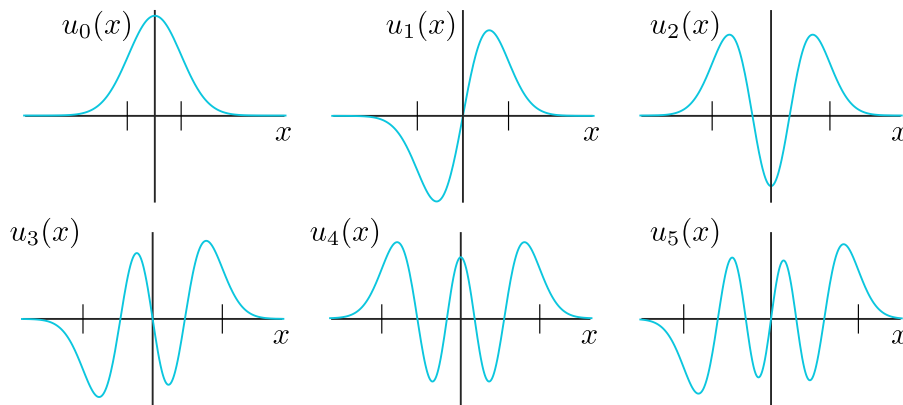


Figure 11.3: **Wavefunctions of energy eigenstates of the harmonic oscillator.** The first six energy eigenstates $u_n(x)$ of the harmonic oscillator. The two markers on the x axis show where tunnelling starts: the classically-allowed region is between the markers, where the total energy of the particle is more than the potential.

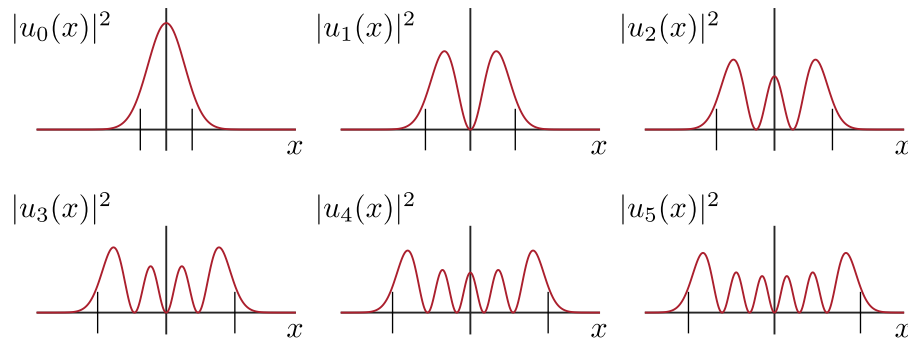


Figure 11.4: **Probability densities of the eigenstates of the harmonic oscillator.** The probability densities for finding the particle at x for the first six energy eigenstates of the harmonic oscillator. The markers again indicate where tunnelling starts.

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (11.34)$$

That is, the ground state energy is $E_0 = \frac{1}{2}\hbar\omega$, and this is the **zero-point energy**, which we encountered for the infinite square well in Sec. 8.3.3. As in all cases, it arises due to the uncertainty principle, since the particle cannot simultaneously be stationary and at the bottom of the well.

Interestingly, we see that the energy levels of the quantum harmonic oscillator are **much denser** than the energy levels of the infinite and finite square well. For the infinite square well we saw that the

energy levels are proportional to n^2 , and for the finite square well we saw that this behaviour is basically unchanged towards the bottom of the well. This means that **the spacing between energy levels increases with energy**.

For the harmonic oscillator, the energies are proportional to n , and hence **the spacing between the levels is constant**, and always equal to $\hbar\omega$.

12. Scattering

When we studied the finite square well, we restricted our attention to finding the energy eigenstates for energies E **less than the depth of the well** V_0 . In this section we would like to understand what happens when we consider energies E larger than the depth of the well. Before doing this, we will first analyse in detail a simpler situation, known as a **potential step**. This contains the important physical effects, while avoiding some complications. We will then return to the finite well at the end of this section.

12.1 Scattering

It will be useful to start by looking a bit more carefully at what we already learnt for the finite square well for $E \leq V_0$. All we asked was that the energy be less than the depth of the well, and from this alone we found the wavefunctions of the energy eigenstates. These are depicted in Fig. 11.3. What we see is that the particle is **essentially confined to the well**. We found a new quantum effect – **quantum tunneling** – whereby, remarkably, the particle can be found outside the well. However, almost all of the probability to find the particle is inside the well, and the probability to find the particle outside drops off exponentially fast in the distance from the well.

This means that if we consider any wavefunction $\Psi(x)$ that has a superposition of energies $E_n \leq V_0$ that the particle will be confined to the well. This is perfectly in line with our classical expectations: classically, if the energy of the particle is low enough, the only places it could possibly be found are inside the well.

With this in mind, we now want to turn our attention to situations where $\Psi(x)$ has an arbitrary superposition of energies, even those larger than V_0 . Classically, if a particle has more energy than the depth of the well, then it can be found outside the well also. That is, the particle will behave like a **free** particle, as we studied in Sec. 4. For example, a particle with energy E and velocity v would travel towards the well, speed up inside the well to velocity $v' > v$ and then slow back down to the initial velocity once it has passed the well, as depicted schematically below in Fig. 12.1

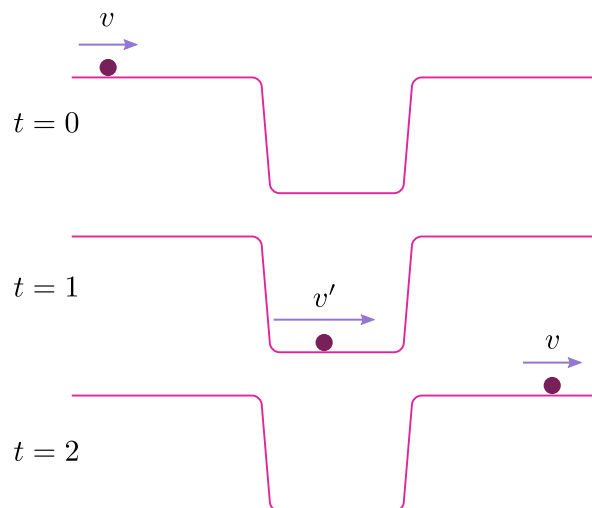


Figure 12.1: **Classical particle passing a potential well.** Classically, if a particle approaches a well, it will fall into it and speed up, converting potential energy into kinetic energy, and then slow down as it leaves the well, to return to its original velocity.

Quantum mechanically we may expect the situation to be somewhat similar. The key point however is that the energy eigenstates for $E > V_0$, just like for a free particle, should now **extend over all space**,

since the particle should not be confined to the well, like when $E < V_0$.

There is however one **new important phenomena** which does not arise in classical mechanics. In quantum mechanics, when a particle enters a region where the potential changes very **rapidly** – either increasing or decreasing abruptly – there is **always** a probability amplitude for the particle to be **reflected** by the potential. Crucially, this is independent of the energy change. In classical mechanics, this would correspond, for example, to a particle approaching a cliff, and bouncing off of it! We call this effect **scattering**.

Quantum scattering is almost the complete **opposite** of quantum tunnelling: whereas in quantum tunnelling particles enter regions that classically they don't have enough energy to enter, in quantum scattering particles fail to enter regions that they do have enough energy to enter.

This is the main new physical effect that arises, which we need to understand in order to properly understand the quantum mechanics of a particle with more energy than a potential well. We therefore start by considering the simplest situation where quantum scattering occurs, namely the **finite step**.

12.2 The finite step potential

Consider the following potential function

$$V(x) = \begin{cases} 0 & \text{if } x < 0, \\ V_0 & \text{if } x \geq 0. \end{cases} \quad (12.1)$$

depicted in Fig. 12.2. This corresponds to an abrupt change in potential from $V(x) = 0$ to $V(x) = V_0$ at the origin. Our goal is to find the energy eigenstates for this potential well when $E > V_0$, by solving the time-independent Schrödinger equation, and to analyse them physically.

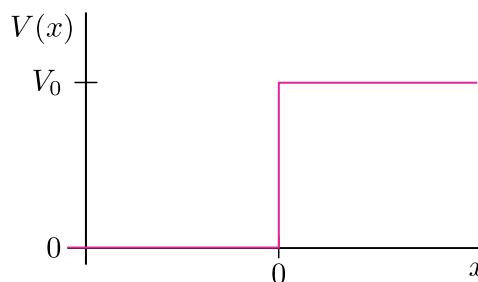


Figure 12.2: **The potential step**. The potential energy vanishes for $x < 0$, and is equal to V_0 for $x \geq 0$.

12.3 Energy eigenstates

In order to find the energy eigenstates we will use our previous understanding from both the free particle, and from the finite square well. On the one hand, for the potential step, it is clear that the particle is not bound, and therefore the situation is very similar to the free particle of Sec. 4. We therefore expect, just like there, that the energy eigenstates **will be unnormalisable** wavefunctions. However, also just like for the free particle, we will ultimately be interested in considering how **wavepackets** evolve in time, and we should expect (rightly so) that we can form **normalised wavepackets** out of the unnormalised energy eigenstates, in the same way as we did previously.

On the other hand, we need to use our knowledge from the finite square well in order to find a solution to the time-independent Schrödinger equation that is continuous everywhere, and has a continuous first derivative everywhere. We will therefore proceed by solving the time-independent Schrödinger equation on either side of the step, and “stitch” the solutions together, just as we did for the energy eigenstates of the finite square well.

To the left of the step, which we denote by Region I, when $x < 0$, the potential vanishes, and the time-independent Schrödinger equation is identical as for the free particle, (4.3). We have already solved this equation, and hence we can write down the solution (as given in (4.8)), which is

$$u_I(x) = Ae^{ikx} + Be^{-ikx} \quad (12.2)$$

where $k = \sqrt{2ME}/\hbar$ is the same as previously, and A and B are arbitrary constants.

❗ In Section 8.1 we said that solutions of the TISE can always be taken to be **real** without loss of generality. You may be wondering therefore why we have written a complex solution. It will turn out to be useful to do so – something which will only become apparent with hindsight. It also means we follow more closely the treatment of the free particle, which is advantageous.

To the right of the step, which we will call region II, such that $x \geq 0$, the time-independent Schrödinger equation is

$$Eu_{II}(x) = -\frac{\hbar^2}{2M} \frac{d^2 u_{II}}{dx^2} + V_0 u_{II}(x), \quad (12.3)$$

Re-arranging, this can be re-expressed as

$$\frac{d^2 u_{II}}{dx^2} = -\frac{2M(E - V_0)}{\hbar^2} u_{II}(x). \quad (12.4)$$

Since $E > V_0$, the constant $\frac{2M(E - V_0)}{\hbar^2}$ on the right-hand side is positive, and we can define

$$k' = \frac{\sqrt{2M(E - V_0)}}{\hbar}, \quad (12.5)$$

so that the time-independent Schrödinger equation becomes

$$\frac{d^2 u_{II}}{dx^2} = -k'^2 u_{II}(x). \quad (12.6)$$

The general solution can be written down, since the only difference to the above is that we now have k' instead of k , and so the solution must have the form

$$u_{II}(x) = Ce^{ik'x} + De^{-ik'x} \quad (12.7)$$

where C and D are two more constants.

We could just now just stitch the solution in the two regions together, but it is better to proceed a bit more thoughtfully by identifying a pair of **physically relevant situations**, which will lead us to two linearly independent solutions.

12.3.1 Right- and left-scattering

Instead of just finding the general solution to the time-independent Schrödinger equation, we will first identify two types of solution which are **very natural**.

As an example of what this means, consider again the free particle from Sec. 4, where $V(x) = 0$ everywhere. In this case the general solution to the TISE is $u(x) = Ae^{ikx} + Be^{-ikx}$. This can very naturally be seen as a **superposition of two solutions**, $u_+(x) = e^{ikx}$, which corresponds to a state of definite momentum $p = \hbar k$, and $u_-(x) = e^{-ikx}$, which corresponds to a state of definite momentum $p = -\hbar k$. That is, this the general solution corresponds to **a superposition of the particle moving to the left and to the right, with the same energy and opposite momentum**.

Let's now come back to the potential step. Things are a little bit more complicated, but we can still think about these two situations – the particle moving to the left, and the particle moving to the right. We just have to be a bit more careful by what we mean by this now.

Consider a particle moving with positive momentum p , hence moving towards the right, starting off somewhere on the left of the step (i.e. with some negative co-ordinate). Classically it would continue moving towards the right forever, even when it reaches and passes the potential step at $x = 0$, much like what we depicted in Fig. 12.1. After the step it will have a smaller momentum, equal to $p' = \sqrt{p^2 - 2MV_0}$, the momentum associated to the final kinetic energy $p^2/2M - V_0$.

Quantum mechanically we expect the behaviour to be different: the new phenomenon we are interested in is the **scattering** of the particle by the potential step. This means that with some probability amplitude we also expect the particle to reflect **backwards** off the step. Said another way, we expect that after reaching the step, the particle will be in a **superposition of having passed the step and of having been reflected by the step**. Crucially, in region II, just as in the classical case, we **only** expect to see a particle with positive momentum p' , i.e. moving to the right.

We can also think of the reverse of this situation – a particle that starts in region II with momentum $-p'$, moving to the left. Now, after the particle has passed the step we expect it to be in a superposition of having passed the step, moving to the left in region I with momentum $-p = -\sqrt{p'^2 + 2MV_0}$, and having been reflected by the step, moving to the right in region II with momentum p' . This is all nicely summarised in Fig. 12.3.

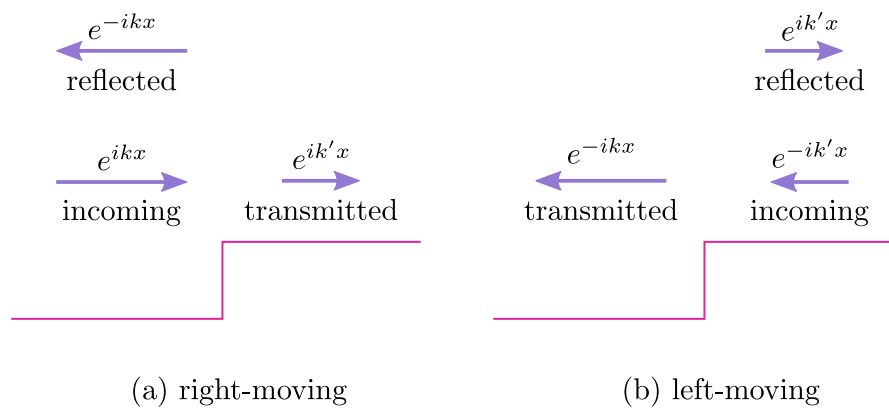


Figure 12.3: **Right-moving and Left-moving situations**. (a) In a ‘right-moving’ situation, a particle approaches the step from the left, with positive momentum. It is then partially reflected by the step, and partially transmitted. (b) In a ‘left-moving’ situation, everything is reversed. The particle approaches the step from the right with negative momentum. It is then partially reflected, and partially transmitted.

What does all this mean for solving the time-independent Schrödinger equation? It means that we can focus on two linearly independent solutions, one corresponding to a left moving particle, and one corresponding to a right-moving particle.

For the right-moving particle, we need to take $D = 0$, so that there is **no wavefunction of the form $e^{-ik'x}$ in region II, which corresponds to the particle having momentum $-\hbar k'$ in region II**. Thus, we are interested in stitching together the following wavefunction

$$u_k^R(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{if } x < 0, \\ Ce^{ik'x} & \text{if } x \geq 0. \end{cases} \quad (12.8)$$

In the above, we have labelled the state using k , which specifies the energy eigenvalue through $E = \hbar^2 k^2 / 2M$ as usual.

For a left-moving particle, as you will show and solve in Problem Sheet 4, we need to consider instead

$$u_k^L(x) = \begin{cases} Be^{-ikx} & \text{if } x < 0, \\ Ce^{ik'x} + De^{-ik'x} & \text{if } x \geq 0. \end{cases} \quad (12.9)$$

$u_k^L(x)$ and $u_k^R(x)$ constitute two linearly independent solutions to the time-independent Schrödinger

equation for each k . These can then be superposed, to form a general normalised wavepacket, as we discuss below.

12.3.2 Applying the continuity conditions

We will now use the continuity of the wavefunction and its first derivative to fix the integration constants for the right-moving particle $u_k^R(x)$. In order to have a continuous wavefunction at $x = 0$ we must have

$$C = A + B. \quad (12.10)$$

For the first derivative, we have

$$\frac{du_k^R}{dx} = \begin{cases} ikAe^{ikx} - ikBe^{ikx} & \text{if } x < 0, \\ ik'Ce^{ik'x} & \text{if } x \geq 0. \end{cases} \quad (12.11)$$

and so to have continuity at $x = 0$ we need

$$ikA - ikB = ik'C. \quad (12.12)$$

Substituting in $C = A + B$ from the continuity of the wavefunction, and re-arranging, we arrive at

$$B = \frac{k - k'}{k + k'} A \quad (12.13)$$

Thus, putting everything together, the right-moving solution is

$$u_k^R(x) = \begin{cases} A \left(e^{ikx} + \frac{k-k'}{k+k'} e^{-ikx} \right) & \text{if } x < 0, \\ \frac{2k}{k+k'} A e^{ik'x} & \text{if } x \geq 0. \end{cases} \quad (12.14)$$

As we should expect by now, all terms are proportional to A , which is just sets the overall normalisation. This wavefunction is depicted below in Fig. 12.4. However, note that we have the same issue arising here as we did for the free particle – the wavefunction $u_k^R(x)$ is **unnormalisable**. Although this is again unpleasant, we just need to use these wavefunctions in the same way as we did for the free particle: we need to form **wave packets** out of the stationary states, i.e. to superpose stationary states with a range of energies, which is equivalent to a range of k . In doing so we will be able to form normalised wavefunctions. We will return to this in the next subsection.

Before going there, we can still interpret more quantitatively the scattering at the potential, in terms of so-called reflection and transmission coefficients.

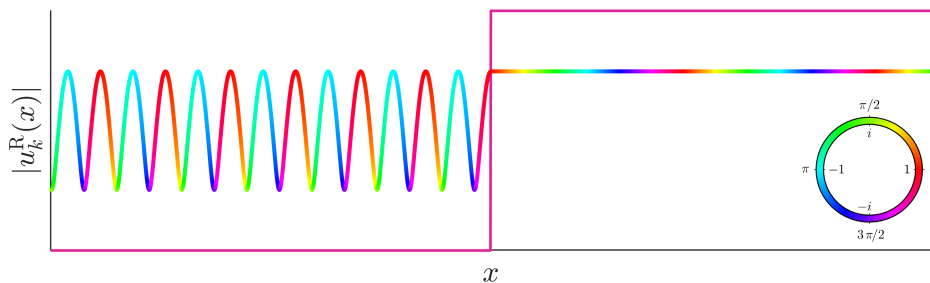


Figure 12.4: **Right-moving energy eigenstate**. Colour plot of a right-moving energy eigenstate, given in (12.14). For illustrative purposes, we also plot the potential step, to highlight where it is in relation to the wavefunction. On the left of the step, where there is both the incoming and reflected component of the wavefunction, there is interference, leading to sinusoidal oscillations. On the right, where there is only the transmitted component, the modulus of the wavefunction is constant.

12.4 Reflection and Transmission coefficients

We will now introduce a pair of coefficients, which tell us, roughly speaking, how **likely** a particle is to reflect off the potential step, or how likely it is to not reflect – i.e. to be transmitted. There are two ways in which this can be done, both of which lead to the same answer. Here we will present the simpler method, which is more heuristic. In Exercise 12.1 we show that the same answer is arrived at more formally by considering the **probability current** $j(x, t)$.

Heuristically, even though the wavefunction $u_k^R(x)$ is not normalisable, we nevertheless treat A as proportional to the amplitude of the ‘**incoming**’ wavefunction – whereby the particle is moving to the right, and B as proportional to the amplitude of the ‘**reflected**’ wavefunction. B tells us the **relative amplitude** to be reflected, and hence we can define the **reflection coefficient** R as the modulus square of the ratio between the reflected and incoming amplitudes,

$$R = \frac{|B|^2}{|A|^2} = \frac{(k - k')^2}{(k + k')^2}. \quad (12.15)$$

We define the transmission coefficient to be such that $R + T = 1$, i.e. such that the particle is **either reflected or transmitted with probability 1**, hence

$$T = 1 - R = \frac{4kk'}{(k + k')^2}. \quad (12.16)$$

It turns out that the transmission coefficient is also equal to

$$T = \frac{k'|C|^2}{k|A|^2}. \quad (12.17)$$

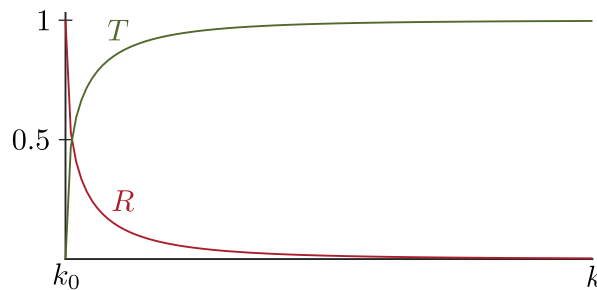


Figure 12.5: **Reflection and transmission coefficients**. Plot of reflection and transmission coefficients for the finite step, as given in (12.15) and (12.17). Here $k_0 = \sqrt{2MV_0}/\hbar$ is the minimum value of k we can consider, corresponding to $E = V_0$. We see that the particle is perfectly reflected in this case, and that the reflection coefficient is large only for k close to k_0 . For large values of k , the particle is transmitted with almost unit probability.

The reflection and transmission coefficients are plotted as a function of k in Fig. 12.5. As we can see, only when the energy E of the incoming particle is close to the height of the step V_0 , corresponding to $k = \sqrt{2ME}/\hbar$ being close to $k_0 = \sqrt{2MV_0}/\hbar$ is there significant amounts of reflection. When the energy is much larger, corresponding to k being much larger than k_0 , then the particle is transmitted with probability quickly approaching 1.

That is, for the transmission, we divide the amplitude squared for the particle to be **transmitted** by the amplitude square of the incoming particle, corrected by a factor of k'/k . This factor comes because the particle **slows down** as it crosses the barrier, causing the probability amplitude to grow. This factor precisely takes into account how much a probability amplitude increases or decreases because of a change of velocity, which is calculated using the probability current.

In Exercise 12.2 we analyse the behaviour of the reflection and transmission coefficients as we vary the physical parameters of the problem – the height of the barrier V_0 , the mass of the particle m , and the energy of the particle E .

Exercise 12.1 — Reflection and transmission coefficients from probability current. In this exercise, we will show that we can also arrive at the expressions for the reflection and transmissions coefficients by considering the probability current $j(x, t_0)$.

- (a) Consider the wavefunction associated to the **incoming** particle, $\Psi_{\text{inc}}(x, t_0) = Ae^{ikx}$ at time t_0 , where k is a positive constant. Show that the probability current for this wavefunction is

$$j_{\text{inc}}(x, t_0) = \frac{\hbar k}{M} |A|^2.$$

- (b) Using your calculation from part (a), explain why the currents for the **reflected** wavefunction $\Psi_{\text{refl}}(x, t_0) = Be^{-ikx}$ and the **transmitted** wavefunction $\Psi_{\text{trans}}(x, t_0) = Ce^{ik'x}$ are

$$j_{\text{refl}}(x, t_0) = -\frac{\hbar k}{M} |B|^2, \quad j_{\text{trans}}(x, t_0) = \frac{\hbar k'}{M} |C|^2.$$

- (c) We will now define the reflection and transmission coefficients as proportion of the incoming current that is reflected and transmitted respectively. We thus define R and T to be

$$R = \frac{|j_{\text{refl}}(x, t_0)|}{j_{\text{inc}}(x, t_0)}, \quad T = \frac{j_{\text{trans}}(x, t_0)}{j_{\text{inc}}(x, t_0)},$$

where we use $|j_{\text{refl}}(x, t_0)|$, since by the physics of the problem, this is a negative quantity. Substitute in the expressions from part (a) and part (b), to show that we recover the expressions (12.15) and (12.17) from the main text.

This shows that the reflection and transmission coefficients can be defined in terms of the probability currents as well as how they were defined in the main text, and both lead to the same answer.

Exercise 12.2 — Dependence of reflection coefficient on physical parameters. In this exercise, we will explore the dependence of the reflection coefficient R on the physical parameters of the problem, namely on the mass of the particle m , and the height of the step V_0 .

- (a) By substituting the definitions of k and k' , show that the reflection coefficient can alternatively be written as

$$R = \frac{(\sqrt{E} - \sqrt{E - V_0})^2}{(\sqrt{E} + \sqrt{E - V_0})^2}$$

- (b) What does this tell us about how the reflection coefficient depends upon the mass of the particle?
 (c) What happens when (i) the potential step vanishes, $V_0 = 0$? (ii) The energy of the particle equals the height of the potential, $E = V_0$?
 (d) Do both of your answers to part (c) make sense physically?

12.5 Dynamics of wavepackets

The most interesting phenomenon that we can study in this context is the motion of a wavepacket as it crosses the potential step. Unfortunately, this problem is actually completely intractable analytically. Nevertheless, conceptually the situation is identical to our treatment of wavepackets when considering a free particle, as we will outline below. In order to actually study anything in this case we have to turn to **numerics**. We will see an example of this at the end of this section.

Starting with the conceptual side, we would like to specify a wavepacket $\Psi(x, 0)$ at time $t = 0$, which is again a complete specification of the state. As a concrete example, we could imagine a packet with

centre at $x_0 \ll 0$, far from the origin, with width $\Delta x \ll x_0$, such that the particle is initially completely on the left-hand side of the step. We can then consider that the particle has positive average momentum $p_{av} \gg 0$, and uncertainty in momentum $\Delta p \ll p_{av}$, so that the momentum of the particle is positive. For example, we could consider a Gaussian wavepacket, as we did for the free particle. Such a packet fits within our general picture of a particle coming from the left and moving to the right.

Such a wavepacket can be expressed as a superposition of energy eigenstates, just like in any other situation. Crucially, given the way we have just set things up, this wavepacket will in fact be a superposition **only of the right-moving energy eigenstates** $u_k^R(x)$. Thus, at $t = 0$ the wavefunction $\Psi(x, 0)$ can be written as

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{k_0}^{\infty} c(k) u_k^R(x) dk, \quad (12.18)$$

for some function $c(k)$ which determines the shape of the wavepacket. Note that the lower limit of integration is $k_0 = \sqrt{2MV_0}/\hbar$, as we want the particle to have enough energy $E > V_0$, i.e. enough energy to pass the potential step.

We can now once again **write down** the wavefunction of the particle at an arbitrary time t . This is because once again (12.18) is a decomposition of the wavefunction at $t = 0$ into energy eigenstates. These are stationary states, whose time evolution is simple, and we know that the superposition principle tells us that the time evolution of a superposition is the superposition of the time evolution, namely

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{k_0}^{\infty} c(k) e^{-i\hbar k^2 t/2M} u_k^R(x) dk, \quad (12.19)$$

Evaluating this integral will in general only be possible numerically, but in principle this is the solution, in complete analogy to any other situation we have studied.

Example 12.1 — Gaussian wavepacket. As an example, we can again consider a Gaussian wavepacket. Therefore, let us take the function $c(k)$ closely related to that from Example 4.1,

$$c(k) = \left(\frac{2a^2}{\pi} \right)^{1/4} e^{-a^2(k-k_{av})^2} e^{ikx_0}. \quad (12.20)$$

The only differences compared to (5.11) are that we centre the Gaussian now at $k_{av} = p_{av}/\hbar$, and the final factor of e^{-ikx_0} , which has the effect of **translating** the spatial wavefunction so that the initial wavepacket is approximately

$$\Psi(x, 0) = \left(\frac{1}{a\sqrt{2\pi}} \right)^{1/2} e^{-(x-x_0)^2/4a^2} e^{ik_{av}x} \quad (12.21)$$

corresponding to a Gaussian with centre at $\langle x \rangle = x_0$ and average momentum $\langle p \rangle = \hbar k_{av} = p_{av}$.

To find the evolution in time, we can numerically evaluate (12.19), for a variety of times t , restricting the range of integration to where the Gaussian $c(k)$ is non-zero, which is around the value of k_0 . In Fig. 12.6 we plot the result for 6 different times, encompassing the wavepacket approaching the step, and being partially reflected by it. We see that the final state of the particle is a **superposition of two wavepackets** – a reflected wavepacket and a transmitted wavepacket.

12.6 Finite square well

Finally, we can return to the finite square well, and consider energy eigenstates with $E > V_0$. Our procedure is identical to above: we need to first need to solve the time-independent Schrödinger equation in the 3 regions – to the left of the well, inside the well, and to the right of the well. We should then identify our two physically relevant situations: a right-moving and a left-moving particle. Mathematically, this will allow us to set one of our integrations constants to 0. Finally, we need to stitch together the solutions in the 3 regions, using the continuity of the wavefunction and its first derivative in order solve

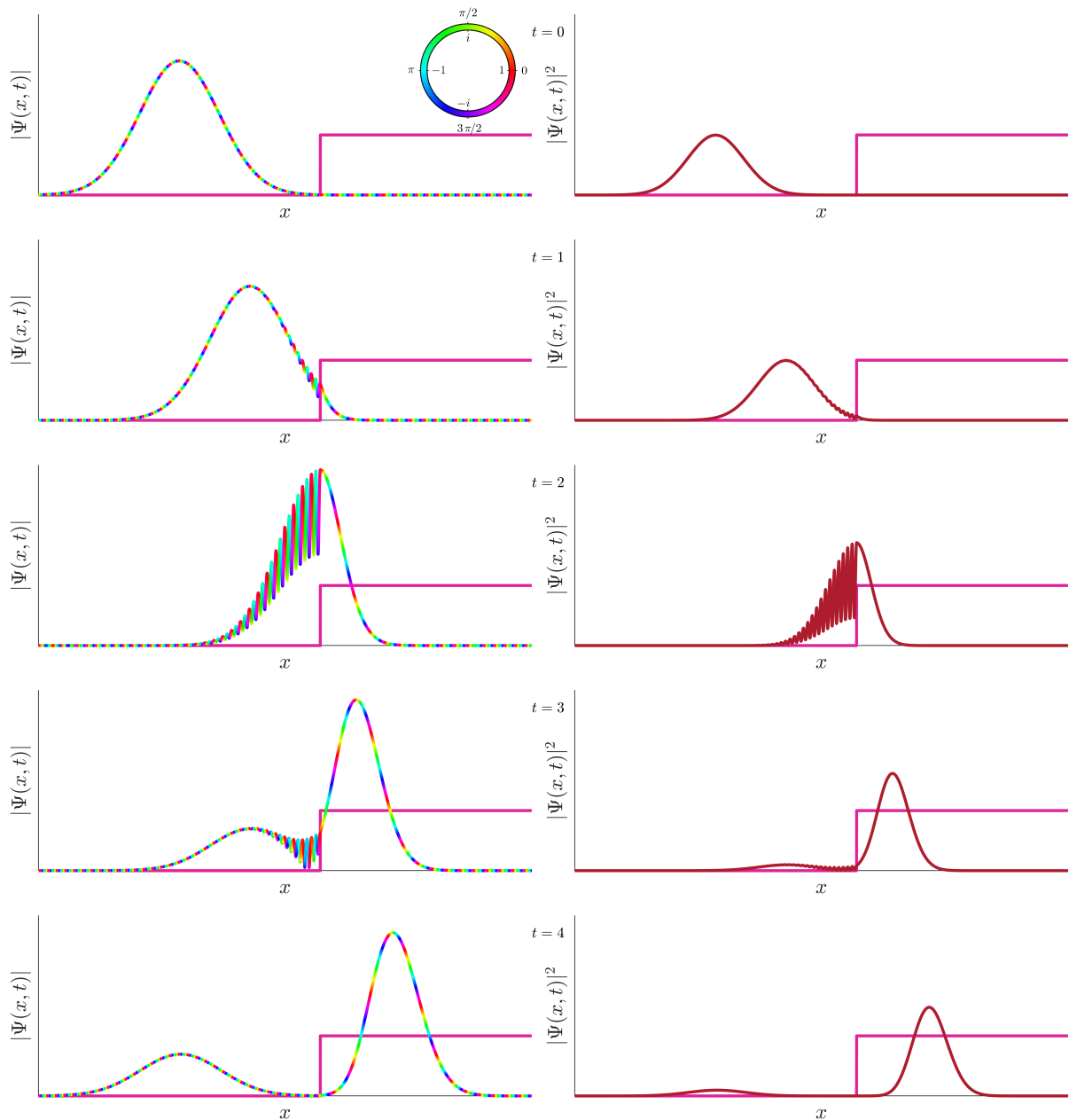


Figure 12.6: **Scattering of a Gaussian wavepacket by a potential step.** A plot of the scattering of a Gaussian wavepacket by a step potential. On the left plot the wavefunction $\Psi(x, t)$ using a colour plot, for various times t . On the right, we plot the associated probability density $|\Psi(x, t)|^2$. The potential step is also plotted, for illustrative purposes. The particle approaches the step from the left, with positive momentum, and energy larger than the potential height V_0 . Nevertheless, the particle is partially reflected by the step, such that the final state of the particle is a superposition of a left-moving packet after the step, and a right-moving packet that has been reflected by the step.

for all but one of the remaining integration constants, with the final one being the normalisation constant, as always.

Here we simply state the final answer, which is obtained after a rather long and intricate calculation, that is carried out in Problem Sheet - Week 11 as a final, challenging, exercise for the course. The

right-moving energy eigenstate with incoming energy $E = \hbar^2 k^2 / 2M$ is

$$u_k^R(x) = \begin{cases} Ae^{ik'x} + Be^{-ik'x} & \text{if } x < 0, \\ Ce^{ikx} + De^{-ikx} & \text{if } 0 \leq x \leq a, \\ Fe^{ik'x} & \text{if } x > a, \end{cases} \quad (12.22)$$

where $k' = \sqrt{2M(E - V_0)}/\hbar$, A is the normalisation constant, and

$$B = \frac{2i(k^2 - k'^2) \sin ka}{(k + k')^2 e^{-ika} - (k - k')^2 e^{ika}} A, \quad C = \frac{2k'(k + k')e^{-ika}}{(k + k')^2 e^{-ika} - (k - k')^2 e^{ika}} A, \quad (12.23)$$

$$D = \frac{2k'(k - k')e^{ika}}{(k + k')^2 e^{-ika} - (k - k')^2 e^{ika}} A, \quad F = \frac{4kk'e^{-ik'a}}{(k + k')^2 e^{-ika} - (k - k')^2 e^{ika}} A. \quad (12.24)$$

This wavefunction is depicted in Fig. 12.7, for two different values of k , the significance of which will become clear below. This wavefunction leads to the following reflection and transmission coefficients

$$R = \frac{(k^2 - k'^2)^2 \sin^2 ka}{4k^2 k'^2 + (k^2 - k'^2)^2 \sin^2 ka}, \quad T = \frac{4k^2 k'^2}{4k^2 k'^2 + (k^2 - k'^2)^2 \sin^2 ka}. \quad (12.25)$$

As you can see, the solutions have a complex form, which is why they are being stated, and not derived. It is most interesting to look at the transmission coefficient graphically, which we plot in Fig. 12.8.

What we see is that for certain values of k the particle is transmitted with probability 1, while for other values this is not the case. The values of k where T becomes unity are those where $R = 0$, which we see from (12.25) is when $\sin^2 ka = 0$. This occurs when $k = n\pi/a$. These are **precisely the values of k we found for the infinite square well!**

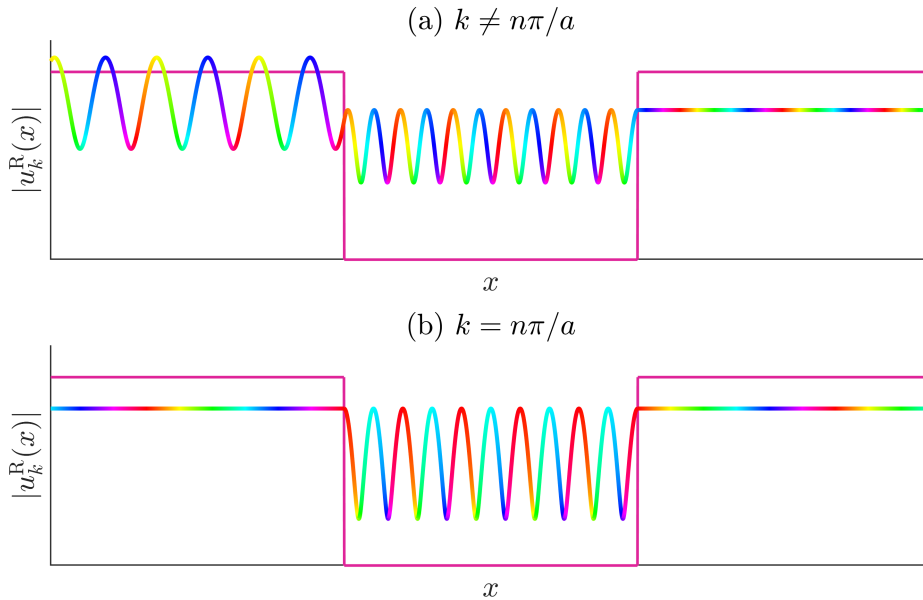


Figure 12.7: **Right-moving energy eigenstates of the finite square well.** Colour plot of a right-moving energy eigenstate, given in (12.22). For illustrative purposes, we also plot the potential step, to highlight where it is in relation to the wavefunction. (a) An example for a value of $k \neq n\pi/a$, for some integer a . The fact that the modulus varies to the left of the well and inside the well is an indication that in these regions the particle is moving both to the left and to the right. (b) An example for a value of k equal to a multiple of π/a . In these special cases, the particle is perfectly transmitted. As a consequence, to the left of the well the modulus is constant, signalling only a right-moving component of the wavefunction.

Thus, if the particle has more energy than the well, i.e. $E > V_0$, so that it is not bound in the well, and the energy happens to match one of the energy levels of the **infinite square well**, then the particle is not reflected at all, but is transmitted with unit probability. For any other value of k , there is a probability that the particle is reflected. Thus, the quantisation condition of the infinite square well again appears for the finite well, now when considering scattering.

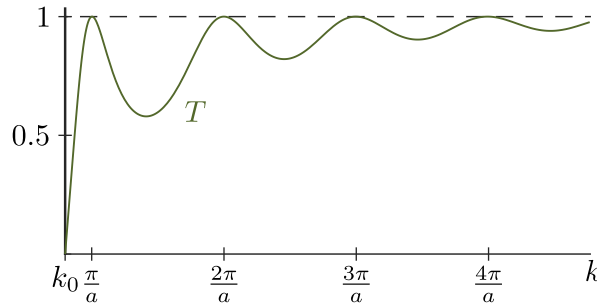


Figure 12.8: **Transmission coefficient of the finite well.** Plot of transmission coefficient for the finite square well, as given in (12.25). Here $k_0 = \sqrt{2MV_0}/\hbar$ is the minimum value of k we can consider, corresponding to $E = V_0$. We see that the particle is perfectly transmitted whenever k is a multiple of π/a , i.e. exactly the values of k which give the energy eigenstates of the infinite square well. Thus, if a particle has energy above E the height of the well V_0 , but this energy happens to match the energy levels of the infinite square well, it is not reflected at all by the potential well.

Finally, we can also consider the dynamics of wavepackets, just as we did in Section 12.5. Considering the same Gaussian wavepacket from Example 12.1, we plot the evolution in Fig. 12.9. The new features we observe now compared to before, is that the particle will now repeatedly be transmitted and reflected by each wall of the well, leading to a much more intricate and complicated form at later times. Nevertheless, the general behaviour is as expected, even though we have the special energies which are perfectly transmitted by the well.

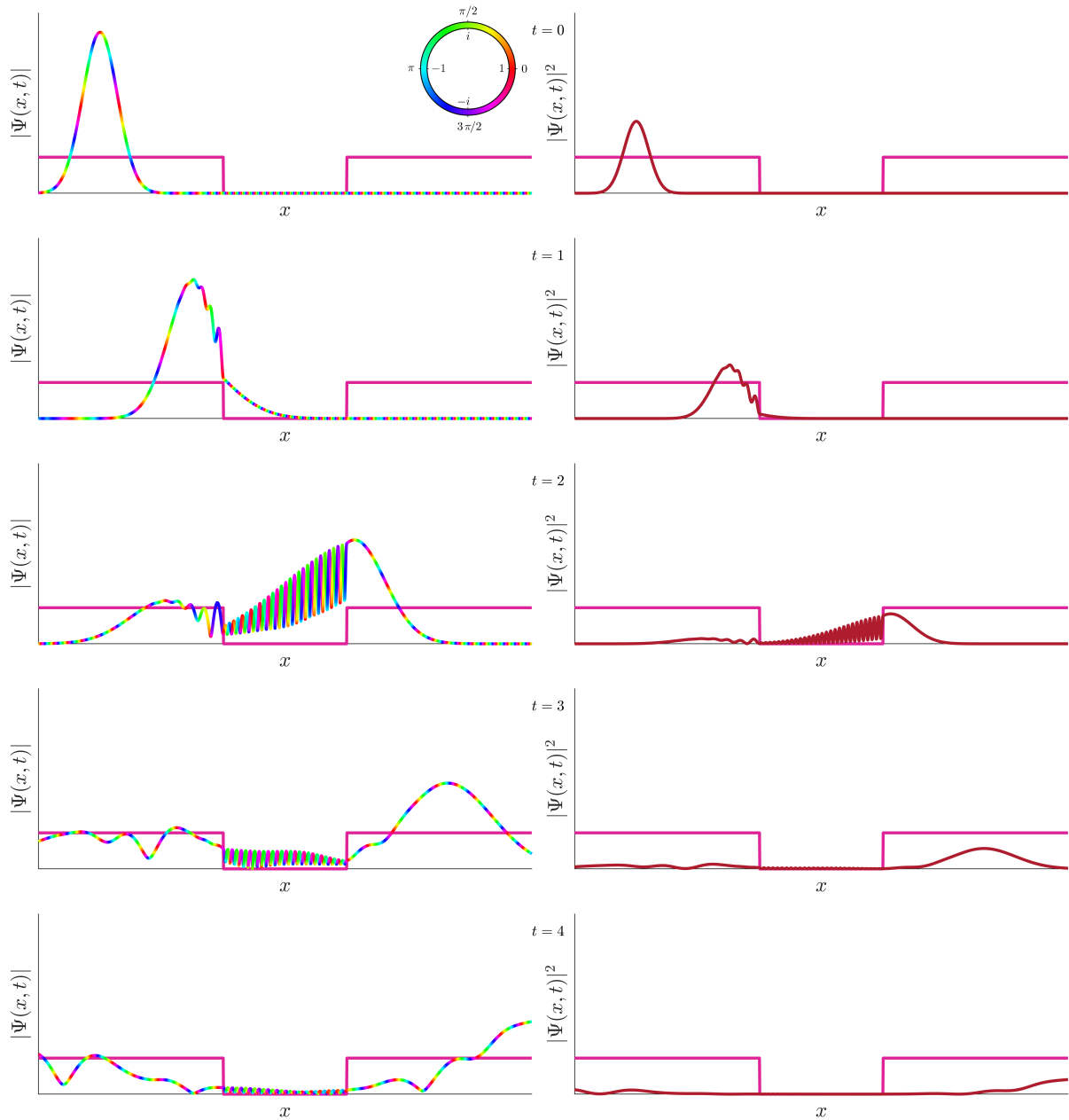


Figure 12.9: **Scattering of a Gaussian wavepacket by a potential well.** A plot of the scattering of a Gaussian wavepacket by the finite square well. On the left we plot the wavefunction $\Psi(x, t)$ using a colour plot, for various times t . On the right, we plot the associated probability density $|\Psi(x, t)|^2$. The potential well is also plotted, for illustrative purposes. The particle approaches the well from the left, with positive momentum, and energy larger than well depth V_0 . The particle is partially reflected by the left-hand wall, with part of the wavepacket entering, and part reflecting. The part which is transmitted then rapidly approaches the right-hand wall, where it is again partially reflected and partially transmitted. The part which is reflected then approaches the left-hand wall, where it can again be partially reflected and transmitted. At late times, the particle will be found outside the well, either travelling to the right or to the left, and with a spread-out form, accounting for the possibility of multiple reflections inside the well before finally escaping.