Introduction to Quantum Mechanics

a Schrödinger approach in one dimension

BY KASPER PEETERS (BASED ON NOTES BY MATHEW BULLIMORE)

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Lecture notes for the 2024-2025 Mathematical Physics II module at Durham University.

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Why Quantum Mechanics?

1.1 A Brief History

In last term's lectures, you have explored a powerful reformulation of 'classical mechanics' using the Lagrangian and Hamiltonian formalisms. This is perfectly adequate for a complete understanding of balls, pendulums, springs, and waves, on macroscopic distance scales familiar to humans.

However, by the early 1900's there was mounting experimental evidence that the elementary constituents of matter, at microscopic distances of atoms and molecules, behave in a wholly different manner. The new theoretical framework that emerged in this period to describe such phenomena is known as 'quantum mechanics'. This has had a profound effect on society: quantum mechanics underpins much of the technological revolution of the last century.

Ultimately, the framework of quantum mechanics is determined by experimental facts. However, many features of quantum mechanics are reminiscent of the Hamiltonian formulation of classical mechanics, and we will emphasise this connection throughout the course. You should keep in mind that quantum mechanics is the more fundamental description of nature, with classical mechanics an approximation valid at macroscopic distances.

Introductory lecture, in which the module is introduced and motivation is given that led to the birth of quantum mechanics.

Quantum mechanics has an extremely rich mathematical framework. In this course, we will encounter techniques from analysis, probability, algebra, and representation theory. Moreover, ideas and techniques from quantum mechanics have inspired many exciting developments in pure mathematics in the last half century, particularly in geometry and topology. This continues to be an active area of research today.

In this lecture and the next, we will explore some of the inconsistencies between classical mechanics and experimental facts about nature at microscopic distances. This will serve as a guide to the development of quantum mechanics in subsequent lectures.

1.2 Bound States

Many potentials which lead to a continuum of bound states in classical mechanics produce, instead, a discrete spectrum in the real world, which can be 'explained' by 'quantisation conditions'.

In classical mechanics, a particle has a definite position and momentum $(x(t), p(t))$ at each time t. We can view this geometrically as a curve in 'phase space' parametrised by time t. Given some initial conditions, the shape of the curve is determined by Hamilton's equations,

$$\dot{x} = \frac{\partial H}{\partial p}\,, \qquad \dot{p} = -\frac{\partial H}{\partial x}\,, \tag{1.1}$$

where H is the Hamiltonian. More precisely, Hamilton's equations specify the tangent space to the curve at each time t, as shown below.

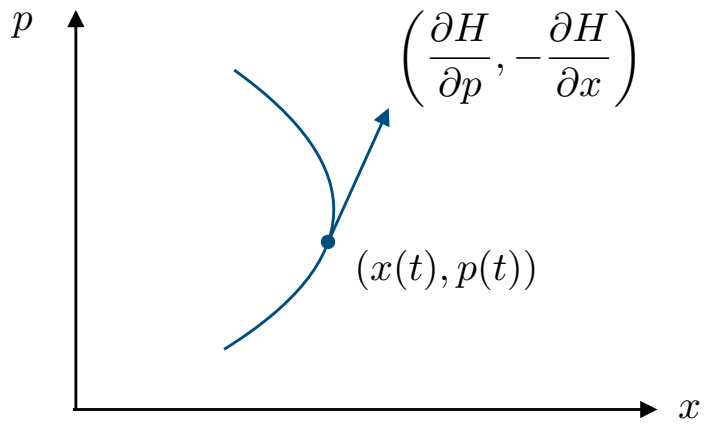

Figure 1.1: Phase space dynamics of a classical system, driven by the Hamiltonian.

- **Example.** A particle of mass m moving in a potential $V(x)$ has

$$H = \frac{p^2}{2m} + V(x)\,. \tag{1.2}$$

The Hamiltonian itself is conserved and equal to the total energy E, given by the sum of kinetic energy and potential energy. In this case, eliminating the momentum p from Hamilton's equations leads back to Newton's law,

$$m\ddot{x} = -\frac{dV}{dx}\,. \tag{1.3}$$

In classical mechanics, a 'bound state' is a solution of Hamilton's equations that is confined to a finite region of phase space. Bound states arise from oscillations around a local minimum of the potential $V(x)$.

- **Example 1** A simple harmonic oscillator has quadratic potential

$$V(x) = \frac{1}{2}m\omega^2 x^2\,, \tag{1.4}$$

where ω is known as the 'angular frequency'. The general solution of Hamilton's equations is given by

$$\begin{aligned} x(t) &= \sqrt{\frac{2E}{m\omega^2}}\sin(\omega t + \phi)\,, \\ p(t) &= \sqrt{2mE}\cos(\omega t + \phi)\,, \end{aligned} \tag{1.5}$$

where the energy $E \geq 0$ and phase ϕ are determined by the initial conditions.

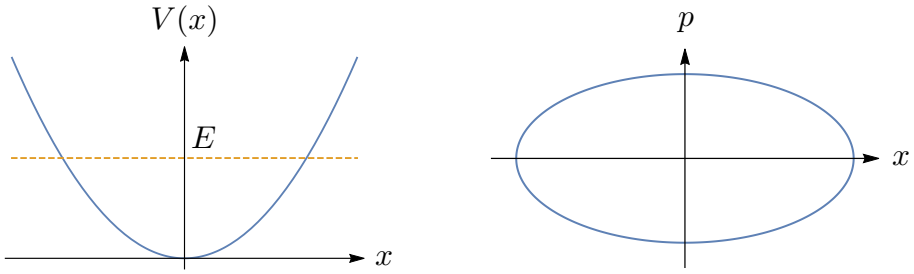

Figure 1.2: Potential energy and phase space dynamics of the simple harmonic oscillator.

The particle is confined to the region where $V(x) \leq E$ and cannot escape to infinity. The curve $(x(t), p(t))$ forms an ellipse in phase space, which is confined to a finite region. There is therefore a continuous spectrum of bound states parametrised by the energy $E \geq 0$.

- **Example 2.** The effective potential for the radial motion of an electron in a hydrogen atom is (in convenient units)

$$V(x) = \frac{J^2}{2mx^2} - \frac{e^2}{x}\,, \tag{1.6}$$

where m, e are the mass and electric charge of the electron and J^2 is the conserved square of the angular momentum vector. The potential has a minimum at $x_0 = J^2/me^2$ and asymptotes to 0 from below as $x \to \infty$. There is a continuous spectrum of bound states parametrised by J^2 and energy $V(x_0) < E < 0$.

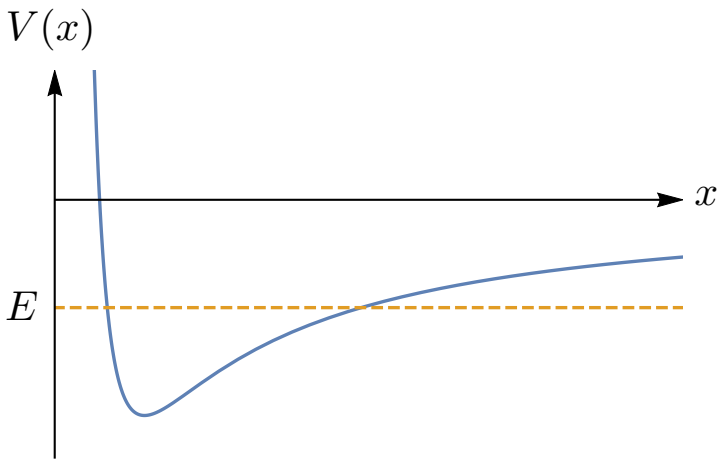

Figure 1.3: Classical potential energy of the hydrogen atom; there is a classical bound state for every energy $V(x_0) < E < 0$.

More generally, any potential $V(x)$ with a local minimum at some point x_0 will classically have a *continuous* spectrum of bound states with energy $V(x_0) < E < E_{\max}$ for some maximum energy $E_{\max}$.

This classical expectation is in striking contradiction with experimental tests of microscopic systems, which typically have a *discrete* spectrum of bound states. For example, from the study of atomic spectra it is known that a hydrogen atom has a

discrete set of bound states where angular momentum and energy take particular values

$$\begin{aligned} J^2 &= j(j+1)(2\pi h)^2 \qquad & j &= 0, 1, \dots , \\ E &= -\frac{(2\pi)^2 m e^4}{2h^2 n^2} & n &= 1, 2, \dots . \end{aligned} \tag{1.7}$$

The quantity h is a new constant of nature known as the Planck constant. This has units of 'energy times time' (just like angular momentum) and is approximately

$$h \approx 6.63 \times 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}\,. \tag{1.8}$$

The notation $\hbar = h/(2\pi)$ is also commonly used, and called the *reduced* Planck constant,

$$\hbar \approx 1.05 \times 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}\,. \tag{1.9}$$

These discrete spectra of bound states cannot be explained in the framework of classical mechanics. Later in the course, we will show that a discrete spectrum of bound states is, however, a characteristic feature of quantum mechanics.

In the beginning days of quantum mechanics, people tried to impose these quantisation rules by hand, for instance by imposing that for the harmonic oscillator,

$$\int_{\text{orbit}} p\mathrm{dx} = nh\,, \quad n \in \mathbb{Z}\,, \tag{1.10}$$

where the integral is over one entire orbit. For the harmonic oscillator, we get (see the problems)

$$\int_{\text{orbit}} p\mathrm{dx} = \frac{2\pi E}{\omega}\,, \tag{1.11}$$

and so with $\omega = 2\pi\nu$, the 'quantisation condition' (1.10) produces $E = \nu h n$. However, such quantisation prescriptions clearly do not constitute a 'theory', and are difficult to generalise to more complicated systems.

1.3 The Photoelectric Effect

Light irradiated onto a metal behaves as if it is made of discrete constituents ('photons').

We now consider another important phenomenon that is inconsistent with classical mechanics. The 'photo-electric effect' is the emission of electrons from certain metals when irradiated by light.

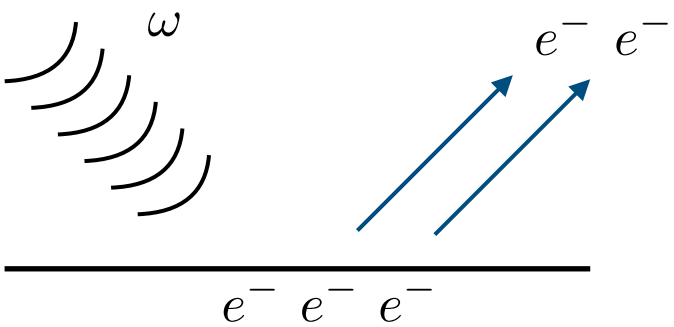

Figure 1.4: Schematic depiction of the photo-electric effect: when light of frequency ω is irradiated onto a metal, it releases electrons.

In classical mechanics, light is a wave. This is a fluctuation in the electromagnetic field that solves the wave equation

$$\frac{\partial^2 \psi}{\partial t^2} - c^2 \frac{\partial^2 \psi}{\partial x^2} = 0 \,, \tag{1.12}$$

where c is the speed of light. You can think about the real part of the amplitude $\psi(x,t)$ as a component of the electric or magnetic field. Let us assume the light is monochromatic and accurately described by a plane wave

$$\psi(x,t) = \psi_0 \, e^{i\omega(x/c - t)} \tag{1.13}$$

with angular frequency ω. This is related to the wavelength by $\lambda = 2\pi/\omega$. The 'intensity' of the light is the energy carried by the electromagnetic field, averaged over time. This is proportional to the modulus squared of the amplitude, $I \sim |\psi(x,t)|^2 = |\psi_0|^2$, and is independent of the angular frequency ω.

Let us assume an electron in the metal must absorb a minimum amount of energy E_{min} from the light to be emitted from the metal. Then the classical description of light as a wave leads to the following expectation:

- The energy of the emitted electrons depends on the intensity I but is independent of the angular frequency ω.
- Electrons are emitted even in low-intensity light, but there is a time-delay as each electron absorbs the minimum energy E_{min}.

However, the experimental result is the following:

- The energy of emitted electrons is independent of the intensity I and is linearly proportional to the angular frequency, $\hbar\omega - E_{\text{min}}$.
- Electrons are only emitted if $\hbar\omega \geq E_{\text{min}}$ and are emitted immediately.

Here $\hbar$ is the same Planck's constant introduced above. This is shockingly different to the classical expectation!

In 1905, Einstein made a remarkable proposal that resolved this contradiction: that light arrives in indivisible packets known as 'quanta' or 'photons'. The energy carried by each individual photon is

$$E = \hbar\omega \,, \tag{1.14}$$

while the intensity is related to the rate that photons are arriving. Assuming an electron can only absorb one photon at a time, this means that an electron can only be emitted if $\hbar\omega \geq E_{\text{min}}$. Its energy is equal to that of the photon it absorbs minus the energy needed to escape the metal, $\hbar\omega - E_{\text{min}}$.

1.4 These lectures

In these lectures we will restrict to one-dimensional quantum mechanics in the Schrödinger wave function approach.

We have seen two examples of how the classical mechanics of particles and waves fails to explain experimental data at microscopic distances. Furthermore, we have seen hints that light has characteristics of a wave, but arrives in indivisible packets like a particle. This is known as 'particle-wave duality' and is a feature not only of light but also electrons and all constituents of matter.

In the following chapters, we will explore this idea much more precisely, starting with the 'double slit' experiment, and then gradually developing a mathematical formalism that can explain the phenomena discussed above.

YouTube
Feynman on the difficulty of understanding quantum mechanics.

As we go along, you will discover that quantum mechanics is a hard topic. This is not only because it requires you to understand a load of new mathematical ingredients, but mostly because, as a beginner, you will be guaranteed to lack an intuition for it. Your classical experience with the real world out there is of no use when it comes to understanding the microscopic world governed by quantum mechanics. So the only way to 'gain intuition' is to solve many problems and slowly get used to the strange miscroscopic world. To make life easier, we will stick exclusively to one-dimensional systems in these lectures.

Another aspect which does not make it simpler for a newcomer to grasp the concepts is that there exist three different mathematical formulations of quantum mechanics, all equivalent in sofar this can be verified, but radically different in their notation and even conceptual interpretation. The present notes follow the so-called *Schrödinger wave function* approach, which connects most clearly to classical wave mechanics which was at the root of the development of quantum mechanics originally.

The first of the other two approaches is the *operator approach*, which formalises much of the wave function approach into the language of operators acting on infinite-dimensional vector spaces. We will touch briefly on this towards the end of the module. Finally, there is the *path integral* approach, which is both conceptually and technically entirely different from the first two. These two other approaches will be discussed in the Quantum Mechanics III module.

1.5 Recommended literature

Read books! No honestly, read books! There is no substitute for solving problems yourself, but the next best thing is to read multiple sources so you get to see things from different angles.

Three books which these notes to a large extent based on are

- *Introduction to Quantum Mechanics*, David J. Griffiths
  A standard textbook. Chapters 1-3 cover the same material as this course but in a different order. Overall, this is the most appropriate textbook.
- *Quantum Physics*, S. Gasiorowicz
  Chapters 3-7 contain lots of worked examples relevant for this course.
- *Principles of Quantum Mechanics*, R. Shankar
  A popular favourite. Chapters 3-7 cover similar material to this course but at a more advanced level. A good investment for ambitious students who wish to progress onto Quantum Mechanics III.

There are various other books which do get referred to frequently, but which are somewhat further away from the present course, e.g.:

- *Modern Quantum Mechanics*, J. J. Sakurai
  Another standard book, with a nice motivation for quantum mechanics at the beginning. It does, however, use the operator approach almost exclusively.
- *Feynman Lectures, Volume III*, R.P. Feynmann, R.B. Leighton, M. Sands
  A classic everyone should have read. Covers a lot more than we will cover in this module, but the first few chapters are worth having a look at. Available for free online at https://www.feynmanlectures.caltech.edu.
- *Notes on Quantum Mechanics*, D.V. Schroeder
  A very new book by an extremely good educator. Has a lot of emphasis on concrete computations, often using Mathematica. Available for free online at https://physics.weber.edu/schroeder/quantum/.

2

The Double Slit Experiment

2.1 Particles and Waves

In classical mechanics, you have learned about two distinct things: particles and waves. In this chapter we will explore the 'double-slit experiment'. This shows that the elementary constituents of matter (electrons, photons, any of the elementary particles) exhibit characteristics of both particles and waves, known as 'particle-wave duality'. The experiment also demonstrates that the laws of nature are fundamentally probabilistic.

Lecture about the double-slit experiment, going through the main maths that describes the interference pattern.

First, a quick reminder about the classical mechanics of particles and waves moving in one dimension.

- A particle has a definite position and momentum $(x(t), p(t))$ at each time t. The time evolution of position and momentum is found by solving Hamilton's equations,

$$\dot{x} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{\partial H}{\partial x}\,, \tag{2.1}$$

  where H is the Hamiltonian function. For a particle of mass m moving in a potential $V(x)$ the Hamiltonian is

$$H = \frac{p^2}{2m} + V(x)\,. \tag{2.2}$$

- A wave is described by an amplitude $\psi(x,t)$. This might be the displacement of a string, or a component of the electromagnetic field, as a function of position x and time t. The amplitude is a solution of a partial differential equation, such as the wave equation

$$\frac{\partial^2 \psi}{\partial t^2} - v^2 \frac{\partial^2 \psi}{\partial x^2} = 0\,, \tag{2.3}$$

  where v is the velocity.

Experiments probing microscopic distances show that the elementary constituents of matter exhibit characteristics of *both* particles and waves. To see this concretely, we are going to examine the 'double-slit experiment'. Although it is very often presented as a thought experiment, it has actually been performed it in the laboratory, for instance with electrons. A more extensive account can be found in Volume III of the Feynman Lectures.

YouTube

Jim Al-Khalili explaining the double-slit experiment.

For arguments sake, we will imagine performing this experiment with electrons. We will first explain the outcome of the experiment according to classical mechanics,

assuming that electrons are particles and then waves. We will then explain how electrons actually behave in nature.

2.2 Double-Slit : Particles

Let us first suppose that electrons are particles. There is a source emitting these particles at a uniform rate in random directions towards a screen with two small slits S_1 and S_2. The particles that pass through one of the slits arrive one at a time at a detector D on the other side of the screen.

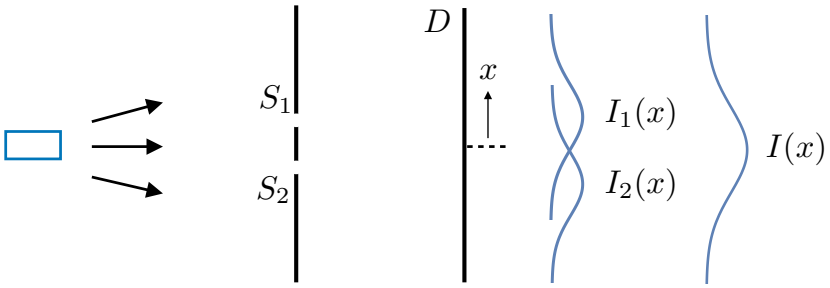

Figure 2.1: Outcome of the double-slit experiment if the source emits particles: intensities add up.

By averaging over a long period of time, the detector measures the rate that particles arrive per unit area, as a function of the vertical direction x. We call this the 'intensity'. Suppose that:

- The intensity measured with only S_1 open is $I_1(x)$.
- The intensity measured with only S_2 open is $I_2(x)$.
- The intensity measured with both S_1 and S_2 open is $I(x)$.

Since particles arrive at the detector one at a time and must pass through either S_1 or S_2, the intensities add up

$$I(x) = I_1(x) + I_2(x)\,. \tag{2.4}$$

The result is thus simply the appearance of one or two peaks, depending on the separation of the slits and the distance to the screen.

2.3 Double-Slit : Waves

Now suppose instead that electrons are waves with amplitude $\psi(x,t)$. There is a source emitting waves uniformly towards a screen with two small slits S_1 and S_2. The waves pass through the slits and arrive continuously at a detector D.

Suppose that

- The amplitude at the detector with only S_1 open is $\psi_1(x)$.
- The amplitude at the detector with only S_2 open is $\psi_2(x)$.

- The amplitude at the detector with both S_1 and S_2 open is $\psi(x)$.

Let us assume that the wave amplitude obeys a *linear* partial differential equation. Then the principle of superposition means that

$$\psi(x) = \psi_1(x) + \psi_2(x)\,. \tag{2.5}$$

Note that we are ignoring the dependence on time t, which is not important in the argument that follows.

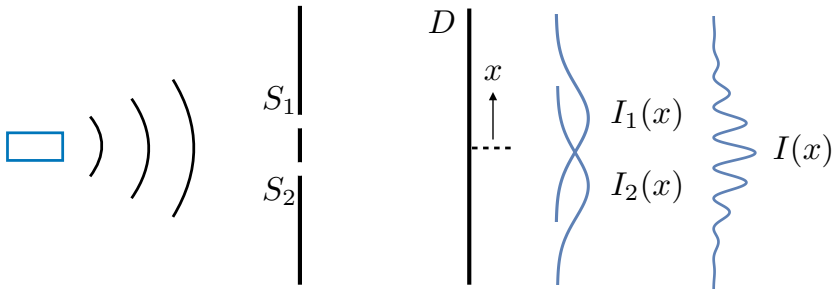

Figure 2.2: Outcome of the double-slit experiment if the source emits waves: there is a characteristic interference pattern.

By averaging over a long period of time, the detector measures the rate that energy is deposited per unit area, as a function of the vertical direction x. We again call this the 'intensity'. The energy carried by a wave is proportional to the modulus squared of the amplitude. Ignoring the constant of proportionality,

$$I_1(x) = |\psi_1(x)|^2\,, \qquad I_2(x) = |\psi_2(x)|^2\,, \qquad I(x) = |\psi(x)|^2\,,$$

are the intensities measured by the detector with only S_1, only S_2, and both S_1 and S_2 open respectively. They are related by

$$\begin{aligned} I(x) &= |\psi(x)|^2 \\ &= |\psi_1(x) + \psi_2(x)|^2 \\ &= |\psi_1(x)|^2 + |\psi_2(x)|^2 + 2\mathrm{Re}(\psi_1(x)\overline{\psi_2(x)}) \\ &= I_1(x) + I_2(x) + 2\sqrt{I_1(x)I_2(x)}\cos(\delta(x))\,, \end{aligned} \tag{2.6}$$

where $\delta(x)$ is the relative phase of $\psi_1(x)$ and $\psi_2(x)$. The additional term compared to the result for particles is known as the 'interference' term. It generates the kind of interference pattern illustrated in the figure above.

Let us compute the interference pattern more explicitly using a series of approximations. For familiarity, let us suppose that the amplitude $\psi(x,t)$ obeys the wave equation with velocity v. We further assume the slits are very thin, so that we are effectively dealing with two pointlike sources, producing the two waves

$$\psi_1(x,t) = C\,e^{i(kr_1-\omega t)}\,, \quad \psi_2(x,t) = C\,e^{i(kr_2-\omega t)}\,, \tag{2.7}$$

where

- C is a normalisation constant that is unimportant in what follows,
- $k = \omega/v$ where ω is the angular frequency of the wave,

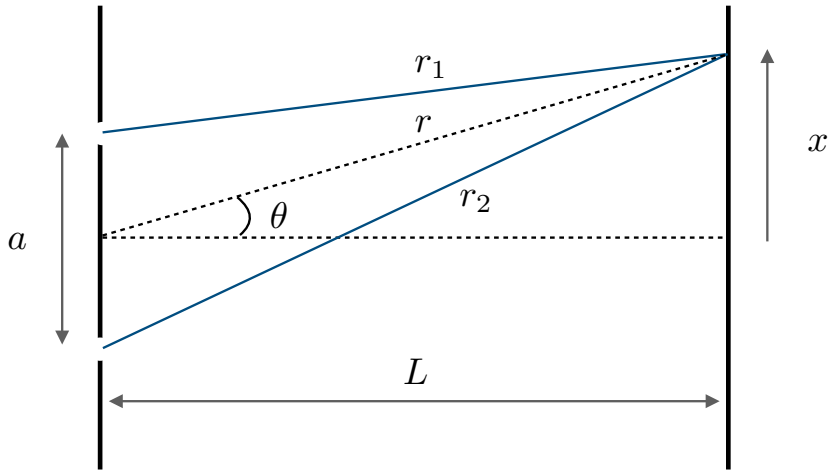

Figure 2.3: Variables used to compute the interference pattern for the double-slit experiment.

- r_1, r_2 are the distances from the slits S_1, S_2 to a point on the detector at height x.

With these approximations, the total amplitude is

$$\psi(x,t) = C(e^{ikr_1} + e^{ikr_2})e^{-i\omega t} \tag{2.8}$$

and therefore the intensity at a point x on the screen will be given by

$$\begin{aligned} I(x) &= C^2 |\, e^{ikr_1} + e^{ikr_2} \,|^2 && (2.9)\\ &= 2C^2 \left(1 + \cos(k(r_1 - r_2))\right) && (2.10)\\ &= 4C^2 \cos^2\left(\frac{k}{2}(r_1 - r_2)\right) . && (2.11) \end{aligned}$$

There is constructive interference when $k(r_1 - r_2) = 2n\pi$ and destructive interference when $k(r_1 - r_2) = (2n+1)\pi$ where $n \in \mathbb{Z}$, so the intensity will clearly display an interference pattern.

To determine the intensity function $I(x)$ explicitly is tricky since the distances r_1, r_2 are complicated functions of x. The two right-angled triangles give

$$r_1^2 = L^2 + \left(x - \frac{a}{2}\right)^2 , \quad r_2^2 = L^2 + \left(x + \frac{a}{2}\right)^2 . \tag{2.12}$$

Taking a square root to obtain r_1 and r_2, we can then subtract these two expressions to get the phase we have in (2.9). To get some more insight into that expression, it is useful to expand r_1 and r_2 for small values of a, that is, for $a \ll x$. Using a Taylor expansion we get

$$r_1 = \sqrt{L^2 + x^2} - \frac{ax}{2\sqrt{L^2 + x^2}} + \mathcal{O}(a^2) , \tag{2.13}$$

and similar for r_2. Subtracting the two and assuming furthermore that $x \ll L$, we get the simple expression $r_2 - r_1 = ax/L$, and using this in (2.9) thus gives

$$I(x) \approx 4C^2 \cos^2\left(\frac{ka}{2L}x\right) . \tag{2.14}$$

The result is thus quite different from that in the previous section: waves give a characteristic intensity interference pattern, with an approximate separation between maxima as given above. To plot the full pattern, just use (2.12) directly.

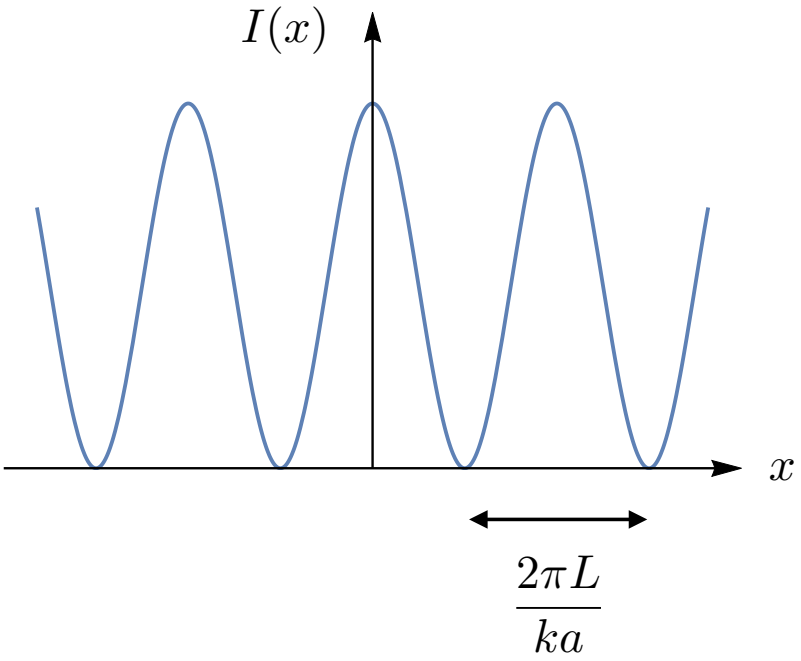

Figure 2.4: Approximate interference pattern computed using the approximations $a \ll x$ and $x \ll L$.

2.4 Double-Slit: the real world

An experiment by Bach et al. reported in 2012 clearly shows how individual electrons in a double-slit experiment gradually build up an interference pattern. This movie shows the electron buildup pattern one electron at a time.

Let us summarise our results for particles and waves and compare to the experimental result for electrons.

Particles

1. Particles arrive one at a time.
2. There is no interference, $I = I_1 + I_2$.

Waves

1. Waves arrive continuously.
2. There is interference, $I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\delta$.

However, when the experiment is performed with real-world electrons, the result is neither of these two. Despite the fact that we can set up the experiment such that we can really register the arrival of electrons on the screen one-by-one, there *nevertheless* is an interference pattern. So we find that:

Real world electrons

1. Electrons arrive one at a time.
2. There is interference, $I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\delta$.

So electrons exhibit characteristics of both particles and waves. They arrive one by one like particles, but the rate that particles arrive exhibits interference like a wave. This behaviour cannot be explained in classical mechanics.

In the double-slit experiment, classical particles would lead to two peaks, and classical waves to an interference pattern. In the real world, the pattern appears dot-by-dot, but nevertheless shows interference.

The double experiment is, however, compatible with the following statements:

- Electrons arrive at the detector one at a time.
- Each of them is described by an amplitude $\psi(x,t)$.
- The modulus squared $|\psi(x,t)|^2$ is the probability distribution for the detector to find an electron at position x at time t.
- The amplitude $\psi(x,t)$ obeys a linear partial differential equation to ensure the principle of superposition.

We must abandon the idea that an electron has a definite position $x(t)$ at all times. Instead, we may only predict the *probability* to measure the position x in a certain region. The same conclusion applies to momentum, energy and any other measurable quantity. The laws of nature are inherently probabilistic!

3

Wave function and Probabilities

Throughout the lecture course, we focus on a particle of mass m moving in one dimension with potential $V(x)$. In classical mechanics, the particle has definite position and momentum $(x(t), p(t))$, which evolve according to Hamilton's equations with Hamiltonian $H = \frac{p^2}{2m} + V(x)$.

Introducing the wave function which leads to the probabilistic character of quantum mechanics.

Motivated by the the double slit experiment, however, we must give up the idea that a particle as a definite position and momentum $(x(t), p(t))$. Instead, the particle is described by a complex wave function $\psi(x,t)$ that encodes the probability for a measurement of position or momentum to yield values in a given range. In this lecture, we consider measurements of position. In the subsequent lectures, we will consider measurements of momentum and energy.

3.1 The Wave function

The wave function $\psi(x,t)$ is a complex function of position x and time t. Putting on our analysis hat, the wave function defines a continuous function

$$\psi_t \quad : \mathbb{R} \to \mathbb{C} \tag{3.1}$$

$$: x \mapsto \psi(x,t) \tag{3.2}$$

at each time $t \in \mathbb{R}$. We will discuss to what extent the wave function should be differentiable later in the course.

The probability density to find a particle at position x at time t is given by $P(x,t) = |\psi(x,t)|^2$.

A basic postulate of quantum mechanics is that the modulus squared of the wave function,

$$P(x,t) := |\psi(x,t)|^2 \,, \tag{3.3}$$

is the 'probability density' for a measurement at time t to find the particle at position x. There are two equivalent ways to say what this means:

- The probability to find the particle between infinitesimally separated points x and $x + dx$ at time t is $P(x,t)dx$.
- The probability to find the particle in a finite interval $a < x < b$ is

$$\int_a^b P(x,t)dx \,. \tag{3.4}$$

We find an immediate constraint on the wave function $\psi(x,t)$ from the requirement that the probability to find the particle anywhere must be 1. In particular, a physical wave function $\psi(x,t)$ should obey

$$\int_{-\infty}^{\infty} P(x,t)dx = 1 \tag{3.5}$$

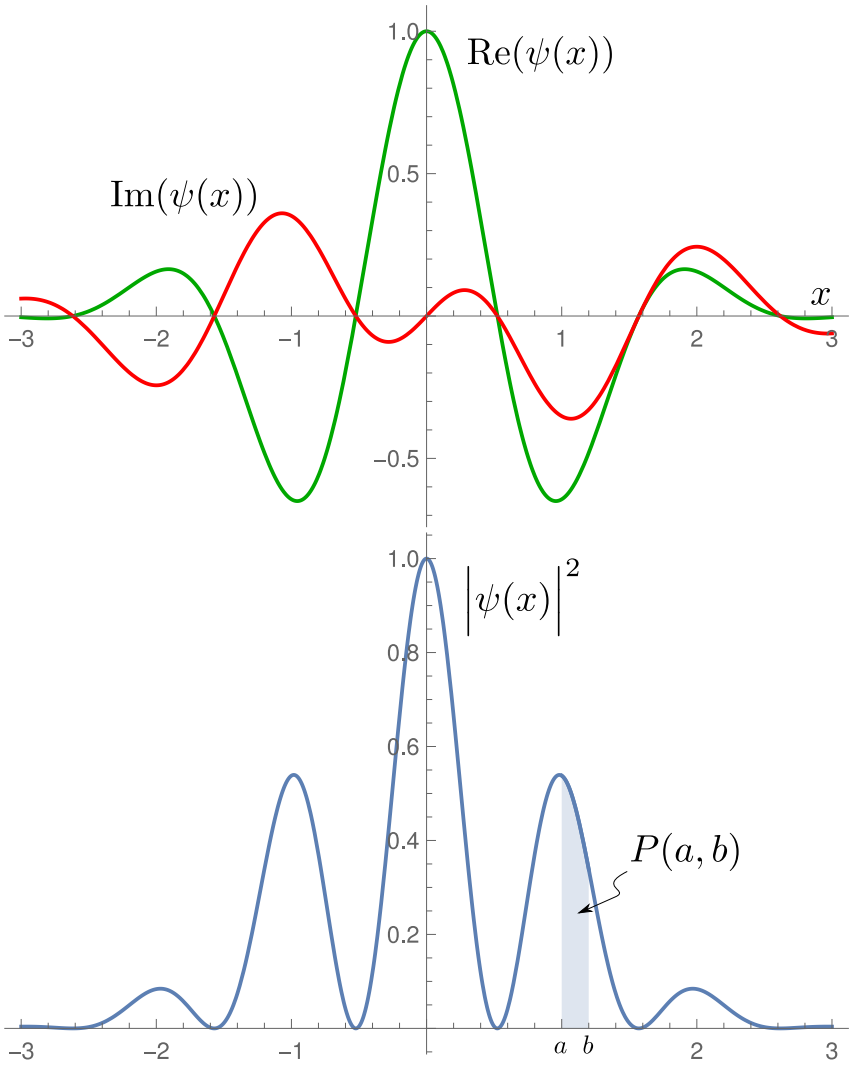

Figure 3.1: A typical wave function (top), having both a real and imaginary part, and the corresponding probability density (bottom). Also indicated is the probability to find the particle in a finite interval $a < x < b$.

at any time t. This constraint typically requires that the wave function should decay fast enough as $x \to \pm\infty$. Some terminology:

- If the above integral exists, the wave function is 'square-normalisable'.
- If the above integral is equal to 1, the wave function is 'normalised'.

3.2 Expectation Values

As for any probability distribution, the expectation value of a polynomial function $f(x)$ is given by

$$\begin{aligned} \langle f(x) \rangle &:= \int_{-\infty}^{\infty} f(x) P(x,t)\, \mathrm{d}x \\ &= \int_{-\infty}^{\infty} f(x) \left|\psi(x,t)\right|^2 \mathrm{d}x\,. \end{aligned} \tag{3.6}$$

The mean of measurements of position, $\langle x \rangle$, for many measurements of particles described by the same wave function, is given by weighing the position by the probability, $\langle x \rangle = \int x |\psi(x,t)|^2 \mathrm{d}x$.

There are two important expectation values that will feature in these lectures:

- First, the expectation value $\langle x \rangle$ is the mean of position measurements on an ensemble of particles with the same wave function $\psi(x,t)$.
- Second, the standard deviation is defined by

  $$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}\,. \tag{3.7}$$

  This is a measure of the spread of the probability distribution around the mean $\langle x \rangle$. In quantum mechanics, it is therefore customary to call Δx the 'uncertainty' in the position.

3.3 Examples

In the first part of the course, we consider wave functions and expectation values at a fixed point in time t - how the wave function evolves in time will be considered later. With this understood, we denote the wave function by $\psi(x)$.

3.3.1 Gaussian Wave function

Consider the wave function

$$\psi(x) = C\, e^{-x^2/4\Delta^2}\,, \tag{3.8}$$

where $\Delta > 0$ has units of length and C is a normalisation constant. To determine the normalisation constant C, we require that the probability to find the particle anywhere is 1,

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 dx \tag{3.9}$$

$$= |C|^2 \int_{-\infty}^{\infty} e^{-x^2/2\Delta^2} dx \tag{3.10}$$

$$= |C|^2 \sqrt{2\Delta^2} \int_{-\infty}^{\infty} e^{-y^2} dy \tag{3.11}$$

$$= |C|^2 \sqrt{2\pi\Delta^2}\,, \tag{3.12}$$

where we have used the substitution $y = \sqrt{2\Delta^2}$ and the standard Gaussian integral

$$\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi}\,. \tag{3.13}$$

We can therefore choose $C = (2\pi\Delta^2)^{-1/4}$. Note that we could have multiplied the normalisation by a constant phase $e^{i\theta}$. This would not change the probability density or position expectation values, so for convenience we can set it to 1.

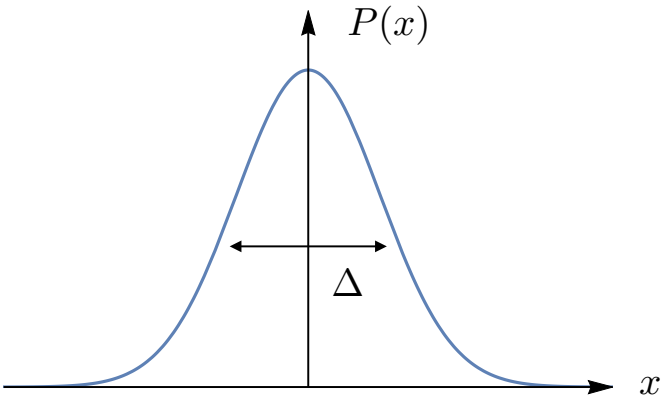

Figure 3.2: Gaussian probability density with width Δ.

The normalised probability distribution is

$$P(x) = \frac{1}{\sqrt{2\pi\Delta^2}} e^{-x^2/2\Delta^2} \tag{3.14}$$

which is a standard Gaussian probability distribution. Before doing any computations, we can immediately say that:

- $\langle x^{2n+1} \rangle = 0$ for $n \in \mathbb{Z}_{\geq 0}$ since the integrand is an odd function of x.
- Since Δ is the only length in the problem, dimensional analysis tells us that $\langle x^{2n} \rangle \propto \Delta^{2n}$ for $n \in \mathbb{Z}_{\geq 0}$.

In one of the problems, you are asked to verify that $\langle x^2 \rangle = \Delta^2$ and therefore the spread $\Delta x = \Delta$.

3.3.2 Infinite Potential Well

Consider a particle confined to the region $0 < x < L$. You can regard this as a particle in an infinite potential well,

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{other} \end{cases}\,. \tag{3.15}$$

The particle would require infinite energy to be found with $x \leq 0$ or $x \geq L$. We therefore require the wave function vanishes in these regions so that the probability to find it there is zero.

A wave function that meets this requirement is

$$\psi(x) = \begin{cases} C\sqrt{x(L-x)} & 0 < x < L \\ 0 & \text{otherwise} \end{cases}\,. \tag{3.16}$$

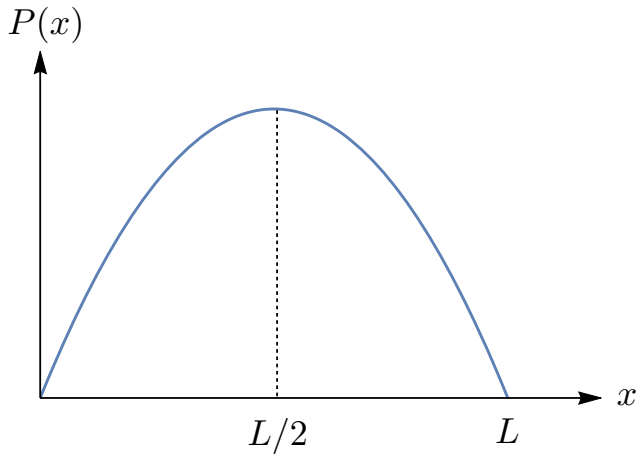

Figure 3.3: Probability density for a particule in an infinite potential well.

To determine the normalisation C, we require that the probability to find the particle anywhere is 1,

$$1 = |C|^2 \int_0^L x(L-x)dx = |C|^2 \frac{L^3}{6}\,, \tag{3.17}$$

and therefore $C = \sqrt{6/L^3}\, e^{i\theta}$. For convenience, we can choose $e^{i\theta} = 1$.

We can now compute some expectation values. Since L is the only length in the problem, dimensional analysis means that $\langle x^n \rangle \propto L^n$ for any $n \in \mathbb{Z}_{\geq 0}$. Computing the first few, we find

$$\begin{aligned} \langle x \rangle &= \frac{6}{L^3} \int_0^L x^2(L-x)\,\mathrm{d}x = \frac{L}{2}\,, \\ \langle x^2 \rangle &= \frac{6}{L^3} \int_0^L x^3(L-x)\,\mathrm{d}x = \frac{3L^2}{10}\,. \end{aligned} \tag{3.18}$$

Since the probability density is symmetric around $L/2$, we should have expected $\langle x \rangle = L/2$. Finally, the uncertainty is

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{L}{\sqrt{20}}\,. \tag{3.19}$$

The wave function is continuous. It is also differentiable, except at places where $V(x)$ is not finite.

This example shows that we will, at some point, have to be more precise about the continuity and differentiability properties of the wave function. For the infinite potential well, we see that $\psi(x)$ is continuous everywhere, and differentiable except at the edges of the well. Jumping ahead a bit, we will find that this holds in general: the wave function $\psi(x)$ will always have to be continuous, and it will have to be differentiable *except* at positions x where the potential $V(x)$ is not finite. We will discuss and derive these conditions in more detail once we have introduced the Schrödinger equation.

3.4 Phases

In is important to note that if we multiply the wave function $\psi(x)$ by a position-dependent phase, the probability density is unchanged

$$\psi(x) \quad \to e^{i\theta(x)}\psi(x)\,, \qquad P(x) \quad \to P(x)\,. \tag{3.20}$$

This means that measurements of position cannot detect the difference between the wave functions $\psi(x)$ and $e^{i\theta(x)}\psi(x)$. In the next lecture, however, we will show that measurements of momentum can detect the difference between these wave functions, unless $\theta(x)$ is constant. On the other hand, a constant phase $e^{i\theta}$ cannot be detected by any measurement and the wave functions $\psi(x)$ and $e^{i\theta}\psi(x)$ describe the same physical state.

3.5 Collapse of the Wave function

We now mention an important subtlety with the interpretation of the probability density $P(x,t)$ in quantum mechanics compared to other areas of mathematical sciences.

Suppose a particle has wave function $\psi(x,t)$ for $t < t_0$. Then at $t = t_0$ the position of the particle is measured and the particle is found at $x = x_0$. What is the wave function after the measurement?

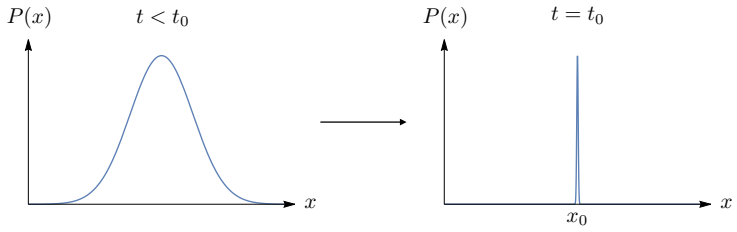

Figure 3.4: When a measurement of position is made, the wave function 'collapses' to one which is sharply peaked at the position where we have found the particle.

It turns out that another measurement immediately after the first will find the particle at $x = x_0$ with probability 1. This is known as wave function collapse. It means that the act of measurement modifies the wave function to something that is tightly localised around $x = x_0$. We will describe this phenomenon more precisely in a future lecture.

When a particle's position is measured, its wave function 'collapses' to a wave function which is sharply peaked at the position where we found the particle.

This is why we must carefully specify the meaning of expectation values such as $\langle x \rangle$. It is not obtained by averaging over repeated measurements of the same wave function. Instead, it is the average of measurements made on an ensemble of particles with the same wave function $\psi(x,t)$.

4

Momentum and Planck's constant

In the last section, we understood the probabilistic interpretation of the wave function $\psi(x,t)$ for measurements of position x at time t. In this lecture we ask the question: how does the wave function $\psi(x,t)$ encode information about measurements of momentum?

On how to extract information about the momentum of particles from the wave function.

4.1 Momentum in Classical Mechanics

For motivation, we first recall the interpretation of momentum in classical mechanics as the generator of translations in space.

Recall from last term's lectures that functions of position and momentum generate infinitesimal canonical transformations in Hamiltonian mechanics. The infinitesimal canonical transformation with parameter ϵ generated by a function $A(x,p)$ is

$$x \to x' = x + \epsilon\{x, A\} \tag{4.1}$$
$$p \to p' = p + \epsilon\{p, A\}\,. \tag{4.2}$$

where

$$\{f,g\} := \frac{\partial f}{\partial x}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial x} \tag{4.3}$$

is the Poisson bracket.

In particular, the canonical transformation generated by the function

$$A(x,p) = p \tag{4.4}$$

is

$$x \to x' = x + \epsilon\{x,p\} = x + \epsilon \tag{4.5}$$
$$p \to p' = p + \epsilon\{p,p\} = p\,. \tag{4.6}$$

Here we have used that

$$\{x,p\} = 1\,. \tag{4.7}$$

The important lesson is that momentum p generates an infinitesimal translation of x.

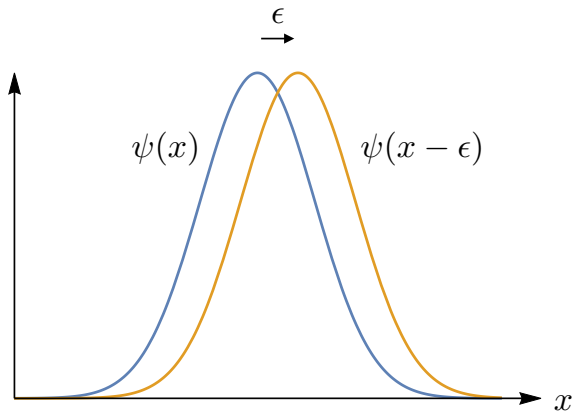

Figure 4.1: Infinitesimal translation of a wave function to the right, $\psi_{\text{trans}}(x) = \psi(x-\epsilon)$ (and note the sign!).

4.2 Momentum in Quantum Mechanics

We now use this idea of momentum to understand momentum in quantum mechanics. Let us consider translating a wave function $\psi(x)$ by a infinitesimal amount ϵ in the positive x direction - as shown below. As in the previous lecture, we work at some fixed moment in time.

The translated wave function is of course $\psi(x-\epsilon)$. To first order in ϵ, the change in the wave function is found by Taylor expanding,

$$\delta_\epsilon \psi(x) = \psi(x-\epsilon) - \psi(x) \tag{4.8}$$

$$= -\epsilon \frac{\partial}{\partial x}\psi(x) + \mathcal{O}(\epsilon^2)\,. \tag{4.9}$$

If we want momentum to generate translations, this suggests we should identify momentum p with the derivative with respect to x.

Let us therefore define a momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}\,, \tag{4.10}$$

such that

$$\delta_\epsilon \psi(x) = -\epsilon \frac{i}{\hbar}\hat{p}\,\psi(x)\,, \tag{4.11}$$

where $\hbar$ is a constant of proportionality. The additional factors of i are introduced for convenience; we will get back to them shortly. Some comments are in order

1. Note that while the momentum p has units of MLT^{-1}, $\partial/\partial x$ has units of L^{-1}. This means $\hbar$ must have units ML^2T^{-1}, or 'energy·time'.

2. Since the wave function is complex, we could imagine $\hbar$ is a complex number. In a moment, we will show that $\hbar$ must be real for momentum measurements to yield real results. This is why we introduced the extra factor of $-i$ in the definition.

Planck's constant has to be present in quantum mechanics for dimensional reasons. It has dimension of 'energy·time' or 'action'.

The constant $\hbar$ is known as the (reduced) Planck constant, and pronounced 'h-bar'.

Its value cannot be determined by mathematical arguments. It must be determined by comparing to experimental data, for example atomic spectra. In our universe,

$$\hbar \approx 1.05 \times 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}\,. \tag{4.12}$$

The smallness of this number, in units that are natural to humans, is why we do not observe quantum mechanical effects in everyday life. You will in the literature also find $h = 2\pi\hbar$, which is usually called Planck's constant (without the 'reduced' prefix).

4.3 A Quick Commutator

In order have position and momentum on an equal footing, we can introduce a position operator $\hat{x}$ that simply multiplies a wave function by x. In summary,

$$\hat{x} = x \tag{4.13}$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}\,. \tag{4.14}$$

The 'commutator' of these operators is defined by

$$[\hat{x}, \hat{p}] := \hat{x}\,\hat{p} - \hat{p}\,\hat{x}\,. \tag{4.15}$$

Here the operators should always be understood to act on everything to the right. Acting with this equation on a wave function $\psi(x)$, we have

$$[\hat{x}, \hat{p}]\ \psi(x) = \hat{x}(\hat{p}\,\psi(x)) - \hat{p}(\hat{x}\,\psi(x)) \tag{4.16}$$

$$= x\left(-i\hbar\frac{\partial}{\partial x}\psi(x)\right) + i\hbar\frac{\partial}{\partial x}\left(x\psi(x)\right) \tag{4.17}$$

$$= i\hbar\,\psi(x)\,. \tag{4.18}$$

where the final line follows from the product rule. Since this holds for any wave function $\psi(x)$, we can summarise this result by

$$[\hat{x}, \hat{p}] = i\hbar\,. \tag{4.19}$$

This is known as the canonical commutation relation.

The commutator is reminiscent of the Poisson bracket formula $\{x, p\} = 1$ from classical mechanics. In fact, the commutator in quantum mechanics is found by replacing

$$\{\,,\,\} \to -\frac{i}{\hbar}[\,,\,]\,. \tag{4.20}$$

This replacement rule is known as 'canonical quantisation'. We study it further in later lectures after introducing some more mathematical machinery.

4.4 Momentum Expectation Values

Just like position, in quantum mechanics we can only compute the probabilities of the outcomes of momentum measurements. For now, we satisfy ourselves with computing expectation values of functions of momentum.

First, recall from the last lecture that the expectation value $\langle x \rangle$ can be written

$$\langle x \rangle = \int_{-\infty}^{\infty} x \, |\psi(x,t)|^2 \, dx \tag{4.21}$$

$$= \int_{-\infty}^{\infty} \overline{\psi(x,t)} \, \hat{x} \, \psi(x,t) \, dx \, . \tag{4.22}$$

We now propose, similarly, that the expectation value of momentum is

$$\langle p \rangle = \int_{-\infty}^{\infty} \overline{\psi(x,t)} \, \hat{p} \, \psi(x,t) \, dx \tag{4.23}$$

$$= -i\hbar \int_{-\infty}^{\infty} \overline{\psi(x,t)} \, \frac{\partial}{\partial x} \, \psi(x,t) \, dx \, . \tag{4.24}$$

As for the position expectation value, we emphasise that $\langle p \rangle$ is interpreted as the average of momentum measurements on an ensemble of particles with the same wave function $\psi(x,t)$.

Let us now return to explain why $\hbar$ must be real. Since the outcomes of momentum measurements are real numbers, we require $\langle p \rangle \in \mathbb{R}$. Let us imagine for a second that $\hbar$ is complex and compute the complex conjugate of $\langle p \rangle$,

$$\overline{\langle p \rangle} = i\bar{\hbar} \int_{-\infty}^{\infty} dx \, \psi(x,t) \frac{\partial}{\partial x} \overline{\psi(x,t)} \tag{4.25}$$

$$= -i\bar{\hbar} \int_{-\infty}^{\infty} dx \, \frac{\partial}{\partial x} \psi(x,t) \, \overline{\psi(x,t)} + i\hbar \left[|\psi(x,t)|^2 \right]_{-\infty}^{\infty} \tag{4.26}$$

$$= -i\bar{\hbar} \int_{-\infty}^{\infty} dx \, \overline{\psi(x,t)} \frac{\partial}{\partial x} \psi(x,t) \tag{4.27}$$

$$= \frac{\bar{\hbar}}{\hbar} \langle p \rangle \, . \tag{4.28}$$

In the passing second line, we have integrated by parts. In passing to the third line, we discarded the boundary term because $|\psi(x,t)|^2$ must vanish as $x \to \pm\infty$ if the wave function is square normalisable. Therefore, the momentum expectation value is real if and only if $\hbar$ is real.

In a similar way, we can compute more general expectation values

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} dx \, \overline{\psi(x,t)} \, f(\hat{p}) \, \psi(x,t) \tag{4.29}$$

$$= \int_{-\infty}^{\infty} dx \, \overline{\psi(x,t)} \, f\left(-i\hbar \frac{\partial}{\partial x} \right) \, \psi(x,t) \, . \tag{4.30}$$

Of particular importance is the momentum uncertainty

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \, , \tag{4.31}$$

which gives a measure of the spread of momentum measurements around $\langle p \rangle$ made on an ensemble of particles with identical wave function $\psi(x,t)$.

4.4.1 Example: Gaussian Wave function

Let us again consider the wave function

$$\psi(x) = Ce^{-x^2/4\Delta^2}\,, \tag{4.32}$$

with normalisation $C = (2\pi\Delta^2)^{-1/4}$. In the last lecture, we showed that the position expectation values are given by $\langle x\rangle = 0$ and $\langle x^2\rangle = \Delta^2$, and therefore the uncertainty in position is $\Delta x = \Delta$.

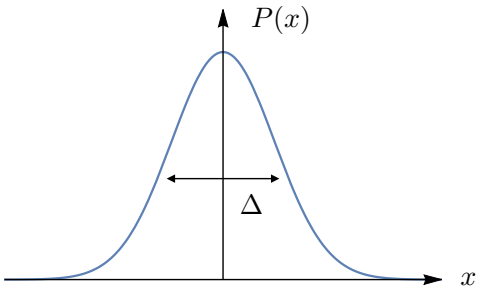

Figure 4.2: Gaussian wave function with width Δ.

The action of the momentum operator on this wave function is

$$\hat{p}\,\psi(x) = \frac{i\hbar}{2\Delta^2}\,x\,\psi(x) \tag{4.33}$$

$$\hat{p}^2\,\psi(x) = \frac{\hbar^2}{2\Delta^2}\,\psi(x) - \frac{\hbar^2}{4\Delta^4}\,x^2\,\psi(x)\,. \tag{4.34}$$

Note that the result is always a polynomial in x times the original wave function. This means we can recycle our results for position expectation values to compute momentum expectation values. For example,

$$\langle p\rangle = \frac{i\hbar}{2\Delta^2}\int_{-\infty}^{\infty} x|\psi(x)|^2 = \frac{i\hbar}{2\Delta^2}\langle x\rangle = 0 \tag{4.35}$$

and similarly

$$\langle p^2\rangle = \frac{\hbar^2}{2\Delta^2}\int_{-\infty}^{\infty}|\psi(x)|^2 - \frac{\hbar^2}{4\Delta^4}\int_{-\infty}^{\infty}x^2|\psi(x)|^2 \tag{4.36}$$

$$= \frac{\hbar^2}{2\Delta^2} - \frac{\hbar^2}{4\Delta^4}\langle x^2\rangle \tag{4.37}$$

$$= \frac{\hbar^2}{4\Delta^2}\,. \tag{4.38}$$

The momentum uncertainty is therefore $\Delta p = \frac{\hbar}{2\Delta}$.

Note that the product of position and momentum uncertainties is independent of Δ,

$$\Delta x\,\Delta p = \frac{\hbar}{2}\,. \tag{4.39}$$

This means that if we attempt to localise the particle in space by making Δx smaller, the the uncertainly in momentum Δp necessarily increases, and vice verse.

4.5 Heisenberg's Uncertainty Principle

This example illustrates an important result known as Heisenberg's uncertainty principle. This states that for any normalised wave function,

$$\Delta x \Delta p \geq \frac{\hbar}{2} \,. \tag{4.40}$$

We will prove this result later in the course. It shows that there is a fundamental limit in quantum mechanics on the degree we can simultaneously reduce the uncertainty in position and momentum. The Gaussian wave function saturates this limit: it is a 'minimal uncertainty' wave function.

Remember that $\hbar$ is an extremely small number in human units. So while we cannot arrange for both Δx and Δp to vanish, both uncertainties can be simultaneously small in human units. This goes some way to explaining why in everyday life, objects appear to have a definite position and momentum.

5

Schrödinger's Equation

About the most important equation in Quantum Mechanics, which determines how systems evolve in time.

In this lecture, we begin to understand how the wave function evolves in time in quantum mechanics. The basic question is: given an initial wave function $\psi(x,0)$, what is the wave function $\psi(x,t)$ at later times $t>0$? This will allow us to determine how statistical predictions for the outcomes of measurements evolve in time. For example, we can determine how expectation values of observables such as $\langle x\rangle$, $\langle p\rangle$, $\langle H\rangle$ depend on time.

5.1 Time Evolution in Classical Mechanics

In the Hamiltonian formulation of classical mechanics, a particle is described by a definite position and momentum $(x(t),p(t))$, which evolve in time according to Hamilton's equations

$$\dot{x}=+\frac{\partial H}{\partial p}\qquad \dot{p}=-\frac{\partial H}{\partial x}\,, \tag{5.1}$$

where H is the Hamiltonian of the system.

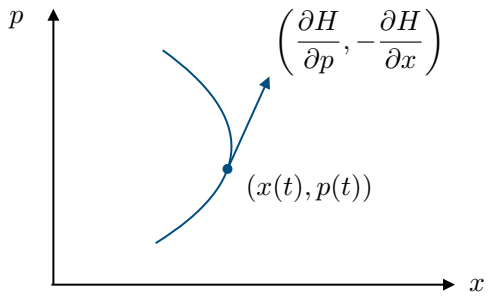

Figure 5.1: Time evolution in phase space is generated by the Hamiltonian.

It is useful to reformulate time-evolution as a canonical transformation. First, we note that Hamilton's equations can be expressed as

$$\dot{x}=\{x,H\}\qquad \dot{p}=\{p,H\}\,, \tag{5.2}$$

where

$$\{A,B\}:=\frac{\partial A}{\partial x}\frac{\partial B}{\partial p}-\frac{\partial A}{\partial p}\frac{\partial B}{\partial x} \tag{5.3}$$

is the Poisson bracket. This shows that an infinitesimal time evolution $t\mapsto t+\epsilon$ of position and momentum can be expressed

$$x\mapsto x+\epsilon\dot{x}=x+\epsilon\{x,H\} \tag{5.4}$$

$$p\mapsto p+\epsilon\dot{p}=p+\epsilon\{p,H\}\,, \tag{5.5}$$

which is an infinitesimal canonical transformation generated by the Hamiltonian H. In other words, the Hamiltonian is the generator of time translations.

This is similar to the statement that momentum is the generator of translations in space from lecture 3. We will follow the same logic here to understand time-evolution in quantum mechanics.

5.2 Schrödinger's Equation

We now use the idea of the Hamiltonian as the generator of time translations to understand time-evolution in quantum mechanics.

Let us consider a wave function $\psi(x,t)$. The small change in the wave function due to an infinitesimal time translation $t \mapsto t+\epsilon$ is

$$\delta_\epsilon \psi(x,t) = \psi(x,t+\epsilon) - \psi(x,t) \tag{5.6}$$

$$= \epsilon \frac{\partial \psi(x,t)}{\partial t} + \mathcal{O}(\epsilon^2)\,. \tag{5.7}$$

We want this transformation to be "generated" by the Hamiltonian operator $\hat{H}$. This means the change in the wave function is proportional to the action of the Hamiltonian H on the wave function,

$$\delta_\epsilon \psi(x,t) = \frac{\epsilon}{\alpha} \hat{H}\,\psi(x,t)\,. \tag{5.8}$$

where $\alpha \in \mathbb{C}$ is an unknown constant of proportionality.

Equating the two expressions for the change in the wave function under the infinitesimal time translation $t \mapsto t+\epsilon$, we find

$$\alpha \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\,\psi(x,t)\,. \tag{5.9}$$

How can we determine the constant of proportionality $\alpha \in \mathbb{C}$?

1. **Dimensional Analysis.** The hamiltonian has units of energy ML^2T^{-2}, while the derivative ∂_t has units T^{-1}. The constant of proportionality α therefore has units of angular momentum ML^2T^{-1}. Note that these are the same units as $\hbar$.

2. **Conservation of Total Probability.** The probability to find the particle anywhere in space should be 1 at any time. This requires that the normalisation $\int \psi^*(x), \psi(x)\,\mathrm{d}x$ is constant in time for any square-normalisable wave function,

$$0 = \partial_t \int \psi^* \psi \,\mathrm{d}x \tag{5.10}$$

$$= \int \partial_t \psi^* \psi \,\mathrm{d}x + \int \psi^*\, \partial_t \psi \,\mathrm{d}x \tag{5.11}$$

$$= \int \frac{1}{\alpha} \big(\hat{H}\,\psi\big)^* \,\psi \mathrm{d}x + \int \psi^* \frac{1}{\alpha} \hat{H}\,\psi \mathrm{d}x \tag{5.12}$$

$$= \left(\frac{1}{\bar{\alpha}} + \frac{1}{\alpha}\right) \int \psi^* \hat{H} \psi \,\mathrm{d}x \tag{5.13}$$

$$= \frac{\alpha + \bar{\alpha}}{|\alpha|^2} \int \psi^* H \psi \,\mathrm{d}x\,. \tag{5.14}$$

In passing to the fourth line, we have used the fact that we know the form of $\hat{H}$ in terms of derivatives with respect to x. We can integrate by parts with respect to those, and hence show that you can 'move' the operator $\hat{H}$ from the $\bar{\psi}$ factor to the ψ factor. We thus conclude that $\alpha = -\bar{\alpha}$ and therefore α is imaginary.

These observations suggest the constant of proportionality is $\alpha = i\hbar$ where $\hbar$ is Planck's constant - this is indeed the value chosen by nature!

The Schrödinger equation determines the time-evolution of the wave function in terms of the Hamiltonian operator acting on the wave function.

In summary we have

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\,\psi(x,t) \tag{5.15}$$

or written out in full

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t)\,. \tag{5.16}$$

This is the "Schrödinger equation". It is a linear partial differential equation for the wave function $\psi(x,t)$. This is probably the most profound equation you will come across in your degree: it is the most fundamental description of nature we have at short distances.

Note that there is also something called the "time-independent Schrödinger equation", which is essentially what you get when $\partial\psi(x,t)/\partial t$ evaluates to a constant times $\psi(x,t)$. We will return to that special case in the chapter on "stationary states".

5.3 Properties

The following properties of Schrödinger's equation are very important in the development of quantum mechanics.

1. **1st Order in Time.** Schrödinger's equation has only a first order time derivative. This means that if we know the initial wave function $\psi(x,0)$, Schrödinger's equation uniquely determines the wave function $\psi(x,t)$ for $t \geq 0$.

2. **Linearity.** Schrödinger's equation is linear PDE for the wave function $\psi(x,t)$. This means that given two solutions $\psi_1(x,t)$ and $\psi_2(x,t)$, any linear combination

$$a_1\psi_1(x,t) + a_2\psi_2(x,t) \tag{5.17}$$

with constants $a_1, a_2 \in \mathbb{C}$ is another solution. This is known as the "principle of superposition".

The combination of these two properties, together with the decomposition of a wave function $\psi(x,t)$ into orthonormal eigenstates of the Hamiltonian $\hat{H}$ provides a powerful and systematic method of solving Schrödinger's equation. The next lecture is dedicated to explaining this method. For now we look at some simple examples.

5.4 Example: Plane Waves

Consider a wave function of the form

$$\psi_p(x,t) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} e^{-iE(p)t/\hbar} ,$$

where $E(p)$ is some function of momentum $p \in \mathbb{R}$. Then,

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = E(p)\psi(x,t) \tag{5.18}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{p^2}{2m}\psi(x,t) . \tag{5.19}$$

If we choose $E(p) = p^2/2m$ then

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} . \tag{5.20}$$

We have therefore found a solution of Schrödinger's equation with $V(x) = 0$. This corresponds to plane wave solution for a free particle of mass m.

5.5 Example: Ground State in Infinite Potential Well

Now consider the wave function

$$\psi(x,t) = \phi_1(x) e^{-iE_1 t/\hbar} \tag{5.21}$$

$$= \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \exp\left(-i\frac{\hbar\pi^2}{2mL^2}t\right) \tag{5.22}$$

in an infinite potential well $0 < x < L$.

We find

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2\pi^2}{2mL^2}\psi(x,t) \tag{5.23}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \psi(x,t) \tag{5.24}$$

and therefore

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} . \tag{5.25}$$

so $\psi(x,t)$ is a solution of Schrödinger's equation in the infinite potential well. Note that $\psi(x,0) = \phi_1(x)$ is the ground state Hamiltonian eigenfunction with lowest energy

$$E_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 = \frac{\hbar\pi^2}{2mL^2} . \tag{5.26}$$

The wave function $\psi(x,t)$ is therefore the unique time evolution of $\phi_1(x)$.

These examples have something in common: they are both of the form

$$\psi(x,t) = \phi(x) e^{-iEt/\hbar} , \tag{5.27}$$

where $\phi(x)$ is an eigenfunction of the Hamiltonian H with eigenvalue E. We will see later (chapter 11) why this is always a solution of Schrödinger's equation and that any solution can be expressed as a linear combination of such solutions.

5.6 Wave function continuity and differentiability

When we first introduced the wave function, and discussed its form in an infinite potential well, we mentioned in passing that the wave fuction is always continuous, and differentiable except at points where $V(x)$ is not finite. We are now in a position to back up this claim.

First look at differentiability. You can prove this formally by writing down the Schrödinger equation for a state of the form (5.27). Re-arranging a bit, this gives

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\phi(x) = (E - V(x))\phi(x)\,. \tag{5.28}$$

Now integrate both sides over a small interval interval around a point of interest. If $E-V(x)$ remains finite, the right-hand side goes to zero in the limit of infinitesimally small interval, so the left-hand side should too. That means that the 2nd derivative of $\phi(x)$ has to remain finite, which can only be true if the 1st derivative is continuous.

You have seen a counterexample of this when we discussed the infinite potential well, where $V(x)$ is infinite outside the range $0 < x < L$. Another counterexample which we will see later is the delta-function potential.

For the continuity of $\phi(x)$ itself, consider what happens if you have the simplest type of discontinuity, namely a step,

$$\phi(x) = \begin{cases} a & \text{for } x < 0, \\ b & \text{for } x > 0. \end{cases} \tag{5.29}$$

Then $\phi'(x) = (b-a)\delta(x)$, which you may still be happy with, but the second derivative is then undefined, and you will struggle to make sense of (5.28) above. For this reason, we take the wave function to be continuous.

6

The Hilbert Space

We now begin to develop the mathematical structures underlying quantum mechanics more systematically. In this lecture, we introduce the idea of wave functions as elements of a complex vector space with Hermitian inner product. With a few additional assumptions, this is known as a 'Hilbert space'.

A mathematical detour, in which we start viewing wave functions as vectors in an infinite-dimensional complex vector space: Hilbert space.

6.1 Linear Algebra

Consider a finite-dimensional complex vector space $V \cong \mathbb{C}^N$. The most important property is that of taking linear combinations: $a_1 v_1 + a_2 v_2 \in V$ for any $v_1, v_2 \in V$ and complex numbers $a_1, a_2 \in \mathbb{C}$.

A Hermitian inner product on V is a map

$$\begin{aligned} \langle \cdot, \cdot \rangle &: V \times V \to \mathbb{C} \\ &: (v_1, v_2) \mapsto \langle v_1, v_2 \rangle \end{aligned} \tag{6.1}$$

that obeys

- $\langle v, w \rangle = \overline{\langle w, v \rangle}$
- $\langle v, a_1 w_1 + a_2 w_2 \rangle = a_1 \langle v, w_1 \rangle + a_2 \langle v, w_2 \rangle$
- $\langle a_1 v_1 + a_2 v_2, v \rangle = \bar{a}_1 \langle v_1, v \rangle + \bar{a}_2 \langle v_2, v \rangle$
- $\langle v, v \rangle \geq 0$ with equality iff $v = 0$.

It is often convenient to introduce an orthonormal basis $\{e_j\}$ such that

$$\langle e_i, e_j \rangle = \delta_{ij} \tag{6.2}$$

and any vector can be expressed

$$v = \sum_{j=1}^{N} v_j e_j \,. \tag{6.3}$$

Computing the inner product with e_j, the components of the vector are $v_j = \langle v, e_j \rangle$. The Hermitian inner product can then be expressed in component form as

$$\langle v, w \rangle = \sum_j \bar{v}_j w_j \,. \tag{6.4}$$

In particular, the squared norm of a vector is $|v|^2 := \langle v, v \rangle = \sum_j |v_j|^2$.

6.2 Wave functions Revisited

At a fixed time t, a wave function is a continuous function

$$\begin{aligned} \psi &: \mathbb{R} \to \mathbb{C} \\ &: x \mapsto \psi(x)\,. \end{aligned} \tag{6.5}$$

In order for the wave function to have a probabilistic interpretation, we require it to be square-normalisable,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \mathrm{d}x < \infty\,. \tag{6.6}$$

This means that by multiplying by a constant, we can ensure that the probability to find the particle anywhere is 1.

The set of continuous square-integrable wave functions forms a complex vector space. That is to say, for any square-integrable ψ_1, ψ_2 and complex numbers $a_1, a_2 \in \mathbb{C}$, the wave function $a_1\psi_1 + a_2\psi_2$ is square-integrable. This can be shown as follows. It is immediate that if ψ is square-integrable then $a\psi$ is square integrable for any complex number $a \in \mathbb{C}$. We can therefore focus on the sum $\psi_1 + \psi_2$. At each point $x \in \mathbb{R}$ we have

$$|\psi_1 + \psi_2|^2 = |\psi_1|^2 + |\psi_2|^2 + 2\mathrm{Re}(\bar{\psi}_1\psi_2) \tag{6.7}$$

$$\leq |\psi_1|^2 + |\psi_2|^2 + 2|\bar{\psi}_1\psi_2| \tag{6.8}$$

$$\leq |\psi_1|^2 + |\psi_2|^2 + 2|\psi_1||\psi_2|\,, \tag{6.9}$$

where we used the properties of complex numbers, $\mathrm{Re}(z) \leq |z|$ and $|z_1 z_2| = |z_1|z_2|$. We also have the elementary inequality

$$2|\psi_1||\psi_2| = |\psi_1|^2 + |\psi_2|^2 - (|\psi_1| - |\psi_2|)^2 \tag{6.10}$$

$$\leq |\psi_1|^2 + |\psi_2|^2\,. \tag{6.11}$$

This implies

$$|\psi_1 + \psi_2|^2 \leq 2|\psi_1|^2 + 2|\psi_2|^2\,. \tag{6.12}$$

and therefore

$$\int_{-\infty}^{\infty} \mathrm{d}x\, |\psi_1 + \psi_2|^2 \leq 2\int_{-\infty}^{\infty} \mathrm{d}x\, |\psi_1|^2 + 2\int_{-\infty}^{\infty} \mathrm{d}x\, |\psi_2|^2\,. \tag{6.13}$$

This makes it clear that if the wave functions ψ_1 and ψ_2 are square-integrable then the sum $\psi_1 + \psi_2$ is square-integrable.

6.3 Inner Product

Let us define

$$\langle \psi_1, \psi_2 \rangle := \int_{-\infty}^{\infty} \mathrm{d}x\, \overline{\psi_1(x)}\psi_2(x)\,. \tag{6.14}$$

We claim this is a Hermitian inner product:

- $\langle \psi_1, \psi_2 \rangle = \overline{\langle \psi_2, \psi_1 \rangle}$

- $\langle \psi_3, a_1\psi_1 + a_2\psi_2 \rangle = a_1\langle \psi_3, \psi_1 \rangle + a_2\langle \psi_3, \psi_2 \rangle$
- $\langle a_1\psi_1 + a_2\psi_2, \psi_3 \rangle = \bar{a}_1\langle \psi_1, \psi_3 \rangle + \bar{a}_2\langle \psi_2, \psi_3 \rangle$
- $\langle \psi, \psi \rangle \geq 0$ with equality iff $\psi(x) = 0$.

The first three properties follow immediately from the definition. To prove the final property, note that

$$\langle \psi, \psi \rangle := \int_{-\infty}^{\infty} \mathrm{d}x \, |\psi(x)|^2 \tag{6.15}$$

and that the integrand is everywhere non-negative, $|\psi(x)|^2 \geq 0$. This immediately implies $\langle \psi, \psi \rangle \geq 0$. Now suppose $\langle \psi, \psi \rangle = 0$. Then $|\psi(x)|^2$ vanishes everywhere except a set of measure zero. However, since $|\psi(x)|^2$ is a continuous function, we must have $|\psi(x)|^2 = 0$ everywhere and therefore $\psi(x) = 0$.

The Hermitian inner product obeys another property known as 'completeness'. We will not need the definition in this course. Including this property, the vector space of wave functions together with the Hermitian inner product form a 'Hilbert space'.

6.4 Orthonormal Bases

It is frequently useful to introduce an orthonormal basis of wave functions. In a later lecture, we will explain that there are natural orthonormal bases that are 'continuous' or 'discrete' in nature and arise from eigenfunctions of operators associated to observables such as position, momentum and energy.

For now we define an orthonormal basis to be a discrete set of wave functions $\{\phi_n(x)\}$ such that

$$\langle \phi_m, \phi_n \rangle = \delta_{mn} \tag{6.16}$$

and any continuous square-integrable wave function can be uniquely expressed

$$\psi(x) = \sum_n c_n \phi_n(x) \,, \tag{6.17}$$

where

$$c_m = \langle \phi_m, \psi \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \, \overline{\phi_m(x)} \, \psi(x) \,. \tag{6.18}$$

The Hermitian inner product can be expressed in terms of the coefficients,

$$\langle \psi_1, \psi_2 \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \, \overline{\psi_1(x)} \psi_2(x) = \sum_n \bar{c}_{1,n} c_{2,n} \tag{6.19}$$

while the the squared norm becomes $\langle \psi, \psi \rangle = \displaystyle\int_{-\infty}^{\infty} \mathrm{d}x \, |\psi(x)|^2 = \sum_n |c_n|^2$.

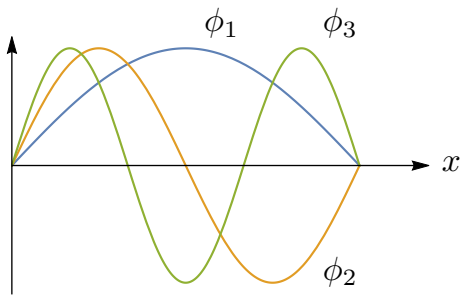

Figure 6.1: The first three basis functions for a particle in a box.

6.5 Example: Particle in a Box

Let us consider an infinite potential well in the region $0 < x < L$. We therefore restrict to continuous square-integrable wave functions that vanish for $x \leq 0$ and $x \geq L$. In this case, we may replace everywhere

$$\int_{-\infty}^{\infty} \mathrm{d}x \to \int_0^L \mathrm{d}x\,. \tag{6.20}$$

Let us define

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad n \in \mathbb{Z}_{>0}\,. \tag{6.21}$$

These wave functions are orthogonal with respect to the inner product

$$\begin{aligned}
\langle \phi_m, \phi_n \rangle &= \int_0^L \bar{\phi}_m(x)\phi_n(x) && (6.22)\\
&= \frac{2}{L}\int_0^L \mathrm{d}x \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\\
&= \frac{1}{L}\int_0^L \mathrm{d}x \left(\cos\left(\frac{(m-n)\pi x}{L}\right) - \cos\left(\frac{(m+n)\pi x}{L}\right)\right) && (6.23)\\
&= \delta_{m,n} - \delta_{m,-n} && (6.24)\\
&= \delta_{m,n} && (6.25)
\end{aligned}$$

where in passing to the final line, we dropped the second contribution because $n + m = 0$ is impossible for $n, m \in \mathbb{Z}_{>0}$.

The fact that any continuous square-integrable wave function has a unique expansion of the form

$$\psi(x) = \sum_{n=0}^{\infty} c_n \phi_n(x) = \sqrt{\frac{2}{L}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{L}\right)\,, \tag{6.26}$$

is the content of Fourier's theorem. The Fourier coefficients are found by taking the Hermitian inner product with $\phi_n(x)$,

$$c_n = \langle \phi_n, \psi \rangle = \sqrt{\frac{2}{L}} \int_0^L \mathrm{d}x\, \sin\left(\frac{n\pi x}{L}\right)\psi(x)\,. \tag{6.27}$$

The norm squared of the wave function is

$$\langle \psi, \psi \rangle = \int_0^L \mathrm{d}x\, |\psi(x)|^2 = \sum_{n=1}^{\infty} |c_n|^2\,,$$

which is precisely the statement of Parseval's theorem.

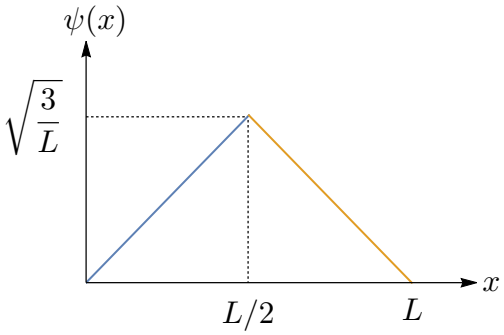

Figure 6.2: The 'pyramid' wave function for a particle in a box.

As an example, consider the 'pyramid' wave function displayed above. With the correct normalisation, this wave function is

$$\psi(x) = \sqrt{\frac{12}{L}} \begin{cases} \dfrac{x}{L} & 0 \leq x \leq \dfrac{L}{2} \\ \dfrac{L-x}{L} & \dfrac{L}{2} \leq x \leq L \end{cases} \tag{6.28}$$

The Fourier coefficients c_n are computed as follows,

$$c_n = \sqrt{\frac{2}{L}} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \psi(x) \mathrm{d}x \tag{6.29}$$

$$= \sqrt{\frac{24}{L^2}} \left(\int_0^{L/2} \frac{x}{L} \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x + \int_{L/2}^{L} \left(1 - \frac{x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x \right)$$

$$= \sqrt{\frac{24}{L^2}} (1 - (-1)^n) \int_0^{L/2} \frac{x}{L} \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x \tag{6.30}$$

$$= \sqrt{24}(1 - (-1)^n) \frac{(-1)^{\frac{n+1}{2}}}{n^2\pi^2} \tag{6.31}$$

$$= \begin{cases} \dfrac{\sqrt{96}(-1)^{m+1}}{(2m+1)^2\pi^2} & \text{if} \quad n = 2m+1 \\ 0 & \text{otherwise} \end{cases} . \tag{6.32}$$

In passing to the final line, the summands are non-zero only when n is odd, so we introduced $n = 2m + 1$. As a consistency check,

$$\langle \psi, \psi \rangle = \sum_{n=1}^{\infty} |c_n|^2 = \frac{96}{\pi^4} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^4} = 1 \,, \tag{6.33}$$

so the wave function is indeed correctly normalised.

7

Hermitian Operators

In the previous lecture, we introduced the mathematical structure behind wave functions. We showed that continuous square-integrable wave functions form a complex vector space with Hermitian inner product, called the Hilbert space. In this lecture, we study the mathematical structures behind observables such as position, momentum and energy.

Introducing Hermitian operators in Hilbert space, and showing how, in the case of a countable basis, their matrix elements are Hermitian matrices.

7.1 More Linear Algebra

We begin with a quick review of some more linear algebra. As before, we first consider a finite-dimensional complex vector space V with Hermitian inner product $\langle \cdot , \cdot \rangle$ and an orthonormal basis $\{e_j\}$.

A linear operator is a map $A : V \to V$ such that

$$A \cdot (a_1 v_1 + a_2 v_2) = a_1 (A \cdot v_1) + a_2 (A \cdot v_2) \tag{7.1}$$

for any vectors $v_1, v_2 \in V$ and complex numbers $a_1, a_2 \in \mathbb{C}$. Any linear combination $a_1 A_1 + a_2 A_2$ and composition $A_1 \cdot A_2$ of two linear operators A_1, A_2 is again a linear operator. The matrix elements of a linear operator in an orthonormal basis $\{e_j\}$ are defined by $A_{ij} = \langle e_i, A \cdot e_j \rangle$.

The adjoint $A^\dagger$ of a linear operator A is defined by

$$\langle v_1, A \cdot v_2 \rangle = \langle A^\dagger \cdot v_1, v_2 \rangle \tag{7.2}$$

for any pair of vectors $v_1, v_2 \in V$. Let us compute the matrix elements of $A^\dagger$ with respect to an orthonormal basis,

$$\begin{aligned} A^\dagger_{ij} &= \langle e_i, A^\dagger e_j \rangle && (7.3) \\ &= \langle A \cdot e_i, e_j \rangle \\ &= \overline{\langle e_j, A \cdot e_i \rangle} && (7.4) \\ &= \overline{A_{ji}} \, . && (7.5) \end{aligned}$$

On other words, the matrix elements of operators A and $A^\dagger$ are related by taking the conjugate transpose of the matrix.

The adjoint operation has the following basic properties

- $(a_1 A_1 + a_2 A_2)^\dagger = \bar{a}_1 A_1^\dagger + \bar{a}_2 A_2^\dagger$
- $(A_1 A_2)^\dagger = A_2^\dagger A_1^\dagger$.

A Hermitian (or symmetric) operator is a linear operator which is equal to its adjoint, $A^\dagger = A$.

It follows from these properties that $(A^n)^\dagger = (A^\dagger)^n$ and therefore $f(A)^\dagger = f(A^\dagger)$ for any polynomial function $f(a)$.

A Hermitian operator is a linear operator that is equal to its adjoint, $A = A^\dagger$. An equivalent way to say this is that a Hermitian operator obeys

$$\langle v_1, A \cdot v_2 \rangle = \langle A \cdot v_1, v_2 \rangle \tag{7.6}$$

for any $v_1, v_2 \in V$. The matrix elements A_{ij} of a Hermitian operator form a Hermitian matrix, $\overline{A_{ji}} = A_{ij}$, hence the name! We will see that Hermitian operators play an incredible important role in quantum mechanics.

As an aside: mathematicians tend to call Hermitian operators 'symmetric operators', and reserve the word Hermitian for matrices. There are subtle issues related to the fact that the domain of A may not be equal to the domain of $A^\dagger$, in which case the operator is symmetric but not 'self-adjoint'. For a lot of physics applications the theory around this is more complicated than the solution, but we may touch on some of this in a problem later. However, if this is your thing and you cannot wait, read [4] (all four volumes of it).

7.2 Linear Differential Operators

We now return to quantum mechanics of a particle moving in one dimension $x \in \mathbb{R}$. In the previous lecture, we learnt that continuous square-integrable wave functions $\psi(x)$ form a complex vector space with Hermitian inner product

$$\langle \psi_1, \psi_2 \rangle = \int_{-\infty}^{\infty} \overline{\psi_1(x)} \psi_2(x) \mathrm{d}x \,. \tag{7.7}$$

Furthermore, it often convenient to introduce a discrete orthonormal basis of wave functions $\{\phi_n(x)\}$. Remember that the index n may run over a set with an infinite number of elements, for example $n \in \mathbb{Z}_{>0}$.

A linear operator now corresponds to a linear differential operator A built from derivatives with respect to x. We have already encountered two important examples of linear differential operators:

- The position operator $\hat{x} = x$
- The momentum operator $\hat{p} = -i\hbar \dfrac{\partial}{\partial x}$

We define the matrix elements of A in a discrete orthonormal basis by

$$A_{mn} := \langle \phi_m, A \cdot \phi_n \rangle = \int_{-\infty}^{\infty} \overline{\phi_m(x)} \left(A \cdot \phi_n(x) \right) \,. \tag{7.8}$$

If there is an infinite number of wave functions $\phi_n(x)$ in the orthonormal basis, this will be an infinite-dimensional matrix.

The adjoint of a linear differential operator is defined by

$$\langle \psi_1, A^\dagger \cdot \psi_2 \rangle = \langle A \cdot \psi_1, \psi_2 \rangle \tag{7.9}$$

and has the same properties as above. It has matrix elements given by the conjugate transpose, $A^\dagger_{mn} = \bar{A}_{nm}$.

A Hermitian operator again satisfies $A^\dagger = A$ or equivalently

$$\langle \psi_1, A \cdot \psi_2 \rangle = \langle A \cdot \psi_1, \psi_2 \rangle \,. \tag{7.10}$$

for any continuous square-normalisable wave functions $\psi_1(x)$, $\psi_2(x)$. The matrix elements of a Hermitian operator form a Hermitian matrix $A_{mn} = \bar{A}_{nm}$.

7.3 Position, Momentum and Energy

Let us prove the position and momentum operators are Hermitian. First, using the fact that x is real we have (on the real line)

$$\begin{aligned} \langle \hat{x} \cdot \psi_1, \psi_2 \rangle &= \int_{-\infty}^{\infty} \overline{x\psi_1(x)}\, \psi_2(x)\, \mathrm{d}x & (7.11)\\ &= \int_{-\infty}^{\infty} \overline{\psi_1(x)}\, x\psi_2(x)\, \mathrm{d}x \\ &= \langle \psi_1, \hat{x} \cdot \psi_2 \rangle \,. & (7.12) \end{aligned}$$

Second, integrating by parts we find

$$\begin{aligned} \langle \hat{p} \cdot \psi_1, \psi_2 \rangle &= \int_{-\infty}^{\infty} \overline{-i\hbar \frac{\partial \psi_1(x)}{\partial x}} \psi_2(x)\, \mathrm{d}x & (7.13)\\ &= \int_{-\infty}^{\infty} i\hbar \frac{\partial \overline{\psi_1(x)}}{\partial x} \psi_2(x)\, \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \overline{\psi_1(x)} \left(-i\hbar \frac{\partial \psi_2(x)}{\partial x} \right) \mathrm{d}x + i\hbar \left[\overline{\psi_1(x)} \psi_2(x) \right]_{-\infty}^{\infty} & (7.14)\\ &= \langle \psi_1, \hat{p} \cdot \psi_2 \rangle \,. & (7.15) \end{aligned}$$

In passing to the final line, we have discarded the boundary term from integrating by parts since the wave functions $\psi_1(x)$, $\psi_2(x)$ vanish as $x \to \pm\infty$ as a necessary condition for square-normalizable.

Proving that operators are Hermitian in general leads to boundary terms which need to vanish for the proof to work; the Hermiticity is thus tightly connected to boundary conditions.

More general Hermitian operators can be constructed from polynomials in the position and momentum operators. An important example is the Hamiltonian operator

$$\begin{aligned} \hat{H} &= \frac{\hat{p}^2}{2m} + V(x) & (7.16)\\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \,, & (7.17) \end{aligned}$$

corresponding to measurements of energy. This suggests that perhaps all measurable quantities are represented by Hermitian operators in quantum mechanics. We will explain why this is the case in upcoming lectures.

7.4 Example: Particle in a Box

In a box, the basis of wave functions is countable, and we can compute the matrix elements of the position, momentum and Hamiltonian operators for the first few basis vectors.

Let us consider an infinite potential well in the region $0 \leq x \leq L$. In the last lecture, we introduced a basis of square-integrable wave functions

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad n \in \mathbb{Z}_{>0}\,. \tag{7.18}$$

The first few of these functions are displayed in figure 7.1; note how they satisfy the boundary conditions that the wave functions vanish at the edge of the box.

We will now compute the matrix elements of position, momentum and Hamiltonian operators in this basis.

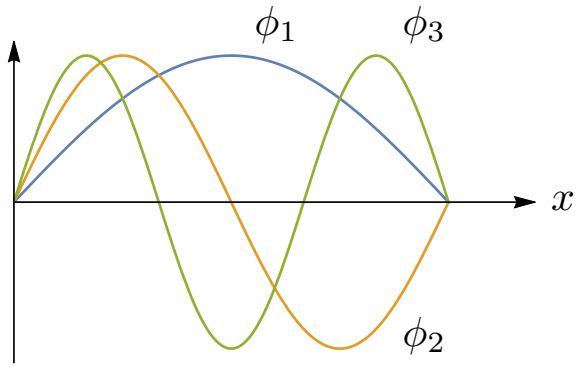

Figure 7.1: Basis of square-integrable wave functions in a box.

7.4.1 Position

First, for position we find

$$\begin{aligned} x_{mn} &:= \langle \phi_m, \hat{x} \cdot \phi_n \rangle && (7.19)\\ &= \int_0^L x\, \overline{\phi_m(x)} \phi_n(x) \mathrm{d}x && (7.20)\\ &= \frac{2}{L} \int_0^L x \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x \\ &= \frac{1}{L} \int_0^L x \left[\cos\left(\frac{(m-n)\pi x}{L}\right) - \cos\left(\frac{(m+n)\pi x}{L}\right)\right] \mathrm{d}x\,. && (7.21) \end{aligned}$$

It is convenient to introduce $y = \pi x/L$ and use

$$\int_0^\pi y \cos(ny) dy = \frac{(-1)^n - 1}{n^2} \qquad n \neq 0\,, \tag{7.22}$$

which you can prove by integration by parts. Combining the two contributions to the integral we find

$$x_{mn} = \begin{cases} \frac{L}{2} & \text{if} \quad m = n \\ \frac{4L}{\pi^2} \frac{mn}{(m^2-n^2)^2} \left((-1)^{m+n} - 1\right) & \text{if} \quad m \neq n \end{cases}, \tag{7.23}$$

which is a Hermitian matrix

$$x_{mn} = \begin{pmatrix} \frac{L}{2} & -\frac{16L}{9\pi^2} & 0 & -\frac{32L}{225\pi^2} & \cdots \\ -\frac{16L}{9\pi^2} & \frac{L}{2} & -\frac{48L}{25\pi^2} & 0 & \\ 0 & -\frac{48L}{25\pi^2} & \frac{L}{2} & -\frac{96L}{49\pi^2} & \\ -\frac{32L}{225\pi^2} & 0 & -\frac{96L}{49\pi^2} & \frac{L}{2} & \\ \vdots & & & & \ddots \end{pmatrix} . \tag{7.24}$$

7.4.2 Momentum

Second, for momentum we find

$$\begin{aligned} p_{mn} &:= \langle \phi_m, \hat{p} \cdot \phi_n \rangle && (7.25)\\ &= -i\hbar \int_0^L \overline{\phi_m(x)} \, \frac{\partial \phi_n(x)}{\partial x} \, \mathrm{d}x && (7.26)\\ &= -i\hbar \frac{2}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right) \mathrm{d}x \\ &= -\frac{i\hbar n\pi}{L^2} \int_0^L \left[\sin\left(\frac{(m+n)\pi x}{L}\right) + \sin\left(\frac{(m-n)\pi x}{L}\right) \right] \mathrm{d}x \, . && (7.27) \end{aligned}$$

It is convenient to introduce $y = \pi x/L$ and use

$$\int_0^\pi \sin(ny)\, dy = \frac{1-(-1)^n}{n} \quad n \neq 0 \tag{7.28}$$

to find

$$p_{mn} = \begin{cases} 0 & \text{if} \quad m = n \\ \frac{2i\hbar}{L} \frac{mn}{(m^2-n^2)} \left((-1)^{m+n} - 1\right) & \text{if} \quad m \neq n \end{cases} . \tag{7.29}$$

This is again a Hermitian matrix

$$\begin{pmatrix} 0 & \frac{8i\hbar}{3L} & 0 & \frac{16i\hbar}{15L} & \cdots \\ -\frac{8i\hbar}{3L} & 0 & \frac{24i\hbar}{5L} & 0 & \\ 0 & -\frac{24i\hbar}{5L} & 0 & \frac{48i\hbar}{7L} & \\ -\frac{16i\hbar}{15L} & 0 & -\frac{48i\hbar}{7L} & 0 & \\ \vdots & & & & \ddots \end{pmatrix} . \tag{7.30}$$

7.4.3 Energy

The Hamiltonian operator is

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \, . \tag{7.31}$$

in the region $0 < x < L$. The matrix elements of the Hamiltonian are then

$$\begin{aligned} H_{mn} &:= \langle \phi_m, H \cdot \phi_n \rangle && (7.32)\\ &= -\frac{\hbar^2}{2m} \int_0^L \overline{\phi_m(x)} \, \partial_x^2 \phi_n(x) \, \mathrm{d}x && (7.33)\\ &= \frac{\hbar^2 \pi^2 n^2}{2mL^2} \cdot \frac{2}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x \\ &= E_n \delta_{mn} \, . && (7.34) \end{aligned}$$

where

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \,. \tag{7.35}$$

This is a diagonal Hermitian matrix. In fact, the above computation shows that the wave functions $\phi_n(x)$ in our orthonormal basis are in fact 'eigenfunctions' of the Hamiltonian operator,

$$\hat{H} \cdot \phi_n(x) = E_n \phi_n(x) \,. \tag{7.36}$$

More about eigenfunctions in the next chapter.

8

The Spectrum of a Hermitian Operator

In this lecture we further develop the properties of Hermitian operators and why they are important in quantum mechanics. In particular we study the eigenfunctions and eigenvalues of Hermitian operators and the difference between a discrete and continuous spectrum.

In which you will learn why Hermitian operators are so important for physics, and we consolidate the computation of expectation values.

8.1 Hermitian Differential Operators

Recall that a linear differential operator A is Hermitian if

$$\langle \psi_1, A \cdot \psi_2 \rangle = \langle A \cdot \psi_1, \psi_2 \rangle \tag{8.1}$$

for all continuous square normalisable wave functions $\psi_1(x)$, $\psi_2(x)$. More succinctly, a Hermitian operator obeys $A^\dagger = A$. We demonstrated last time that position, momentum and energy are represented by Hermitian differential operators,

$$\hat{x} = x\,, \qquad \hat{p} = -i\hbar \frac{\partial}{\partial x}\,, \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\,. \tag{8.2}$$

Our working assumption is that all measurable quantities are represented by Hermitian differential operators in quantum mechanics.

A wave function $\psi_a(x)$ is an eigenfunction of a Hermitian differential operator A with eigenvalue a if it obeys

$$A \cdot \psi_a(x) = a\psi_a(x)\,. \tag{8.3}$$

Such wave functions play a distinguished role in quantum mechanics due to the following observations.

- **Expectation values:** let us first compute the expectation value of measurements of A. Assuming $\psi_a(x)$ is normalised, we find

$$\langle A \rangle = \langle \psi_a, A \cdot \psi_a \rangle = \langle \psi_a, a\psi_a \rangle = a\langle \psi_a, \psi_a \rangle = a\,. \tag{8.4}$$

  Similarly, $\langle A^n \rangle = a^n$ for any positive integer $n > 0$.

- **Uncertainty:** the uncertainty in measurements of A is therefore

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} = \sqrt{a^2 - a^2} = 0\,. \tag{8.5}$$

Hermitian operators are important for physics because their eigenvalues are real. If the system is in an eigenstate of this operator, measurement of the observable will yield a real answer given by the corresponding eigenvalue.

This is therefore a wave function with a definite value a for the measurable quantity A. In other words, measurements of A should yield the result a with probability 1.

In addition, the eigenfunctions and eigenvalues of Hermitian operators have the following important properties.

Theorem: Let A be a Hermitian operator.

(i) The eigenvalues of A are real: $a \in \mathbb{R}$.

(ii) Two eigenfunctions $\psi_1(x)$, $\psi_2(x)$ of A with distinct eigenvalues $a_1 \neq a_2$ are orthogonal.

Proof: Suppose $\psi_1(x)$, $\psi_2(x)$ are eigenfunctions of A with eigenvalues a_1, a_2,

$$A \cdot \psi_1(x) = a_1\psi_1(x) \qquad A \cdot \psi_2(x) = a_2\psi_2(x)\,. \tag{8.6}$$

Then

$$\langle \psi_1, A \cdot \psi_2 \rangle = \langle \psi_1, a_2\psi_2 \rangle = a_2\langle \psi_1, \psi_2 \rangle \tag{8.7}$$

$$\langle A \cdot \psi_1, \psi_2 \rangle = \langle a_1\psi_1, \psi_2 \rangle = \bar{a}_1\langle \psi_1, \psi_2 \rangle\,. \tag{8.8}$$

Subtracting these two equations we find $0 = (\bar{a}_1 - a_2)\langle \psi_1, \psi_2 \rangle$.

(i) First suppose that $a_2 = a_2 = a$ and $\psi_1 = \psi_2 = \psi$. Then we find

$$(\bar{a} - a)\langle \psi, \psi \rangle = 0\,. \tag{8.9}$$

Recall that $\langle \psi, \psi \rangle = 0$ if and only if $\psi(x) = 0$ identically. Therefore, provided the eigenfunction is not zero, we have $\bar{a} = a$ or equivalently $a \in \mathbb{R}$.

(ii) Second suppose that $a_1 \neq a_2$. Importing the result from part (i) we now have

$$(a_1 - a_2)\langle \psi_1, \psi_2 \rangle = 0 \tag{8.10}$$

and therefore $\langle \psi_1, \psi_2 \rangle = 0$.

Furthermore, an extension of the second part of this theorem is that the eigenfunctions of a Hermitian operator can be chosen to form an orthonormal basis. However, what we mean by “orthonormal basis" depends on whether the spectrum of eigenvalues is discrete or continuous.

8.2 Discrete Spectrum

Suppose A has a discrete spectrum of eigenvalues $\{a_n\}$ labelled by an index n. We will for simplicity assume the spectrum is non-degenerate: there is one linearly independent eigenfunction $\phi_n(x)$ for each distinct eigenvalue a_n.

In this case, we can choose the eigenfunctions $\phi_n(x)$ to form a complete orthonormal basis in the standard sense. This means that as well as eigenfunctions with different eigenvalues being orthogonal, all of the eigenfunctions are normalised. In summary,

$$\langle \phi_m, \phi_n \rangle = \delta_{mn}\,. \tag{8.11}$$

where δ_{mn} is the unit matrix. Furthermore, any continuous square-integrable wave function has a unique expansion

$$\psi(x) = \sum_n c_n \phi_n(x) \tag{8.12}$$

with coefficients $c_n \in \mathbb{C}$ (yes, there are subtleties here which we ignore for now).

1. The coefficients are found using the inner product and orthonormality,

$$\langle \phi_m, \psi \rangle = \sum_n c_n \langle \phi_m, \phi_n \rangle = \sum_n c_n \delta_{mn} = c_m \,. \tag{8.13}$$

2. The norm of a wave function is

$$\langle \psi, \psi \rangle = \sum_{mn} \bar{c}_m c_n \langle \phi_m, \phi_n \rangle = \sum_n |c_n|^2 \,. \tag{8.14}$$

3. If the wave function is normalised,

$$\langle \psi, \psi \rangle = \sum_n |c_n|^2 = 1 \,. \tag{8.15}$$

   This suggests that we interpret $|c_n|^2$ as the probability for a measurement of A to yield the result a_n: these probabilities should add up to 1.

The decomposition of a wave function in an eigenbasis $\{\phi_m\}$ of an Hermitian operator, with coefficients c_n, strongly suggests $|c_n|^2$ is the probability of finding the system in the state ϕ_n for which measurement leads to the value a_n.

Example: Energy in an Infinite Square Well

Consider the Hamiltonian operator for an infinite potential well in the region $0 < x < L$,

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \,. \tag{8.16}$$

It is straightforward to see that

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad n \in \mathbb{Z}_{>0} \tag{8.17}$$

are Hamiltonian eigenfunctions with eigenvalues

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \,. \tag{8.18}$$

We have already shown that these eigenfunctions are orthonormal. The fact that any continuous wave function can be expressed uniquely as a linear combination of these wave functions is the content of Fourier's theorem.

In particular, if we expand any wave function

$$\psi(x) = \sum_{n>0} c_n \phi_n(x) \tag{8.19}$$

then $|c_n|^2$ is the probability that a measurement of energy will yield the result E_n. The fact that these probabilities sum to 1 is Parceval's theorem.

8.3 Continuous Spectrum

A Hermitian operator A can also have a continuous spectrum of eigenvalues, say $a \in \mathbb{R}$, or some interval in $\mathbb{R}$. In this case, we cannot choose the eigenfunctions to form a complete orthonormal basis in the standard sense - we need a “continuous" version of the unit matrix δ_{mn}.

For this purpose, we will introduce the Dirac delta function, denoted by $\delta(a)$. This is not a function but a ‘distribution’. This means it behaves as a function inside integrals. You can think about it roughly as a function with

$$\delta(a) = \begin{cases} 0 & a \neq 0 \\ \infty & a = 0 \end{cases} \tag{8.20}$$

but where the area under the function is 1,

$$\int_{-\infty}^{\infty} \delta(a)\,\mathrm{d}a = 1\,. \tag{8.21}$$

A more precise definition is as a limit of a Gaussian function

$$\delta_\epsilon(a) = \frac{1}{\epsilon\sqrt{\pi}} e^{-a^2/\epsilon^2} \tag{8.22}$$

as it becomes infinitely thin $\epsilon \to 0^+$.

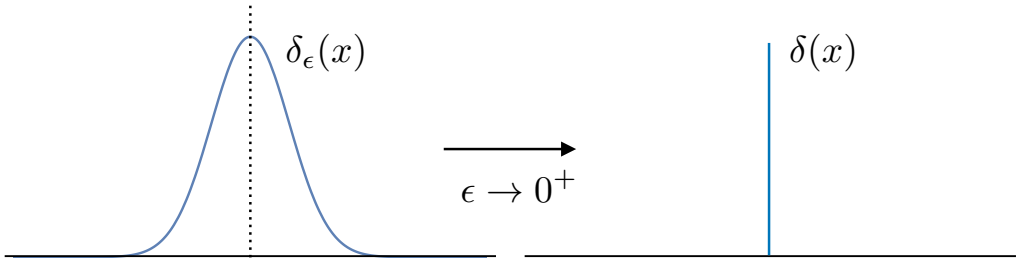

Figure 8.1: A Gaussian function becomes a Dirac delta function in the limit that the width goes to zero.

For the calculations that we need to do in this course, we will accept the following important properties of the Dirac delta function.

- For any continuous function $f(a)$,

$$\int_{-\infty}^{\infty} \delta(a - a')f(a')\,\mathrm{d}a' = f(a)\,. \tag{8.23}$$

  This is the continuous analogue of the discrete formula $\sum_n \delta_{mn} f_n = f_m$ and so $\delta(a - a')$ is a continuous analogue of the unit matrix δ_{mn}.

- The Dirac delta function is the Fourier transform of 1,

$$\delta(a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iaa'}\,\mathrm{d}a'\,. \tag{8.24}$$

The Dirac delta is for a continuous basis what a Kronecker delta is for a discrete basis.

- It follows from the above that $\delta(a) = \delta(-a) = \overline{\delta(a)}$.

For a Hermitian operator A with a continuous spectrum, it is possible to find a basis of eigenfunctions $\phi_a(x)$ with eigenvalues $a \in \mathbb{R}$ such that

$$\langle \phi_a, \phi_{a'} \rangle = \delta(a - a') \,. \tag{8.25}$$

This means the eigenfunctions $\psi_a(x)$ are not square-normalisable since $\langle \psi_a, \psi_a \rangle = \infty$. Nevertheless, any square-normalisable wave function can still be uniquely expanded

$$\psi(x) = \int_{-\infty}^{\infty} c(a)\, \phi_a(x)\, \mathrm{d}a \,, \tag{8.26}$$

with complex coefficients $c(a)$ depending continuously on a.

Eigenfunctions of an operator with continuous spectrum are not unit-normalisable, but can be 'delta-function normalised'.

1. The coefficients can be calculated using the inner product,

$$\begin{aligned} \langle \phi_a, \psi \rangle &= \int_{-\infty}^{\infty} c(a') \, \langle \phi_a, \phi_{a'} \rangle \, \mathrm{d}a' && (8.27)\\ &= \int_{-\infty}^{\infty} c(a') \, \delta(a - a') \, \mathrm{d}a' && (8.28)\\ &= c(a) \,. && (8.29) \end{aligned}$$

   This is the continuous analogue of the discrete result $\langle \phi_n, \psi \rangle = c_n$.

2. The norm of a wave function can be expressed

$$\begin{aligned} \langle \psi, \psi \rangle &= \int_{-\infty}^{\infty} \overline{c(a)} c(a') \langle \phi_a, \phi_{a'} \rangle \, \mathrm{d}a\mathrm{d}a' && (8.30)\\ &= \int_{-\infty}^{\infty} \overline{c(a)} c(a') \delta(a - a') \, \mathrm{d}a\mathrm{d}a' && (8.31)\\ &= \int_{-\infty}^{\infty} |c(a)|^2 \, \mathrm{d}a \,. && (8.32) \end{aligned}$$

   This is the continuous analogue of the discrete result $\langle \psi, \psi \rangle = \sum_n |c_n|^2$.

3. For a normalised wave function

$$\langle \psi, \psi \rangle = \int_{-\infty}^{\infty} |c(a)|^2 \, \mathrm{d}a = 1 \,. \tag{8.33}$$

   This suggests that we should treat $|c(a)|^2$ as a probability distribution for measurements of A.

Example:

An example is the momentum operator $\hat{p} = -i\hbar\partial_x$ for a particle moving in one dimension. It is straightforward to see that the eigenfunctions are plane waves $e^{ipx/\hbar}$ with eigenvalue p. We choose the normalisation

$$\phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \,. \tag{8.34}$$

so that

$$\langle \psi_p, \psi'_p \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} \mathrm{d}x = \delta(p - p') \,. \tag{8.35}$$

as required.

Expanding a wave function as a linear combination of momentum eigenfunctions

we find

$$\psi(x) = \int_{-\infty}^{\infty} c(p)\phi_p(x)\,\mathrm{d}p \tag{8.36}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p)\, e^{ipx/\hbar}\,\mathrm{d}p\,. \tag{8.37}$$

This is nothing other than the Fourier transform (we will see later that this is the Fourier transform between the position and momentum space wave functions).

9

Postulates of Quantum Mechanics

In this lecture, we bring together everything that we have learned so far to describe the postulates of quantum mechanics. These are the assumptions about how the maths relates to the physics.

A quick walk-through of the five postulates of quantum mechanics.

9.1 Statement of Postulates

1. A particle is described by a normalised wave function $\psi(x)$. Recall that the space of square-normalisable wave functions forms a complex vector space with Hermitian inner product

$$\langle \psi_1, \psi_2 \rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, \overline{\psi_1(x)} \psi_2(x)\,. \tag{9.1}$$

   In this notation, a normalised wave function obeys $\langle \psi, \psi \rangle = \int_{-\infty}^{\infty} |\psi(x)|^2 = 1$.

There are five postulates in quantum mechanics: 1) wave function postulate, 2) observables postulate, 3) measurement outcome postulate, 4) collapse postulate, 5) evolution postulate.

2. Measurable quantities or observables are represented by Hermitian operators $A(x,p)$ constructed from polynomial or real analytic functions of the elementary position and momentum operators,

$$\hat{x} = x \tag{9.2}$$

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}\,. \tag{9.3}$$

   For example, the Hamiltonian operator is $\hat{H} = \dfrac{\hat{p}^2}{2m} + V(x)$.

3. The possible outcomes of a measurement of A are its eigenvalues a. How we assign probabilities to these outcomes depends on whether the spectrum of eigenvalues is discrete or continuous:

   - **Discrete**: $\{a_j\}$. Choose a basis of eigenfunctions $\psi_j(x)$ that obey $\langle \phi_i, \phi_j \rangle = \delta_{ij}$. The probability to find the eigenvalue a_j is $P_j := |\langle \phi_j, \psi \rangle|^2$.
   - **Continuous**: $a \in \mathbb{R}$. Choose a basis of eigenfunctions $\psi_a(x)$ that obey $\langle \phi_a, \phi_{a'} \rangle = \delta(a - a')$. The probability density for measurements of the observable is $P(a) := |\langle \phi_a, \psi \rangle|^2$.

4. If a measurement of A yields the result a_j (or a for a continuous spectrum), the wave function immediately after the measurement is $\phi_j(x)$ (or $\phi_a(x)$ for a continuous spectrum).

5. As long as no measurements are made, the wave function evolves in time according to the Schrödinger equation,

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\psi(x,t)\,. \tag{9.4}$$

Of these, the 4th postulate is perhaps the least understood and the most mysterious. It has led to various interpretations of quantum mechanics. For actual computations, it often does not matter how this postulate is interpreted, and we will not go into these matters here.

9.2 Discussion of Postulates

Let us emphasise some important observations / consistency checks:

- The outcomes of measurements are real numbers. This is consistent with the fact that observables are represented by Hermitian operators, whose eigenvalues are real numbers.
- To compute probabilities it is convenient to expand the wave function in an orthonormal basis of eigenfunctions of A
  - **Discrete**: If we expand the wave function
    $$\psi(x) = \sum_j c_j \phi_j(x)\,, \tag{9.5}$$
    where $c_j = \langle \phi_j, \psi \rangle$. The probability to measure a_j is therefore the the modulus squared of the coefficient,
    $$P_j := |\langle \phi_j, \psi \rangle|^2 = |c_j|^2\,. \tag{9.6}$$
    Consistency requires that the total probability is 1. This follows from the normalisation of the wave function,
    $$\langle \psi, \psi \rangle = \sum_j |c_j|^2 = \sum_j P_j = 1\,. \tag{9.7}$$
  - **Continuous**: We expand the wave function
    $$\psi(x) = \int_{-\infty}^{\infty} \mathrm{d}a\, c(a) \phi_a(x)\,, \tag{9.8}$$
    where $c(a) = \langle \phi_a, \psi \rangle$. The probability distribution is therefore the modulus squared of the coefficient function,
    $$P(a) := |\langle \phi_a, \psi \rangle|^2 = |c(a)|^2\,. \tag{9.9}$$
    Consistency requires the total probability is 1. This follows from the normalisation of the wave function,
    $$\langle \psi, \psi \rangle = \int_{-\infty}^{\infty} \mathrm{d}a\, |c(a)|^2 = \int_{-\infty}^{\infty} \mathrm{d}a\, P(a) = 1\,. \tag{9.10}$$
- A measurement of A that yields an eigenvalue a_j / a causes the wave function to immediately collapse to the corresponding eigenfunction,
  $$\psi(x) \to \psi_j(x) \,/\, \psi_a(x) \tag{9.11}$$
  in the discrete / continuous case. In the continuous case, you should be concerned that the wave function immediately after the measurement is a not square-normalisable,
  $$\langle \phi_a, \phi_a \rangle = \infty\,. \tag{9.12}$$

This assumes an “idealised" measurement of a continuous parameter where the outcome is determined with infinite accuracy. A real-world measurement will always have some experimental uncertainty ϵ. The wave function immediately after the measurement is then a square-normalisable wave function

$$\int \mathrm{d}a'\, \delta_\epsilon(a-a')\phi_{a'}(x)\,, \tag{9.13}$$

where $\delta_\epsilon(a-a')$ is sharply peaked around $a'=a$ with width ϵ. The idealised measurement corresponds to the limit $\epsilon \to 0$ where $\delta_\epsilon(a-a') \to \delta(a-a')$. This is a convenient and useful mathematical ideal.

9.3 Expectation Values

The expectation value of a Hermitian operator is defined by

$$\langle A\rangle = \langle \psi, A\psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, \overline{\psi(x)}\, A\cdot\psi(x)\,. \tag{9.14}$$

The definition $\langle A\rangle = \langle\psi, A\psi\rangle$ is backed up by a computation of the expectation value using a decomposition of the wave function in terms of eigenfunctions of $\hat{A}$.

This expectation value can be computed by acting with the differential operator A and evaluating the integral. However, it is often more convenient to first expand the wave function in an orthonormal basis of eigenfunctions of A. This leads to the expected formulae using the probabilities P_j or probability distribution $P(a)$.

- **Discrete**: The expectation value is

$$\begin{aligned}
\langle A\rangle &= \sum_{ij} \bar{c}_i c_j \langle \phi_i, A\cdot\phi_j\rangle && (9.15)\\
&= \sum_{ij} a_j \bar{c}_i c_j \langle \phi_i, \phi_j\rangle && (9.16)\\
&= \sum_{j} a_j |c_j|^2 && (9.17)\\
&= \sum_{j} a_j P_j\,. && (9.18)
\end{aligned}$$

- **Continuous**: The expectation value is

$$\begin{aligned}
\langle A\rangle &= \int_{-\infty}^{\infty} \mathrm{d}a\,\mathrm{d}a'\, \overline{c(a)}\, c(a')\langle \phi_a, A\cdot\phi_{a'}\rangle && (9.19)\\
&= \int_{-\infty}^{\infty} \mathrm{d}a\,\mathrm{d}a'\, a'\,\overline{c(a)}\, c(a')\langle \phi_a, \phi_{a'}\rangle && (9.20)\\
&= \int_{-\infty}^{\infty} \mathrm{d}a\,\mathrm{d}a'\, a'\,\overline{c(a)}\, c(a')\delta(a-a') && (9.21)\\
&= \int_{-\infty}^{\infty} \mathrm{d}a\, a|c(a)|^2 && (9.22)\\
&= \int_{-\infty}^{\infty} \mathrm{d}a\, aP(a)\,. && (9.23)
\end{aligned}$$

A similar result holds for the expectation value of any real analytic function $f(A)$.

These expressions make it manifest that we are computing an average, because we are summing/integrating the possible outcomes of the measurement – the eigenvalues – with the probabilities to find the system in the state corresponding to each eigenvalue.

9.4 Position Revisited

Eigenfunctions of the position operator are Dirac delta functions. If you insist on square-normalisable wave functions, use narrow-width Gaussians instead.

The position operator $\hat{x}$ multiplies a wave function by x. The spectrum of the position operator is continuous with an orthonormal basis of eigenfunctions

$$\phi_{x'}(x) = \delta(x - x') \tag{9.24}$$

labelled by $x' \in \mathbb{R}$.

They form eigenfunctions because

$$\hat{x} \cdot \phi_{x'}(x) = x\delta(x - x') = x'\delta(x - x') = x'\phi_{x'}(x) \tag{9.25}$$

and are orthonormal,

$$\begin{aligned} \langle \phi_{x_1}, \phi_{x_2} \rangle &= \int_{-\infty}^{\infty} \mathrm{d}x\, \phi_{x_1}(x)\phi_{x_2}(x) && (9.26) \\ &= \int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x - x_1)\delta(x - x_2) \\ &= \delta(x_1 - x_2)\,. && (9.27) \end{aligned}$$

As mentioned above, these wave functions are not square-normalisable: $\langle \phi_{x'}, \phi_{x'} \rangle = \infty$. Nevertheless, we regard $\phi_{x'}(x)$ as the wave function immediately after an "idealised" measurement that measures the position x' with infinite accuracy.

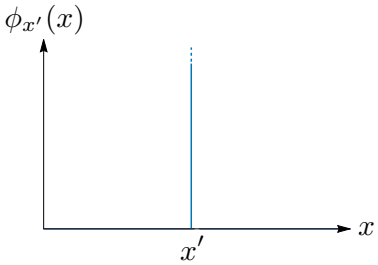

Figure 9.1: An eigenstate of the position operator, with eigenvalue x'.

We can expand any wave function in this basis,

$$\begin{aligned} \psi(x) &= \int_{-\infty}^{\infty} \mathrm{d}x' c(x')\phi_{x'}(x) && (9.28) \\ &= \int_{-\infty}^{\infty} \mathrm{d}x' c(x')\delta(x - x') \\ &= c(x)\,, && (9.29) \end{aligned}$$

so the coefficient function is the wave function itself. The probability density for position measurements according to the postulates are

$$P(x) = |\langle \phi_x, \psi \rangle|^2 = \left| \int_{-\infty}^{\infty} \mathrm{d}x' \delta(x - x')\psi(x') \right|^2 = |\psi(x)|^2\,. \tag{9.30}$$

This recovers our original probabilistic interpretation of the wave function!

9.5 Momentum Revisited

Eigenfunctions of the momentum operator are plane waves, which are not unit-normalisable on the real line either.

The momentum operator is $\hat{p} = -i\hbar\partial_x$. In the last lecture we showed that the spectrum of the momentum operator is continuous with an orthonormal basis of eigenfunctions labelled by $p \in \mathbb{R}$,

$$\phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \,. \tag{9.31}$$

In particular,

$$\langle \phi_p, \phi_{p'} \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}p \, e^{i(p'-p)x/\hbar} = \delta(p - p') \,. \tag{9.32}$$

As above, these wave functions are not square-normalisable, but arise from an “idealised" measurement that determines the momentum with infinite accuracy.

We can expand any wave function in the momentum basis

$$\psi(x) = \int_{-\infty}^{\infty} \mathrm{d}p \, c(p) \phi_p(x) \tag{9.33}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p \, c(p) e^{ipx/\hbar} \,. \tag{9.34}$$

The coefficients can be computed using the inner product and orthonormality,

$$c(p) = \langle \phi_p, \psi \rangle \tag{9.35}$$

$$= \int_{-\infty}^{\infty} \mathrm{d}x \, \overline{\phi_p(x)} \psi(x) \tag{9.36}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x \, \psi(x) e^{-ipx/\hbar} \,. \tag{9.37}$$

The momentum probability density is

$$\widetilde{P}(p) = |c(p)|^2 \,. \tag{9.38}$$

10

Commutators and Uncertainty Principle

Discussing two effects of non-commuting operators: on the measurement process, and on the limitation of the wave function description of particles.

This lecture is motivated by the question:

- *Suppose I measure an observable A, such as position, momentum or energy. How does that measurement affect subsequent measurements of another observable B?*

To answer this question, we introduce the commutator $[A, B]$ of two Hermitian operators and explore its physical interpretation. We will prove a generalisation of Heisenberg's uncertainty principle, which is a fundamental limitation on the precision that observables A and B can be determined simultaneously.

10.1 The Commutator

Two commuting operators share an (orthonormal) basis of eigenfunctions. This is extremely important, because eigenfunctions and eigenvalues are related to possible measurement outcomes.

Suppose we have two linear operators A and B, such as position x, momentum p or the Hamiltonian H. The commutator is defined by

$$[A, B] := AB - BA\,. \tag{10.1}$$

It has the following properties:

- Anti-symmetry: $[A, B] = -[B, A]$.
- Linear: $[a_1 A_1 + a_2 A_2, B] = a_1[A_1, B] + a_2[A_2, B]$.
- $[A, \cdot]$ is a derivation: $[A, BC] = B[A, C] + [A, B]C$.
- Jacobi identity: $[A[B, C]] + [B, [C, A]] + [C, [A, B]] = 0$.

The commutator plays an important role in quantum mechanics due to the following theorem:

Theorem: *"Two commuting matrices are simultaneously diagonalizable."* If A and B are Hermitian operators with $[A, B] = 0$, it is possible to find an orthonormal basis of wave functions that are simultaneous eigenfunctions of A and B.

Proof: To keep things simple, we will assume the spectrum of eigenvalues $\{a_j\}$ of A is discrete and non-degenerate. This means that up to normalisation there is a unique solution to $A\,\phi_j(x) = a_j\phi_j(x)$ for each eigenvalue a_j. The normalisation can be chosen to make the basis orthonormal, $\langle\phi_i, \phi_j\rangle = \delta_{ij}$.

We want to prove that $\phi_j(x)$ is simultaneously an eigenfunction of B. The commutator $[A, B] = 0$ is equivalent to $AB = BA$. This means

$$A\,(B\,\phi_j) = B\,(A\,\phi_j) = B\,(a_j\phi_j) = a_j(B\,\phi_j) \tag{10.2}$$

so $B\,\phi_j$ is also an eigenfunction A with eigenvalue a_j. But such wave function is unique up to normalisation and therefore

$$B\,\phi_j(x) = b_j\phi_j(x) \tag{10.3}$$

for some $b_j \in \mathbb{R}$. So $\phi_j(x)$ is simultaneously an eigenfunction of B.

10.2 Compatibility

Quantum operators which originate from classical observables which have a vanishing Poisson bracket are called “compatible”.

This theorem motivates the following definition.

- **Definition:** Two observables represented by Hermitian operators A and B are called “compatible" if their commutator vanishes, $[A, B] = 0$.

Let us first determine whether the observables we have encountered so far are compatible. Recall that the position and momentum operators are

$$\hat{x} = x \qquad \hat{p} = -i\hbar\frac{\partial}{\partial x} \tag{10.4}$$

while

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\,. \tag{10.5}$$

1. **Position and Momentum.** Let us compute the commutator of position and momentum acting on a generic wave function,

$$[\hat{x}, \hat{p}]\,\psi = x\left(-i\hbar\frac{\partial\psi}{\partial x}\right) + i\hbar\frac{\partial}{\partial x}\,(x\psi) = i\hbar\psi\,. \tag{10.6}$$

   This is the “canonical commutation relation"

$$[\hat{x}, \hat{p}] = i\hbar\,, \tag{10.7}$$

   which shows position and momentum are not compatible.

2. **Momentum and Energy.** A similar computation shows that

$$[H, p] = [V(x), p] = i\hbar\frac{\partial V(x)}{\partial x}\,. \tag{10.8}$$

   So momentum p and energy H are compatible only if $V(x)$ is constant. We will return to this result later in the course.

3. **Position and Energy.** From the commutator of position and momentum,

$$[H, x] = \frac{1}{2m}[p^2, x] = \frac{1}{2m}\,(p[p, x] + [p, x]p) = -\frac{i\hbar}{m}p\,, \tag{10.9}$$

   so position and energy are never compatible.

If A and B do not commute, and we measure A, immediately after that, the uncertainty of B has to be nonzero. This is a statement about subsequent measurements.

10.3 Compatibility and Measurement

To understand the physical significance of compatibility, suppose we measure A and find the eigenvalue a_j. Then the wave function immediately after the measurement is the eigenfunction $\phi_j(x)$.

- What happens if we make another measurement of A immediately afterwards? As $\phi_j(x)$ is an eigenfunction of A, the measurement will again find a_j with probability 1. Correspondingly, the uncertainty of a normalised eigenfunction vanishes,

$$\begin{aligned}(\Delta A)^2 &= \langle A^2\rangle - \langle A\rangle^2 && (10.10)\\ &= \langle \phi_j, A^2\phi_j\rangle - \langle \phi_j A, \phi_j\rangle^2 && (10.11)\\ &= a_j^2\langle\phi_j,\phi_j\rangle - (a_j\langle\phi_j,\phi_j\rangle)^2 && (10.12)\\ &= a_j^2 - a_j^2 = 0\,. && (10.13)\end{aligned}$$

- What happens if we make a measurement of B immediately afterwards?
  - If $[A,B]=0$, $\phi_j(x)$ is also an eigenfunction of B with eigenvalue b_j. So a measurement of B will find b_j with probability 1. Correspondingly, the same argument as above shows that $\Delta B = 0$. In other words, we can simultaneously determine the values of both A and B.
  - If $[A,B]\neq 0$, $\phi_j(x)$ is not an eigenfunction of B and there are multiple potential outcomes. Suppose the measurement of B yields a particular eigenvalue, say b. Then the wave function jumps to the corresponding eigenfunction of B with $\Delta B = 0$. But now $\Delta A > 0$.

It is important to emphasise that the subsequent measurements discussed in this section are measurements *without* time between them. A generic eigenstate of an operator will not stay an eigenstate under time evolution, so a measurement of A, followed by a delay and then another measurement of A, will typically still lead to a non-zero spread. Only eigenstates of the Hamiltonian operator, or operators which commute with it, remain eigenstates under time evolution.

10.4 The Generalised Uncertainty Principle

If $[A,B]\neq 0$, we cannot necessarily find simultaneous eigenfunctions of A and B with both $\Delta A = 0$ and $\Delta B = 0$. In fact, there is a fundamental limitation in quantum mechanics on the how small we can simultaneously make the uncertainties ΔA and ΔB. This is quantified by the "Generalised Uncertainty Principle":

Theorem: For any square-normalisable wave function,

$$\Delta A \Delta B \geq \frac{1}{2}|\langle [A,B]\rangle|\,. \qquad (10.14)$$

The generalised uncertainty principle relates the product of uncertainties of two operators to their commutator. It says something about the spread of two observables in the same state, not about subsequent measurements.

Proof: We will assume here that $\langle A\rangle = \langle B\rangle = 0$ for the wave function in question. This will simplify the argument without losing any of its essence. The translation to $\langle A\rangle \neq 0$, $\langle B\rangle \neq 0$ as an exercise for the interested reader.

With our assumption, the uncertainty in A can be expressed,

$$(\Delta A)^2 = \langle A^2 \rangle = \langle \psi, A^2 \psi \rangle = \langle A\psi, A\psi \rangle = \langle \psi_A, \psi_A \rangle \,, \tag{10.15}$$

where $\psi_A := A \cdot \psi$. There is an identical statement for B and therefore we can write

$$(\Delta A)^2 (\Delta B)^2 = \langle \psi_A, \psi_A \rangle \langle \psi_B, \psi_B \rangle \,. \tag{10.16}$$

We can now use the Cauchy-Schwarz inequality,

$$\langle \psi_A, \psi_A \rangle \langle \psi_B, \psi_B \rangle \geq |\langle \psi_A, \psi_B \rangle|^2 \,. \tag{10.17}$$

This result holds for any Hermitian inner product. It is analogous to the standard result $|\mathbf{a}|^2 |\mathbf{b}|^2 \geq |\mathbf{a} \cdot \mathbf{b}|^2$ from real euclidean geometry, which follows from the formula $\mathbf{a} \cdot \mathbf{b} = |\mathbf{a}||\mathbf{b}| \cos(\theta)$ for the dot product.

The right-hand side of this inequality can be expressed as

$$\begin{aligned} \langle \psi_A, \psi_B \rangle &= \langle AB \rangle & (10.18) \\ &= \frac{1}{2} \langle (AB - BA) \rangle + \frac{1}{2} \langle (AB + BA) \rangle & (10.19) \\ &= \frac{1}{2} \langle [A, B] \rangle + \frac{1}{2} \langle \{A, B\} \rangle & (10.20) \end{aligned}$$

where $[A, B] := AB - BA$ is the commutator and $\{A, B\} := AB + BA$ is the "anti-commutator". It is straightforward to check that,

1. $[A, B]$ is anti-Hermitian $\Rightarrow \langle [A, B] \rangle \in i\mathbb{R}$.
2. $\{A, B\}$ is Hermitian $\Rightarrow \langle \{A, B\} \rangle \in \mathbb{R}$.

so the commutator and anti-commutator provide the imaginary and real parts of $\langle \psi_A, \psi_B \rangle$. Recalling the formula $|z|^2 = x^2 + y^2$ for the modulus squared of a complex number $z = x + iy$, we have

$$\begin{aligned} |\langle \psi_A, \psi_B \rangle|^2 &= \frac{1}{4} |\langle [A, B] \rangle|^2 + \frac{1}{4} |\langle \{A, B\} \rangle|^2 & (10.21) \\ &\geq \frac{1}{4} |\langle [A, B] \rangle|^2 \,. & (10.22) \end{aligned}$$

This concludes the proof.

1. **Position and Momentum.** For position and momentum,

$$\Delta x \, \Delta p \geq \frac{\hbar}{2} \,, \tag{10.23}$$

   which is Heisenberg's uncertainty principle.

2. **Momentum and Energy.** For momentum and energy,

$$\Delta p \, \Delta H \geq \frac{\hbar}{2} \langle V'(x) \rangle \,, \tag{10.24}$$

   which vanishes automatically when $V(x)$ is constant.

3. **Position and Energy.** For position and energy,

$$\Delta x \, \Delta H \geq \frac{\hbar}{2m} \langle p \rangle \, . \tag{10.25}$$

   This implies that square-normalisable Hamiltonian eigenfunctions must have $\langle p \rangle = 0$. In fact, square-normalisable Hamiltonian eigenfunctions may always be chosen real, compatible with this statement.

Note that what is derived here is a statement which is different from the one in the previous section: the generalised uncertainty principle as derived above says nothing about subsequent measurements (see also [1]).

The uncertainty relation always contains $\hbar$ on the right hand side, and is thus fundamentally "quantum".

It should be emphasised that this is a fundamental feature of quantum mechanics. Only in the classical limit, $\hbar \to 0$, can we simultaneously determine exactly the values of non-compatible observables such as position and momentum.

11

Energy Revisited

In the last two lectures, we summarised the postulates of quantum mechanics and revisited what we learnt earlier in the course about measurements of position and momentum. In this lecture, we will do the same for measurements of energy and prove a couple of very important theorems about the spectrum of the Hamiltonian operator.

Discussing two important properties of the energy spectrum in quantum mechanics, quite different from the classical world.

11.1 Reminder about Energy Measurements

Given the wave function $\psi(x)$ of a particle moving in some potential $V(x)$, the basic question we want to answer is: how can we determine the possible outcomes of a measurement of energy and their probabilities?

The starting point is to construct an orthonormal basis of eigenfunctions of the Hamiltonian operator $\hat{H}$. For now, let's *assume* the spectrum of the Hamiltonian has the following properties:

1. **Discrete:** There is a discrete set of eigenvalues $\{E_j\}$.
2. **Non-degenerate**: There is a unique eigenfunction $\phi_j(x)$ solving

$$\hat{H} \cdot \phi_j(x) = E_j \phi_j(x) \tag{11.1}$$

   for each eigenvalue E_j.

In this case, we can choose the eigenfunctions to be orthonormal,

$$\langle \psi_i, \psi_j \rangle = \delta_{ij} \,. \tag{11.2}$$

We then expand the wave function

$$\psi(x) = \sum_j c_j \phi_j(x) \tag{11.3}$$

and, provided the wave function is normalised, the probability to measure energy E_j is $P_j = |c_j|^2$. As a consistency check, it is straightforward to check that $\sum_j P_j = 1$.

Finally, we can compute expectation value of energy measurements by summing the possible outcomes of an energy measurement weighted by their probabilities, $\langle H \rangle = \sum_j P_j E_j$.

11.2 Examples with Bound States

Examples of bound states suggest two important properties of the energy spectrum which hold in a variety of situations (but not all).

The Hamiltonian could in principle have a continuous spectrum or both discrete and continuous eigenvalues. It may also be degenerate with multiple linearly independent eigenfunctions with the same eigenvalue. It is therefore important to qualify when the assumptions made in the previous section are valid.

For concreteness, let us consider a particle of mass m moving on a line with potential $V(x)$. The Hamiltonian operator is then

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{11.4}$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{11.5}$$

and Hamiltonian eigenfunctions are solutions to the differential equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \tag{11.6}$$

that satisfy appropriate boundary conditions as $x \to \pm\infty$ and at any discontinuities in the potential $V(x)$.

The Hamiltonian operator typically has a discrete spectrum for energies E where the corresponding classical solutions $x(t)$ would be bounded in space. For this reason, the corresponding eigenfunctions are sometimes called “bound states". This is perhaps best illustrated with examples.

- **Infinite square well.** Consider the potential

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{other} \end{cases} . \tag{11.7}$$

  The classical motion is certainly bounded for any energy $E > 0$: the particle bounces back and forth from the walls of the box. The spectrum of the Hamiltonian is indeed discrete and non-degenerate with eigenvalues

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \qquad n \in \mathbb{Z}_{>0} . \tag{11.8}$$

- **Simple harmonic oscillator.** Consider the quadratic potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 . \tag{11.9}$$

  The classical motion is bounded: the particle oscillates with angular frequency ω for any finite energy $E > 0$. Later in the course, we will show that the spectrum is again discrete and non-degenerate with eigenvalues

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n \in \mathbb{Z}_{\geq 0} . \tag{11.10}$$

- **Hydrogen Atom:** The effective potential of an electron in a hydrogen atom is

$$V(x) = \frac{J^2}{2mx^2} - \frac{e^2}{x} . \tag{11.11}$$

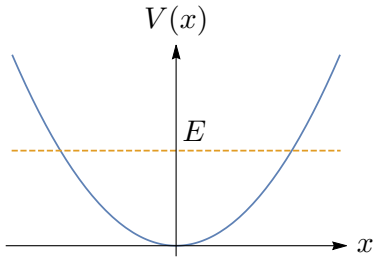

Figure 11.1: Simple harmonic oscillator potential.

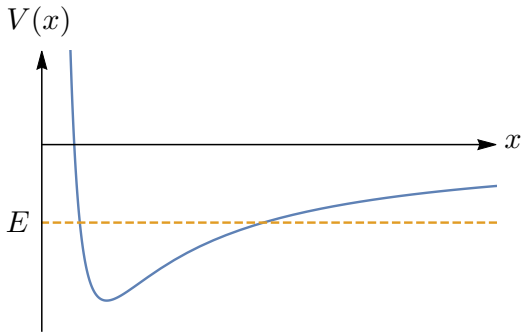

Figure 11.2: Effective potential of an electron in a hydrogen atom.

The classical motion is bounded for $E < 0$ and unbounded for $E \geq 0$. Correspondingly, there is a discrete set of bound states with energy $E < 0$, given by

$$E_n = -\frac{me^4}{2\hbar^2 n^2} \qquad n \in \mathbb{Z}_{>0}\,. \tag{11.12}$$

There is also a continuous spectrum of “scattering states" with $E > 0$ that will also be studied later in the course.

These examples illustrate some important universal features of a particle moving on a real line:

1. The Hamiltonian eigenvalues obey $E > V_0$ where V_0 is the minimum of the potential $V(x)$.
2. The spectrum of the Hamiltonian is non-degenerate.

We prove these properties in the following sections.

11.3 Minimum Energy

In quantum mechanics, the lowest lying energy eigenvalue is always strictly larger than the minimal value of the potential. This is called the zero-point energy.

Suppose the potential is bounded below, meaning $V(x) \geq V_0$ for all $x \in \mathbb{R}$. The point x_0 where $V(x_0) = V_0$ is typically a local minimum.

In classical mechanics there is a continuum of bound states with energy $E \geq V_0$ with the minimum energy configuration $E = V_0$ corresponding to a stationary particle at $x = x_0$. In contrast, in quantum mechanics we must have $E > V_0$.

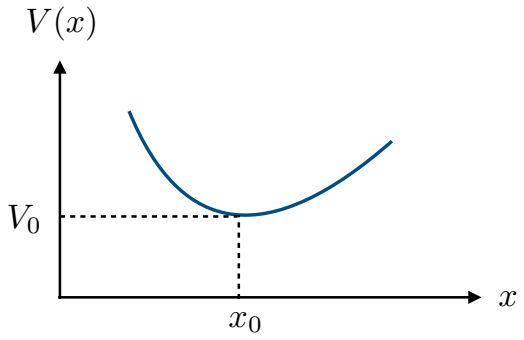

Figure 11.3: A potential with a local minimum at $x = x_0$.

Theorem: If the wave function is normalised, $\langle H \rangle > V_0$.
Proof: The energy expectation value is

$$\langle H \rangle = \langle \psi, \hat{H}\psi \rangle \tag{11.13}$$

$$= \frac{1}{2m}\langle \psi, \hat{p}^2\psi \rangle + \langle \psi, V(x)\psi \rangle \tag{11.14}$$

$$= \frac{1}{2m}\langle \hat{p}\psi, \hat{p}\psi \rangle + \langle \psi, V(x)\psi \rangle \,, \tag{11.15}$$

since the momentum operator p is Hermitian. The first term is necessarily non-negative,

$$\langle \hat{p}\psi, \hat{p}\psi \rangle = \int_{-\infty}^{\infty} |\hat{p}\psi(x)|^2 \, \mathrm{d}x = \int_{-\infty}^{\infty} \left| -i\psi'(x) \right|^2 \, \mathrm{d}x \geq 0 \tag{11.16}$$

and therefore

$$\langle H \rangle \geq \langle \psi, V(x)\psi \rangle = \int_{-\infty}^{\infty} V(x)|\psi(x)|^2 \, \mathrm{d}x \geq V_0 \int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x = V_0 \,. \tag{11.17}$$

We therefore conclude that $\langle H \rangle \geq V_0$.

The next step is to rule out equality. A necessary condition for equality is $\langle \hat{p}\psi, \hat{p}\psi \rangle = 0$. From positive definiteness of the inner product, this would require that $\hat{p}\psi = 0$ and therefore

$$-i\hbar \frac{\partial \psi(x)}{\partial x} = 0 \quad \Rightarrow \quad \psi(x) = c \,, \tag{11.18}$$

where $c \in \mathbb{C}$ is constant. However, square-normalisability requires $\psi(x) \to 0$ for $x \to \pm\infty$ and hence $c = 0$, so such a wave function would vanish identically. We therefore conclude that $\langle H \rangle > V_0$.

Corollary: If $\psi(x)$ is a normalized eigenfunction of H with eigenvalue E, then $E > V_0$.
Proof: This is a simple consequence of the above theorem: $\langle H \rangle = \langle \psi, H\psi \rangle = E\langle \psi, \psi \rangle = E > 0$.

This means that states with the minimum energy in classical mechanics, $E = V_0$, corresponding to a stationary particle, cannot exist in quantum mechanics. This is compatible with our intuition from Heisenberg's uncertainty principle. It is a very important result.

The smallest eigenvalue $E > V_0$ is sometimes known as the 'zero-point energy' in quantum mechanics. This is a characteristic feature of quantum mechanics that leads ultimately to some of the greatest mysteries in theoretical physics.

11.4 Non-degeneracy

For a particle on the real line, the energy spectrum is non-degenerate: there exists only one eigenfunction for each energy eigenvalue. The proof generalises to some other situations, but not all.

Theorem: The spectrum of the Hamiltonian is non-degenerate.
Proof: Consider a pair of square-normalizable eigenfunctions with the same eigenvalue,

$$\hat{H} \cdot \psi_1(x) = E\psi_1(x) \tag{11.19}$$
$$\hat{H} \cdot \psi_2(x) = E\psi_2(x)\,. \tag{11.20}$$

We will prove that $\psi_1(x) \propto \psi_2(x)$, which implies there is a unique normalised eigenfunction for each eigenvalue E.

Expanding out, we have

$$-\frac{\hbar}{2m}\partial_x^2\psi_1(x) + V(x)\psi_1(x) = E\psi_1(x) \tag{11.21}$$
$$-\frac{\hbar}{2m}\partial_x^2\psi_2(x) + V(x)\psi_2(x) = E\psi_2(x)\,. \tag{11.22}$$

Subtracting the top equation multiplied by $\psi_2(x)$ from the bottom equation multiplied by $\psi_1(x)$, the contributions propotional to $V(x)$ and E vanish and we find

$$0 = \psi_1\partial_x^2\psi_2 - \psi_2\partial_x^2\psi_1 \tag{11.23}$$
$$= \partial_x(\psi_1\partial_x\psi_2 - \psi_2\,\partial_x\psi_1)\,. \tag{11.24}$$

Therefore,

$$\psi_1\partial_x\psi_2 - \psi_2\partial_x\psi_1 = c \in \mathbb{C}\,. \tag{11.25}$$

Boundary conditions are crucial in proving non-degeneracy of the energy spectrum.

But since the wave functions are normalizable, $\psi_1(x)$, $\psi_2(x)$ necessarily vanish at $x \to \pm\infty$. Evaluating the equation at infinity, we therefore determine that $c = 0$. We can then solve the equation,

$$\psi_1\partial_x\psi_2 - \psi_2\partial_x\psi_1 = 0 \tag{11.26}$$
$$\Rightarrow \frac{\partial_x\psi_1}{\psi_1} - \frac{\partial_x\psi_2}{\psi_2} = 0 \tag{11.27}$$
$$\Rightarrow \partial_x(\log\psi_1 - \log\psi_2) = 0 \tag{11.28}$$
$$\Rightarrow \log\frac{\psi_1}{\psi_2} = A \tag{11.29}$$
$$\Rightarrow \psi_1 = e^A\psi_2\,, \tag{11.30}$$

for some constant $A \in \mathbb{C}$. This shows that $\psi_1(x)$ and $\psi_2(x)$ are the same eigenfunction.

11.5 The Evader

We have encountered a potential counterexample to the above theorem: a free particle moving on a circle of circumference L with potential $V(x) = 0$. There is an orthonormal basis of Hamiltonian eigenfunctions

$$\phi_{\pm n}(x) = \frac{1}{\sqrt{L}}e^{\pm 2\pi i n x/L} \qquad n \in \mathbb{Z} \tag{11.31}$$

with eigenvalues

$$E_n = \frac{\hbar^2}{2m}\left(\frac{2\pi n}{L}\right)^2 . \tag{11.32}$$

The spectrum is degenerate because $E_n = E_{-n}$. The above proof fails at the stage where we required the wave function to vanish as $x \to \pm\infty$. Here, instead we have imposed periodic boundary conditions $\psi(x+L) = \psi(x)$, which is not strong enough to determine the constant $c = 0$ in (11.25).

12

Stationary states

We have seen that the generic time-evolution of the wave function is governed by the Schrödinger equation,

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\,\psi(x,t)\,, \tag{12.1}$$

which is a PDE for the wave function, and takes the explicit form

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t)\,. \tag{12.2}$$

It is linear and 1st order in time.

In this lecture, we will introduce a powerful method to find the unique solution for the wave function $\psi(x,t)$ given an initial condition $\psi(x,0)$. This is known as the method of “separation of variables".

Stationary states can be used to solve for the time evolution of a generic initial wave function.

12.1 Stationary Wave functions

A simple class of solutions to Schrödinger's equation may be found by assuming that the dependence on position and time is factorised,

$$\psi(x,t) = \phi(x)T(t)\,. \tag{12.3}$$

Substituting into Schrödinger's equation we find

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\phi(x)}\frac{\partial^2\phi(x)}{\partial x^2} + V(x)\,. \tag{12.4}$$

Schrödinger's equation can be reduced to the time-independent Schrödinger equation for wave functions which factorise into a space-dependent factor and a time-dependent factor.

The left hand side is now a function of t only, while the right hand side is a function of x only. Since Schrödinger's equation holds for all x and t, we conclude that both sides are equal to the same constant,

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = E \tag{12.5}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\phi(x)}\frac{\partial^2\phi(x)}{\partial x^2} + V(x) = E\,. \tag{12.6}$$

where for now $E \in \mathbb{C}$. Notice we have implicitly assumed the potential $V(x)$ is independent of time - this will always be the case in this course.

The first equation can be immediately solved,

$$T(t) = e^{-iEt/\hbar}\,, \tag{12.7}$$

up to a normalisation that we can absorb into $\phi(x)$. The second equation says that $\phi(x)$ is an eigenfunction of the Hamiltonian $\hat{H}$ with eigenvalue E. In particular, since $\hat{H}$ is a Hermitian operator, $E \in \mathbb{R}$.

- **Summary:** we have found a class of solutions to Schrödinger's equation

$$\psi(x,t) = \phi(x)e^{-iEt/\hbar}\,, \tag{12.8}$$

where $\phi(x)$ is an eigenfunction of the Hamiltonian with energy E,

$$\hat{H}\,\phi(x) = E\phi(x)\,. \tag{12.9}$$

This is the time evolution of an initial wave function $\psi(x,0) = \phi(x)$. Equation (12.9) is also often called the "time-independent Schrödinger equation".

The time-independent Schrödinger equation is obtained from the full Schrödinger equation when the wave function is stationary. Solving that equation is equivalent to solving for a particular eigenstate of the Hamiltonian operator.

We have encountered a number of examples in the previous lecture. The key property of such solutions is that probabilities of measurements of any observable are independent of time t, since the contribution from the overall phase $e^{-iEt/\hbar}$ always cancels out. For example,

- **Position:** The probability density for position is

$$P(x,t) = |\psi(x,t)|^2 = |\phi(x)e^{-iEt/\hbar}|^2 = |\phi(x)|^2\,. \tag{12.10}$$

- **Energy:** The probability to measure energy E is

$$P_E = |\langle\phi,\psi\rangle|^2 = |\langle\phi,\phi\rangle e^{-iEt/\hbar}|^2 = |\langle\phi,\phi\rangle|^2 = 1\,. \tag{12.11}$$

For this reason, such solutions are known as "stationary wave functions". They are the unique time-evolution of Hamiltonian eigenfunctions.

12.2 Complete Solution

The stationary wave functions are simple but extremely important. Due to the fact that Schrödinger's equation is linear, we can build all possible solutions of Schrödinger's equation by taking linear combinations of stationary wave functions!

Suppose we have an initial wave function $\psi(x,0)$. We now provide a recipe for constructing the solution of Schrödinger's equation $\psi(x,t)$ at later times $t > 0$.

1. **Step 1:** As always, we first construct an orthonormal basis of Hamiltonian eigenfunctions $\phi_j(x)$ with eigenvalues E_j. We assume here that the spectrum is discrete and non-degenerate. We then have stationary wave functions,

$$\psi_j(x,t) = \phi_j(x)e^{-iE_jt/\hbar}\,. \tag{12.12}$$

These wave functions remain orthonormal for all time t as the dependence on the phase $e^{-iE_jt/\hbar}$ cancels out,

$$\langle\psi_i,\psi_j\rangle = e^{i(E_i-E_j)t/\hbar}\langle\phi_i,\phi_j\rangle = e^{i(E_i-E_j)t/\hbar}\delta_{ij} = \delta_{ij}\,. \tag{12.13}$$

2. **Step 2:** We expand the initial wave function $\psi(x,0)$ as a linear combination of the orthonormal basis of Hamiltonian eigenfunctions,

$$\psi(x,0) = \sum_j c_j\phi_j(x)\,. \tag{12.14}$$

The wave function is correctly normalized if $\langle\psi,\psi\rangle = \sum_j |c_j|^2 = 1$.

3. **Step 3:** We promote this to the wave function,

$$\psi(x,t) = \sum_j c_j \psi_j(x,t) \tag{12.15}$$

$$= \sum_j c_j \phi_j(x) e^{-iE_j t/\hbar} \,. \tag{12.16}$$

Since Schrödinger's equation is linear, this is automatically a solution by the principle of superposition. Furthermore, it coincides with the initial wave function $\psi(x,0)$ at $t = 0$. Since Schrödinger's equation is first order in time, we expect the initial wave function to uniquely determine the solution for $t > 0$. We therefore claim that the solution is unique.

How do probabilities and expectation values depend on time?

- **Energy.** The probabilities of energy measurements are always independent of time because the phases $e^{-iE_j t/\hbar}$ cancel out

$$P_j = |\langle \phi_j, \psi \rangle|^2 = |c_j e^{-iE_j t/\hbar}|^2 = |c_j|^2 \,. \tag{12.17}$$

The expectation value $\langle H \rangle = \sum_j P_j E_j$ is therefore also independent of t.

- **Position and Momentum.** The probability distributions and expectation values of position and momentum will typically vary in time.

Let us see this explicitly in some examples.

12.3 Example: Sum of Two Eigenfunctions

Consider a normalized initial wave function

$$\psi(x,0) = c_1 \phi_1(x) + c_2 \phi_2(x) \tag{12.18}$$

with $|c_1|^2 + |c_2|^2 = 1$. The wave function at later times is

Most time-dependent wave functions are not separable, and hence not stationary. An example is the sum of two stationary states with different energy.

$$\psi(x,t) = c_1 \psi_1(x,t) + c_2 \psi(x,t) \tag{12.19}$$

$$= c_1 \phi_1(x) e^{-iE_1 t/\hbar} + c_2 \phi_2(x) e^{-iE_2 t/\hbar} \,. \tag{12.20}$$

The outcomes of energy measurements and their probabilities are independent of t,

$$\begin{aligned} E_1 \quad &: \quad P_1 = |c_1|^2 \\ E_2 \quad &: \quad P_2 = |c_2|^2 \,. \end{aligned} \tag{12.21}$$

On the other hand, the probability density is

$$P(x,t) = |\psi(x,t)|^2 \tag{12.22}$$

$$= |c_1 \phi_1(x) e^{-iE_1 t/\hbar} + c_2 \phi_2(x) e^{-iE_2 t/\hbar}|^2 \tag{12.23}$$

$$= |c_1|^2 |\phi_1(x)|^2 + |c_2|^2 |\phi_2(x)|^2 \tag{12.24}$$

$$+ 2\mathrm{Re}\left(c_1 \bar{c}_2 \phi_1(x) \overline{\phi_2(x)} e^{-i(E_1 - E_2)t/\hbar} \right) \,. \tag{12.25}$$

Due to the final "interference term", the position probability density and position expectation values oscillate in time with frequency

$$\omega = (E_2 - E_1)/\hbar \,. \tag{12.26}$$

12.4 Example: Infinite Square Well

Let us consider the infinite square well $0 < x < L$ with initial wave function

$$\psi(x,0) = \frac{1}{\sqrt{2}}(\phi_1(x) + \phi_2(x))\,. \tag{12.27}$$

The unique solution of Schrödinger's equation is

$$\psi(x,t) = \frac{1}{\sqrt{2}}\left(\phi_1(x)e^{-iE_1t/\hbar} + \phi_2(x)e^{-iE_2t/\hbar}\right)\,.$$

The outcomes of energy measurements and their probabilities are independent of t,

$$\begin{aligned} E_1 \quad &: \quad P_1 = \frac{1}{2} \\ E_2 \quad &: \quad P_2 = \frac{1}{2}\,. \end{aligned} \tag{12.28}$$

On the other hand, the probability density is

$$\begin{aligned} P(x,t) &= |\psi(x,t)|^2 \qquad (12.29)\\ &= \frac{1}{2}|\phi_1(x)|^2 + \frac{1}{2}|\phi_2(x)|^2 + \frac{1}{2}\left(\phi_1(x)\overline{\phi_2(x)}e^{-i(E_1-E_2)t/\hbar} + \text{c.c.}\right) \\ &= \frac{1}{L}\left(\sin^2\left(\frac{\pi x}{L}\right) + \sin^2\left(\frac{2\pi x}{L}\right) + 2\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\cos(\omega t)\right)\,, \qquad (12.30) \end{aligned}$$

which oscillates with frequency

$$\omega = \frac{E_2 - E_1}{\hbar} = \frac{3\hbar\pi^2}{2mL^2}\,. \tag{12.31}$$

13

Case Study: The Free Particle

Determining the full time evolution of a free particle wave function, illustrated on a Gaussian.

This lecture is an extended example consisting of a “free particle" moving on a line. This means that the potential $V(x) = V_0$ is a constant. In this lecture, we assume for simplicity that the potential vanishes $V_0 = 0$. You might think this is the simplest possible example, but it exhibits a number of important subtleties.

- **Classical Mechanics.** The classical solutions of Hamilton’s equations are

$$x(t) = x_0 + \frac{p_0}{m}t \tag{13.1}$$

$$p(t) = p_0\,. \tag{13.2}$$

  where (x_0, p_0) are the initial position and momentum. In the absence of a force, we have uniform motion with constant velocity p_0/m.

- **Quantum mechanics**. Suppose we have an initial wave function $\psi(x, 0)$ with expectation values $\langle x\rangle = x_0$ and $\langle p\rangle = p_0$. Then we would like to determine the wave function $\psi(x, t)$ at later times $t > 0$. We follow the recipe introduced in the previous lecture!

13.1 Step 1: Hamiltonian Eigenfunctions

Once we know the decomposition of an initial Gaussian wave function in terms of energy eigenfunctions, we can compute its time evolution.

The starting point for understanding is to construct an orthonormal basis of eigenfunctions of the Hamiltonian operator

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\,.$$

In this case, it is first convenient to first discuss the momentum operator $\hat{p}$. This is because an eigenfunction of the momentum operator $\hat{p}$ with eigenvalue p is automatically an eigenfunction of the Hamiltonian operator $\hat{H}$ with eigenvalue $E = p^2/2m$.

The momentum eigenfunctions are solutions to the differential equation

$$-i\hbar\frac{\partial}{\partial x}\phi_p(x) = p\phi_p(x)\,. \tag{13.3}$$

The solutions are

$$\phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \tag{13.4}$$

for any $p \in \mathbb{R}$. The momentum operator therefore has a continuous spectrum and correspondingly the normalisation is chosen so that

$$\langle \phi_p, \phi_{p'} \rangle = \int_{-\infty}^{\infty} \overline{\phi_p(x)} \phi_{p'}(x) \mathrm{d}x \tag{13.5}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i(p-p')x/\hbar} \mathrm{d}x \tag{13.6}$$

$$= \delta(p - p') \,. \tag{13.7}$$

The spectrum of the momentum operator is also non-degenerate: there is a unique eigenfunction $\phi_p(x)$ for each eigenvalue $p \in \mathbb{R}$.

The same wave functions are also Hamiltonian eigenfunctions

$$\hat{H} \cdot \phi_p(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi_p(x) = E_p \phi_p(x)$$

where

$$E_p = \frac{p^2}{2m} \,.$$

However, the spectrum of the Hamiltonian is degenerate since $\phi_p(x)$ and $\phi_{-p}(x)$ have the same energy since $E_p = E_{-p}$. This is a consequence of "parity" symmetry $x \mapsto -x$ that sends

$$\phi_p(x) \mapsto \phi_p(-x) = \phi_{-p}(x) \,,$$

while leaving the Hamiltonian operator $\hat{H}$ invariant. Nevertheless, the wave functions $\phi_p(x)$ can be taken as an orthonormal basis of Hamiltonian eigenfunctions.

13.2 Step 2: Stationary Solutions

We can immediately promote the Hamiltonian eigenfunctions $\phi_p(x)$ to stationary solutions of Schrödinger's equation,

$$\psi_p(x,t) = \phi_p(x) e^{-iE_p t/\hbar} \tag{13.8}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} e^{i(px - E_p t)/\hbar} \,. \tag{13.9}$$

These stationary wave functions correspond to plane waves. In particular, $\psi_p(x,t)$ and $\psi_{-p}(x,t)$ are plane waves with equal magnitude of momentum in opposite directions and therefore equal energy.

13.3 Step 3: Time Evolution of Wave function

We now return to the problem at hand: how to determine the solution of Schrödinger's equation $\psi(x,t)$ given an initial wave function $\psi(x,0)$.

We expand $\psi(x,0)$ as a linear combination of the Hamiltonian eigenfunctions. In this case, the spectrum of the Hamiltonian operator is continuous and the expansion becomes an integral

$$\psi(x,0) = \int_{-\infty}^{\infty} \mathrm{d}p \, c(p) \, \phi_p(x) \tag{13.10}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p \, c(p) \, e^{ipx/\hbar} \,. \tag{13.11}$$

The coefficients function $c(p)$ is computed via the inverse relation,

$$c(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x,0)\, e^{-ipx/\hbar}\,. \tag{13.12}$$

This is of course the Fourier transform between the initial wave function $\psi(x,0)$ and the initial momentum space wave function, $c(p) = \widetilde{\psi}(p,0)$

To compute the wave function at later times, we promote the Hamiltonian eigenfunctions $\phi_p(x)$ to stationary wave functions,

$$\psi(x,t) = \int_{-\infty}^{\infty} \mathrm{d}p\, c(p)\psi_p(x,t) \tag{13.13}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p\, c(p)\, e^{ipx/\hbar} e^{-ip^2t/2m\hbar}\,. \tag{13.14}$$

We can express this in terms of the initial wave function $\psi(x,0)$ by substituting in the inverse Fourier transform for the coefficients $c(p)$ and interchanging the order of integration,

$$\psi(x,t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}p \left(\int_{-\infty}^{\infty} \mathrm{d}x'\, \psi(x',0)\, e^{-ipx'/\hbar} \right) e^{ipx/\hbar} e^{-ip^2t/2m\hbar} \tag{13.15}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}x' \psi(x',0) \int_{-\infty}^{\infty} \mathrm{d}p\, e^{ip(x-x')/\hbar} e^{-ip^2t/2m\hbar}\,. \tag{13.16}$$

The integral over momentum can now be computed using the standard Gaussian integral formula

$$\int_{-\infty}^{\infty} \mathrm{d}y\, e^{-\alpha y^2 + \beta y} = \sqrt{\frac{\pi}{\alpha}}\, e^{\beta^2/4\alpha}\,. \tag{13.17}$$

With the substitution

$$\alpha = \frac{it}{2m\hbar} \qquad \beta = i\frac{(x-x')}{\hbar}\,, \tag{13.18}$$

we find

$$\int_{-\infty}^{\infty} \mathrm{d}p\, e^{ip(x-x')/\hbar} e^{-ip^2t/2m\hbar} = \left(\frac{2\pi\hbar m}{it}\right)^{1/2} e^{im(x-x')^2/2\hbar t}\,. \tag{13.19}$$

We therefore have

$$\psi(x,t) = \left(\frac{m}{2\pi\hbar it}\right)^{1/2} \int_{-\infty}^{\infty} \mathrm{d}x'\, \psi(x',0)\, \exp\left(\frac{im(x-x')^2}{2\hbar t}\right)\,, \tag{13.20}$$

The propagator allows us to compute, by doing a single integral, the wave function at arbitrary times if we know the wave function at an initial time.

which allows us to compute $\psi(x,t)$ from the initial wave function $\psi(x,0)$. The object

$$G(x,x';t) = \left(\frac{m}{2\pi\hbar it}\right)^{1/2} \exp\left(\frac{im(x-x')^2}{2\hbar t}\right) \tag{13.21}$$

is sometimes called the "propagator".

- **Important Subtlety.** The Gaussian integral above converges for $\mathrm{Re}(\alpha) > 0$ whereas our α is purely imaginary. A more careful analysis would add a small imaginary time $t \to t - i\epsilon$ and consider the limit $\epsilon \to 0$, or deform the contour of integration slightly into the complex p-plane. This will not be necessary in this course - the above formulae will be correct for all examples we come across. An example is the Gaussian wave function, which we now turn to.

13.4 Example: Time-Evolution of Gaussian

Gaussian wave functions spread in time, but preserve their Gaussian nature. They also preserve their minimal spread.

Consider an initial Gaussian wave function

$$\psi(x,0) = Ce^{ip_0x/\hbar}e^{-x^2/4\Delta^2} \tag{13.22}$$

with normalisation $C = (2\pi\Delta^2)^{-1/4}$. The initial probability distribution is

$$P(x,0) = |\psi(x,0)|^2 \tag{13.23}$$

$$= \frac{1}{\sqrt{2\pi\Delta^2}}e^{-x^2/2\Delta^2} \tag{13.24}$$

The initial wave function has the characteristic properties

$$\langle x\rangle = 0 \qquad \Delta x = \Delta \tag{13.25}$$

$$\langle p\rangle = p_0 \qquad \Delta p = \frac{\hbar}{2\Delta}\,. \tag{13.26}$$

In particular, Heisenberg's uncertainty principle is saturated, $\Delta x\Delta p = \hbar/2$.

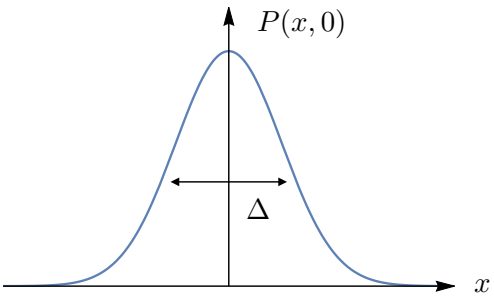

Figure 13.1: Probability density for a Gaussian wave packet with width Δ.

The wave function at later times is

$$\psi(x,t) = \left(\frac{m}{2\pi\hbar it}\right)^{1/2}\int_{-\infty}^{\infty}\mathrm{d}x'\,\exp\left(\frac{im(x-x')^2}{2\hbar t}\right)\psi(x',0) \tag{13.27}$$

$$= C\left(\frac{m}{2\pi\hbar it}\right)^{1/2}\int_{-\infty}^{\infty}\mathrm{d}x'\,\exp\left(\frac{im(x-x')^2}{2\hbar t}\right)e^{ip_0x'/\hbar}e^{-x'^2/4\Delta^2}\,. \tag{13.28}$$

This can be evaluated by performing another Gaussian integral with parameters

$$\alpha = \frac{m}{2i\hbar t}\left(1+\frac{i\hbar t}{2m\Delta^2}\right) \tag{13.29}$$

$$\beta = -\frac{im}{\hbar t}\left(x-\frac{p_0t}{m}\right)\,. \tag{13.30}$$

Notice that $\mathrm{Re}(\alpha) > 0$ so the Gaussian integral converges and there is no subtlety in computing it. After some simplification, the final result for the wave function at later times is

$$\psi(x,t) = \left[2\pi\Delta^2\left(1+\frac{i\hbar t}{2m\Delta^2}\right)\right]^{1/4}\exp\left[ip_0\left(x-\frac{p_0t}{2m}\right)\right]\exp\left[\frac{-(x-p_0t/m)^2}{4\Delta^2(1+i\hbar t/2m\Delta^2)}\right]\,. \tag{13.31}$$

The probability distribution is particularly simple,

$$P(x,t) = \frac{1}{\sqrt{2\pi\Delta(t)^2}} \exp\left[-\frac{x(t)^2}{4\Delta(t)^2}\right] \tag{13.32}$$

where

$$x(t) = x - \frac{p_0 t}{m} \qquad \Delta(t) = \Delta\sqrt{1 + \frac{\hbar^2 t^2}{4m^2\Delta^4}}\,. \tag{13.33}$$

This is a time-dependent Gaussian characterised by

$$\langle x\rangle = \frac{p_0}{m}t \qquad \Delta x = \Delta(t) \tag{13.34}$$

$$\langle p\rangle = p_0 \qquad \Delta p = \frac{\hbar}{2\Delta(t)} \tag{13.35}$$

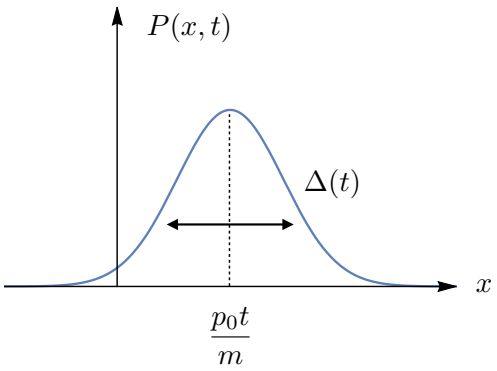

Figure 13.2: Probability density for a moving Gaussian wave packet with width Δ and momentum p_0.

Time-evolution of a free Gaussian wave packet with non-zero momentum p_0. Note how the wave packet width Δ increases in size over time.

- $\langle x\rangle$, $\langle p\rangle$ obey the classical equations of motion: the centre of the wavepacket $\langle x\rangle$ is moving with constant velocity p_0/m. In a later lecture, we will prove this result in generality.
- The position uncertainty $\Delta(t)$ is increasing in time. Intuitively, the initial uncertainty in momentum (and therefore velocity) leads to an increasing uncertainty in position over time.
- Heisenberg's uncertainty principle is saturated $\Delta x \Delta p = \frac{\hbar}{2}$ for all t: the wave function remains Gaussian.
- For a macroscopic object of mass $1g = 10^{-3}kg$ with initial position determined up to uncertainty $\Delta \sim 10^{-15}m$ equal to the width of a proton, it would take $300,000$ years for the uncertainty in position to grow to $\Delta \sim 1mm = 10^{-3}m$. It is therefore reasonable to treat macroscopic objects classically over long periods of time.

14

Two-particle systems

Introducing two-particle quantum mechanics and entanglement.

We have so far only looked at the quantum mechanics of a single particle in one dimension. That certainly provided some interesting results and contrasts with classical mechanics. But the full glory of quantum mechanics only becomes visible if we allow ourselves to look at somewhat more complicated systems, with more degrees of freedom. The system which is closest to what we have analysed so far is that of *two* particles in one dimension. The mathematics is not all that much more complicated than what we have seen so far, but the results we get out will challenge our intuition, as we touch on the important concept of *entanglement*.

14.1 Two-particle wave functions

A system of two (or three, or one hundred) particles only has one wave function.

If we have two particles in one dimension, our system is described by two positions (and classically, two momenta). So instead of having a wave function $\psi(x)$, we will now need a wave function $\psi(x_1, x_2)$, and a probability density $P(x_1, x_2) = \left|\psi(x_1, x_2)\right|^2$. It is important to understand what this probability density describes. It gives us, for any pair of positions of the first and second particle, the probability density of finding the system in that particular situation (state). Whereas for a single particle we had

$$\text{probability to find particle in } a < x < b \quad = \int_a^b P(x)\,\mathrm{d}x\,, \tag{14.1}$$

we now have a

$$\begin{aligned}\text{probability to find particle 1 in } a < x_1 < b \\ \text{and particle 2 in } c < x_2 < d\end{aligned} \quad = \int_a^b \int_c^d P(x_1, x_2)\,\mathrm{d}x_1 \mathrm{d}x_2\,. \tag{14.2}$$

Note that this is probabilitity density is constructed from *one* function of *two* variables. You may have thought that a system of two particles requires two wave functions, one for the first and one for the second particle. But that is not how things work. You have *one* wave function, which maps any point in the space of classical configurations (with points labelled by (x_1, x_2)) to a single complex number.

If you are only interested in the probability density of one of the particles, we need to integrate the density over the position of the other. So we can write

$$P(x_1) = \int P(x_1, x_2)\mathrm{d}x_2\,, \tag{14.3}$$

and similar for $P(x_2)$. Intuitively this should make sense: if you do not care about where particle 2 is located, you need to 'collect' all situations which lead to particle 1 being at position x_1.

By analogy with the one-particle situation, you will not be surprised to learn that if you measure *both* the positions of particle 1 and particle 2 to be $\tilde{x}_1$ and $\tilde{x}_2$, the wave function collapses to the product of position eigenstates of the two particles,

$$\psi_{\text{before}}(x_1, x_2) \;\to\; \psi_{\text{after}}(x_1, x_2) \propto \delta(x_1 - \tilde{x}_1)\delta(x_2 - \tilde{x}_2) \tag{14.4}$$

What happens if you decide to only measure the position of, say, particle 1, but not measure particle 2? Well, in that case the wave function collapses according to

$$\begin{aligned} \psi_{\text{before}}(x_1, x_2) \;\to\; \psi_{\text{after}}(x_1, x_2) &\propto \delta(x_1 - \tilde{x}_1)\psi_{\text{before}}(x_1, x_2) \\ &= \delta(x_1 - \tilde{x}_1)\psi_{\text{before}}(\tilde{x}_1, x_2)\,. \end{aligned} \tag{14.5}$$

That is to say, the wave function now is a 'slice' of the original wave function, taken at the position where we found particle 1.

14.2 Hamiltonian eigenfunctions in a box

The eigenfunctions of a the Hamiltonian of two free particles are simply products of single-particle eigenfunctions; these are separable.

To keep things concrete, let us now assume that our two particles are put in a box of size L, so that the positions x_1 and x_2 satisfy $0 < x_1 < L$ and $0 < x_2 < L$. We will also assume that the potential vanishes. The Hamiltonain for two free, or non-interacting, particles is simply the sum of two single-particle Hamiltonians. If they have equal masses, then we have

$$\hat{H} = \frac{1}{2m}\hat{p_1}^2 + \frac{1}{2m}\hat{p_2}^2 = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial}{\partial x_2^2}\,. \tag{14.6}$$

It is therefore easy to find eigenfunctions: they are simply products of single-particle eigenfunctions. So

$$\phi(x_1, x_2) = \frac{2}{L}\sin\left(\frac{n\pi x_1}{L}\right)\sin\left(\frac{m\pi x_2}{L}\right) \tag{14.7}$$

is a unit-normalised eigenfunction of (14.6) for any two integers m and n. The time-dependence can be found easily by using our knowledge of stationary states. We simply need to find the eigenvalue of this wave function, and then the time-dependence is a simple factor $\exp(-iEt/\hbar)$. The Hamiltonian acting on the wave function above gives

$$\hat{H}\phi(x_1, x_2) = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(n^2 + m^2\right)\phi(x_1, x_2)\,. \tag{14.8}$$

and the energy eigenvalue is simply the sum of the eigenvalues of the individual particle wave functions.

A wave function of the type (14.7) is called 'separable', as it separates into a product of an x_1-dependent function and an x_2-dependent function.

14.3 Non-separable wave functions: entanglement

Non-separable wave functions describe entangled particles, for which measurement of the position of one particle influences the subsequent measurement of the position of the other.

Interesting things happen when we add two basis functions (14.7) together (remember, Schrödinger's equation is linear, so we can do that). An example is

$$\psi(x_1,x_2) = \sqrt{\frac{18}{5}}\frac{1}{L}\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{3\pi x_2}{L}\right) + \frac{1}{3}\sin\left(\frac{3\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right)\right]. \tag{14.9}$$

This is no longer a separable wave function; you cannot write it as the product of one function of only x_1 and another one of only x_2. The probability density is plotted in the figure on the right below.

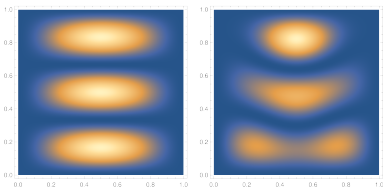

Figure 14.1: A separable wave-function on the left (the first term in (14.9)), versus a non-separable wave function on the right (both terms of (14.9)), for the two-particle system. Lighter colours indicate larger probability density $P(x_1,x_2)$. The horizontal axis corresponds to x_1, the vertical to x_2. We have set $L=1$ for simplicity.

The probability density of the position of particle 1 is obtained as above by integrating over x_2. This computation gives

$$P_{\text{before } x_2 \text{ measurement}}(x_1) = \int_0^L \left|\psi(x_1,x_2)\right|^2 \mathrm{d}x_2\,. \tag{14.10}$$

However, if you *first* measure the position of particle x_2 to be $\tilde{x}_2$, the wave function collapses to $\psi(x_1,\tilde{x}_2)$. In this case the probability density is

$$P_{\text{after } x_2 \text{ measurement}}(x_1) \propto \left|\psi(x_1,\tilde{x}_2)\right|^2. \tag{14.11}$$

The probability density (14.10) integrates, for every value of x_1 the density along a vertical line in the plot. The density (14.11), on the other hand, simply takes a horizontal slice through the plot. These clearly do not have to agree. To make this concrete, the density for our example state (14.9) before the measurement is

$$P_{\text{before } x_2 \text{ measurement}}(x_1) = \frac{2}{5L}\sin(\pi x_1)^2\Big[6+2\cos(2\pi x_1)+\cos(4\pi x_1)\Big], \tag{14.12}$$

On the other hand, if we measure, for example, the position of particle 2 to be $x_2 = L/3$, then the density for the other particle after that measurement will be

$$P_{\text{after } x_2 = L/3 \text{ measurement}}(x_1) = \frac{2}{L}\sin(3\pi x_1)^2\,. \tag{14.13}$$

This clearly is not the same.

We thus see that the measurement of one particule *influences* the subsequent measurement of the other particle. Quantum states with that property are called *entangled* states. Non-separable wave functions thus describe entangled particles.

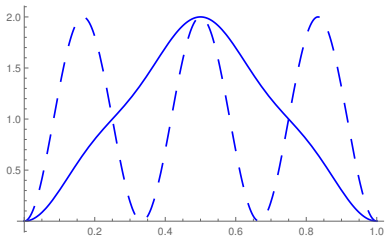

Figure 14.2: Probability density $P(x_1)$ before (solid curve) and after (dashed curve) the measurement of $x_2 = L/3$, for the example wave function used in this section ($L = 1$ for convenience).

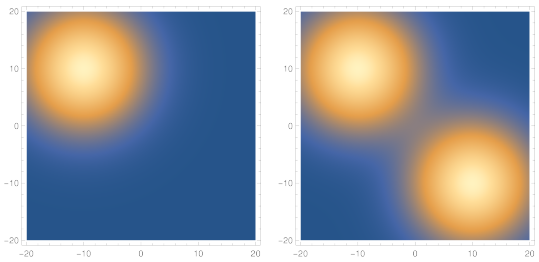

Figure 14.3: A separable and a non-separable two-particle wave function, built by multiplying and adding single-particle Gaussian wave functions.

Now that you have seen how one-particle wave functions can be used to build two-particle wave functions, you can of course apply knowledge from previous chapters to construct more interesting two-particle states. One useful example is the combination of Gaussian wave functions. A Gaussian for two particles is given by

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2\pi\Delta^2}} \exp\left[-\frac{x_1^2 + x_2^2}{4\Delta^2}\right] . \tag{14.14}$$

This is clearly a separable state. It can be considered an initial wave function, and its time evolution then follows by using the results computed in the previous chapter. More complicated wave functions can be obtained by linear superposition. A separable and a non-separable example are given in the figure below.

More complicated things happen when we consider interacting particles, that is, systems for which $V(x_1, x_2) \neq 0$. Needless to say, solving the Schrödinger equation for such systems is even more complicated than for a single particle with a non-zero potential, and this almost always requires numerical techniques. This goes beyond the scope of the current module. We may touch on these briefly in a problem session later.

For further reading on the topic in this chapter, see [3], and also see Schroeder's book.

15

Simple Harmonic Oscillator

"The career of a young theoretical physicist consists of treating the harmonic oscillator in ever-increasing levels of abstraction." – Sydney Coleman.

The simple harmonic oscillator potential is

$$V(x) = \frac{1}{2}m\omega^2 x^2 \tag{15.1}$$

where ω is known as the "angular frequency".

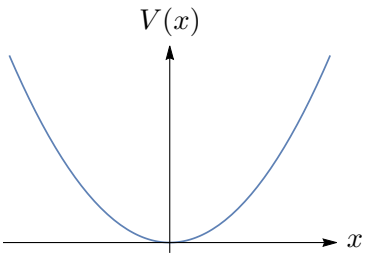

Figure 15.1: Potential of the simple harmonic oscillator

How to find the complete analytic spectrum (eigenvalues and eigenfunctions) of the Hamiltonian of the Simple Harmonic Oscillator in quantum mechanics. And a quick comparison with the classical version.

In the present chapter we will see how many quantum mechanical properties of a particle in a harmonic oscillator potential can be found exactly using very simple methods, without recourse to approximations.

15.1 Importance

Any small-fluctuation problem is a simple harmonic oscillator, hence its importance.

The harmonic oscillator potential is an extremely important example in mathematical physics and quantum mechanics in particular:

- It can be solved exactly!
- It is universal: any physical system involving small fluctuations around equilibrium is described by a collection of simple harmonic oscillators. Concretely, we can expand a potential around a local minimum $x = x_0$ as

  $$V(x) = V(x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots . \tag{15.2}$$

  Provided the distance $|x - x_0|$ remains small this is well approximated by a simple harmonic oscillator with

  $$m\omega^2 = \frac{1}{2}V''(x_0) . \tag{15.3}$$

- It is prototypical: the techniques we will introduce to in solving the simple harmonic oscillator can be applied to a wide range of other problems.

15.2 Classical Solution

Hamilton's equation for the simple harmonic oscillator are

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}\,, \tag{15.4}$$

$$\dot{p} = -\frac{\partial H}{\partial x} = -m\omega^2 x\,, \tag{15.5}$$

with general solution

$$x(t) = \sqrt{\frac{2E}{m\omega^2}}\sin(\omega t + \delta) \tag{15.6}$$

$$p(t) = \sqrt{2mE}\cos(\omega t + \delta)\,. \tag{15.7}$$

The conserved energy $E \geq 0$ and phase δ are determined by the initial conditions $(x(0), p(0))$. The motion oscillates between the points $x = \pm\sqrt{\frac{2E}{m\omega^2}}$ where the kinetic energy vanishes and $V(x) = E$.

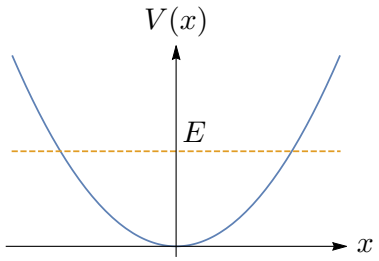

Figure 15.2: Motion in the simple harmonic oscillator potential turns around at the points where $E = V(x)$.

15.3 Energy Spectrum - First Attempt

In quantum mechanics, the basic question is to determine the spectrum of eigenvalues and eigenfunctions of the Hamiltonian operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\,. \tag{15.8}$$

We can attempt to solve the Hamiltonian eigenvalue ODE directly, but that is hard, and the wave functions are not simple.

There can gain some information on the spectrum from general theorems we proved in lecture 11 about square-normalisable Hamiltonian eigenfunctions.

1. The Hamiltonian eigenvalues obey $E > V_{\min}$ where $V_{\min}$ is the minimum value of the potential. We immediately conclude that $E > 0$.
2. The spectrum is **non-degenerate**: there is one linearly independent eigenfunction for each energy $E > 0$.

Furthermore, our experience with confining potentials leads us to expect that the spectrum will be **discrete**.

To make further progress, we could try to construct the Hamiltonian eigenfunctions and eigenvalues using the following method.

- Look for solutions to the differential equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi}{\partial x^2}+\frac{1}{2}m\omega^2x^2\phi(x)=E\phi(x)\,. \tag{15.9}$$

- Determine $E>0$ such that there exist square-normalizable solutions $\phi(x)$.

This is perfectly reasonable but unilluminating.

15.4 Ladder Operators

The simple harmonic oscillator can be formulated using so-called ladder operators instead of $\hat{x}$ and $\hat{p}$.

Instead, we follow a more powerful approach using "ladder operators". We emphasise that this method is completely algebraic: we can find the spectrum of the Hamiltonian operator without solving any differential equations!

Recall that physical observables in quantum mechanics are represented by Hermitian operators obeying $A=\hat{a}^\dagger$. For example, position $\hat{x}$ and momentum $\hat{p}$. Let us now introduce the ladder operators,

$$\hat{a}=\frac{1}{\sqrt{2\hbar m\omega}}\left(m\omega\hat{x}+i\hat{p}\right)\,, \tag{15.10}$$

$$\hat{a}^\dagger=\frac{1}{\sqrt{2\hbar m\omega}}\left(m\omega\hat{x}-i\hat{p}\right)\,. \tag{15.11}$$

They are not Hermitian operators, rather $\hat{a}^\dagger$ is the adjoint of a.

Why did we introduce these strange combinations? The reason is it allows the Hamiltonian operator to be expressed in a particularly useful form. To see this, we first invert these relations to express position and momentum in terms of the ladder operators,

$$\hat{x}=\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^\dagger)\,, \tag{15.12}$$

$$\hat{p}=-i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}-\hat{a}^\dagger)\,. \tag{15.13}$$

We then write the Hamiltonian operator

$$\begin{aligned}\hat{H}&=\frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2 &(15.14)\\ &=-\frac{1}{2m}\frac{\hbar m\omega}{2}(\hat{a}-\hat{a}^\dagger)^2+\frac{1}{2}m\omega^2\frac{\hbar}{2m\omega}(\hat{a}+\hat{a}^\dagger)^2 &(15.15)\\ &=\frac{\hbar\omega}{4}\left((\hat{a}+\hat{a}^\dagger)^2-(\hat{a}-\hat{a}^\dagger)^2\right) &(15.16)\\ &=\frac{\hbar\omega}{2}\left(\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a}\right)\,. &(15.17)\end{aligned}$$

This form of the Hamiltonian operator will allow us to determine tge spectrum of eigenvalues E. First, however, it is important to understand the relation between the combinations $\hat{a}\hat{a}^\dagger$ and $\hat{a}^\dagger\hat{a}$ appearing in the Hamiltonian. In other words, we need to compute the commutator $[\hat{a},\hat{a}^\dagger]$.

15.5 Commutators

The ladder operators satisfy the Heisenberg algebra.

Recall that the commutator is defined by

$$[A, B] := AB - BA\,. \tag{15.18}$$

Using the canonical commutator between position and momentum, $[x, p] = i\hbar$, we can compute the commutation relations between the ladder operators,

$$\begin{aligned}\left[\hat{a}, \hat{a}^\dagger\right] &= \frac{1}{2\hbar m\omega}[m\omega x + ip, m\omega x - ip] && (15.19)\\ &= \frac{1}{2\hbar}\left(-i[x, p] + i[p, x]\right) && (15.20)\\ &= 1\,, && (15.21)\end{aligned}$$

in addition to $[\hat{a}, \hat{a}] = [\hat{a}^\dagger, \hat{a}^\dagger] = 0$. This is known as a the Heisenberg algebra. We can use it to express the Hamiltonian operator in two more equivalent ways

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)\,. \tag{15.22}$$

Finally, let us compute the commutators between the Hamiltonian and ladder operators using $[a, \hat{a}^\dagger] = 1$. We find

$$\begin{aligned}\left[\hat{H}, a\right] &= \hbar\omega[\hat{a}^\dagger\hat{a}, \hat{a}] && (15.23)\\ &= \hbar\omega(\hat{a}^\dagger[\hat{a}, \hat{a}] + [\hat{a}^\dagger, \hat{a}]\hat{a}) && (15.24)\\ &= -\hbar\omega\hat{a}\,, && (15.25)\end{aligned}$$

and similarly

$$\begin{aligned}\left[\hat{H}, \hat{a}^\dagger\right] &= \hbar\omega[\hat{a}^\dagger\hat{a}, \hat{a}^\dagger] && (15.26)\\ &= \hbar\omega(\hat{a}^\dagger[\hat{a}, \hat{a}^\dagger] + [\hat{a}^\dagger, \hat{a}^\dagger]\hat{a}) && (15.27)\\ &= \hbar\omega\hat{a}^\dagger\,. && (15.28)\end{aligned}$$

These equations are extremely important to determine the spectrum.

15.6 Energy Spectrum Revisited

Ladder operators convert any Hamiltonian eigenfunction of the simple harmonic oscillator into another one, with one unit less or more energy.

Now, suppose $\phi(x)$ is a Hamiltonian eigenfunction with energy E. Then we can construct more eigenfunctions by acting with the ladder operators. For example,

$$\begin{aligned}\hat{H}\hat{a}^\dagger\phi &= [\hat{H}, \hat{a}^\dagger]\phi + \hat{a}^\dagger\hat{H}\phi && (15.29)\\ &= \hbar\omega\hat{a}^\dagger\phi + \hat{a}^\dagger E\phi && (15.30)\\ &= (E + \hbar\omega)\hat{a}^\dagger\phi\,, && (15.31)\end{aligned}$$

and similarly,

$$\hat{H}\hat{a}\phi = [\hat{H}, \hat{a}]\phi + \hat{a}\hat{H}\phi \tag{15.32}$$

$$= -\hbar\omega\hat{a}\phi + \hat{a}E\phi \tag{15.33}$$

$$= (E - \hbar\omega)\hat{a}\phi\,. \tag{15.34}$$

By induction, we find

- $(\hat{a}^\dagger)^n\phi(x)$ is a Hamiltonian eigenfunction with energy $E + n\hbar\omega$.
- $\hat{a}^n\phi(x)$ is a Hamiltonian eigenfunction with energy $E - n\hbar\omega$,

For this reason, $\hat{a}^\dagger$ and $\hat{a}$ are sometimes called 'creation' and 'annihilation' operators respectively: they create and annihilate energy in units of $\hbar\omega$.

However, recall that normalizable eigenfunctions must have $E > 0$. This means we cannot act indefinitely with $\hat{a}$ because the eigenvalue E would eventually become negative. There must therefore exist an eigenfunction $\phi_0(x)$ with the property that it is annihilated by $\hat{a}$,

$$\hat{a}\,\phi_0 = 0\,. \tag{15.35}$$

We have proven that square-normalisable Hamiltonian eigenfunctions are non-degenerate, so this wave function is unique up to normalisation.

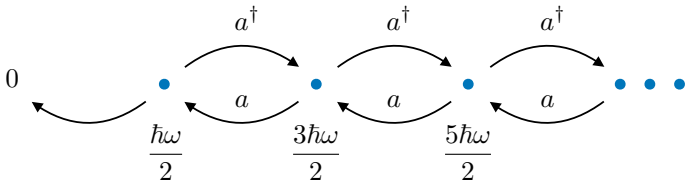

Figure 15.3: Action of the ladder operators of the simple harmonic oscillator.

Since the Hamiltonian can be expressed

$$\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \tfrac{1}{2})\,, \tag{15.36}$$

we immediately find that $\phi_0(x)$ has eigenvalue $\frac{1}{2}\hbar\omega$. It is known as the "ground state" of the simple harmonic oscillator. We can then construct eigenfunctions $(\hat{a}^\dagger)^n\phi_0(x)$ with eigenvalues $\hbar\omega(n + \frac{1}{2})$ where $n > 0$ by acting with the creation operator $\hat{a}^\dagger$. They are known as "excited states".

In summary, the spectrum of the Hamiltonian operator for the simple harmonic oscillator is

$$E_n = \hbar\omega(n + \tfrac{1}{2}) \qquad n \in \mathbb{Z}_{\geq 0}\,. \tag{15.37}$$

This is the key result of this lecture. We will construct the corresponding Hamiltonian eigenfunctions and study their properties more systematically next.

15.7 Normalisation

We can write down unit-normalised eigenfunctions purely in terms of ladder operators.

Let us first determine the normalisation of the wave functions $\phi_n(x)$ systematically. We are going to proceed by induction on n. We therefore first assume that the ground state wave function is correctly normalized, $\langle\phi_0, \phi_0\rangle = 1$. We then introduce constants C_n such that

$$\hat{a}^\dagger \phi_{n-1}(x) = C_n \phi_n(x) \tag{15.38}$$

and therefore

$$\phi_n(x) = \frac{1}{C_n}\hat{a}^\dagger \phi_{n-1}(x) \tag{15.39}$$

$$\vdots \tag{15.40}$$

$$= \frac{1}{C_n \cdots C_1}(\hat{a}^\dagger)^n \phi_0(x)\,. \tag{15.41}$$

We want to determine C_n such that $\phi_n(x)$ is normalised for all $n > 0$.

Let us assume that the $(n-1)$-th wave function is correctly normalized, $\langle\phi_{n-1}, \phi_{n-1}\rangle = 1$, and compute the normalisation of the n-th wave function. Using the inner product notation,

$$\langle\phi_n, \phi_n\rangle = \langle\frac{1}{C_n}\hat{a}^\dagger\phi_{n-1}, \frac{1}{C_n}\hat{a}^\dagger\phi_{n-1}\rangle \tag{15.42}$$

$$= \frac{1}{|C_n|^2}\langle\phi_{n-1}, \hat{a}\hat{a}^\dagger\phi_{n-1}\rangle \tag{15.43}$$

$$= \frac{1}{|C_n|^2}\langle\phi_{n-1}, \left(\frac{\hat{H}}{\hbar\omega} + \frac{1}{2}\right)\phi_{n-1}\rangle \tag{15.44}$$

$$= \frac{1}{|C_n|^2} n\langle\phi_{n-1}, \phi_{n-1}\rangle \tag{15.45}$$

$$= \frac{1}{|C_n|^2} n\,. \tag{15.46}$$

We can therefore choose $C_n = \sqrt{n}$ giving the normalisation

$$\phi_n(x) = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^n \phi_0(x)\,. \tag{15.47}$$

The action of the ladder operators on the wave functions ϕ_n is

$$\hat{a}^\dagger \phi_n(x) = \sqrt{n+1}\,\phi_{n+1}(x)\,, \tag{15.48}$$

$$\hat{a}\,\phi_n(x) = \sqrt{n}\,\phi_{n-1}(x)\,. \tag{15.49}$$

The first equation is our definition of C_n. The second equation follows from the first by acting with $\hat{a}$, expressing the result in terms of the Hamiltonian operator $\hat{H} = \hbar\omega(a\hat{a}^\dagger - \frac{1}{2})$, using the fact that $\phi_n(x)$ is a Hamiltonian eigenfunction with energy $E_n = \hbar\omega(n + \frac{1}{2})$ and finally shifting $n \to n - 1$.

Notice that

$$\hat{a}^\dagger\hat{a}\,\phi_n(x) = n\phi_n(x)\,. \tag{15.50}$$

For this reason, $\hat{a}^\dagger a$ is sometimes called the "number operator". In particular, we can recover the correct Hamiltonian eigenvalues

$$\hat{H}\phi_n(x) = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})\phi_n(x) \tag{15.51}$$

$$= \hbar\omega(n + \frac{1}{2})\phi_x(x) \tag{15.52}$$

$$= E_n\phi_n(x)\,, \tag{15.53}$$

as expected.

15.8 Orthogonality

In the lecture on Hermitian operators, we proved that square-normalisable eigenfunctions of a Hermitian operator with different eigenvalues are orthogonal. It is worth verifying this fact here using the ladder operators.

Without loss of generality, we will show that $\langle\phi_{n+j}, \phi_n\rangle = 0$ for all $n \geq 0$ and $j > 0$. Since the result must vanish, we do not keep track of the normalisation. Therefore,

$$\langle\phi_{n+j}, \phi_n\rangle \propto \langle(\hat{a}^\dagger)^{n+j}\phi_0, \phi_n\rangle \tag{15.54}$$

$$= \langle\phi_0, \hat{a}^{n+j}\phi_n\rangle \tag{15.55}$$

$$\propto \langle\phi_0, \hat{a}^j\phi_0\rangle \tag{15.56}$$

$$= 0\,, \tag{15.57}$$

since $\hat{a}\,\phi_0(x) = 0$. In summary, we indeed find that

$$\langle\phi_n, \phi_m\rangle = \delta_{nm} \tag{15.58}$$

for any $n, m \in \mathbb{Z}_{\geq 0}$.

15.9 Expectation Values

Expectation values of polynomials of x or p can be computed using the ladder operators, without knowing the wave functions explicitly, and without doing any integrals.

We can now compute the expectation value of physical observables $A(x, p)$ in any Hamiltonian eigenfunction. First, we express of position and momentum in terms of the ladder operators,

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)\,, \tag{15.59}$$

$$\hat{p} = -i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a} - \hat{a}^\dagger)\,. \tag{15.60}$$

Using this result, we can express $A(x, p)$ in terms of the ladder operators $\hat{a}$, $\hat{a}^\dagger$. Finally, $\langle A(x, p)\rangle$ can be computed using the known action of $\hat{a}$, $\hat{a}^\dagger$ (or the Hamiltonian $\hat{H}$ if it is more convenient) on $\phi_n(x)$ and the orthonormality of $\phi_n(x)$.

For example, let us compute the expectation value of position in the n-th stationary

wave function as follows

$$\langle x\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle\phi_n, (\hat{a}+\hat{a}^\dagger)\phi_n\rangle \tag{15.61}$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\langle\phi_n, \sqrt{n}\,\phi_{n-1} + \sqrt{n+1}\,\phi_{n+1}\rangle$$

$$= \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n}\,\delta_{n,n-1} + \sqrt{n+1}\,\delta_{n,n+1}) \tag{15.62}$$

$$= 0\,. \tag{15.63}$$

The expectation value of position squared is computed similarly,

$$\langle x^2\rangle = \frac{\hbar}{2m\omega}\langle\phi_n, (\hat{a}+\hat{a}^\dagger)^2\phi_n\rangle \tag{15.64}$$

$$= \frac{\hbar}{2m\omega}\langle\phi_n, (\hat{a}^2 + a^{\dagger 2} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a})\phi_n\rangle$$

$$= \frac{\hbar}{2m\omega}\langle\phi_n, (\hat{a}^2 + a^{\dagger 2} + 2\hat{a}^\dagger\hat{a} + 1)\phi_n\rangle \tag{15.65}$$

$$= \frac{\hbar}{2m\omega}(\sqrt{n(n-1)}\delta_{n,n-2} + \sqrt{(n+1)(n+2)}\delta_{n,n+2} + (2n+1)\delta_{n,n}) \tag{15.66}$$

$$= \frac{\hbar}{2m\omega}(2n+1) \tag{15.67}$$

$$= \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right)\,. \tag{15.68}$$

By similar computations, the expectation values of momentum and momentum squared are

$$\langle p\rangle = 0\,, \qquad \langle p^2\rangle = \hbar m\omega\left(n+\frac{1}{2}\right)\,. \tag{15.69}$$

Note the following points:

- We have $\Delta x\Delta p = \hbar(n+\frac{1}{2})$, compatible with Heisenberg's uncertainty principle. Furthermore, Heisenberg's uncertainty principle is saturated for $n = 0$. Indeed, we show below that $\phi_0(x)$ is a Gaussian.
- As a consistency check, we can reproduce the expectation value of the Hamiltonian,

$$\langle H\rangle = \frac{1}{2m}\langle p^2\rangle + \frac{1}{2}m\omega^2\langle x^2\rangle \tag{15.70}$$

$$= \frac{1}{2m}\hbar m\omega\left(n+\frac{1}{2}\right) + \frac{1}{2}m\omega^2\frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right) \tag{15.71}$$

$$= \hbar\omega\left(n+\frac{1}{2}\right) \tag{15.72}$$

$$= E_n\,. \tag{15.73}$$

15.10 Wave functions

The (complicated) wave functions of the simple harmonic oscillator can be constructed by acting with the differential operator form of the creation operator on the ground state wave function (which is a Gaussian).

Everything in the simple harmonic oscillator can be computed using the properties of $\hat{a}$, $\hat{a}^\dagger$, $\hat{H}$ and how they act on the wave functions $\phi_n(x)$. That said, we could not finish without briefly exploring what these wave functions look like!

First, using the momentum operator $\hat{p} = -i\hbar\partial_x$, the ladder operators become differential operators acting on wave functions

$$a = \frac{1}{\sqrt{2\hbar m\omega}}\left(m\omega x + \hbar\frac{\partial}{\partial x}\right), \tag{15.74}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}\left(m\omega x - \hbar\frac{\partial}{\partial x}\right). \tag{15.75}$$

The defining equation $\hat{a}\,\psi_0(x) = 0$ for the ground state wave function becomes a differential equation,

$$\left(m\omega x + \hbar\frac{\partial}{\partial x}\right)\phi_0(x) = 0\,, \tag{15.76}$$

whose normalised solution is the Gaussian

$$\phi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}\,. \tag{15.77}$$

This explains the observation that the ground state wave function saturates Heisenberg's uncertainty principle.

The normalized exited state wave functions are then given by

$$\phi_n(x) = \frac{1}{\sqrt{n!}}\frac{1}{(2\hbar m\omega)^{n/2}}\left(m\omega x - \hbar\frac{\partial}{\partial x}\right)^n \phi_0(x)\,. \tag{15.78}$$

They take the form of a polynomial in x, known as a "Hermite polynomial", multiplying a Gaussian wave function. Some comments:

- The wave functions are even or odd: $\phi(-x) = (-1)^n\phi(x)$. This explains why $\langle x\rangle = 0$.
- The wave functions are real. This explains why $\langle p\rangle = 0$.

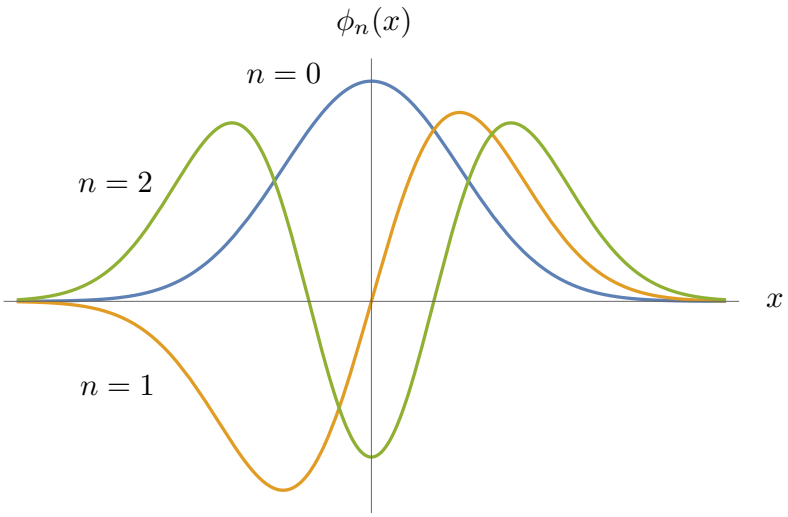

Figure 15.4: The first three energy eigenstates of the simple harmonic oscillator.

16

The Continuity Equation

In various earlier lectures, we have discussed how expectation values such as

$$\langle x \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \, x \, P(x,t) \tag{16.1}$$

depend on time. In this lecture, we investigate how the probability density $P(x,t)$ depends on time t. This question leads us to introduce the probability current $J(x,t)$, which measures the flow of probability and prove the continuity equation

$$\partial_t P + \partial_x J = 0 \,. \tag{16.2}$$

This important equation expresses the idea that probability cannot be created and destroyed but flows from one region to the next. This is known as the local conservation of probability. It is an important concept when we come to discuss scattering and tunneling in the following chapters.

16.1 The Continuity Equation

The probability density and the probability current density satisfy an equation known as the "continuity equation".

Our starting point is the probability density

$$P(x,t) := \left|\psi(x,t)\right|^2 . \tag{16.3}$$

We would like to understand how the probability density depends on time t. Let us therefore first recall Schrödinger's equation for the wave function and its complex conjugate,

$$\partial_t \psi(x,t) = -\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\partial_x^2 + V(x)\right)\psi(x,t) \,, \tag{16.4}$$

$$\partial_t \overline{\psi}(x,t) = \frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\partial_x^2 + V(x)\right)\overline{\psi}(x,t) \,, \tag{16.5}$$

where we recall that the potential $V(x)$ is a real analytic function. We can now compute the time derivative of the probability density,

$$\partial_t P = \partial_t |\psi|^2 \tag{16.6}$$

$$= \psi\,(\partial_t \overline{\psi}) + \overline{\psi}\,(\partial_t \psi) \tag{16.7}$$

$$= \frac{i}{\hbar}\psi\left(-\frac{\hbar^2}{2m}\partial_x^2 + V\right)\overline{\psi} - \frac{i}{\hbar}\overline{\psi}\left(-\frac{\hbar^2}{2m}\partial_x^2 + V\right)\psi \,. \tag{16.8}$$

Note that the dependence on the potential $V(x)$ cancels out between the two terms and the remainder becomes

$$\partial_t P = \frac{\hbar}{2mi}\left(\psi\,\partial_x^2\overline{\psi} - \bar{\psi}\,\partial_x^2\psi\right) \tag{16.9}$$

$$= \frac{\hbar}{2mi}\partial_x\left(\psi\partial_x\overline{\psi} - \overline{\psi}\partial_x\psi\right) \tag{16.10}$$

$$= -\partial_x J\,, \tag{16.11}$$

where the symbol J,

$$J := \frac{\hbar}{2mi}(\bar{\psi}\partial_x\psi - \psi\partial_x\bar{\psi}) \tag{16.12}$$

is known as the "probability current density". The result

$$\partial_t P + \partial_x J = 0\,, \tag{16.13}$$

is known as the "continuity equation".

16.2 Physical Interpretation

Physically, the continuity equation expresses that a change of the probability contained in a given region is due to probability flowing in or out of the region through the boundaries.

To understand the physical interpretation of $J(x,t)$ and the continuity equation it is convenient to integrate it over an interval. Let us define

$$P_{ab}(t) = \int_a^b P(x,t)\,\mathrm{d}x \tag{16.14}$$

to be the probability to find the particle in the interval $a < x < b$. The time derivative of this probability can be expressed in terms of the probability current at the boundaries of the interval,

$$\frac{d}{dt}P_{ab}(t) = \int_a^b \partial_t P(t,x)\,\mathrm{d}x \tag{16.15}$$

$$= -\int_a^b \partial_x J(t,x)\,\mathrm{d}x \tag{16.16}$$

$$= J(a,t) - J(b,t)\,. \tag{16.17}$$

This has the following interpretation:

- $J(x,t)$ is the rate that probability is "flowing" from left to right at x.
- The rate of change of the probability $P_{ab}(t)$ to find the particle in the interval $a < x < b$ is equal to the rate that probability is flowing in at the boundaries $x = a$ and $x = b$.

Put simply, this expresses the conservation of probability: probability cannot be created or destroyed but flows from one region to the next.

It is illuminating to consider the following limits:

1. Sending $a \to -\infty$ and $b \to \infty$, the equation becomes

$$\frac{d}{dt}\int_{-\infty}^{\infty} P(x,t)\,\mathrm{d}x = 0\,, \tag{16.18}$$

since if the wave function is normalizable then $\psi(x,t) \to 0$ and hence $J(x,t) \to 0$ as $x \to \pm\infty$. We therefore recover the conservation of the total probability to find the probability. In particular, if the wave function is normalised at $t = t_0$,

$$\int_{-\infty}^{\infty} P(x, t=t_0)\,\mathrm{d}x = 1\,, \tag{16.19}$$

this will remain normalised for $t > 0$. This is an important property that you proved in one of the problems in the chapter where we first introduced the Schrödinger's equation.

2. Setting $a = x$ and $b = x + \mathrm{d}x$ we find

$$\partial_t P(x,t)\,\mathrm{d}x = J(x,t) - J(x+\mathrm{d}x,t)\,. \tag{16.20}$$

In the limit $\mathrm{d}x \to 0$, we recover the continuity equation $\partial_t P(x,t) + \partial_x J(x,t)$, which therefore expresses the local conservation of probability in the neighbourhood of the point x.

16.3 Example: Stationary Wave functions

Let us consider a stationary wave function,

$$\psi(x,t) = \phi(x)e^{-iEt/\hbar}\,, \qquad \hat{H}\,\phi(x) = E\phi(x)\,.$$

Normalisable stationary wave functions have vanishing probability current density: no probability flows in or out of any given region.

The probability density and current are independent of time,

$$P(x,t) = |\phi(x)|^2\,, \tag{16.21}$$

$$J(x,t) = \frac{\hbar}{2mi}\big(\bar{\phi}(x)\partial_x\phi(x) - \phi(x)\partial_x\bar{\phi}(x)\big)\,. \tag{16.22}$$

The continuity equation tells us that $\partial_x J(x,t) = 0$ and therefore $J(x,t) = J_0$ is constant. Furthermore, if $\phi(x)$ is square-normalizable then $J(x,t) \to 0$ as $x \to \pm\infty$. However, if $J(x,t)$ is constant, then it must vanish $J(x,t) = 0$.

As an explicit example, suppose we have a Hamiltonian eigenfunction in the infinite potential well $0 < x < L$,

$$\phi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\,, \tag{16.23}$$

for some $n \in \mathbb{Z}_{>0}$. Since $\phi(x)$ is a real function,

$$J = \frac{\hbar}{2mi}(\bar{\psi}\partial_x\psi - \psi\partial_x\bar{\psi}) = \frac{\hbar}{2mi}(\phi\partial_x\phi - \phi\partial_x\phi) = 0\,, \tag{16.24}$$

as required.

In fact, square-normalizable Hamiltonian eigenfunctions can always be chosen real (up to a constant phase) and this argument is completely general. It provides another proof of $J(x,t) = 0$ for a square-normalisable stationary solution.

16.4 Example: Sum of Two Stationary Wave functions

Sums of normalisable stationary wave functions can have interference, leading to probability density flowing in or out of a region. The probability current density for such sums is typically not zero.

Now consider the normalized sum of two stationary wave functions,

$$\psi(x,t) = \frac{1}{\sqrt{2}}\left(\phi_1(x)e^{-iE_1t/\hbar} + \phi_2(x)e^{-iE_2t/\hbar}\right), \tag{16.25}$$

where we assume the Hamiltonian eigenfunctions $\phi_1(x)$, $\phi_2(x)$ are normalized and real with energy eigenvalues E_1, E_2. Introducing the frequency

$$\omega = \frac{E_2 - E_1}{\hbar},$$

the probability current is

$$J(x,t) = \frac{\hbar}{2mi}\left(\bar{\psi}\,\partial_x\psi - \psi\,\partial_x\bar{\psi}\right) \tag{16.26}$$

$$= \frac{\hbar}{4mi}\left(\phi_1\partial_x\phi_1 + \phi_2\partial_x\phi_2 + \phi_1\partial_x\phi_2\, e^{-i\omega t} + \phi_2\partial_x\phi_1\, e^{i\omega t} - c.c.\right) \tag{16.27}$$

$$= \frac{\hbar}{2m}\left(\phi_2\partial_x\phi_1 - \phi_1\partial_x\phi_2\right)\sin(\omega t)\,. \tag{16.28}$$

The probability current therefore oscillates in time with frequency ω.

16.5 Example: Plane Waves

For (non-normalisable) plane waves, which we will use for scattering problems, the probability current density is proportional to the velocity of the wave.

Now consider the stationary plane wave solution for a free particle on a line,

$$\psi_p(x,t) = C\, e^{i(px - E_p t)/\hbar}, \tag{16.29}$$

where $E_p = p^2/2m$. The probability density and current are constant

$$P(x,t) = |C|^2, \tag{16.30}$$

$$J(x,t) = |C|^2\frac{p}{m}. \tag{16.31}$$

Note that the probability current is equal to the probability density multiplied by the velocity p/m of the wave. This is consistent with the continuity equation. It evades the statement that $J(x,t) = 0$ for a stationary wave function because it is not square-normalisable.

Despite the fact that they are not square-normalizable, plane wave solutions are useful in "scattering problems" in quantum mechanics. This will be the starting point for the next lecture.

17

Scattering Problems

17.1 Introduction to Scattering Problems

Consider a potential that becomes constant as $x \to \pm\infty$. For instance,

$$V(x) \to \begin{cases} 0 & x \to -\infty \\ V_0 & x \to +\infty \,. \end{cases} \tag{17.1}$$

In a scattering problem, we ask the question: what is the fate of a particle with energy E incoming from $x = -\infty$?

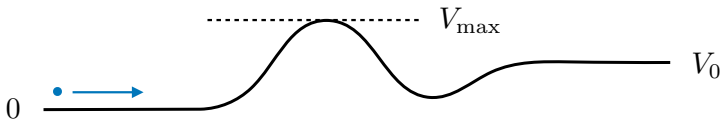

Figure 17.1: A classical particle incident on a potential barrier. It either reflects (if the energy is smaller than $V_{\max}$), or it passes over the barrier.

The answer in classical mechanics is simple. Let $V_{\max}$ denote the maximum value of the potential. Conservation of energy tells us that:

- If $E < V_{\max}$, the particle will be "reflected" back to $x = -\infty$ with probability 1.
- If $E > V_{\max}$, the particle will be "transmitted" to $x = \infty$ with probability 1.

The answer in quantum mechanics is much more interesting!

Quantum particles scattering off a potential barrier typically have both a non-zero probability to reflect as well as a non-zero probability to transmit.

17.2 Scattering Wavepackets

What do we mean by the scattering of particles in quantum mechanics? The proper answer is to consider the scattering of "wavepackets", which you can imagine as Gaussian wave functions.

- For $t \to -\infty$, the wave function has the form of an incoming wavepacket,

$$\psi(x,t) \to \psi_I(x,t)\,. \tag{17.2}$$

- The incoming wavepacket will then "scatter" from the potential and as $t \to \infty$, the wave function tends to a sum of reflected and transmitted wavepackets,

$$\psi(x,t) \to \psi_R(x,t) + \psi_T(x,t)\,. \tag{17.3}$$

A quantum-mechanical wave packet incident on a potential barrier will split into a reflected part and a transmitted part, in contrast to classical mechanics.

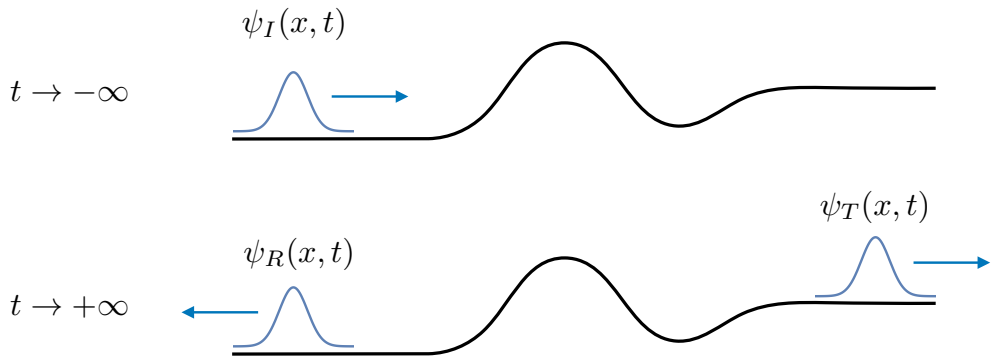

Figure 17.2: A quantum mechanical wave packet incident on a potential barrier. Part of it reflects, and part of it gets transmitted.

In the limit $t \to \infty$, the reflected and transmitted wavepackets are completely separated in space and show no interference. The probability for the particle to be reflected or transmitted is then defined by

$$R = \lim_{t\to\infty} \int |\psi_R(x,t)|^2 \mathrm{d}x \,, \tag{17.4}$$

$$T = \lim_{t\to\infty} \int |\psi_T(x,t)|^2 \mathrm{d}x \,, \tag{17.5}$$

such that

$$R + T = 1 \tag{17.6}$$

if the total wave function is correctly normalized.

For a general potential $V(x)$ and incoming wave function $\psi_I(x,t)$, computing R and T is extremely hard. Fortunately, we do not need to solve this problem in general to answer important questions about scattering experiments.

17.3 Scattering Plane Waves

Scattering plane waves is easier computationally (than wave packets), but still captures the reflection and transmission behaviour, by making using of the probability current density.

Scattering experiments typically involve incoming particles with a small energy uncertainty ΔE. This suggests that instead it is useful to consider stationary wave functions with energy $E > 0$,

$$\psi(x,t) = \phi(x) e^{-iEt/\hbar} \,, \qquad \hat{H} \cdot \phi(x) = E\phi(x) \,. \tag{17.7}$$

It is straightforward to find the form of the Hamiltonian eigenfunction $\phi(x)$ in the asymptotic regions where the potential is constant: these are plane waves.

- For $x \to -\infty$, Hamiltonian eigenfunctions obey

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -k^2 \phi(x) \,, \qquad k = \sqrt{2mE/\hbar^2} \,. \tag{17.8}$$

  The general solution is

$$\phi(x) = e^{ikx} + re^{-ikx} \,. \tag{17.9}$$

  This is a superposition of incoming and reflected waves. Since the wave functions are not square-normalizable, the overall constant is not physically meaningful: for convenience we have set the coefficient of the incoming wave to 1.

- For $x \to +\infty$, $V(x) = V_0$. For scattering problems we assume that $E > V_0$. The Hamiltonian eigenfunctions are solutions to

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -k'^2 \psi(x)\,, \qquad k' = \sqrt{2m(E - V_0)/\hbar^2}\,. \tag{17.10}$$

  We consider the solution

$$\psi(x) = te^{ik'x} \tag{17.11}$$

  corresponding to a transmitted wave. There is another solution $e^{-ik'x}$. which corresponds to a wave incoming from $x = +\infty$. We discard this solution as we only want waves incoming from $x = -\infty$.

In summary we have asymptotic plane waves,

$$\phi(x) \to \begin{cases} e^{ikx} + re^{-ikx} & x \to -\infty \\ te^{ik'x} & x \to +\infty \end{cases}. \tag{17.12}$$

How do we extract physical information from these wave functions? To answer this question, we consider the probability current. For stationary solutions this takes the form

$$J = \frac{\hbar}{2mi}\left(\bar{\psi}\partial_x\psi - \psi\partial_x\bar{\psi}\right) \tag{17.13}$$

$$= \frac{\hbar}{2mi}\left(\bar{\phi}\partial_x\phi - \phi\partial_x\bar{\phi}\right)\,, \tag{17.14}$$

where the phase $e^{-iEt/\hbar}$ has cancelled out. For a plane wave $\phi(x) = e^{ikx}$, the probability current is

$$J(\phi = e^{ikx}) = \frac{\hbar}{2mi}\left(e^{-ikx}\partial_x e^{ikx} - e^{ikx}\partial_x e^{-ikx}\right) = \frac{\hbar k}{m}\,. \tag{17.15}$$

(once again, this does not violate the statement that the probability current vanishes for *square-normalisable* stationary solutions because plane waves are not square-normalisable). The probability current in the asymptotic regions is therefore

$$J(x) \to \begin{cases} J_I - J_R & x \to -\infty \\ J_T & x \to +\infty\,, \end{cases} \tag{17.16}$$

where

$$J_I := \frac{\hbar k}{m}\,, \qquad J_R := \frac{\hbar k}{m}|r|^2\,, \qquad J_T := \frac{\hbar k'}{m}|t|^2\,, \tag{17.17}$$

are defined such that $J_I, J_R, J_T > 0$. They are the contributions to the probability current in the asymptotic regions from the incident, reflected, and transmitted waves.

There is an immediate constraint on these currents from the continuity equation $\partial_t P + \partial_x J = 0$. Since the the wave functions are stationary, $\partial_t P = 0$, and the probability current is constant in space. We conclude that

$$J(-\infty) = J(\infty) \tag{17.18}$$

and therefore

$$J_I - J_R = J_T \,. \tag{17.19}$$

This means that if we define

$$R := \frac{J_R}{J_I} = |r|^2 \qquad\qquad T := \frac{J_T}{J_I} = \frac{k'}{k}|t|^2 \tag{17.20}$$

then $R + T = 1$.

This suggests we interpret R and T as the probability for an incoming particle with definite energy $E > V_0$ to be reflected and transmitted by the potential. This in fact coincides with a careful analysis of the scattering of wavepackets in the limit $\Delta E \to 0$ of small uncertainty in energy. We are therefore justified in using the simpler definition in terms of plane waves.

For more information, see section 5.4 of [5].

17.4 Example: Finite Step Potential

For a finite step potential the plane wave functions on the left- and right-hand side can be written down explicitly, and imposing continuity and differentiability at the step then determines the reflection and transmission coefficients.

Let us consider the finite step potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \tag{17.21}$$

where we assume that $V_0 > 0$. This is a simple approximation for a more realistic smooth potential interpolating between 0 and V_0. It might represent the boundary between two different materials.

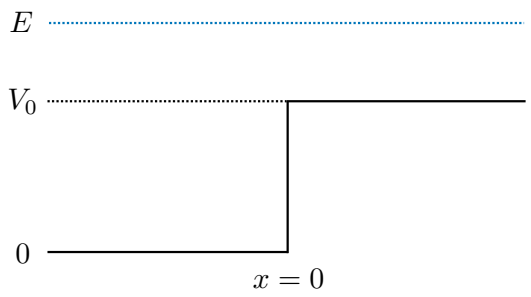

Figure 17.3: A finite step potential.

There are two cases to consider: $E > V_0$ or $E < V_0$. The "scattering problem" considered above corresponds to $E > V_0$. However, $0 < E < V_0$ is also extremely interesting and is known as the "tunnelling problem". We consider it further in the next lecture.

Let us therefore restrict here to $E > V_0$. In this example, the asymptotic plane wave solutions considered above are valid all the way up to $x = 0$. In summary,

$$\phi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ te^{ik'x} & x > 0 \end{cases} . \tag{17.22}$$

We now need to impose boundary conditions at the discontinuity in the potential at $x = 0$. Since the potential remains finite we require that both $\phi(x)$ and $\partial_x\phi(x)$ are

continuous across $x = 0$. This requires

$$1 + r = t \qquad k(1 - r) = k't\,. \tag{17.23}$$

We have two equations for two unknowns r, t and the solution is unique

$$r = \frac{k - k'}{k + k'}\,, \qquad t = \frac{2k}{k + k'}\,, \tag{17.24}$$

and hence

$$R = \left(\frac{k - k'}{k + k'}\right)^2\,, \qquad T = \frac{k'}{k}\left(\frac{2k}{k + k'}\right)^2 = \frac{4kk'}{(k + k')^2}\,. \tag{17.25}$$

As a consistency check we see that $R + T = 1$ as required.

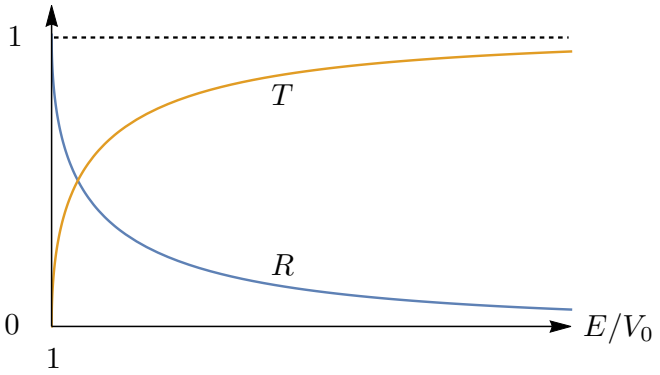

Figure 17.4: The transmission and reflection probabilities for scattering of a quantum plane wave of energy E off a finite-step potential of height V_0.

The reflection and transmission probabilities as a function of the dimensionless ratio E/V_0 are shown above. There are two important limits:

- As $E \to \infty$ or $V_0 \to 0$ we find $R \to 0$ and $T \to 1$: the potential step effectively disappears and the incoming particle is transmitted with probability 1. Note that this coincides with the classical expectation for particles with $E > V_0$.
- As $E \to V_0$ from above we find $R \to 1$ and $T \to 0$: the incoming particle is reflected with probability 1. This coincides with the classical expectation for particles with $E \leq V_0$.

As mentioned above, an important question is what happens in quantum mechanics when $E < V_0$. We will address this problem in the next lecture!

18

Tunnelling

Consider the potential barrier shown below. In classical mechanics, an incoming particle with energy $E < V_{\max}$ is reflected with probability 1 and cannot reach $x = +\infty$. In quantum mechanics, there can be a non-zero probability for the particle to be transmitted through to $x = +\infty$. This phenomenon is known as "quantum tunnelling".

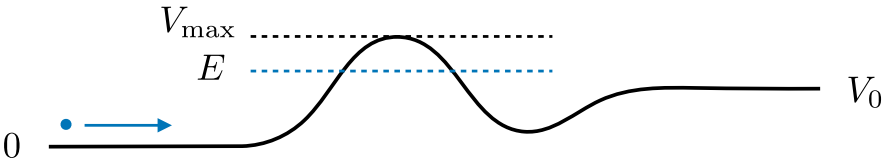

Figure 18.1: When $E < V_{\max}$ a quantum mechanical wave packet will still partially tunnel through the barrier, while a classical particle would be fully reflected.

In quantum mechanics, particles can tunnel through a potential barrier which is classically fully reflective.

18.1 Finite Step Revisited

Let us revisit the finite step potential,

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases}, \tag{18.1}$$

where we assume $V_0 > 0$. We consider incoming particles of definite energy $E > 0$. There are two regimes to consider:

1. "Scattering" : $E > V_0$.
2. "Tunnelling" : $0 < E < V_0$.

18.1.1 Scattering on a step

The scattering regime $E > V_0$ corresponds to the case where classically an incoming particle would be automatically transmitted. We covered this in the last lecture so we summarise the results here.

In the scattering regime of the finite step problem, the wave function is oscillatory on both sides of the step. There is an incoming part, as well as a reflected and transmitted part, all described by plane waves.

The Hamiltonian eigenfunctions take the form

$$\phi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ te^{ik'x} & x > 0 \end{cases}, \tag{18.2}$$

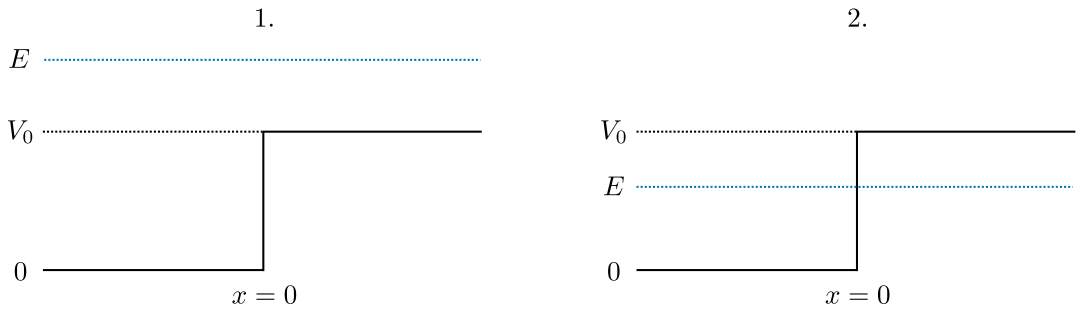

Figure 18.2: Two regimes for the finite step potential: when $E > V_0$ we are in the scattering regime, while for $E < V_0$ we are in the tunnelling regime.

where

$$k = \sqrt{2mE/\hbar^2} \qquad k' = \sqrt{2m(E - V_0)/\hbar^2}\,. \tag{18.3}$$

The coefficients r, t are found by requiring that the wave function and its derivative are continuous at $x = 0$, with the result

$$r = \frac{k - k'}{k + k'} \qquad t = \frac{2k}{k + k'}\,. \tag{18.4}$$

The wave functions are not square-normalizable and to extract physical information we instead compute ratios of probability currents. The probability current is

$$J(x) = \begin{cases} J_I - J_R & x < 0 \\ J_T & x > 0 \end{cases} \tag{18.5}$$

where

$$J_I = \frac{\hbar k}{m} \qquad J_R = \frac{\hbar k}{m}|r|^2 \qquad J_T = \frac{\hbar k'}{m}|t|^2\,. \tag{18.6}$$

The reflection and transmission probabilities are then

$$\begin{aligned} R &= \frac{J_R}{J_I} = |r|^2 = \left(\frac{k - k'}{k + k'}\right)^2 \\ T &= \frac{J_T}{J_I} = \frac{k'}{k}|t|^2 = \frac{4kk'}{(k + k')^2}\,. \end{aligned} \tag{18.7}$$

As a consistency check, we have $R + T = 1$. The reflection and transmission coefficients are sketched below for $V_0 < E < \infty$.

18.1.2 Tunnelling into a step

In the tunnelling regime of the finite step problem, the wave function is oscillatory to the left of the step, but exponentially damped (but nonzero) to the right of the step.

Now consider $0 < E < V_0$. In the region $x > 0$, where $E - V_0$ has changed sign, the Hamiltonian eigenfunction now has an exponential decay

$$\phi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ te^{-\kappa x} & x > 0 \end{cases}\,, \tag{18.8}$$

where now $\kappa = \sqrt{2m(V_0 - E)/\hbar^2}$. We discard the other potential solution $e^{\kappa x}$ which would diverge at $x \to +\infty$.

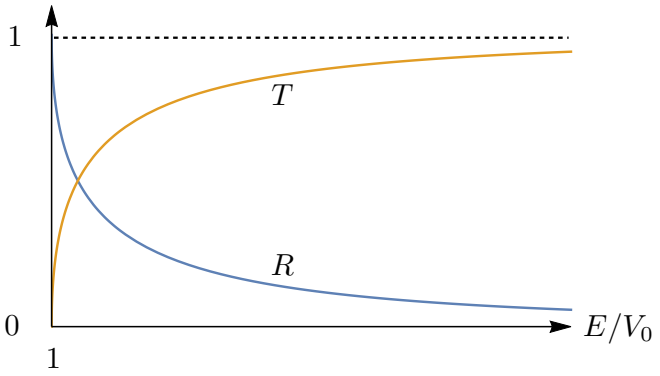

Figure 18.3: The transmission and reflection coefficients for the scattering regime, as a function of the dimensionless ratio of the energy of the incoming wave divided by the height of the step.

Notice that the above wave function can be obtained from the scattering problem by replacing $k' \to i\kappa$. This means we can immediately write down the solution for the coefficients r, t,

$$r = \frac{k - i\kappa}{k + i\kappa} \qquad t = \frac{2k}{k + i\kappa}\,. \tag{18.9}$$

This dramatically changes the computation of the probability currents, which involve both the wave function and its conjugate. In particular, the reflected probability current is now equal to the incoming probability current,

$$J_R = \frac{\hbar k}{m}|r|^2 = \frac{\hbar k}{m}\left|\frac{k - i\kappa}{k + i\kappa}\right|^2 = \frac{\hbar k}{m} = J_I\,. \tag{18.10}$$

Meanwhile, the transmitted probability current now vanishes,

$$\begin{aligned} J_T &= \frac{\hbar}{2mi}(\overline{\phi(x)}\partial_x\phi(x) - \phi(x)\partial_x\overline{\phi(x)}) \qquad x > 0 && (18.11)\\ &= \frac{\hbar}{2mi}(e^{-\kappa x}\partial_x e^{-\kappa x} - e^{-\kappa x}\partial e^{-\kappa x}) \\ &= 0\,, && (18.12) \end{aligned}$$

because $e^{-\kappa x}$ is a real function of x.

In summary, we conclude that

$$R = 1 \qquad T = 0 \tag{18.13}$$

in the tunnelling regime $0 < E < V_0$. Note the following points:

- This is consistent with the limit $E \to V_0^+$ in the scattering regime $E > V_0$.
- It coincides with the classical expectation that the particle is always reflected when $0 < E < V_0$.

Despite the fact that $T = 0$, the probability density is non-zero in the region $x > 0$ so there is therefore a non-vanishing probability to find the particle with $x > 0$. The probability density is sketched below. In contrast, the particle is forbidden from the region $x > 0$ in classical mechanics

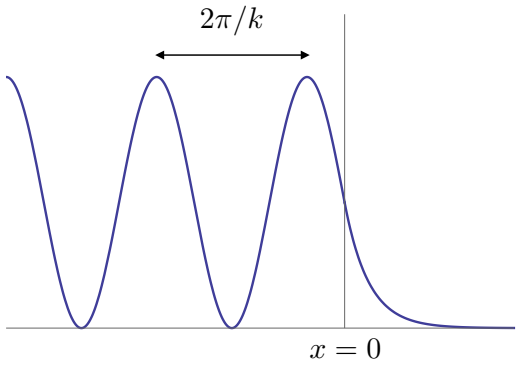

Figure 18.4: The probability density in the presence of a finite step potential, for the tunnelling regime, which clearly shows that the wave function can penetrate into the barrier.

This has important consequences if we were to add a step down to $V(x) = 0$ at some finite distance $x = L$. The wave function would then be expected to decay exponentially for $0 < x < L$, but then become trigonometric again for $x > L$ and there is a possibility for the particle to escape to $x \to +\infty$. This is known as "quantum tunnelling". We explore this in more detail now.

18.2 Finite Potential Barrier

Let us now consider the finite barrier potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 \leq x \leq L \\ 0 & x > L \end{cases} . \tag{18.14}$$

In this case, we will see that there is a non-zero probability to find the particle to

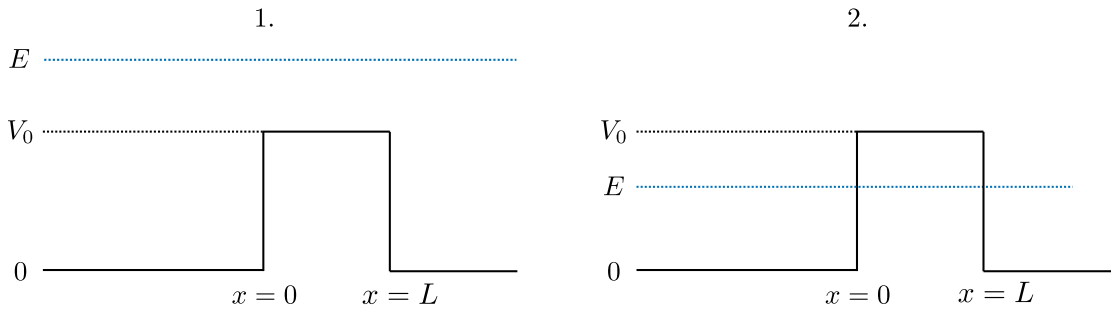

Figure 18.5: Scattering and tunnelling regimes for the finite barrier problem.

the right of the barrier *even* when $E < V_0$.

18.2.1 Scattering off a barrier

The scattering regime corresponds again to $E > V_0$. The Hamiltonian eigenfunctions are trigonometric in all regions,

$$\phi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ Ae^{ik'x} + Be^{-ik'x} & 0 < x < L \\ te^{ikx} & x > L \end{cases} , \tag{18.15}$$

For a finite width potential barrier, the scattering regime exhibits full transmission ('resonance') for a discrete set of energies, corresponding to a wave-length which fits an integer number of times 'inside' the barrier.

where the wavenumbers k, k' are defined as above.

Since the potential remains finite at $x = 0$ and $x = L$, we need to impose that the wave function and its derivative are continuous there. This gives the constraints

$$1 + r = A + B \tag{18.16}$$
$$k(1 - r) = k'(A - B) \tag{18.17}$$

from $x = 0$ and

$$Ae^{ik'L} + Be^{-ik'L} = te^{ikL} \tag{18.18}$$
$$k'(Ae^{ik'L} - Be^{-ik'L}) = kte^{ikL}\,. \tag{18.19}$$

from $x = L$. We have four linear equations for four variables r, t, A, B. The solution is found by elementary but tedious linear algebra that I will not reproduce here. The important output is the reflection / transmission probabilities

$$R = |r|^2 = \frac{(k^2 - k'^2)^2 \sin^2(k'L)}{(k^2 + k'^2)^2 \sin^2(k'L) + 4k^2k'^2 \cos^2(k'L)} \tag{18.20}$$
$$T = |t|^2 = 1 - R\,. \tag{18.21}$$

The important features are summarized below.

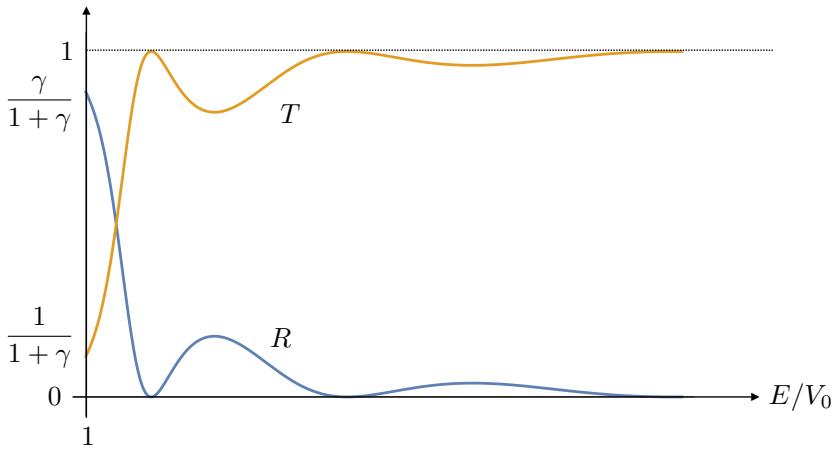

Figure 18.6: Transmission and reflection for a finite barrier, as a function of the incident energy, for the scattering regime. The case $E/V_0 = 1$ is called "critical scattering".

- The limit $E \to \infty$ corresponds to $k, k' \to \infty$ with $k/k' \to 1$. We find $R \to 0$, $T \to 1$ reproducing the classical expectation for $E > V_0$. The potential barrier is negligible compared to the energy and the particle is transmitted with probability 1.
- The limit $E \to V_0^+$ corresponds to $k' \to 0^+$, with

  $$R \to \frac{\gamma}{1+\gamma} \qquad T \to \frac{1}{1+\gamma} \tag{18.22}$$

  where $\gamma = mL^2V_0/2\hbar^2$ is a dimensionless parameter.

- The function has trigonometric dependence on k'. In particular, the transmission probability becomes 1 whenever $k'L = n\pi$ or equivalently

$$E = V_0 + \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 . \tag{18.23}$$

These "transmission resonances" correspond to a standing wave in $0 < x < L$. If we remember that the wavelength is $\lambda = 2\pi/k'$, the condition becomes $2L = n\lambda$ so the distance from $x = 0$ to $x = L$ and back is an integer number of wavelengths. Intuitively, there is constructive interference between incident wave at $x = 0$ and the standing wave in the region $0 < x < L$.

18.2.2 Tunnelling through a barrier

In the tunnelling regime there are no resonances, and the transmission goes to zero as the barrier height goes to infinity.

The tunnelling regime is $0 < E < V_0$. The Hamiltonian eigenfunctions are now

$$\phi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ Ae^{\kappa x} + Be^{-\kappa x} & 0 < x < L \\ te^{ikx} & x > L \end{cases} , \tag{18.24}$$

where k and κ are defined as above.

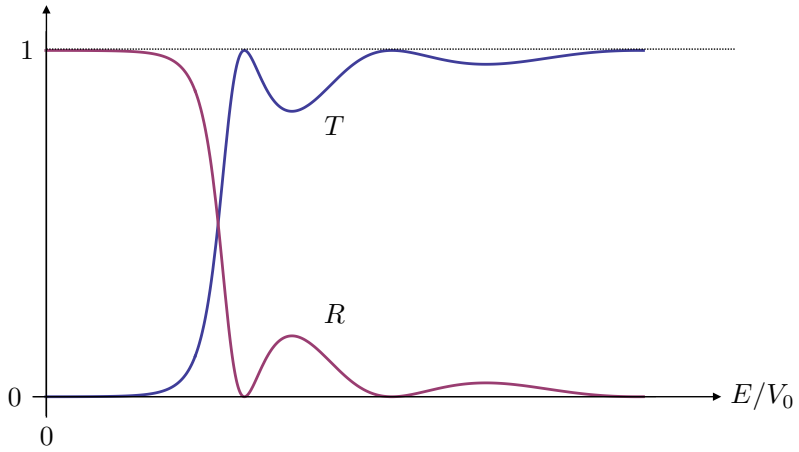

Figure 18.7: Transmission and reflection coefficients for a finite size potential barrier, for all potential heights.

A Jupyter notebook (on Colab) to compute the time dependence of a wave packet incident on a finite-height barrier, and see the effect of tunnelling.

As before, the coefficients r, t are found by replacing $k' \to i\kappa$ in the scattering regime. This modifies the reflection and transmission coefficients to

$$R = \frac{\left(k^2+\kappa^2\right)^2 \sinh^2(\kappa L)}{\left(k^2-\kappa^2\right)^2 \sinh^2(\kappa L) + 4\kappa^2 k^2 \cosh^2(\kappa L)} \tag{18.25}$$

$$T = 1 - R\,. \tag{18.26}$$

Note that there is a non-vanishing probability for the particle to be transmitted through the potential barrier and reach $x = +\infty$, which is forbidden in classically. This is known as "quantum tunnelling".

- The limit $E \to 0$ corresponds to $k \to 0$ with κ fixed. We find $R \to 1$, $T \to 0$ reproducing the classical expectation for $E < V_0$.

- The limit $E \to V_0^-$ in the tunnelling regime coincides with the limit $E \to V_0^+$ in the scattering regime.
- Note the exponential rather than trigonometric dependence on κ in $0 < x < L$. In particular, there are no "resonances" like in the scattering regime.

Finally, we can combine the results in the scattering and tunnelling regimes to sketch the reflection / transmission probabilities across the entire range $0 < E < \infty$.

19

Momentum-space Wave function

So far position and momentum have appeared asymmetrically in quantum mechanics. In this lecture, we rectify the situation by introducing a 'momentum-space' wave function. We work at a fixed time t.

The symmetry between position and momentum is restored by the momentum-space representation of quantum mechanics.

19.1 Motivation

In the Hamiltonian formulation of classical mechanics, position and momentum appear in a symmetrical way as coordinates (x, p) on phase space. Moreover, there is a canonical transformation that exchanges them!

In classical mechanics position and momentum appear very symmetrically, and there is a map (a canonical transformation) which exchanges them and leaves Hamilton's equations unchanged.

Recall that a canonical transformation is a change of coordinates $(x, p) \to (x', p')$ that leaves Hamilton's equations invariant. Under the transformation

$$(x, p) \to (p, -x)\,, \tag{19.1}$$

we find

$$\dot{x} = +\frac{\partial H}{\partial p} \quad \to \quad \dot{p} = -\frac{\partial H}{\partial x} \tag{19.2}$$

$$\dot{p} = -\frac{\partial H}{\partial x} \quad \to \quad \dot{x} = +\frac{\partial H}{\partial p}\,. \tag{19.3}$$

So Hamilton's equations are indeed unchanged but the role of position and momentum has been reversed.

19.2 The Fourier Transform

In contrast, position and momentum appear quite asymmetrically in our description of quantum mechanics so far. We have introduced a 'position-space' wave function $\psi(x)$ on which position and momentum act as operators

The Fourier transform translates things in position-space to things in momentum-space.

$$\hat{x} = x\,, \tag{19.4}$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}\,. \tag{19.5}$$

The canonical transformation $(x, p) \to (p, -x)$ from classical mechanics suggests there should another formulation of quantum mechanics with a 'momentum-space' wave function $\widetilde{\psi}(p)$ on which position and momentum act as operators

$$\hat{x} = i\hbar\frac{\partial}{\partial p}\,, \tag{19.6}$$

$$\hat{p} = p\,. \tag{19.7}$$

We claim that the position and momentum wave functions are in fact related by the following pair of integrals

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p\, \widetilde{\psi}(p)\, e^{ipx/\hbar}\,, \tag{19.8}$$

$$\widetilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x)\, e^{-ipx/\hbar}\,. \tag{19.9}$$

This is an example of a 'Fourier transform'.

Let us see that these are consistent with the expected form of the position and momentum operators above.

- First acting with $i\hbar\dfrac{\partial}{\partial p}$ on the momentum-space wave function,

$$i\hbar\frac{\partial}{\partial p}\,\widetilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x) \left(i\hbar\frac{\partial}{\partial p} e^{-ipx/\hbar} \right) \tag{19.10}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x)\, \left(x e^{-ipx/\hbar} \right) \tag{19.11}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \left(x\psi(x) \right)\, e^{-ipx/\hbar}\,, \tag{19.12}$$

  which corresponds to multiplying the position-space wave function by x.

- Second multiplying the momentum-space wave function by p,

$$p\,\widetilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x) \left(p\, e^{-ipx/\hbar} \right) \tag{19.13}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x)\, \left(i\hbar\frac{\partial}{\partial x} e^{-ipx/\hbar} \right) \tag{19.14}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, \left(-i\hbar\frac{\partial}{\partial x}\psi(x) \right)\, e^{-ipx/\hbar}\,, \tag{19.15}$$

  which corresponds to acting with $-i\hbar\dfrac{\partial}{\partial x}$ on the position-space wave function.

The action of position and momentum operators on position and momentum wave functions is summarised in the following table.

	$\psi(x)$	$\widetilde{\psi}(p)$
$\hat{x}$	x	$+i\hbar\dfrac{\partial}{\partial p}$
$\hat{p}$	$-i\hbar\dfrac{\partial}{\partial x}$	p

(19.16)

Because we can formulate quantum mechanics using a wave function which is a function of momentum rather than position, there is indeed a symmetry between the two.

19.3 The Momentum-space Wave function

The function $\widetilde{\psi}(x)$ is known as the momentum-space wave function. Everything we have learnt about the position-space wave function has analogues for the momentum-space wave function.

- $\widetilde{P}(p) := |\widetilde{\psi}(p)|^2$ is the momentum probability density. In particular, the probability that a momentum measurement will find $a < p < b$ is

$$\int_a^b \mathrm{d}p\, \widetilde{P}(p) = \int_a^b \mathrm{d}p\, |\widetilde{\psi}(p)|^2 \,.$$

  This is an improvement on previous lectures where we could only compute expectation values of momentum.

- We can compute momentum expectation values using

$$\langle f(p) \rangle = \int_{-\infty}^{\infty} \mathrm{d}p\, f(p)\, |\widetilde{\psi}(p)|^2 \tag{19.17}$$

  for any polynomial function $f(p)$.

- We can compute position expectation values using

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \mathrm{d}p\, \overline{\widetilde{\psi}(p)}\, f\left(i\hbar \frac{\partial}{\partial p}\right) \widetilde{\psi}(p) \tag{19.18}$$

  for any polynomial function $f(x)$.

19.4 Examples

19.4.1 Example 1: bound state of the delta-function potential

In general, the momentum-space wave function is different from the position-space wave function (the Fourier transform is non-trivial).

Consider the wave function

$$\psi(x) = Ce^{-\lambda|x|/\hbar} \tag{19.19}$$

where $\lambda > 0$ is a constant; we have seen this wave function in the discussion of the delta function potential. To find the normalisation C, we require the probability to find the particle anywhere is 1,

$$1 = |C|^2 \int_{-\infty}^{\infty} e^{-2\lambda|x|/\hbar}\, \mathrm{d}x \tag{19.20}$$

$$= 2|C|^2 \int_0^{\infty} e^{-2\lambda x/\hbar}\, \mathrm{d}x \tag{19.21}$$

$$= |C|^2 \frac{\hbar}{\lambda}\,, \tag{19.22}$$

and therefore $C = \sqrt{\lambda/\hbar}$ up to a constant phase.

Let us now compute the momentum-space wave function,

$$\widetilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}p\, e^{-ipx/\hbar} \psi(x) \tag{19.23}$$

$$= \sqrt{\frac{\lambda}{2\pi\hbar^2}} \int_{-\infty}^{\infty} \mathrm{d}p\, e^{-ipx/\hbar} e^{-\lambda|x|/\hbar} \tag{19.24}$$

$$= \sqrt{\frac{\lambda}{2\pi\hbar^2}} \left(\int_0^{\infty} e^{(-ip-\lambda)x/\hbar} + \int_{-\infty}^{0} e^{(-ip+\lambda)x/\hbar} \right) \tag{19.25}$$

$$= \sqrt{\frac{\lambda}{2\pi}} \left(\frac{1}{ip+\lambda} + \frac{1}{-ip+\lambda} \right) \tag{19.26}$$

$$= \sqrt{\frac{2}{\pi}} \frac{\lambda^{3/2}}{p^2+\lambda^2} \,. \tag{19.27}$$

You may wish to verify that $\widetilde{\psi}(p)$ is correctly normalised!

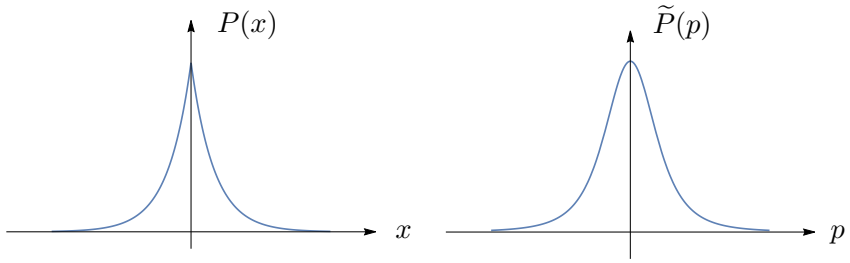

Figure 19.1: The position-space wave probability density for the delta potential bound state, and its momentum-space version.

19.4.2 Example 2: Gaussian wave function

The momentum wave function corresponding to a Gaussian in position-space is again a Gaussian, but now in momentum-space.

Consider the normalised Gaussian wave function

$$\psi(x) = Ce^{-x^2/4\Delta^2} \,. \tag{19.28}$$

where $C = 1/(2\pi\Delta^2)^{1/4}$.

The momentum-space wave function is computed by completing the square in the exponential,

$$\widetilde{\psi}(p) = \frac{C}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\, e^{-x^2/4\Delta^2} e^{-ipx/\hbar} \tag{19.29}$$

$$= \frac{C}{\sqrt{2\pi\hbar}} e^{-p^2\Delta^2/\hbar^2} \int_{-\infty}^{\infty} \mathrm{d}x\, e^{-(x+2ip\Delta/\hbar)^2/4\Delta^2} \tag{19.30}$$

$$= \frac{C}{\sqrt{2\pi\hbar}} e^{-p^2\Delta^2/\hbar^2} \int_{\gamma} \mathrm{d}y\, e^{-y^2/4\Delta^2} \tag{19.31}$$

where

$$y = x + 2ip\Delta^2/\hbar \,. \tag{19.32}$$

In performing the substitution, we are now integrating over a 'contour' γ in the complex y-plane that is shifted by an amount $2ip\Delta^2/\hbar$ in the imaginary direction. However, as there are no poles in the intermediate region we can deform the contour

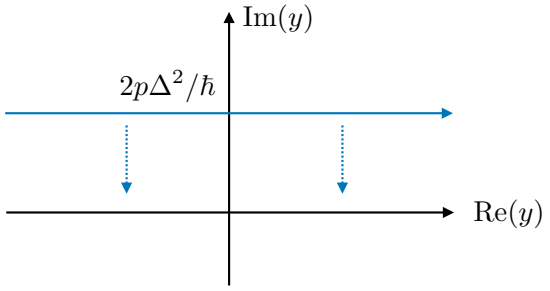

Figure 19.2: The integration over y in (19.31) is a line in the complex plane, which can, however, be shifted to the real line because the integrand does not have any poles in the intermediate region.

back to the real axis. We then have a standard Gaussian integral,

$$\widetilde{\psi}(p) = \frac{C}{\sqrt{2\pi\hbar}} e^{-p^2\Delta^2/\hbar^2} \int_{-\infty}^{\infty} \mathrm{d}y e^{-y^2/4\Delta^2} \tag{19.33}$$

$$= \frac{C\sqrt{4\pi\Delta^2}}{\sqrt{2\pi\hbar}} e^{-p^2\Delta^2/\hbar^2} \,. \tag{19.34}$$

Now defining

$$\widetilde{\Delta} := \hbar/2\Delta \,, \tag{19.35}$$

and substituting in the normalisation factor C, this becomes a normalised Gaussian wave function in momentum-space

$$\widetilde{\psi}(p) = \frac{1}{(2\pi\widetilde{\Delta}^2)^{1/4}} e^{-p^2/4\widetilde{\Delta}^2} \,. \tag{19.36}$$

We can therefore immediately determine that $\langle p \rangle = 0$ and $\Delta p = \widetilde{\Delta}$ in complete agreement with what we computed earlier explicitly in position space using $\Delta p = \sqrt{\langle p^2 \rangle - (\langle p \rangle)^2}$.

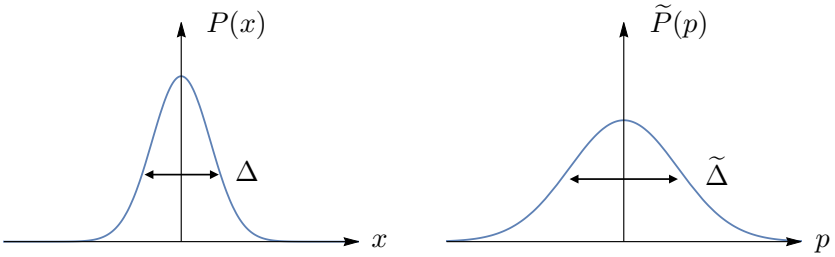

Figure 19.3: The position-space wave probability density for a Gaussian wave function, and its momentum-space version. The momentum-space wave function is again a Gaussian, but with a different width (in momentum-space).

- This is a very important result: the Fourier transformation of a Gaussian wave function is a Gaussian wave function with uncertainties related by

$$\Delta x \, \Delta p = \frac{\hbar}{2} \,. \tag{19.37}$$

19.5 Properties

The Fourier transform preserves the normalisation of the wave function. In addition, a translation in position-space corresponds to a phase factor multiplication in momentum-space, and vice versa.

We conclude by listing a couple of important properties of the Fourier transforms relating position and momentum wave functions.

First, you may have noticed from the Gaussian example that the momentum wave function was automatically normalised. This is generally true: $\psi(x)$ is normalised if and only if $\widetilde{\psi}(p)$ is normalised.

Second, the Fourier transformations interchange 'translations' and 'phases'. To be concrete, it is straightforward to check from the definitions that if

$$\psi(x) \quad \longleftrightarrow \quad \widetilde{\psi}(p) \tag{19.38}$$

are related by Fourier transform then so are

$$\psi(x - x_0) \quad \longleftrightarrow \quad \widetilde{\psi}(p) e^{-ipx_0/\hbar} \tag{19.39}$$

$$\psi(x) e^{ip_0 x/\hbar} \quad \longleftrightarrow \quad \widetilde{\psi}(p - p_0) \tag{19.40}$$

In words:

- If I translate the position wave function $\psi(x)$ by an amount x_0, this is equivalent to multiplying the momentum wave function $\widetilde{\psi}(p)$ by the phase $e^{-ipx_0/\hbar}$.
- If I translate the momentum wave function $\widetilde{\psi}(p)$ by an amount p_0, this is equivalent to multiplying the position wave function $\psi(x)$ by the phase $e^{ip_0 x/\hbar}$.

This has some important consequences. For example, suppose $\psi(x) = \phi(x) e^{ip_0 x/\hbar}$. Then we should expect the momentum expectation values obey $\langle p \rangle_\psi = \langle \phi \rangle + p_0$. To see this explicitly using the momentum wave function

$$\langle p \rangle_\psi = \int \mathrm{d}p \, p \, |\widetilde{\phi}(p - p_0)|^2 \tag{19.41}$$

$$= \int \mathrm{d}p' \, (p' + p_0) \, |\widetilde{\phi}(p')|^2 \tag{19.42}$$

$$= \langle p \rangle_\phi + p_0 \, , \tag{19.43}$$

assuming $\widetilde{\phi}(p)$ is normalised.

20

Ehrenfest's Theorem

Ehrenfest's theorem states that classical equations of motion hold inside expectation values.

In this last lecture, we will explore how the expectation values of Hermitian operators, such the expectation values of position $\langle x \rangle$ and momentum $\langle p \rangle$, evolve in time. We will derive an important equation, known as "Ehrenfest's Theorem" [2], which shows that the classical equations of motion hold inside expectation values. We will illustrate this theorem with a number of examples and point out some subtleties.

20.1 A Classical Reminder

In classical mechanics, a particle has definite position and momentum $(x(t), p(t))$ at each time t that evolve according to Hamilton's equations

$$\dot{x} = +\frac{\partial H}{\partial p} = \{x, H\} \tag{20.1}$$

$$\dot{p} = -\frac{\partial H}{\partial x} = \{p, H\}\,, \tag{20.2}$$

where $\{\,,\,\}$ is the Poisson bracket. Furthermore, the evolution of any quantity $A(x,p)$ constructed from position and momentum is

$$\dot{A} = \{A, H\}\,. \tag{20.3}$$

This is the idea we have already exploited that the Hamiltonian generates time translations. Notice that a quantity A is constant in time if and only if its Poisson bracket with the Hamiltonian vanishes,

$$\{H, A\} = 0\,. \tag{20.4}$$

This notion of conserved quantity will carry over naturally to quantum mechanics.

For the standard Hamiltonian

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

we find

$$\dot{x} = \frac{p}{m} \qquad \dot{p} = -\frac{dV}{dx}$$

and recover Newton's law

$$m\ddot{x} = -\frac{dV}{dx}\,.$$

20.2 Ehrenfest's Theorem

Ehrenfest's theorem roughly states that the classical equations of motion hold inside expectation values. It is easily misinterpreted or misused though.

Let us consider a Hermitian operator A such as position $\hat{x}$, momentum $\hat{p}$ or the Hamiltonian operator $\hat{H}$. Recall that the expectation value of A in a wave function $\psi(x,t)$ is

$$\langle A\rangle := \langle \psi, A\psi\rangle = \int_{-\infty}^{\infty} dx\, \overline{\psi(x,t)}\,(A\cdot\psi(x,t))\ . \tag{20.5}$$

We would like to to understand how this expectation value depends on time.

Theorem: For a Hermitian operator A,

$$\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H},A]\rangle\,. \tag{20.6}$$

Proof: We will compute the time derivative of the expectation value using the compact inner product notation. First, using the product rule inside the integral,

$$\frac{d\langle A\rangle}{dt} = \frac{d}{dt}\langle\psi,A\psi\rangle \tag{20.7}$$

$$= \langle\partial_t\psi, A\psi\rangle + \langle\psi, A\partial_t\psi\rangle\,. \tag{20.8}$$

The partial time derivatives can be replaced by the Hamiltonian operator using Schrödinger's equation,

$$i\hbar\partial_t\psi = \hat{H}\cdot\psi\,. \tag{20.9}$$

Using properties of the inner product and Hermitian operators, we find

$$\frac{d\langle A\rangle}{dt} = \langle -\frac{i}{\hbar}H\psi, A\psi\rangle + \langle\psi, -A\frac{i}{\hbar}H\psi\rangle \tag{20.10}$$

$$= \frac{i}{\hbar}\left(\langle H\psi, A\psi\rangle - \langle\psi, AH\psi\rangle\right) \tag{20.11}$$

$$= \frac{i}{\hbar}\left(\langle\psi, HA\psi\rangle - \langle\psi, AH\psi\rangle\right) \tag{20.12}$$

$$= \frac{i}{\hbar}\langle\psi,[H,A]\psi\rangle \tag{20.13}$$

$$= \frac{i}{\hbar}\langle[H,A]\rangle \tag{20.14}$$

where

$$[A,B] := AB - BA$$

is the commutator. This complete the proof.

This result is reminiscent of the classical equations of motion,

$$\dot{A} = -\{H,A\}\,.$$

To make this precise, recall that commutators in quantum mechanics can be obtained from Poisson brackets in classical mechanics by replacing

$$\{\,\cdot\,,\cdot\,\}\mapsto -\frac{i}{\hbar}[\,\cdot\,,\cdot\,]\,. \tag{20.15}$$

For example,

$$\{x, p\} = 1 \quad \mapsto \quad [\hat{x}, \hat{p}] = i\hbar\,.$$

gives the canonical commutation relation. Ehrenfest's theorem can therefore be interpreted as the statement that the classical equations of motion hold "inside" expectation values.

Let us verify this statement explicitly for the Hamiltonian

$$H = \frac{p^2}{2m} + V(x) \tag{20.16}$$

where $V(x)$ is a real analytic function of x. The commutators of this Hamiltonian with position and momentum were computed in lecture 11,

$$[H, x] = -\frac{i\hbar}{m}p \qquad [H, p] = i\hbar\frac{dV(x)}{dx}\,. \tag{20.17}$$

From Ehrenfest's theorem,

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m}\,, \qquad \frac{d\langle p\rangle}{dt} = -\left\langle \frac{dV}{dx}\right\rangle \tag{20.18}$$

and therefore

$$m\frac{d^2\langle x\rangle}{dt^2} = -\left\langle \frac{\partial V}{\partial x}\right\rangle\,. \tag{20.19}$$

20.3 Conserved Quantities

In quantum mechanics, a conserved quantity is defined to be a Hermitian operator A that commutes with the Hamiltonian: $[H, A] = 0$. This is the natural analogue of the classical statement that $\{A, H\} = 0$. Note that the Hamiltonian itself is always a conserved quantity!

Conserved quantities correspond to operators which commute with the Hamiltonian.

An immediate consequence of Ehrenfest's theorem is that if A is conserved then its expectation value is constant in time,

$$\partial_t\langle A\rangle = 0\,, \tag{20.20}$$

justifying the definition of a conserved quantity.

20.4 Example: Free Particle

In a previous lecture, we completely solved Schrödinger's equation for the wave function of a free particle with vanishing potential $V(x) = 0$. In particular, we found that an initial Gaussian wave function remains a Gaussian with expectation values depending on time,

A Gaussian wave packet with momentum p_0 has a centre of mass moving with velocity $\langle p\rangle/m$; this follows directly from Ehrenfest's theorem.

$$\langle x\rangle = x_0 + \frac{p_0}{m}t\,, \qquad \langle p\rangle = p_0\,.$$

The important point here is that

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m} \qquad \frac{d\langle p\rangle}{dt} = 0\,,$$

so the expectations values solve the classical equations of motion with $V(x) = 0$: the centre $\langle x\rangle$ of the Gaussian wave function is moving with a uniform velocity $\langle p\rangle/m$.

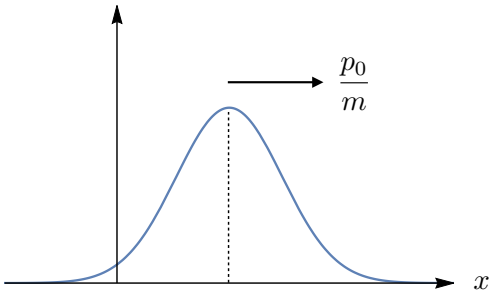

Figure 20.1: A Gaussian wave function with momentum p_0. Ehrenfest's theorem states that centre of the peak $\langle x \rangle$ moves with velocity $\langle p \rangle / m$, without doing the long explicit computation we did earlier.

20.5 Example: Infinite Square Well

The expectation value of a function of x is not the same as the function of the expectation value of x. Be aware of this subtlety when using Ehrenfest's theorem.

While Ehrenfest's theorem states the classical equations of motion hold inside expectation values, this does not necessarily imply that the expectation values obey the classical equations of motion. That is to say, while we have seen that

$$m\frac{d^2\langle x\rangle}{dt^2} = -\left\langle \frac{\partial V}{\partial x} \right\rangle . \tag{20.21}$$

for a system with Hamiltonian (20.16), this does not mean that you can replace the right hand side with

$$-\frac{\partial V(\langle x\rangle)}{\partial x} .$$

The example in the present section illustrates this explicitly. Moreover, it shows that sometimes Ehrenfest's theorem takes a different form, because boundary terms need to be taken into account.

The example to consider is the infinite square well $0 < x < L$, with an initial wave function that is an equal linear combination of the Hamiltonian eigenfunctions with the lowest energy,

$$\psi(x,0) = \frac{1}{\sqrt{2}}(\phi_1(x) + \phi_2(x)) . \tag{20.22}$$

The solution of Schrödinger's equation at times $t > 0$ is

$$\psi(x,0) = \frac{1}{\sqrt{2}}(\phi_1(x)e^{-iE_1t/\hbar} + \phi_2(x)e^{-iE_2t/\hbar}) . \tag{20.23}$$

In a tutorial problem in the chapter on stationary states, we have shown that the position expectation value oscillates in time around the centre of the box,

$$\langle x\rangle = \frac{L}{2} - A\cos(\omega t) \tag{20.24}$$

$$\tag{20.25}$$

with frequency

$$\omega = \frac{E_2 - E_1}{\hbar} . \tag{20.26}$$

and amplitude $A < \frac{L}{2}$.

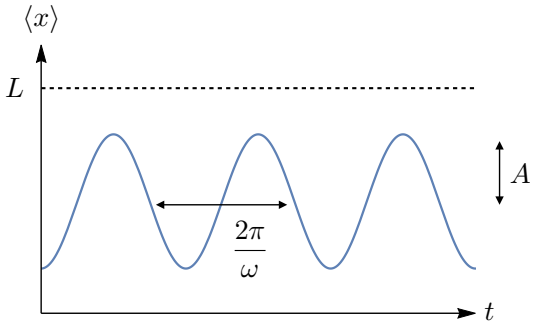

Figure 20.2: Expectation value $\langle x\rangle$ as a function of time for a particle in a box described by the sum of the two lowest-energy Hamiltonian eigenstates. Clearly $\langle x\rangle$ does not satisfy the classical equations of motion, which yield constant-velocity motion except at the boundaries.

This is clearly not a solution of the classical equation of motion. Since the potential vanishes for $0 < x < L$, a classical particle would feel no force except at the boundaries $x = 0$ and $x = L$. The particle would simply bounce backwards and forwards between the two walls of the infinite potential well with a uniform velocity. So the expectation value $\langle x\rangle$ does not satisfy the classical equation of motion.

Does the classical equations of motion hold inside expectation values, as Ehrenfest's theorem states? Well, that is rather subtle in this case. It is straightforward to check that the momentum expectation value satisfies

$$\langle p\rangle = Am\omega\sin(\omega t) = m\frac{d\langle x\rangle}{dt}\,.$$

and thus is in agreement with the first of (20.18), derived from Ehrenfest's theorem. We should also be able to show that

$$\frac{d\langle p\rangle}{dt} = Am\omega^2\cos(\omega t) = -\left\langle\frac{dV}{dx}\right\rangle\,. \tag{20.27}$$

But computing $\langle V'(x)\rangle$ is subtle because the potential jumps at $x = 0$ and $x = L$ and the derivative of the potential diverges there.

Sometimes a generalised form of Ehrenfest's theorem is required, namely when boundary terms ignored in its derivation are actually non-vanishing.

To treat this problem properly, we need to return to the proof of Ehrenfest's theorem for momentum, paying more careful attention to the boundary conditions at $x = 0$ and $x = L$. The starting point is the definition of the momentum expectation value,

$$\langle p\rangle = -i\hbar\int_0^L dx\,\overline{\psi}(\partial_x\psi)\,.$$

Using Schrödinger's equation and its complex conjugate,

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\partial_x^2\psi \qquad -i\hbar\partial_t\overline{\psi} = -\frac{\hbar^2}{2m}\partial_x^2\overline{\psi}\,, \tag{20.28}$$

we find

$$\frac{d\langle p\rangle}{dt} = -i\hbar \int_0^L dx \, \left[(\partial_t \overline{\psi})(\partial_x \psi) + \overline{\psi}(\partial_x \partial_t \psi)\right] \tag{20.29}$$

$$= -\frac{\hbar^2}{2m} \int_0^L dx \, \left[(\partial_x^2 \bar{\psi})(\partial_x \psi) - \overline{\psi}(\partial_x^3 \psi)\right] \tag{20.30}$$

$$= -\frac{\hbar^2}{2m} \int_0^L dx \, \partial_x \left[|\partial_x \psi|^2 - \overline{\psi}\partial_x^2 \psi\right] \tag{20.31}$$

$$= -\frac{\hbar^2}{2m} \, |\partial_x \psi|^2 \big|_0^L \tag{20.32}$$

where in the final step we have used that the wave function vanishes at $x = 0$ and $x = L$. As expected, the non-vanishing contribution comes only from the boundaries $x = 0$ and $x = L$, and we did not see these terms when doing integrations by parts in the derivation of Ehrenfest's theorem ealier. Be aware of subtleties like these.

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