PH20013/60
Quantum and Atomic Physics

Part 1 – Quantum Physics

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Contents

Chapter 1

Introduction

Quantum mechanics was one of the most important developments in 20th Century physics. It has been incredibly successful for describing the properties of matter at atomic and sub-atomic levels, the fundamental behaviour of light, and how light and matter interact. Over 100 years on, the desire to understand the pioneering realisations that light and matter are quantised still influences huge swathes of research throughout physics and other subjects. Through these research efforts, we are rapidly increasing our ability to control systems at the quantum level and build devices that exploit quantum effects.

In the first half of the unit we will study some basic quantum mechanics. We will look at how wave propagation must be used to describe the behaviour of sub-atomic particles. We will meet the central equation of wavefunction quantum mechanics – the Schrödinger equation – and solve it to make precise predictions of the outcomes of measurements. The systems that we will study are simple one-dimensional models but nevertheless they will reveal many interesting and unexpected phenomena. This will equip you with the tools to go on and solve more realistic three-dimensional systems, starting with the hydrogen atom, in the second half of the unit, *Atomic Physics*. The same concepts that we will demonstrate in the one-dimensional systems will eventually be used to explain the structure of atoms and the form of the periodic table.

We will begin with a brief look at the background to quantum physics, starting at the beginning of the 20th Century.

1.1 The origins of quantum physics

1.1.1 Quantisation of atomic energies

By the end of the 19th Century it was generally agreed that most important problems in physics were solved. However two anomalies remained:

- **UV catastrophe**: Classical electromagnetism (the Rayleigh-Jeans Law) predicted that the frequency-dependence of the intensity of radiation from a black body was $I(\lambda) \propto \lambda^{-4}$, suggesting that $I(\lambda) \to \infty$ at short wavelengths. This was in contrast to measured black-body spectra, as shown in Figure 1.1.
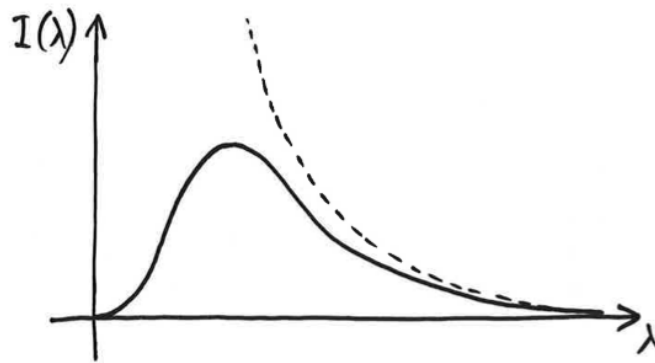
Figure 1.1 Comparison of Rayleigh-Jeans Law and Planck's Law black body emission spectra.

- **Atomic radiation** was observed to be composed of a set of discrete lines rather than having a continuous distribution. These lines could not be explained by any existing theory of light and matter.

Max Planck realised that these effects could be explained by the quantisation of atomic energy levels into steps of

$$\Delta E = hf = \hbar\omega \qquad \text{where} \quad \begin{aligned} \Delta E &= \text{energy of one excitation} \\ f &= \text{frequency of light} \\ \omega &= \text{angular frequency} = 2\pi f \\ h &= \text{Planck's constant} = 6.63 \times 10^{-34}\,\text{Js} \\ \hbar &= \frac{h}{2\pi} = 1.06 \times 10^{-34}\,\text{Js}. \end{aligned} \qquad (1.1)$$

1.1.2   Wavepackets of light

Experimental evidence of the particle-like behaviour of light was provided by

- **Photoelectric effect**: Electron emission from a charged metal surface only occurs when illuminated with light above a certain frequency. Above this threshold the number of electrons emitted depends only on the intensity of the light and not its frequency.

- **Compton scattering**: Monochromatic X-rays scattered by free electrons in a graphite sample are observed to undergo a discrete wavelength shift dependent on the scattering angle.

Explaining these effects required the quantisation of electromagnetic radiation into discrete wavepackets, each with energy $E = \hbar\omega$.

1.1.3   de Broglie waves

Louis de Broglie postulated that matter has wavelike properties with

$$p = \frac{h}{\lambda} = \hbar k \qquad \text{where} \quad p = \text{momentum of particle} \qquad (1.2)$$

$$\lambda = \text{de Broglie wavelength}$$

$$k = \frac{2\pi}{\lambda} = \text{wavenumber}.$$

The wave-like behaviour of matter was later confirmed experimentally by electron diffraction from layers of atoms in crystals in the Davisson-Germer experiment and by G. P. Thompson.

1.1.4   Other points to recall

- Classical physics breaks down at the atomic scale ($\sim 10^{-10}$ m), where quantum mechanics take over.

- Quantum effects are apparent only on these tiny scales as the de Broglie wavelength quickly becomes too small to measure for larger objects (even large molecules).

Exercise Calculate the de Broglie wavelength of:

1. A dust particle of radius $1\,\mu$m, density $3000\,\text{kg}\,\text{m}^{-3}$, moving at $1\,\text{cm}\,\text{s}^{-1}$;

$$
\begin{aligned}
\lambda &= \frac{h}{p} \\
&= \frac{h}{mv} \\
&= \frac{6.63 \times 10^{-34}}{(4\pi/3) \times 10^{-18} \times 3000 \times 10^{-2}} = 5 \times 10^{-18}\,\text{m};
\end{aligned}
$$

$\therefore$ $\lambda <$ diameter of a nucleus.

2. An electron with kinetic energy $10\,$eV.

$$
\begin{aligned}
E &= \frac{1}{2}mv^2 \quad \rightarrow \quad v = \sqrt{\frac{2E}{m}} \\
\lambda &= \frac{h}{p} \\
&= \frac{h}{\sqrt{2mE}} \\
&= \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 10^{-30} \times 10 \times 1.6 \times 10^{-19}}} = 4 \times 10^{-10}\,\text{m};
\end{aligned}
$$

$\therefore$ $\lambda \sim$ atomic dimensions.

- The discretization of energy forces us to adopt a statistical description of quantum systems. We must abandon the deterministic nature of the classical world and start dealing with probabilities.

- Hence, in order to observe quantities experimentally we must repeat measurements many times to make an ensemble average (e.g. double slit interference with electrons).

- The wave and particle descriptions are complementary; if a measurement demonstrates wave characteristics we will not observe particle-like behaviour and vice-versa.

- Pairs of variables display complementary behaviour, for example position and momentum cannot simultaneously be measured precisely. This gives rise to the Heisenberg uncertainly principle:

$$\Delta x \times \Delta p \geq \hbar.$$

This is not due to poor measurement techniques, it is intrinsic to quantum physics.

- As a result of the wave-like features of quantum mechanics, Erwin Schrödinger introduced the wavefunction, Ψ, to represent the de Broglie wave associated with each particle. Ψ describes the evolution of the probability distribution of a quantum system. We will see how to calculate wavefunctions and the properties of the associated particles in the first half of this course.

Chapter 2

The framework of quantum mechanics

We saw in the preceding section that particles display wave-like properties, and that the behaviour of a particle can be described by an associated de Broglie wave. The de Broglie wave is known as a *wavefunction* and it is central to Schrödinger's theory of quantum mechanics. In this section, we will set out the framework that will form the basis of our description of how quantum systems behave and will allow us to deal with complicated cases in later sections. For each system, we need to specify not only the equation that the wavefunction obeys (we will do this in Section 3) but also how the wavefunction is linked to measurable properties of the particle; we will make that connection in this section. The framework that we will establish may seem a little abstract at first, but when we look at some specific examples in later sections you will see how we can use it to make verifiable predictions about the behaviour of quantum systems.

2.1 Wavefunctions

Associated with each particle is a wavefunction, usually represented by the symbol Ψ. In general, Ψ will be a function of all the independent variables upon which the properties of the particle could depend. For the first half of this unit – Quantum Physics – we will be thinking about point-like particles such as electrons[1] so we only need to consider position and time, so in general the wavefuntion will be $\Psi(\vec{r}, t)$. Furthermore we will be working in one spatial dimension only, simplifying the wavefunction to $\Psi(x, t)$.

The wavefunction $\Psi(x, t)$ contains all the information that it is possible to know about the particle. Once we have found the wavefunction for a particular type of particle in a specific system (by solving the equation that we will look at in Section 3) we have a complete description of how the particle behaves. However,

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[1] In Atomic Physics you will take into account additional degrees of freedom such as spin.

extracting useful information from the wavefunction – information describing the outcomes of measurements that we can make on the particle – requires additional calculations. In Section 2.3 we will look at how that is done.

In general wavefunctions are complex and therefore have imaginary parts. Hence they cannot be measured directly and should not be interpreted as physical entities in themselves. Wavefunctions are computational tools that allow us to predict how their associated particles behave. They are a useful way of describing particles and encapsulate the sum of our knowledge about the particles, but they are only relevant within the framework of Schrödinger's quantum theory.

2.2   Probability density and normalisation

Max Born postulated that the wavefunction $\Psi(x,t)$ has a related *probability density*, $P(x,t)$, defined as

$$P(x,t) = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2, \tag{2.1}$$

where Ψ^* is the complex conjugate of Ψ. The probability of finding a particle in the infinitesimal length between x and $x + \mathrm{d}x$ at time t is then

$$P(x,t)\,\mathrm{d}x = \Psi^*(x,t)\Psi(x,t)\,\mathrm{d}x = |\Psi(x,t)|^2\,\mathrm{d}x. \tag{2.2}$$

The probability density provides a link between the complex wavefunction and the measurable properties of the associated particle. It simply states that the particle is more likely to be found in regions where the wavefunction has a larger amplitude[2]. $\Psi^*(x,t)\Psi(x,t)$ was postulated by Born as the probability density because it satisfies the requirements for the physical behaviour of $P(x,t)$, including being real and non-negative.

We can integrate (2.2) to obtain the probability of finding the particle between two points a and b as follows

$$\int_a^b P(x,t)\,\mathrm{d}x = \int_a^b |\Psi(x,t)|^2\,\mathrm{d}x. \tag{2.3}$$

Furthermore, we know that the particle exists somewhere. Hence, the probability

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[2]In three dimensions the probability of finding a particle in volume $\mathrm{d}V$ at time dt is

$$P(\vec{r},t)\,\mathrm{d}V = |\Psi(\vec{r},t)|^2\,\mathrm{d}V.$$

of finding the particle between $x = -\infty$ and $x = +\infty$ must be equal to 1:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, \mathrm{d}x = 1. \tag{2.4}$$

This is known as the *normalisation* condition for a wavefunction $\Psi(x,t)$. If it is satisfied then $\Psi(x,t)$ is said to be *normalised*.

It is essential to normalise any wavefunction before calculating any absolute values from it. For example, it would not make much sense to calculate the probability of finding a particle between $x = a$ and $x = b$ using an un-normalised wavefunction that suggested the total probability of the particle existing anywhere was only 0.5. Our wavefunctions will include a multiplicative constant (typically represented as A) that ensures the wavefunction is normalised; we find the value of the constant by solving (2.4).

Exercise A particle is restricted to the region between $x = 0$ and $x = L$ such that its wavefunction is

$$\Psi(x,t) = \begin{cases} A\mathrm{e}^{i(kx-\omega t)} & 0 \le x \le L \\ 0 & x < 0 \text{ or } x > L. \end{cases}$$

Apply (2.4) to find the normalisation constant A.

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, \mathrm{d}x = \int_0^L A^* \mathrm{e}^{-i(kx-\omega t)} A \mathrm{e}^{i(kx-\omega t)} \, \mathrm{d}x$$
$$= \int_0^L A^2 \, \mathrm{d}x$$
$$= A^2 L$$
$$= 1$$
$$\therefore \quad A = \sqrt{\frac{1}{L}}.$$

So the normalised wavefunction is

$$\Psi(x,t) = \sqrt{\frac{1}{L}} \mathrm{e}^{i(kx-\omega t)}.$$

2.3   Observables and expectation values

Born's postulate shows that we can use the wavefunction to calculate the probability of finding a particle in a given region. However, there are many additional dynamical quantities that we might wish to measure, for example the momentum of the particle or its kinetic energy. In quantum mechanics, these measurable quantities are known as *observables*, and the average values obtained when they are measured are known as their *expectation values*. Expectation values of observables can be calculated from wavefunctions. We will look at some more complex examples later on in Section 6; we lay the groundwork now by looking at how to calculate the expectation value of the particle's position.

2.3.1   Expectation value of position

A particle's wavefunction gives rise to a probability distribution that describes where we are more or less likely to find the particle. This statistical description is central to quantum physics; it implies that repeated position measurements of a particle that is prepared identically every time will yield different results. Each measurement may find the particle in a region of high or low probability, but if enough measurements are carried out we will build up a complete picture of the probability distribution. The expectation value of the position is the average (mean) value of the distribution.

Exercise Consider a discrete probability distribution for the position of a classical object:

Position (m)	Probability
1	0.1
2	0.5
3	0.4

What is the mean position of the object?

$$\text{Mean position} = 0.1 \times 1 + 0.5 \times 2 + 0.4 \times 3 = 2.3\,\text{m}$$

What did we do to find the mean position? We multiplied the position variable by the probability distribution and integrated. Exactly the same technique is used

to find the expectation value of position in quantum mechanics. Therefore at time t the expectation value of position, denoted by angle brackets $\langle x \rangle$, is

$$\langle x \rangle = \int_{-\infty}^{\infty} x\, P(x,t)\, \mathrm{d}x. \tag{2.5}$$

Substituting Born's postulate (2.1) for the probability density we find

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, x\, \Psi(x,t)\, \mathrm{d}x. \tag{2.6}$$

The reason behind the ordering of this equation will become clear later.

Exercise Calculate the expectation value of the position of the particle we looked at in the previous example:

$$\Psi(x,t) = \begin{cases} \sqrt{\frac{1}{L}}\mathrm{e}^{i(kx-\omega t)} & 0 \le x \le L \\ 0 & x < 0 \text{ or } x > L \end{cases}$$

by applying (2.6).

$$\begin{aligned} \langle x \rangle &= \int_{0}^{L} \sqrt{\frac{1}{L}}\mathrm{e}^{-i(kx-\omega t)} x \sqrt{\frac{1}{L}}\mathrm{e}^{i(kx-\omega t)}\, \mathrm{d}x \\ &= \frac{1}{L} \int_{0}^{L} x\, \mathrm{d}x \\ &= \frac{1}{L}\frac{L^2}{2} \\ &= \frac{L}{2} \end{aligned}$$

Therefore on average the particle will be found half-way between the boundaries.

In fact, the same formalism may be extended to any arbitrary function $f(x)$:

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) f(x) \Psi(x,t)\, \mathrm{d}x, \tag{2.7}$$

and can even be used to find the expectation values of time-dependent functions too. We will revisit expectation values in Section 6.

Chapter 3

The time-independent Schrödinger equation in one dimension

We now know how to relate wavefunctions to probability distributions and physical observables, but how do we find the wavefunctions themselves? We require an equation describing how the wavefunctions behave that we can solve for the systems we wish to study. Such an equation has been provided for us by Erwin Schrödinger. We will not derive the Schrödinger equation (like Born's rule, it is a postulate of quantum mechanics) but we will consider why it is a reasonable equation to use. Beyond that, the proof is in the pudding – the solutions of the Schrödinger equation will be demonstration enough of its validity.

3.1 Time-dependent Schrödinger equation

Schrödinger postulated the following equation to find the wavefunction $\Psi(x,t)$ of a particle of mass m moving in one dimension with potential energy $V(x,t)$:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial \Psi(x,t)}{\partial t}. \tag{3.1}$$

This is the time-dependent Schrödinger equation (TDSE) and is the basis of the wavefunction formulation of quantum mechanics, but why does it have this form?

3.1.1 Necessary conditions

If we are to construct an equation with solutions fulfilling the requirements of wavefunctions within the framework of quantum mechanics, there are four fundamental conditions that our equation must satisfy:

1. Consistency with de Broglie waves and with energy quantisation,

$$\lambda = \frac{h}{p}, \qquad E = hf; \tag{3.2}$$

2. Consistency with classical (non-relativistic) equations of motion,

$$E = \frac{p^2}{2m} + V; \tag{3.3}$$

3. Linearity in $\Psi(x,t)$. This implies that all terms (including derivatives) must be of order $\Psi(x,t)$; terms without any $\Psi(x,t)$-dependence or including $\Psi^2(x,t)$ or higher are not allowed. This condition means that functions $\Psi_{\rm j}(x,t)$ that are solutions of our equation can be added together to form new solutions, $\Psi(x,t) = a\Psi_1(x,t) + b\Psi_2(x,t) + \cdots$. These are called *superpositions*;

4. The solutions in free space are sinusoidal travelling waves. In free space the potential energy is constant, $V(x,t) = V_0$. The force acting on a particle,

$$F = -\frac{\partial V(x,t)}{\partial x} = 0, \tag{3.4}$$

and thus the solutions must be travelling waves, $\Psi_0(x,t) = Ae^{i(kx-\omega t)}$.

3.1.2   Justification

We now apply these four conditions and see where they take us. Substituting (3.2) into (3.3) we find

$$\frac{h^2}{2m\lambda^2} + V = hf. \tag{3.5}$$

Then using $k = 2\pi/\lambda$ and $\omega = 2\pi f$ we obtain

$$\frac{\hbar^2 k^2}{2m} + V = \hbar\omega. \tag{3.6}$$

Considering a sinusoidal wave, $\sin(kx - \omega t)$, we see that

$$\frac{\partial^2}{\partial x^2} \sin(kx - \omega t) \propto -k^2, \tag{3.7}$$

$$\frac{\partial}{\partial t} \sin(kx - \omega t) \propto -\omega,$$

and comparing these to the form of (3.6) it becomes clear that our equation should include:

- one $\partial^2/\partial x^2$ term (corresponding to the term dependent on k^2 in (3.6));

- one $\partial/\partial t$ term (corresponding to the ω-dependent term in (3.6));

- a term containing a factor of $V(x,t)$. This term must contain a multiple of $\Psi(x,t)$ in order to remain linear in $\Psi(x,t)$.

Putting these three terms together we obtain

$$\alpha\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta\frac{\partial\Psi(x,t)}{\partial t}. \tag{3.8}$$

In order to find the constants α and β we make use of condition 4. Setting $V(x,t) = V_0$ and using a travelling-wave, free-space solution of the form

$$\Psi_0(x,t) = \cos(kx - \omega t) + \gamma\sin(kx - \omega t) \tag{3.9}$$

in (3.8) and equating factors of $\sin$ and $\cos$, we find $\gamma = \pm i$ and $-\alpha k^2 + V_0 = \mp i\beta\omega$. Then, by comparing this with (3.6) we find that

$$\alpha = -\frac{\hbar^2}{2m}, \qquad \mp i\beta = \hbar. \tag{3.10}$$

We are then free to choose $\gamma = i$, yielding $\beta = i\hbar$. Substituting these relations into (3.8) we recover the time-dependent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}. \tag{3.11}$$

3.1.3   Points to note

- This is not a rigorous derivation of the Schrödinger equation; it is not even the reasoning that Schrödinger himself used to find his equation. It is simply to show that the equation arises naturally if we start from classical wave mechanics and introduce the concepts of de Broglie waves and energy quantisation.

- This demonstrates that the Schrödinger equation is a reasonable equation to take as a starting point from which to calculate quantum mechanical wavefunctions.

- So far, this has been a fairly abstract discussion, however, we will now apply this to several model situations. We will see that the solutions it gives are

both reasonable within the framework that we have set up and also make meaningful (and measurable) predictions about the systems that we will study.

3.2 Time-independent potentials

3.2.1 Separation of variables in the TDSE

Many systems have potential energies that depend only on position and do not change in time:

$$V(x,t) = V(x). \tag{3.12}$$

In these cases, we can rewrite the TDSE as a time-dependent part and a time-independent part.

Firstly, we separate the position and time variables in the wavefunction

$$\Psi(x,t) = \psi(x)\phi(t), \tag{3.13}$$

substitute it into the TDSE (3.1)

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}\phi(t) + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}, \tag{3.14}$$

and divide by $\psi(x)\phi(t)$ to obtain

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)}_{\text{function of } x} = \underbrace{i\hbar\frac{1}{\phi(t)}\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}}_{\text{function of } t}. \tag{3.15}$$

Each side of (3.15) is a function of one independent variable only. The only way to satisfy this equation for all values of x and t is if both sides are equal to a constant. We will call this constant G.

We can now study each side of (3.15) separately, beginning with the time-dependent part (RHS):

$$\frac{i\hbar}{\phi(t)}\frac{\mathrm{d}\phi(t)}{\mathrm{d}t} = G. \tag{3.16}$$

We see straightforwardly that the solution to this first-order differential equation is

$$\phi(t) = \mathrm{e}^{-\frac{iGt}{\hbar}}. \tag{3.17}$$

Comparing the solution (3.17) with a wave of angular frequency ω whose time-

dependence is described by $\mathrm{e}^{-i\omega t}$ we see that

$$\omega = \frac{G}{\hbar} \quad \rightarrow \quad G = \hbar\omega. \tag{3.18}$$

We know from (1.2) that in our description of quantised energy levels, the total energy of a system $E = \hbar\omega$, so we see that the constant G is in fact the total energy. Substituting $G = E$ yields

$$\phi(t) = \mathrm{e}^{-\frac{iEt}{\hbar}}, \tag{3.19}$$

and we find the time-dependent part of the solution to the TDSE.

3.2.2 The time-independent Schrödinger equation

Returning to the position-dependent part of (3.15) (LHS) we have

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x) = G. \tag{3.20}$$

Making the substitution $G = E$ and multiplying through by $\psi(x)$ we find

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x). \tag{3.21}$$

This is the time-independent Schrödinger equation (TISE) in one dimension. It allows us to find $\psi(x)$ for any general time-independent potential $V(x)$. I hope you will learn lots of interesting and useful physics during this unit, but if you learn only one thing then make sure it is this equation!

3.2.3 Stationary-state solutions

In the case of a potential with no time-dependence, the function $\psi(x)$ is a solution to the TISE with energy E. We can write down the full solution to the TDSE, which is the wavefunction $\Psi(x, t)$, in terms of the time-independent solution:

$$\Psi(x, t) = \psi(x)\phi(t) = \psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{3.22}$$

Thence, we find that the probability density for the complete wavefunction $\Psi(x,t)$ is

$$
\begin{aligned}
|\Psi(x,t)|^2 &= \psi^*(x)\mathrm{e}^{\frac{iEt}{\hbar}}\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \\
&= \psi^*(x)\psi(x) \\
&= |\psi(x)|^2.
\end{aligned}
\tag{3.23}
$$

So we see that the solutions described by the functions $\psi(x)$ have probability densities that are constant in time. These functions $\psi(x)$, the solutions to the TISE, are called *eigenfunctions* and they describe *stationary states* of the system. The linguistic root of the term eigenfunction is the German word "eigen" meaning "characteristic". Similarly, the expectation values of observables of stationary states do not change in time.

Exercise   Using (2.6), show that the expectation value of position for a stationary state does not change in time.

$$
\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} \Psi^*(x,t)\, x\, \Psi(x,t)\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty} \psi^*(x)\mathrm{e}^{\frac{iEt}{\hbar}}\, x\, \psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}}\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty} \psi^*(x)\, x\, \psi(x)\,\mathrm{d}x.
\end{aligned}
$$

3.2.4   Superposition states

As discussed in Section 3.1 the Schrödinger equation is linear. As a result we can form *superpositions* which are linear combinations of stationary states. For example, if $\psi_1(x)$ and $\psi_2(x)$ are solutions to the TISE with energies E_1 and E_2 respectively then we can form a superposition state by including the time dependence of each stationary state and adding them, as follows:

$$
\begin{aligned}
\Psi(x,t) &= a\Psi_1(x,t) + b\Psi_2(x,t) \\
&= a\psi_1(x)\mathrm{e}^{-\frac{iE_1 t}{\hbar}} + b\psi_2(x)\mathrm{e}^{-\frac{iE_2 t}{\hbar}}.
\end{aligned}
\tag{3.24}
$$

Note that superpositions are *not* themselves stationary states of the system (as we will see later, and in question 6 of Problem Sheet 1).

3.3   Boundary conditions

We will use the TISE extensively to find the eigenfunctions, energy levels, and associated probability density functions for particles in a range of time-independent potentials $V(x)$. The TISE is a second-order differential equation, and therefore its general solutions will contain constants, and we must eliminate these constants by using boundary conditions.

The general conditions that the eigenfunctions (and therefore also the wavefunctions) are required to satisfy are:

1. **Finite** – $\psi(x)$ must be normalisable and therefore finite. Similarly, the particle must exist somewhere so $\psi(x)$ cannot be zero everywhere.

2. **Single-valued** – the probability density for the particle must only have one value at each position therefore $\psi(x)$ must be single-valued.

3. **Continuous** – $\psi(x)$ must be continuous so that $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ remains finite.

4. **Continuous derivative** – $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ must be continuous so that $\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}$ remains finite.

There is an exception to the fourth condition: if there is an infinite discontinuity in $V(x)$, for example $V(x) \to \infty$ then $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ does not need to be continuous.

For a particular potential $V(x)$, the TISE combined with the boundary conditions above will allow us to find a set of eigenfunctions $\psi(x)$ that describe the behaviour of the particle. The method we will use will be:

1. Write down the TISE with the specific potential $V(x)$ substituted into it.

2. Find a general solution.

3. Apply the boundary conditions to eliminate any unknown constants.

During the next sections, we will see how this method works in a number of different systems. Simply solving the TISE for different one-dimensional potentials will lead us to some remarkable conclusions about how the world around us behaves at its most fundamental level.

Chapter 4

The infinite square well

The first situation that we will consider is a particle with mass m that is strictly confined to a one-dimensional length L. Within the length L it moves freely. This is known as the *infinite square well* or *particle in a box* and it is the simplest potential that we will solve. The unphysical presence of a potential energy that goes abruptly to infinity makes the infinite square well a somewhat artificial example; nevertheless it is a useful system to solve for three reasons:

- The solutions are straightforward and can be found analytically.

- These solutions demonstrate some of the key physics that we will be looking at in this course.

- The infinite square well is a useful (approximate) model for particles tightly confined in one dimension.

4.1 Solution to the Schrödinger equation

We will now solve the Schrödinger equation for the infinite square well to find the eigenfunctions and energy levels of the particle in the well. As this is our first time solving the Schrödinger equation, we will go through it in detail.

The infinite square well potential is written

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \text{ or } x > L. \end{cases} \tag{4.1}$$

Clearly the potential energy does not change over time so we will be solving the TISE. It's always useful to start with a sketch of the potential that we are solving for; this is shown in Figure 4.1.
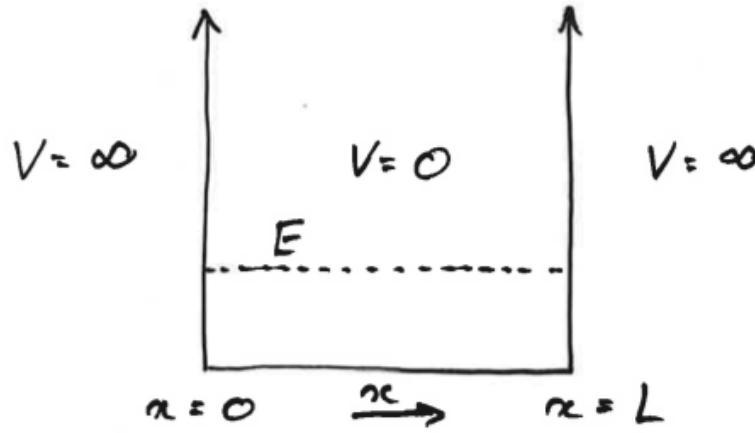
Figure 4.1 The potential energy of a particle in the infinite square well.

First we apply some logic. Because $V = \infty$ outside the well, the particle would need to have infinite energy to exist there. The particle cannot have infinite energy, so it must exist only inside the well, and

$$\psi(x < 0) = \psi(x > L) = 0. \tag{4.2}$$

Therefore the only region we have to solve for is inside the well.

Next we follow the three steps written down in Section 3.3. We begin by writing down the TISE (3.21)

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x). \tag{4.3}$$

and set $V = 0$ inside the well (N.B. from now on we will drop the explicit x-dependence from ψ):

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi. \tag{4.4}$$

Next, we need to find a general solution to this second-order differential equation. We rearrange and introduce a simplifying parameter k

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi, \tag{4.5}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}. \tag{4.6}$$

From our knowledge of second-order differential equations we can "guess" a gen-

eral solution for ψ

$$\psi = A \sin kx + B \cos kx. \tag{4.7}$$

Exercise Show explicitly that (4.7) is a solution to (4.5).

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = Ak \cos kx - Bk \sin kx$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -Ak^2 \sin kx - Bk^2 \cos kx$$

$$= -k^2 \psi.$$

Therefore this is a solution to the TISE in the infinite well.

Exercise Find a solution to (4.5) without writing down any trigonometric functions.

$$\psi = \tilde{A}\mathrm{e}^{ikx} + \tilde{B}\mathrm{e}^{-ikx}$$

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = i\tilde{A}k\mathrm{e}^{ikx} - i\tilde{B}k\mathrm{e}^{-ikx}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\tilde{A}k^2\mathrm{e}^{ikx} - \tilde{B}k^2\mathrm{e}^{-ikx}$$

$$= -k^2 \psi.$$

Convince yourself that this solution is equivalent to (4.7). We will revisit it later!

We're now ready for the third step in our process, applying the boundary conditions. Outside the well $V = \infty$ and $\psi = 0$; therefore for ψ to be single-valued and continuous at the edges of the well we require

$$\psi(x = 0) = 0 \quad \text{and} \quad \psi(x = L) = 0. \tag{4.8}$$

Note that because $V \to \infty$ at $x = 0$ and $x = L$ we do not need the first derivative of ψ to be continuous at the edges of the well. We then substitute the boundary

conditions into our general solution (4.7):

$$
\begin{aligned}
x = 0: \qquad 0 &= A\sin 0 + B\cos 0 \\
&\rightarrow B = 0
\end{aligned}
\tag{4.9}
$$

$$
\begin{aligned}
x = L: \qquad 0 &= A\sin kL + 0 \\
&\rightarrow \sin kL = 0 \\
&\rightarrow kL = n\pi,
\end{aligned}
\tag{4.10}
$$

where n is a positive integer ($n = 1, 2, 3, \dots$). Therefore, as a direct result of imposing boundary conditions on ψ, the parameter k is restricted to a set of discrete values:

$$
k_n = \frac{n\pi}{L},
\tag{4.11}
$$

and the eigenfunctions form a discrete set,

$$
\psi_n = A_n \sin k_n x = A_n \sin\left(\frac{n\pi x}{L}\right).
\tag{4.12}
$$

Furthermore, we find discrete energy levels for the particle in the box by equating (4.6) and (4.11):

$$
k_n = \frac{n\pi}{L} = \frac{\sqrt{2mE_n}}{\hbar}
\tag{4.13}
$$

$$
\therefore\ E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}.
\tag{4.14}
$$

This is the essence of quantisation. The boundary conditions tied the wavefunction to zero at the edges of the well and as a direct consequence, the energy of the particle in the box was restricted to discrete values E_n. The energy levels are represented in Figure 4.2. Although this is a toy system, the way in which energy quantisation occurs is completely analogous to that which you will come across in the Bohr model of the atom at the beginning of the second half of this course.

The integer n is known as the *quantum number* of the particle. Note that it starts from 1, not from zero! We will come back to this point later. The parameter k_n is called the *wavenumber*.
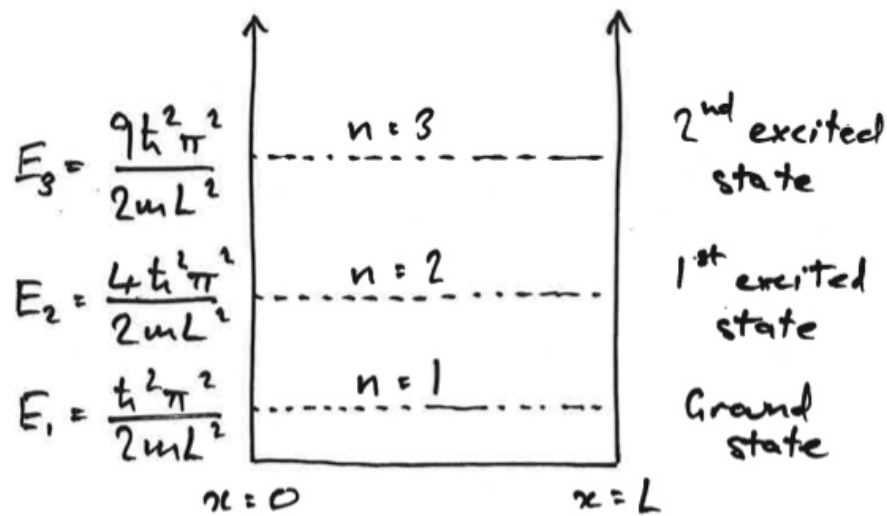
Figure 4.2 Energy levels in the infinite square well.

Exercise Why is $n \neq 0$?

$$\text{If} \quad n = 0 \rightarrow \sin\left(\frac{n\pi x}{L}\right) = 0 \;\therefore\; \psi = 0. \tag{4.15}$$

This would imply that the particle does not exist

4.2 Normalising the wavefunctions

Now is a good time to practise normalisation. We can find the constants A_n by applying the normalisation condition

$$\int_{-\infty}^{\infty} |\psi|^2 \, \mathrm{d}x = 1 \tag{4.16}$$

to the eigenfunctions (4.12). The normalisation condition becomes

$$\int_0^L A_n^2 \sin^2 k_n x \, \mathrm{d}x = 1, \tag{4.17}$$

which can be integrated using the identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$ to give

$$\int_0^L \frac{A_n^2}{2}(1 - \cos 2k_n x)\, \mathrm{d}x = 1$$

$$\frac{A_n^2}{2}\left[x - \frac{1}{2k_n}\sin 2k_n x\right]_0^L = 1$$

$$\frac{A_n^2}{2}\left(L - \frac{1}{2k_n}\sin 2k_n L - 0\right) = 1. \tag{4.18}$$

Then substituting from (4.11), $k_n = \frac{n\pi}{L}$

$$\frac{A_n^2}{2}\left(L - \frac{1}{2k_n}\sin 2n\pi\right) = 1$$

$$\therefore \frac{A_n^2 L}{2} = 1$$

$$\rightarrow A_n = \sqrt{\frac{2}{L}}. \tag{4.19}$$

Hence we see that, in this case, the normalisation constant is the same for all n.

We can now write down the full solution to the TISE for the infinite square well, along with the energy levels associated with each eigenfunction:

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \qquad\qquad E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2}. \tag{4.20}$$

4.3   Visualising the wavefunctions

It is straightforward to sketch the eigenfunctions and probability densities in the infinite square well. The eigenfunctions are standing waves (the nodes do not move) resulting from a superposition of travelling waves moving in the positive and negative directions. We plot these in Figure 4.3.

4.4   Parity

You may have noticed in the previous section that the eigenfunctions have certain symmetry properties about the centre of the well. We can see this more explicitly by changing the x-coordinate so that the origin is in the centre of the well, as shown in Figure 4.4.

Now that we have made the potential symmetric in $\tilde{x}$ such that $V(-\tilde{x}) = V(\tilde{x})$, all the eigenfunctions are either odd or even functions of $\tilde{x}$ with the following pattern:
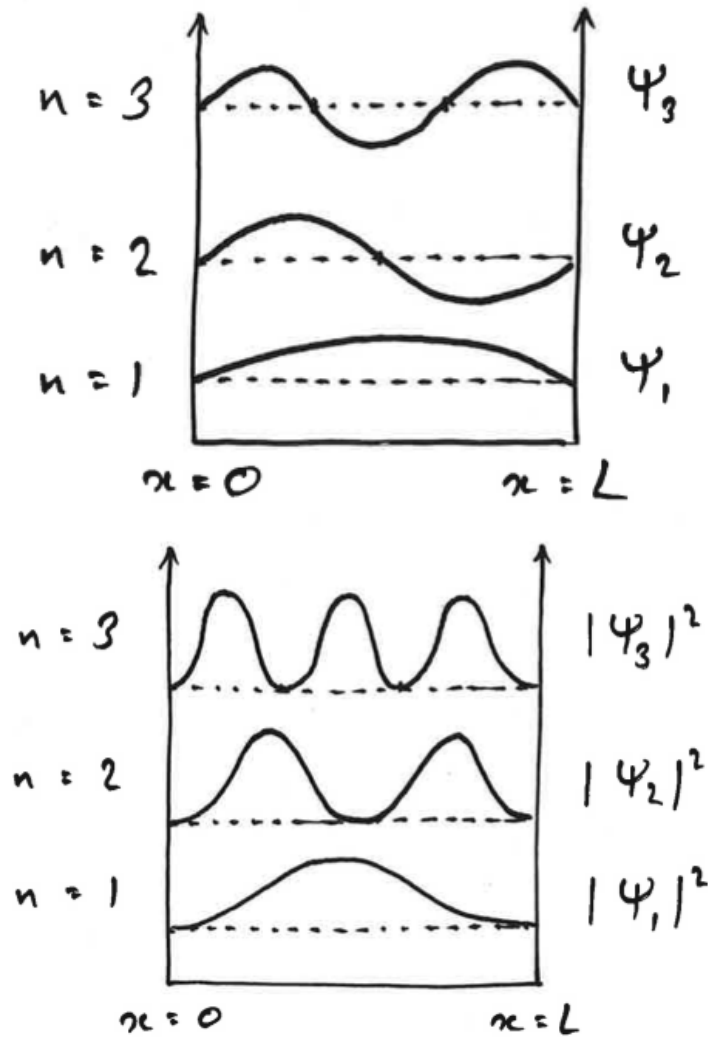
Figure 4.3 Eigenfunctions and probability densities in the infinite square well.

- odd quantum numbers → even eigenfunctions, $\psi(-\tilde{x}) = \psi(\tilde{x})$

- even quantum numbers → odd eigenfunctions, $\psi(-\tilde{x}) = -\psi(\tilde{x})$

The symmetry of each eigenfunction is known as its *parity*. In this case, every eigenfunction has a definite parity (either odd or even) and cannot be a mixture of both odd and even.

The fact that each eigenfunction has definite parity arises from the symmetry of the potential. Because the potential is the same for positive and negative $\tilde{x}$, $V(-\tilde{x}) = V(\tilde{x})$, any observable quantity related to the particle moving in the potential must also be symmetric in $\tilde{x}$. For example, the probability of finding the particle at $+\tilde{x}$ must be the same as the probability of finding it at $-\tilde{x}$:
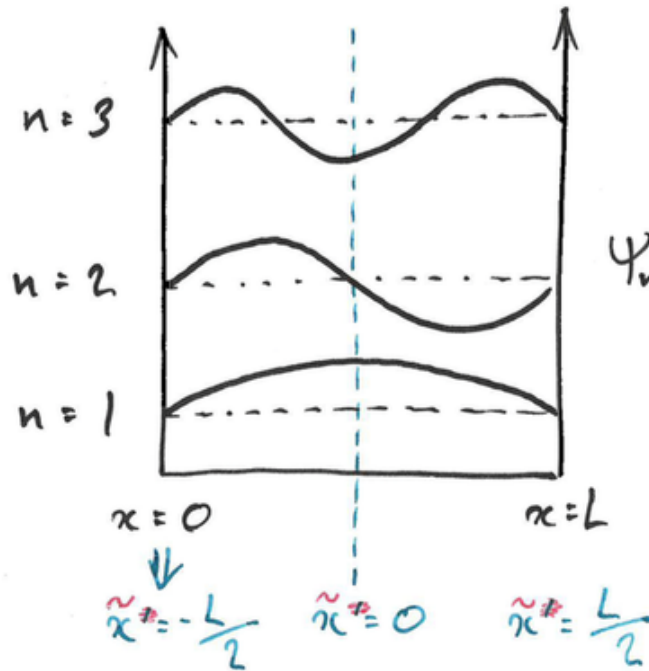
$$|\psi(-\tilde{x})|^2 = |\psi(\tilde{x})|^2. \tag{4.21}$$

Figure 4.4 Parity of eigenfunctions in the infinite square well.

The only way to ensure that this condition is met is if

$$\text{either} \quad \psi(-\tilde{x}) = \psi(\tilde{x}) \qquad\qquad \text{or} \qquad \psi(-\tilde{x}) = -\psi(\tilde{x}) \qquad\qquad (4.22)$$

$$\therefore \quad |\psi(-\tilde{x})|^2 = \psi^*(-\tilde{x})\psi(-\tilde{x}) \qquad\qquad \therefore \quad |\psi(-\tilde{x})|^2 = \psi^*(-\tilde{x})\psi(-\tilde{x})$$

$$= \psi^*(\tilde{x})\psi(\tilde{x}) \qquad\qquad\qquad = [-\psi^*(\tilde{x})][-\psi(\tilde{x})]$$

$$= |\psi(\tilde{x})|^2 \qquad\qquad\qquad\qquad = |\psi(\tilde{x})|^2.$$

Therefore the eigenfunctions must have definite parity. This is the case for all symmetric potentials:

- Bound-state eigenfunctions of any symmetric potential have definite parity about the point of symmetry.

We will use this fact in the next potential that we solve for (as well as explaining what we mean by "bound state").

4.5   Zero-point energy

Look back to the allowed energy levels in (4.20). What is the energy of the ground state? Remember that the ground state has quantum number $n = 1$; therefore its total energy is

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} > 0. \tag{4.23}$$

This result is at odds with what we would expect from a classical particle in a box (by "classical" we mean a particle that obeys Newtonian dynamics rather than the Schrödinger equation - think of a tennis ball). Its lowest energy state is when it is at rest in the box and in this state it has zero total energy (zero kinetic energy and zero potential energy if we have chosen our scale appropriately).

The energy of the ground-state solution to the TISE is known as the *zero-point energy*. It is a statement that a particle obeying the Schrödinger equation can *never be at rest* even when in its lowest energy state. One way to think of the zero point energy is as a manifestation of the Heisenberg uncertainty principle: because we have some information about the position of the particle (the wavefunction is confined to the box), there must be some uncertainty in the momentum of the particle (that is to say, the particle must be moving and therefore cannot be at rest). Note that as the box is made smaller (the uncertainty in position is reduced), the ground-state energy increases ($E_1 \propto L^{-2}$) and therefore the uncertainty in the momentum of the particle increases.

The zero-point energy is common to all quantum systems. It is remarkable that, simply by solving the TISE subject to some simple boundary conditions, we have arrived at a concept so fundamental.

4.6   Orthogonality of the eigenfunctions

So far by solving the TISE we have found a set of eigenfunctions for the infinite square well. These solutions, labelled $\psi_n(x)$, form an infinite set and each has energy E_n. The eigenfunctions are also mutually orthogonal, that is to say

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}. \tag{4.24}$$

You will demonstrate this for yourself in the first problem set. As a result of this property, a normalised set of eigenfunctions is said to comprise an *orthonormal set*.

4.7   Superpositions in the infinite square well

As we have seen, the probability densies associated with the eigenfunctions, the solutions to the TISE, do not change with time. However, we stated in Section 3.2.4 that linear combinations of eigenfunctions are solutions to the TDSE. According to (3.24)

$$
\begin{aligned}
\Psi(x,t) &= a\Psi_1(x,t) + b\Psi_2(x,t) + \dots \\
&= a\psi_1(x)\mathrm{e}^{-\frac{iE_1 t}{\hbar}} + b\psi_2(x)\mathrm{e}^{-\frac{iE_2 t}{\hbar}} + \dots
\end{aligned} \tag{4.25}
$$

is a solution to the TDSE formed from a linear combination of eigenfunctions and their associated time dependencies. In the following exercise, we will investigate the properties of such solutions.

Exercise   A superposition state formed from an equally-weighted sum of the ground and first-excited state eigenfunctions of the infinite square well discussed above ($x = 0$ to $x = L$) can be written

$$
\Psi(x,t) = \frac{1}{\sqrt{2}}\psi_1(x)\mathrm{e}^{-\frac{iE_1 t}{\hbar}} + \frac{1}{\sqrt{2}}\psi_2(x)\mathrm{e}^{-\frac{iE_2 t}{\hbar}}
$$

What is the probability density associated with the superposition state?

$$
\begin{aligned}
|\Psi(x,t)|^2 &= \left| \frac{1}{\sqrt{2}}\psi_1\mathrm{e}^{-\frac{iE_1 t}{\hbar}} + \frac{1}{\sqrt{2}}\psi_2\mathrm{e}^{-\frac{iE_2 t}{\hbar}} \right|^2 \\
&= \frac{1}{2}\left(\psi_1\mathrm{e}^{\frac{iE_1 t}{\hbar}} + \psi_2\mathrm{e}^{\frac{iE_2 t}{\hbar}} \right)\left(\psi_1\mathrm{e}^{-\frac{iE_1 t}{\hbar}} + \psi_2\mathrm{e}^{-\frac{iE_2 t}{\hbar}} \right) \\
&= \frac{1}{2}\left(\psi_1^2 + \psi_2^2 + \psi_1\psi_2\mathrm{e}^{\frac{i(E_1-E_2)t}{\hbar}} + \psi_1\psi_2\mathrm{e}^{\frac{i(E_2-E_1)t}{\hbar}} \right).
\end{aligned}
$$

So we see that the probability density for the superposition state is time-dependent. This is investigated further in problem sheet 1.

4.7.1   Superpositions and measurement

What is the energy of an electron in the superposition state above? When we derived the eigenfunctions $\psi_n(x)$ for an electron in the infinite square well we

found that it can exist only in certain "allowed" energy levels E_n. At first glance, the superposition state that we wrote down in the exercise appears not to possess one of these allowed energies (for example we might assume that it has an energy of $\frac{1}{2}E_1 + \frac{1}{2}E_2$) even though it is a solution to the TDSE. So how can we resolve this paradox?

If a measurement is made of the energy of an electron prepared in the super-position state above, the measurement must yield one of the well-defined values E_1 or E_2; after all, these are the only energies that the electron can have when confined to the well. Hence, after the measurement, the electron will have a definite energy E_1 or E_2 whereas before the measurement the energy of the electron was not well-defined. Likewise, after the measurement the electron must exist in a definite eigenstate, either $\psi_1(x)$ or $\psi_2(x)$ because it has energy E_1 or E_2 respectively, whereas before the measurement it did not. Hence the act of measurement alters the state of the electron.

Chapter 5

The finite square well

The infinite square well was easy to solve and gave us considerable insight into how the solutions to the TISE behave, but it contained unphysical regions in which the potential energy of the particle was infinite. In the second potential that we will study, the *finite square well*, the particle is still free to move within the well as before, but outside the well it has a finite potential energy V_0. This is a much more realistic model of forces holding a particle in a certain region because, unlike the infinite well, if we give the particle in the finite well enough energy it will escape. We will look for solutions to the Schrödinger equation for which the particle remains localized in the region of the well; these are known as *bound states*. For the particle to be in a bound state, its total energy, E, must be less than its potential energy outside the well, V_0.

First we will go through the full mathematical solution, then we will think about the physical implications of the solutions we have found.

5.1 Solution to the Schrödinger equation

We will define the one-dimensional finite well to be symmetric about the origin:

$$V(x) = \begin{cases} 0 & -a \leq x \leq a \\ V_0 & x < -a \text{ or } x > a. \end{cases} \tag{5.1}$$

A sketch of the finite well is shown in Figure 5.1.

The well is split into three regions; we will solve the TISE separately in each region. A reminder of the equation we are trying to solve:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi \tag{5.2}$$
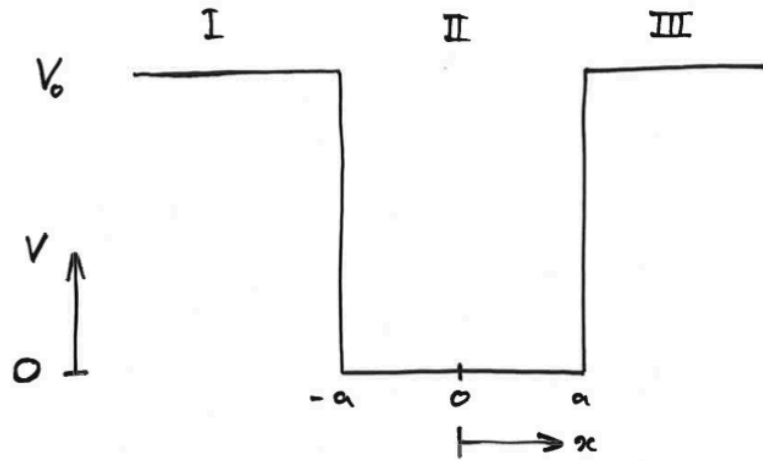
Figure 5.1 The potential energy of a particle in the finite square well.

We will follow exactly the same process as before, finding general solutions and then applying the boundary conditions.

5.1.1 Region II - inside the well

For $-a \leq x \leq a$, $V = 0$ and the TISE becomes:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$
$$\rightarrow \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi$$
$$= -\alpha^2\psi, \tag{5.3}$$

where

$$\alpha = \frac{\sqrt{2mE}}{\hbar}. \tag{5.4}$$

As in Section 4.1, the general solution to this is

$$\psi_{\text{II}} = A\sin\alpha x + B\cos\alpha x. \tag{5.5}$$

5.1.2   Region III - outside the well

For $x > a$, $V = V_0$ and the TISE becomes:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V_0\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = (E - V_0)\psi$$

$$\rightarrow \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi$$

$$= \beta^2\psi, \tag{5.6}$$

where

$$\beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{5.7}$$

Here we will draw breath and note the following important points:

- we are looking for bound states, therefore $E < V_0$;

- $(V_0 - E) > 0 \rightarrow \beta$ is real;

- the RHS of (5.6) is positive (c.f. RHS of (5.3)).

Hence the general solution to (5.6) is

$$\psi_{\mathrm{III}} = C\mathrm{e}^{-\beta x} + D\mathrm{e}^{\beta x}. \tag{5.8}$$

Note the difference with the previous solution in region II. The general solution (5.8) can be further simplified by applying the boundary condition that ψ must remain finite for all x. As a result, $D = 0$ and

$$\psi_{\mathrm{III}} = C\mathrm{e}^{-\beta x}. \tag{5.9}$$

Exercise Show explicitly that (5.8) is a solution to (5.6) the TISE in region III.

$$\frac{\mathrm{d}\psi_{\mathrm{III}}}{\mathrm{d}x} = -C\beta\mathrm{e}^{-\beta x} + D\beta\mathrm{e}^{\beta x}$$

$$\frac{\mathrm{d}^2\psi_{\mathrm{III}}}{\mathrm{d}x^2} = C\beta^2\mathrm{e}^{-\beta x} + D\beta^2\mathrm{e}^{\beta x}$$

$$= \beta^2\psi_{\mathrm{III}}.$$

Therefore this is a solution to the TISE in region III.

5.1.3   Region I - outside the well

We can apply similar reasoning to the region $x < -a$ where we also have $V = V_0$. After applying the same boundary condition on ψ we find the general solution is

$$\psi_\mathsf{I} = F\mathrm{e}^{\beta x}. \tag{5.10}$$

5.1.4   Complete solution

Having found the general solutions, we now apply boundary conditions to eliminate the constants. Firstly we enforce the continuity of ψ at $x = a$ (i.e. $\psi_\mathsf{II}(a) = \psi_\mathsf{III}(a)$):

$$A \sin \alpha a + B \cos \alpha a = C\mathrm{e}^{-\beta a} \tag{5.11}$$

and secondly the continuity of the first derivative of ψ at $x = a$:

$$\alpha A \cos \alpha a - \alpha B \sin \alpha a = -\beta C\mathrm{e}^{-\beta a}. \tag{5.12}$$

Dividing (5.11) by (5.12) we find

$$\frac{A \sin \alpha a + B \cos \alpha a}{\alpha(A \cos \alpha a - B \sin \alpha a)} = -\frac{1}{\beta}. \tag{5.13}$$

We can simplify this expression using arguments based on parity (see Section 4.4). Recall the general solution inside the well:

$$\psi_\mathsf{II} = A \sin \alpha x + B \cos \alpha x. \tag{5.14}$$

Because $V(x)$ is symmetric about the origin, the eigenfunctions must have either odd or even parity and cannot be a mixture of both odd and even functions. Therefore valid eigenfunctions must have either $A = 0$ or $B = 0$, and the solutions split into two groups:

- Even parity, $A = 0$ • Odd parity, $B = 0$

$$\rightarrow \psi_\mathsf{II} = B \cos \alpha x \qquad\qquad \rightarrow \psi_\mathsf{II} = A \sin \alpha x. \tag{5.15}$$

Applying the parity conditions to (5.13) we see

- Even parity   • Odd parity

$$-\frac{1}{\alpha}\cot\alpha a = -\frac{1}{\beta} \qquad\qquad \frac{1}{\alpha}\tan\alpha a = -\frac{1}{\beta}$$

$$\therefore \tan\alpha a = \frac{\beta}{\alpha} \qquad\qquad \therefore -\cot\alpha a = \frac{\beta}{\alpha} \qquad (5.16)$$

These equations are transcendental and must be solved numerically (there is no analytic solution). We make the substitution

$$\gamma = \frac{\sqrt{2mV_0a^2}}{\hbar}, \quad X = \gamma\sqrt{\frac{E}{V_0}}, \qquad (5.17)$$

and after some straightforward algebra (see problem sheet) we find (5.16) for the even and odd solutions become

- Even parity   • Odd parity

$$\tan X = \sqrt{\left(\frac{\gamma}{X}\right)^2 - 1} \qquad\qquad -\cot X = \sqrt{\left(\frac{\gamma}{X}\right)^2 - 1} \qquad (5.18)$$

To find the solutions, we plot $y = \tan X, y = -\cot X,$ and $y = \sqrt{(\gamma/X)^2 - 1}$; these curves are plotted for $\gamma = 1, 4, 5$ in Figure 5.2. From this plot we can infer that:
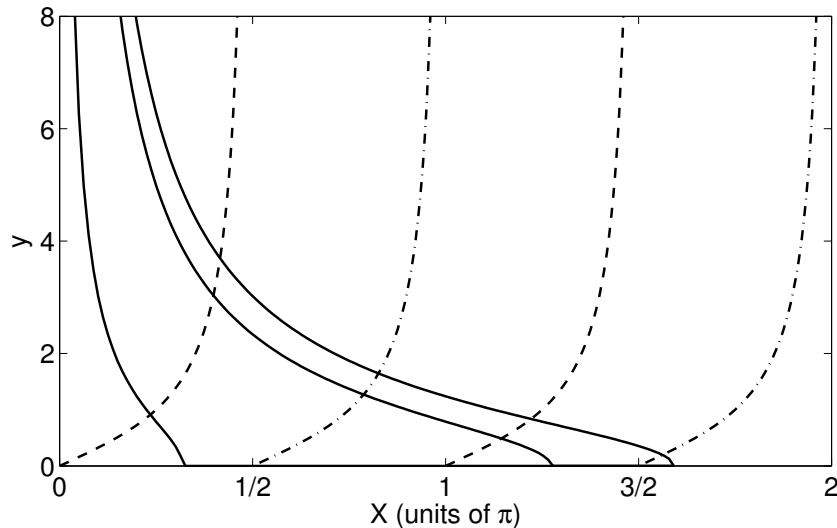

Figure 5.2   Plots for $\gamma = 1, 4, 5$.

- A finite number of discrete bound-state solutions occur at the loci of points

where the lines intersect.

- Larger values of γ give more bound-state solutions:

γ	No. of solutions (bound states)
1	1
4	3
5	4

- γ dictates the strength of the well and indicates the number of bound-state solutions. It increases with both the depth of the well ($\gamma \propto \sqrt{V_0}$) and the width of the well ($\gamma \propto a$).

- For a given value of γ, the number of bound states can be found by noting that $y = \sqrt{(\gamma/X)^2 - 1}$ crosses the X-axis at $X = \gamma$, whereas $\tan X$ and $-\cot X$ intersect the axis at multiples of $\pi/2$. So we see that:

γ_{min}	γ_{max}	No. of bound states
0	$\pi/2$	1
$\pi/2$	π	2
π	$3\pi/2$	3

- There is always at least one bound state regardless of the value of γ. It is the even-parity ground state. The first odd-parity solution appears when

$$\gamma \geq \frac{\pi}{2} \quad \rightarrow \quad V_0 a^2 \geq \frac{\hbar^2 \pi^2}{8m}. \tag{5.19}$$

- So, to calculate the number of bound states from a given set of finite well parameters, calculate γ, express it as a multiple of $\pi/2$ and round up to the nearest integer.

Exercise Find the number of bounds states of an electron in a well of width 2 nm and depth 1 eV.

$$\gamma = \frac{\sqrt{2mV_0a^2}}{\hbar}$$

$$= \frac{\sqrt{2 \times 9.11 \times 10^{-31} \times 1.6 \times 10^{-19} \times (1 \times 10^{-9})^2}}{1.06 \times 10^{-34}}$$

$$= 5.1$$

$$= 3.3 \times \frac{\pi}{2}$$

$\rightarrow$ No of bound states = 4.

5.2   Visualising the wavefunctions

We can construct the eigenfunctions valid for all x even though we do not know the exact energy levels. Qualitatively, we take the general solutions to TISE in each of the regions I, II, and III and join them at the boundaries, ensuring that we maintain the continuity of ψ and its first derivative. The resulting eigenfunctions are shown in Figure 5.3 and their associated probability densities in Figure 5.4.
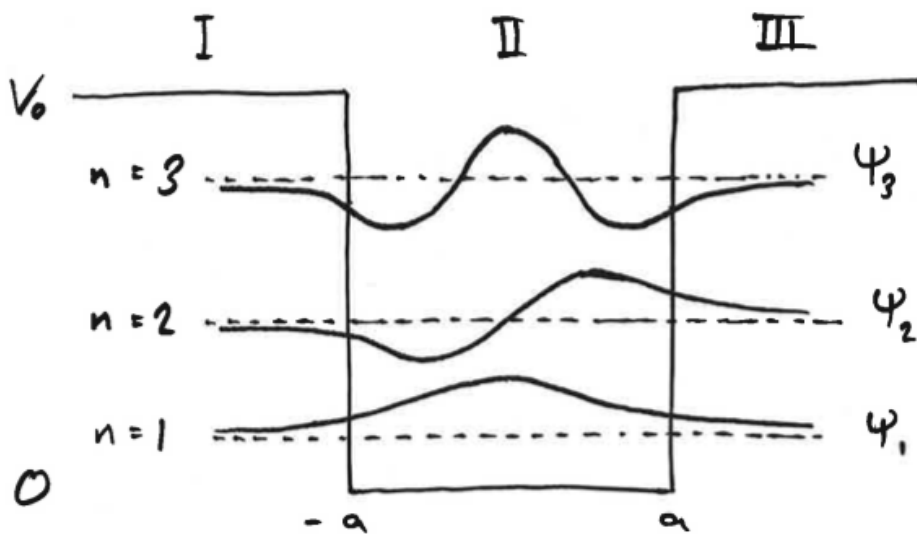

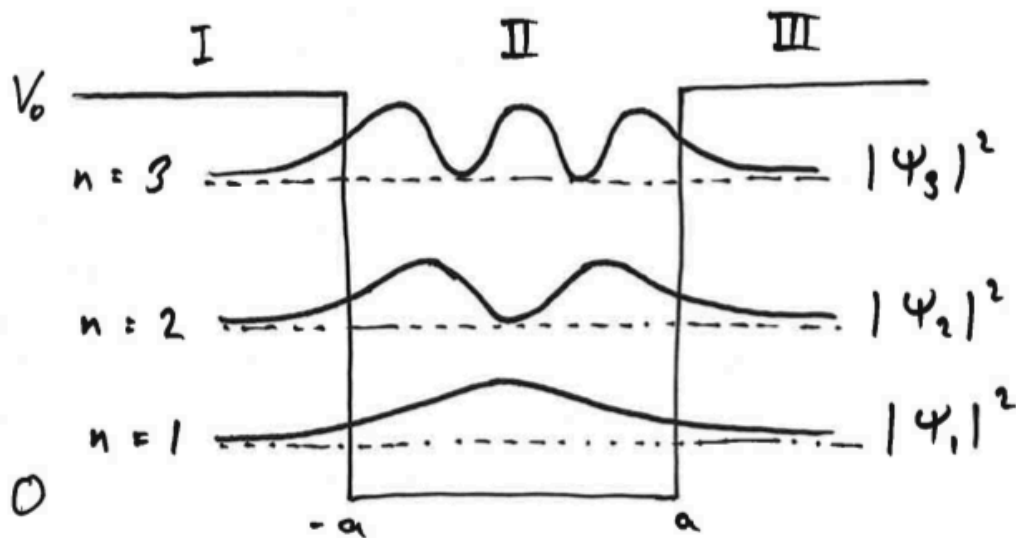**Figure 5.3**   The eigenfunctions for the finite square well.

Figure 5.4 The probability densities for the finite square well.

5.2.1 New physical phenomena

As we can see from Figure 5.3, the probability density functions for the bound states of the finite square well are similar to those of the infinite square well, with the addition of exponential tails extending into the walls of the well. The presence of these tails force us to conclude that the probability of finding the particle outside the well (in regions I and III) is not zero. This is a surprising result as a classical particle obeying Newtonian dynamics would have negative kinetic energy outside the well (simply because $E < V_0$).

The presence of a non-zero probability of finding the particle in a classically forbidden region has arisen simply from solving the TISE subject to the boundary conditions imposed by the finite well. Although contrary to our everyday experience, if we believe that Schrödinger's equation describes how wavefunctions behave, and that these wavefunctions allow us to make predictions about measurable quantities, then we are just going to have to accept that at the quantum level the universe does not behave as we would expect!

5.3 Energy levels

Without going into the numerical solution, we can estimate the allowed energy levels of the finite square well by comparison with the infinite square well. For a

well of width $2a$, (4.20) becomes

$$E_n^\infty = \frac{\hbar^2 \pi^2 n^2}{8ma^2}. \tag{5.20}$$

We can see from Figure 5.3 that the exponential tails make the *effective width* of the finite well larger than the actual width of a corresponding infinite well

$$a_{\text{eff}} > a, \tag{5.21}$$

and therefore the energy levels will be lower for the finite well than an infinite well of equal width

$$E^{(V_0)} < E^\infty. \tag{5.22}$$

However, as $V_0 \to \infty$, the exponential tails become less pronounced and $E^{(V_0)} \to E^\infty$.

Chapter 6

Free particles

We now turn our attention to particles that are travelling through space, rather than being bound to a potential well as in the previous two sections. We will look at what happens when moving particles encounter changes in potential and thus uncover more interesting quantum behaviour. Before we do so, we must look at the properties of free particles moving in uniform potentials. Although this is not a particularly interesting situation, we will use it to find general solutions for travelling waves and examine how to find expectation values of other dynamical variables.

6.1   Particles in free space

When the potential is uniform, a particle will propagate freely without changing its velocity because

$$F \propto -\frac{\mathrm{d}V}{\mathrm{d}x} = 0. \tag{6.1}$$

For convenience, we choose that $V = 0$ everywhere and proceed as usual from the TISE:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

$$\rightarrow \quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

$$\text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}$$

$$\therefore \quad \psi(x) = Ae^{ikx} + Be^{-ikx} \tag{6.2}$$

As we are looking for travelling-wave solutions, we include time-dependence using (3.22) and the energy of the travelling wave, $E = \hbar\omega$:

$$
\begin{aligned}
\Psi(x,t) &= \psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \\
&= (A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx})\mathrm{e}^{-i\omega t} \\
&= \underbrace{A\mathrm{e}^{i(kx-\omega t)}}_{\text{+ve wave}} + \underbrace{B\mathrm{e}^{-i(kx+\omega t)}}_{\text{-ve wave}} \\
&= \Psi_+ + \Psi_-
\end{aligned}
\tag{6.3}
$$

So the general solution contains components representing waves travelling in the positive and negative x directions.

Exercise Show that $\Psi_+ = A\mathrm{e}^{i(kx-\omega t)}$ represents a travelling wave.
Nodes of the real part of Ψ_+ occur at

$$
\begin{aligned}
kx - \omega t &= \frac{\pi}{2} \\
\rightarrow \quad x &= \frac{1}{k}\left(\omega t + \frac{\pi}{2}\right).
\end{aligned}
$$

Therefore the position of the nodes move in time and Ψ_+ is a travelling wave.

Taking a particle travelling in the positive x direction, we can easily calculate its probability density:

$$
\begin{aligned}
P(x,t) = \Psi_+^*\Psi_+ &= A^*\mathrm{e}^{-i(kx-\omega t)}A\mathrm{e}^{i(kx-\omega t)} \\
&= A^*A \\
&= A^2.
\end{aligned}
\tag{6.4}
$$

The probability density is constant in time and uniform in space, as illustrated in Figure 6.1. The particle is equally likely to be found anywhere from $x = -\infty$ to $x = \infty$, a reasonable consequence of the particle not being confined by any potentials.

Exercise What is the consequence of Figure 6.1 for the Heisenberg uncertainty principle?
Uncertainty in position is infinite, therefore uncertainty in momentum is zero!
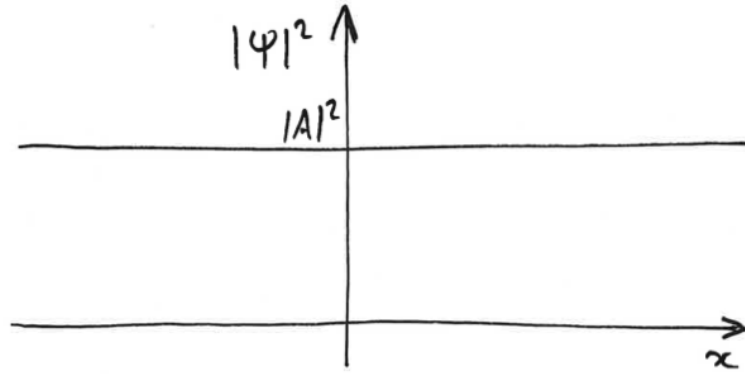

Figure 6.1   Probability density for a particle in free space.

6.2   Expectation values

The case of free particles gives us a good opportunity to look at how to calculate the expectation values of observables other than position. We will start with momentum.

6.2.1   Momentum

Consider a free particle moving in the positive x direction:

$$\Psi_+(x,t) = A\mathrm{e}^{i(kx-\omega t)} \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}. \tag{6.5}$$

in which the potential energy $V = 0$ everywhere. By equating the wavenumber to its standard definition in terms of the de Broglie wavelength λ

$$k = \frac{2\pi}{\lambda} = \frac{\sqrt{2mE}}{\hbar} \tag{6.6}$$

and considering the total energy

$$E = \frac{p^2}{2m} \tag{6.7}$$

we see that the particle has a well-defined momentum, $p = \hbar k$. Now consider

$$\begin{aligned}
-i\hbar\frac{\partial}{\partial x}\Psi_+ &= -i\hbar\frac{\partial}{\partial x}A\mathrm{e}^{i(kx-\omega t)} \\
&= -i\hbar \,.\, ikA\mathrm{e}^{i(kx-\omega t)} \\
&= \hbar k\, A\mathrm{e}^{i(kx-\omega t)} \\
&= \hbar k\, \Psi_+
\end{aligned} \tag{6.8}$$

so we see that

$$-i\hbar\frac{\partial}{\partial x}\Psi_+ = p\,\Psi_+. \tag{6.9}$$

We can apply exactly the same reasoning to a particle moving in the negative x direction to find

$$-i\hbar\frac{\partial}{\partial x}\Psi_- = -\hbar k\,\Psi_-$$
$$= p\,\Psi_-. \tag{6.10}$$

It is apparent that there is an association

$$p \leftrightarrow -i\hbar\frac{\partial}{\partial x}. \tag{6.11}$$

This expression is true in general, and is known as an *operator*, specifically in this case the *momentum operator*. It is usually denoted by a hat:

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{6.12}$$

When applied to a wavefunction, $\hat{p}$ returns the value of the momentum multiplied by the wavefunction.

So far we have looked at the special case of free particles, but we can construct a general expression for the expectation value of any function of x or t in the same manner as we did for position (see (2.6)). For momentum,

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{p}\,\Psi(x,t)\,\mathrm{d}x$$
$$= \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)\,\mathrm{d}x. \tag{6.13}$$

Now the reason for the ordering in (2.6) becomes clear: the operator acts only on the following wavefunction and not on the preceding conjugated wavefunction. For example, with Ψ_+:

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi_+^*\left(-i\hbar\frac{\partial}{\partial x}\Psi_+\right)\mathrm{d}x$$
$$= \int_{-\infty}^{\infty} \Psi_+^*\,\hbar k\,\Psi_+\,\mathrm{d}x$$
$$= \hbar k \int_{-\infty}^{\infty} \Psi_+^*\,\Psi_+\,\mathrm{d}x$$
$$= \hbar k, \tag{6.14}$$

and we recover the known value of the momentum.

6.2.2 Kinetic energy

We can write down an expression for the expectation value of p^2:

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right)^2 \Psi(x,t) \, \mathrm{d}x$$

$$= \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t) \, \mathrm{d}x. \tag{6.15}$$

Thence, using the classical relationship between momentum and kinetic energy we can write down the expectation value of the kinetic energy:

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

$$\rightarrow \quad \langle K.E. \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x,t) \, \mathrm{d}x. \tag{6.16}$$

6.2.3 Time-indepedence

In all these expressions, if we are considering a time-independent potential $V = V(x)$ we can make the substitution (3.22)

$$\Psi(x,t) = \psi(x) \mathrm{e}^{-\frac{iEt}{\hbar}}, \tag{6.17}$$

all time-dependent terms cancel with their complex conjugates, and the partial derivatives in x become ordinary derivatives. We are left with the following expressions for the expectation values:

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

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) \psi(x) \, \mathrm{d}x \tag{6.19}$$

$$\langle K.E. \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} \right) \psi(x) \, \mathrm{d}x. \tag{6.20}$$

These relationships allow us to find the average values of repeated measurements of properties of eigenfunctions. You should learn them!

Exercise Calculate the kinetic energy associated with the eigenfunctions for an infinite square well of width L using (4.20):

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad 0 \le x \le L.$$

$$
\begin{aligned}
\langle K.E. \rangle &= \int_{-\infty}^{\infty} \psi_n^* \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2}\right)\,\mathrm{d}x \\
&= \int_0^L \psi_n^* \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \psi_n\,\mathrm{d}x \\
&= \frac{\hbar^2\pi^2 n^2}{2mL^2}\int_0^L \psi_n^* \psi_n\,\mathrm{d}x \\
&= \frac{\hbar^2\pi^2 n^2}{2mL^2} \\
&= E_n.
\end{aligned}
$$

In the well $V = 0$ therefore the total energy is equal to the kinetic energy.

6.3   Operators and eigenvalues

(6.8) and (6.10) are examples of *eigenvalue equations*. More generally, when an operator acts on an eigenfunction it returns the expectation value of the observable – known as the *eigenvalue* – multiplied by the eigenfunction itself:

$$\text{Operator} \times \psi = \text{Eigenvalue} \times \psi. \tag{6.21}$$

Exercise Construct the TISE from the operators you have seen in this section.

$$\frac{p^2}{2m} + V = E \qquad \rightarrow \qquad \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + V = E$$

$$\left[\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + V\right]\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi.$$

So we see that the TISE is just an eigenvalue equation for the total energy. In fact, forming the TISE from operators is the way in which it was first conceived by Schrödinger.

Chapter 7

Potential steps and barriers

In this section we will study what happens when a particle that is initially travelling in free space (moving subject to a constant potential) encounters a sudden change in potential. In doing so we will uncover yet more interesting quantum phenomena. We will consider situations in which the energy of the incident particle is higher or lower than the step, and also a barrier potential (a narrow region of high potential). In all cases we will model the change in potential to be immediate; although this is unphysical (consider the implications of (6.1)) it will nevertheless illustrate the essential points and it makes the maths easier!

7.1   Probability flux

To begin, we need to define a new quantity, the *probability flux*. Probability flux is defined as the probability per unit time that a particle will be found passing a reference point in a given direction. It is also known as *probability current* and often given the symbol j. The probability flux has a simple form for a particle moving in a region of constant potential[1]. If we consider a particle travelling with speed v in the positive x-direction (see Figure 7.1), then

$$\text{Prob of passing } x_0 \text{ in time } \mathrm{d}t = \text{Prob of being in length } v\,\mathrm{d}t$$

$$= \psi^*\psi v\,\mathrm{d}t$$

$$= \psi^*\psi \frac{\hbar k}{m}\,\mathrm{d}t$$

$$\rightarrow \quad \text{Prob of passing } x_0 \text{ in unit time} = \psi^*\psi \frac{\hbar k}{m}. \tag{7.1}$$

---

[1] In other situations a more complicated expression for probability flux is required; you may see it in textbooks. It is not given here because in the cases that we are considering the full expression for probability flux reduces to the simpler expression shown in these notes.

This is equal to the probability flux j of the particle, so we have

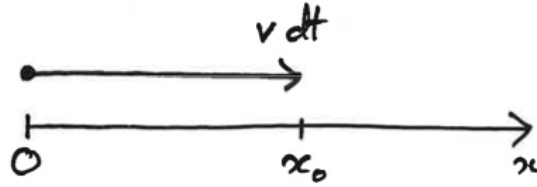$$j = \frac{\hbar k}{m}\psi^*\psi. \tag{7.2}$$

We will use this expression later.

Figure 7.1 Illustration of probability flux.

7.2 Potential steps

We consider a particle with energy E propagating in the positive x-direction towards a sharp boundary where its potential energy increases from 0 to V_0:

$$V(x) = \begin{cases} 0 & x \le 0 \\ V_0 & x > 0. \end{cases} \tag{7.3}$$

We will label these regions I and II respectively. We will solve the TISE for two separate cases in which the particle has different energies.

7.2.1 Energy greater than step height

The first case is when $E > V_0$ as shown in Figure 7.2. Classically, the particle would simply pass through the barrier, travelling with reduced velocity on the other side. In order to find out what happens according to quantum mechanics, we will solve the TISE for the two regions.
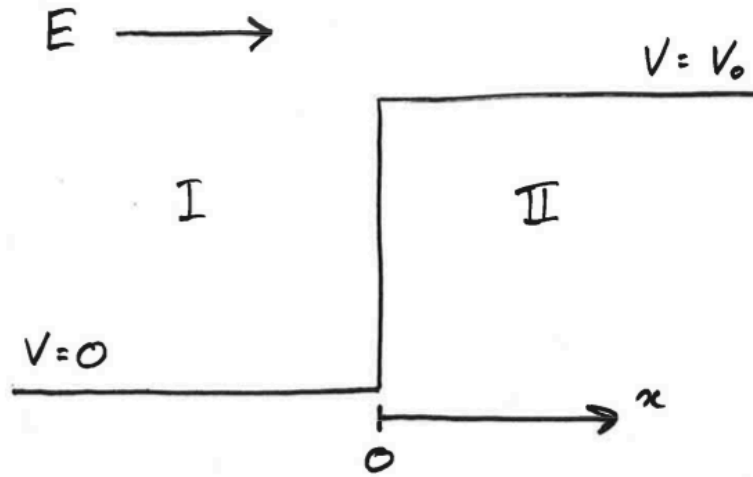
Figure 7.2   Potential step with $E > V_0$.

Region I $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi_\mathrm{I}}{\mathrm{d}x^2} = E\psi_\mathrm{I}$

$$\rightarrow \quad \psi_\mathrm{I} = \underbrace{A\mathrm{e}^{ik_\mathrm{I}x}}_{\text{incident}} + \underbrace{B\mathrm{e}^{-ik_\mathrm{I}x}}_{\text{reflected}}, \quad \text{where} \quad k_\mathrm{I} = \dfrac{\sqrt{2mE}}{\hbar} \tag{7.4}$$

Region II $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi_\mathrm{II}}{\mathrm{d}x^2} + V_0\psi_\mathrm{II} = E\psi_\mathrm{II}$

$$\rightarrow \quad \psi_\mathrm{II} = \underbrace{C\mathrm{e}^{ik_\mathrm{II}x}}_{\text{trans}} + \underbrace{D\mathrm{e}^{-ik_\mathrm{II}x}}_{\text{?}}, \quad \text{where} \quad k_\mathrm{II} = \dfrac{\sqrt{2m(E - V_0)}}{\hbar} \tag{7.5}$$

"?" represents a wave in region II moving in the negative direction. This is unphysical and therefore $D = 0$. We now apply boundary conditions at the step.

$$\text{Continuity of } \psi \text{ at } x = 0: \quad A + B = C \tag{7.6}$$

$$\text{Continuity of } \dfrac{\mathrm{d}\psi}{\mathrm{d}x} \text{ at } x = 0: \quad k_\mathrm{I}(A - B) = k_\mathrm{II}C. \tag{7.7}$$

Rearranging these expressions we can express B and C in terms of A:

$$B = \dfrac{k_\mathrm{I} - k_\mathrm{II}}{k_\mathrm{I} + k_\mathrm{II}} A \quad \text{and} \quad C = \dfrac{2k_\mathrm{I}}{k_\mathrm{I} + k_\mathrm{II}} A, \tag{7.8}$$

yielding the eigenfunction

$$
\psi(x) = \begin{cases} A\mathrm{e}^{ik_\mathsf{I}x} + B\mathrm{e}^{-ik_\mathsf{I}x} & x \le 0 \\ C\mathrm{e}^{ik_\mathsf{II}x} & x > 0 \end{cases} \tag{7.9}
$$

where B and C are given by (7.8).

Exercise Calculate the probability density for the step potential with $E > V_0$, expressing your result in terms of A, k_I, and k_II.

$$
\begin{aligned}
|\psi_\mathsf{I}(x)|^2 &= |A\mathrm{e}^{ik_\mathsf{I}x} + B\mathrm{e}^{-ik_\mathsf{I}x}|^2 \\
&= A^2 + B^2 + AB(\mathrm{e}^{-2ik_\mathsf{I}x} + \mathrm{e}^{2ik_\mathsf{I}x}) \\
&= A^2 + B^2 + 2AB\cos(2k_\mathsf{I}x) \\
&= A^2 \left[1 + \left(\frac{k_\mathsf{I} - k_\mathsf{II}}{k_\mathsf{I} + k_\mathsf{II}} \right)^2 + 2\left(\frac{k_\mathsf{I} - k_\mathsf{II}}{k_\mathsf{I} + k_\mathsf{II}} \right)\cos(2k_\mathsf{I}x) \right]
\end{aligned}
$$

$$
|\psi_\mathsf{II}(x)|^2 = C^2 = \left(\frac{2k_\mathsf{I}}{k_\mathsf{I} + k_\mathsf{II}} \right)^2 A^2. \tag{7.10}
$$

Therefore $|\psi_\mathsf{I}(x)|^2$ is oscillatory in x but $|\psi_\mathsf{II}(x)|^2$ is constant. Note that the maximum value of $|\psi_\mathsf{I}(x)|^2$ is equal to the value of $|\psi_\mathsf{II}(x)|^2$.
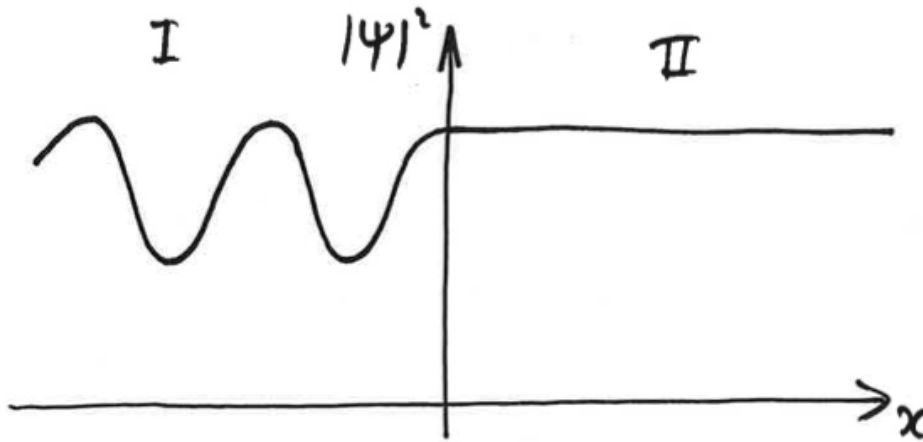

Figure 7.3 Probability density for the step potential with $E > V_0$.

7.2.2   Reflection and transmission probabilities

Although (7.9) is not normalised, we can still use it to find the reflection and transmission probabilities at the step, R and T respectively, using the probability flux (7.2).

$$
\begin{aligned}
R = \frac{j_{\text{reflected}}}{j_{\text{incident}}} &= \frac{\frac{\hbar k_{\text{I}}}{m}|\psi_{\text{reflected}}|^2}{\frac{\hbar k_{\text{I}}}{m}|\psi_{\text{incident}}|^2} = \frac{|\psi_{\text{reflected}}|^2}{|\psi_{\text{incident}}|^2} \\
&= \frac{B^* e^{ik_{\text{I}}x}\, B e^{-ik_{\text{I}}x}}{A^* e^{-ik_{\text{I}}x}\, A e^{ik_{\text{I}}x}} \\
&= \frac{B^* B}{A^* A} \\
&= \left(\frac{k_{\text{I}} - k_{\text{II}}}{k_{\text{I}} + k_{\text{II}}}\right)^2 .
\end{aligned}
\tag{7.11}
$$

Substituting values of k_{I} and k_{II} we find (see problem sheet)

$$
R = \left(\frac{1 - \sqrt{1 - V_0/E}}{1 + \sqrt{1 - V_0/E}}\right)^2 .
\tag{7.12}
$$

The same method can be used for T:

$$
\begin{aligned}
T = \frac{j_{\text{trans}}}{j_{\text{incident}}} &= \frac{\frac{\hbar k_{\text{II}}}{m}|\psi_{\text{trans}}|^2}{\frac{\hbar k_{\text{I}}}{m}|\psi_{\text{incident}}|^2} \\
&= \frac{k_{\text{II}}}{k_{\text{I}}}\frac{C^* e^{-ik_{\text{I}}x}\, C e^{ik_{\text{I}}x}}{A^* e^{-ik_{\text{I}}x}\, A e^{ik_{\text{I}}x}} \\
&= \frac{k_{\text{II}}}{k_{\text{I}}}\frac{C^* C}{A^* A} \\
&= \frac{4 k_{\text{I}} k_{\text{II}}}{(k_{\text{I}} + k_{\text{II}})^2}.
\end{aligned}
\tag{7.13}
$$

Note that, as we would expect, $R + T = 1$; each particle must be either reflected or transmitted.

In order to illustrate the implications of these results, we consider firing a monoenergetic beam of electrons with energy 5 keV at a 4 kV potential step. We can calculate the proportion that will be reflected using (7.12):

$$
V_0 = qV = 4 \,\text{keV}
$$

$$
R = \left(\frac{1 - \sqrt{1 - 4/5}}{1 + \sqrt{1 - 4/5}}\right)^2 = \left(\frac{\sqrt{5} - 1}{\sqrt{5} + 1}\right)^2 = 0.15
$$

The precise value that we have found here is not important, the point is that R *is greater than zero*: even though the electrons have energy that is higher

than the barrier they face, some of them are reflected by it. Approached with our classical notions of how particles behave, this is a very surprising result. It is the equivalent of throwing tennis balls onto a flat roof and finding that some of them bounce back to you even though you threw every ball high enough to clear the side of the building! Nevertheless, in classical wave phenomena, similar situations exist; think of the small fraction of light that is reflected by a window, or water waves being reflected where there is a sudden change in depth. In fact in any situation where a wave encounters an interface at which its wavenumber k changes suddenly (or equivalently the impedance of the medium changes the phase velocity of the wave) some of the wave will be reflected. The behaviour of the wavefunction at the potential step is exactly the same.

7.2.3 Energy less than step height

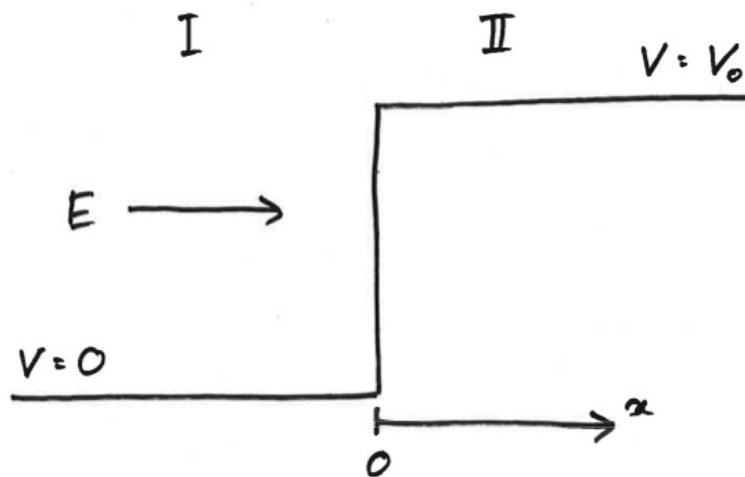The second case is when $E < V_0$, shown in Figure 7.4.

Figure 7.4 Potential step with $E < V_0$.

We solve the TISE again for the two regions, noting the similarity with the finite potential well:

Region I $\quad -\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi_\mathrm{I}}{\mathrm{d}x^2} = E\psi_\mathrm{I}$

$$\rightarrow \quad \psi_\mathrm{I} = \underbrace{A\mathrm{e}^{ik_\mathrm{I}x}}_{\text{incident}} + \underbrace{B\mathrm{e}^{-ik_\mathrm{I}x}}_{\text{reflected}}, \quad \text{where} \quad k_\mathrm{I} = \frac{\sqrt{2mE}}{\hbar} \tag{7.14}$$

Region II $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi_{\mathsf{II}}}{\mathrm{d}x^2} + V_0\psi_{\mathsf{II}} = E\psi_{\mathsf{II}}$

$\rightarrow \quad \dfrac{\mathrm{d}^2\psi_{\mathsf{II}}}{\mathrm{d}x^2} = \dfrac{2m}{\hbar^2}(V_0 - E)\psi_{\mathsf{II}} = \beta^2\psi_{\mathsf{II}}$

$\rightarrow \quad \psi_{\mathsf{II}} = C\mathrm{e}^{-\beta x} + D\mathrm{e}^{\beta x}, \quad \text{where} \quad \beta = \dfrac{\sqrt{2m(V_0 - E)}}{\hbar}$

ψ_{II} must remain finite as $x \rightarrow \infty$ $\therefore$ $D = 0$

$\therefore \quad \psi_{\mathsf{II}} = C\mathrm{e}^{-\beta x}$ $\hfill (7.15)$

So we see that the eigenfunction decays exponentially into the barrier. As for the finite well, the region where $V = V_0$ is forbidden for classical particles. Hence, we once again recover a non-zero probability of finding the particle in a region where a classical particle could never be found. Note that this is a short-range effect and there are no travelling-wave solutions for $x > 0$; hence $R = 1$.

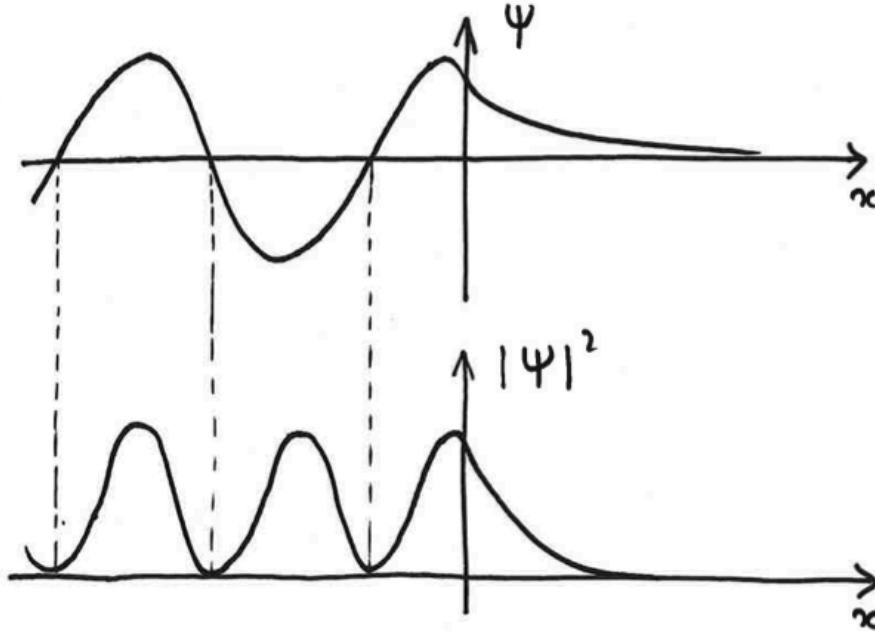The eigenfunctions and probability density for the step potential with $E < V_0$ is shown in Figure 7.5.

Figure 7.5   Probability density for the step potential with $E < V_0$.

7.3   Potential barriers

We now consider what happens when a particle with $E < V_0$ approaches a step where the region with potential energy V_0 is narrow; it no longer continues to $x = \infty$ but only to position $x = a$. At $x = a$, V returns abruptly to zero.

$$V(x) = \begin{cases} V_0 & 0 \leq x \leq a \\ 0 & x < 0 \quad \text{and} \quad x > a, \end{cases} \tag{7.16}$$
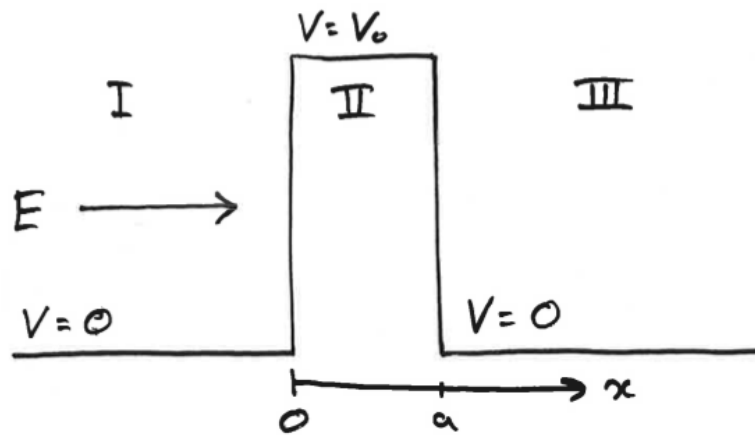
as illustrated in Figure 7.6.

Figure 7.6   Potential barrier.

We can think qualitatively about what happens in this situation. If the barrier is sufficiently narrow, the exponential decay of the wavefunction will still have appreciable amplitude at $x = a$. Upon applying the boundary conditions on ψ at the second interface we will find that the wavefunction (and hence $|\psi|^2$) is non-zero on the other side of the barrier. The particle has some probability of traversing the barrier and continuing to propagate on the far side, even though its energy is lower than the barrier height. This phenomenon is called *tunnelling* – another remarkable result!

We can look at this mathematically by (as ever!) solving the TISE. The form of the solutions is very similar to those in the preceding section, so we will just write down the results:

Region I $\psi_{\mathrm{I}} = \underbrace{A\mathrm{e}^{ik_{\mathrm{I}}x}}_{\text{incident}} + \underbrace{B\mathrm{e}^{-ik_{\mathrm{I}}x}}_{\text{reflected}}$,   where $k_{\mathrm{I}} = \dfrac{\sqrt{2mE}}{\hbar}$ (7.17)

Region II $\psi_{\mathrm{II}} = C\mathrm{e}^{-\beta x} + D\mathrm{e}^{\beta x}$,   where $\beta = \dfrac{\sqrt{2m(V_0 - E)}}{\hbar}$ (7.18)

Region III $\psi_{\mathrm{III}} = \underbrace{F\mathrm{e}^{ik_{\mathrm{I}}x}}_{\text{trans}}$,   (7.19)

where we have omitted the unphysical negative-propagating wave in region III. Note that $D \neq 0$ in region II. The corresponding probability density is sketched in Figure 7.7.
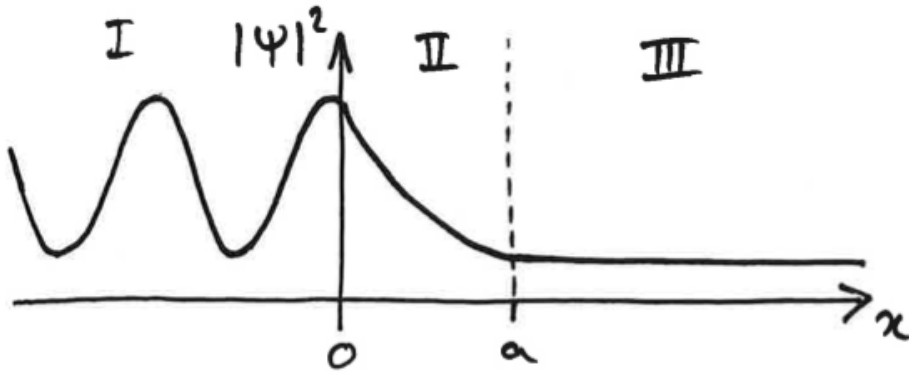

Figure 7.7   Probability density for the potential barrier with $E < V_0$.

By applying the standard continuity conditions at $x = 0$ and $x = a$ we find

$$A + B = C + D$$
$$ik_{\mathrm{I}}(A - B) = -\beta(C - D)$$
$$C\mathrm{e}^{-\beta a} + D\mathrm{e}^{\beta a} = F\mathrm{e}^{ik_{\mathrm{I}}a}$$
$$-\beta(C\mathrm{e}^{-\beta a} - D\mathrm{e}^{\beta a}) = ik_{\mathrm{I}}F\mathrm{e}^{ik_{\mathrm{I}}a}.$$ (7.20)

With these equations, we can eliminate four of the five unknowns and substitute

into an expression for the transmission probability T, given by

$$
\begin{aligned}
T &= \frac{j_{\text{trans}}}{j_{\text{incident}}} \\
&= \frac{\frac{\hbar k_\text{l}}{m}|\psi_{\text{trans}}|^2}{\frac{\hbar k_\text{l}}{m}|\psi_{\text{incident}}|^2} \\
&= \frac{F^* \mathrm{e}^{-ik_\text{l}x}\, F\mathrm{e}^{ik_\text{l}x}}{A^* \mathrm{e}^{-ik_\text{l}x}\, A\mathrm{e}^{ik_\text{l}x}} = \frac{F^*F}{A^*A}.
\end{aligned}
\tag{7.21}
$$

After some tedious algebra and subject to the approximation that the barrier is wide compared to the rate of exponential decay, i.e. $\beta a \gg 1$, we find

$$
T = 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)\mathrm{e}^{-2\beta a}.
\tag{7.22}
$$

So we see that the transmission probability is exponentially dependent on the barrier width a.

Exercise What is the momentum of a particle that has passed through the barrier?

$$
\hat{p}\,\psi_{\text{III}} = \left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)F\mathrm{e}^{ik_\text{l}x} = \hbar k_\text{l}\,\psi_{\text{III}}
$$

So its momentum is unchanged after passing through the barrier!

Chapter 8

The harmonic oscillator

The final one-dimensional potential that we will study is the simple harmonic oscillator. It is the most physically realistic so far because the potential is a smooth function of position, without any of the step-like discontinuities present in the potentials that we have looked at before. The simple harmonic potential is incredibly important because it can be used to describe any system exhibiting small oscillations about a stable equilibrium point.

Consider a continuous potential with a (local) minimum, as shown in Figure 8.1. The minimum is a point of stable equilibrium, and the potential close by can be approximated by a parabola, as shown by the dotted line in the figure. If we set the origin of both the x-axis and the potential energy at the minimum then

$$V(x) = \frac{1}{2}Cx^2. \tag{8.1}$$

For small displacements about the minimum, the system only experiences the parabolic potential, and will be subject to a restoring force proportional to the small displacement:

$$F = -\frac{\mathrm{d}V}{\mathrm{d}x} = -Cx. \tag{8.2}$$

Thus the system will exhibit simple harmonic motion about the equilibrium point.

Mathematically, this is equivalent to making a Taylor expansion about the minimum:

$$
\begin{aligned}
V(x) &= V(0) + x\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)_{x=0} + \frac{x^2}{2}\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_{x=0} + \dots \\
&= \frac{x^2}{2}\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_{x=0} + \dots
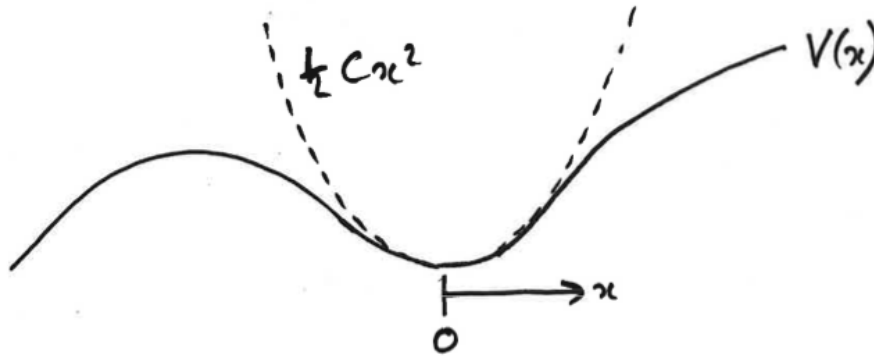\end{aligned}
\tag{8.3}
$$

Figure 8.1 A general potential approximated by the simple harmonic potential.

So, if we ignore terms in x^3 and higher (valid for small x)

$$V(x) \approx \frac{1}{2}Cx^2 \quad \text{where} \quad C = \left(\frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\right)_{x=0} \tag{8.4}$$

and we recover the simple harmonic potential.

We will begin by reviewing the simple harmonic oscillator for a classical particle and then look at the solution of the TISE for the quantum mechanical case.

8.1   Classical simple harmonic oscillator

For a classical simple harmonic oscillator (for example a mass on a spring), we solve the differential equation obtained from (8.2) and Newton's Second Law:

$$m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -Cx. \tag{8.5}$$

We find solutions that are sinusoidal functions

$$x = A\sin(\omega t + \phi) \qquad \text{where} \qquad \omega = \sqrt{\frac{C}{m}}, \tag{8.6}$$

A is the amplitude of the oscillations, ω is the angular frequency, and ϕ is the initial phase. The total energy of the oscillations is

$$E = V(x) + \text{K.E.} = \frac{1}{2}Cx^2 + \frac{1}{2}mv^2, \tag{8.7}$$

but when $x = \pm A$ then $v = 0$, so $E = \frac{1}{2}CA^2$. Note that this constant value is continuous. The probability distribution associated with the motion has maxima at $x = \pm A$ as shown in Figure 8.2; this makes sense intuitively as the oscillator is

more likely to be found at the extremities where it is moving more slowly than in the centre where it is moving fastest.
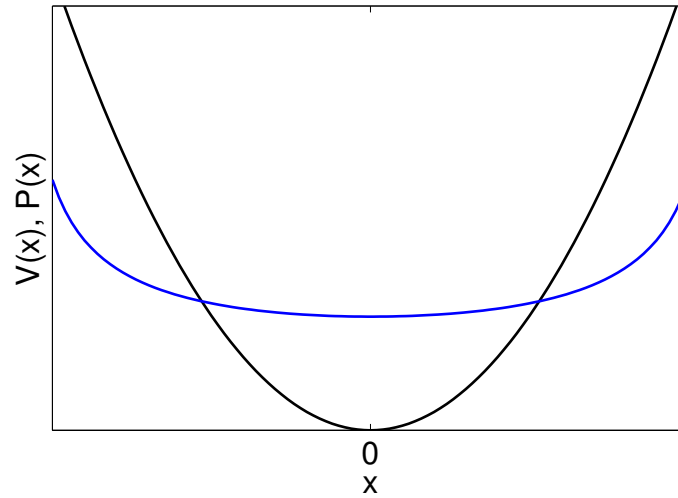

Figure 8.2   Classical simple harmonic oscillator probability density.

8.2   Quantum harmonic oscillator

We will now look at the wavefunctions of a quantum harmonic oscillator using the TISE:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}Cx^2\psi = E\psi. \tag{8.8}$$

The full solution to this equation is involved and we will not go through it here[1]. Instead, we will adopt our familiar technique of "guessing" a solution, though in this case we will only find the ground state solution not a general solution for all bound states.

8.2.1   Ground-state solution

Our trial solution will be a Gaussian function:

$$\psi = A\mathrm{e}^{-\frac{\alpha}{2}x^2} \tag{8.9}$$

---

[1] The interested reader is referred to Appendix I in Eisberg and Resnick

with derivatives

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = -\alpha x \, A\mathrm{e}^{-\frac{\alpha}{2}x^2}$$
$$= -\alpha x \, \psi, \tag{8.10}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\alpha \, \psi - \alpha x \, \frac{\mathrm{d}\psi}{\mathrm{d}x}$$
$$= -\alpha \, \psi + \alpha^2 x^2 \, \psi. \tag{8.11}$$

We substitute into the TISE

$$-\frac{\hbar^2}{2m} \left(-\alpha + \alpha^2 x^2\right) \psi + \frac{1}{2} C x^2 \, \psi = E \, \psi, \tag{8.12}$$

and collect terms with x^2 and no x-dependence on the LHS:

$$\left[\left(\frac{C}{2} - \frac{\hbar^2 \alpha^2}{2m}\right) x^2 + \left(\frac{\hbar^2 \alpha}{2m} - E\right) \right] \psi = 0. \tag{8.13}$$

We know that $\psi \neq 0$, so to satisfy this equation for all x we require both expressions in parentheses to equal zero individually, therefore

$$C = \frac{\hbar^2 \alpha^2}{m} \qquad \text{and} \qquad E = \frac{\hbar^2 \alpha}{2m}. \tag{8.14}$$

We now evaluate the force constant C in terms of the classical oscillation frequency $\omega = \sqrt{\frac{C}{m}}$

$$m\omega^2 = \frac{\hbar^2 \alpha^2}{m} \qquad \rightarrow \qquad \alpha = \frac{m\omega}{\hbar} \tag{8.15}$$

$$\therefore \quad E = \frac{\hbar\omega}{2}. \tag{8.16}$$

So in conclusion we have demonstrated that the ground-state solution is

$$\psi_0 = A\mathrm{e}^{-\frac{\xi^2}{2}}, \quad \text{where} \quad \xi = \sqrt{\alpha}x = \sqrt{\frac{m\omega}{\hbar}}x \tag{8.17}$$

and the ground-state energy level is

$$E_0 = \frac{\hbar\omega}{2}. \tag{8.18}$$

Hence we see that the quantum harmonic oscillator also exhibits zero-point energy. The reason for labelling this solution 0 rather than 1 will become clear in the next section.

8.2.2   Excited-state solutions

The eigenfunctions of the quantum harmonic oscillator are

$$\psi_n = A_n H_n(\xi) \mathrm{e}^{-\frac{\xi^2}{2}}, \qquad (8.19)$$

where the functions $H_n(\xi)$ are the *Hermite polynomials*. These are polynomials of order n, the first few of which are

$$H_0(\xi) = 1$$
$$H_1(\xi) = 2\xi$$
$$H_2(\xi) = 2 - 4\xi^2$$
$$H_3(\xi) = 12\xi - 8\xi^3$$
$$\vdots$$

The form of these solutions is shown in Figure 8.3. The common factor of $\mathrm{e}^{-\frac{\xi^2}{2}}$ ensures that the eigenfunctions tend to zero as $x \to \pm\infty$ and the Hermite polynomials give the solutions their oscillatory form.
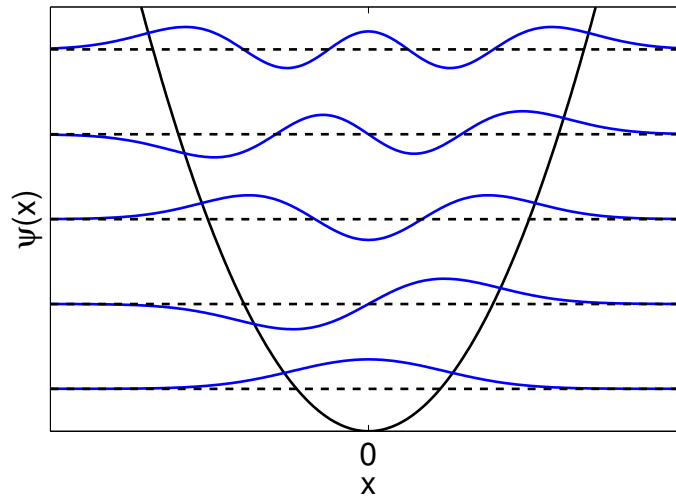

Figure 8.3   Eigenfunctions of the quantum harmonic oscillator.

The energy levels of the quantum harmonic oscillator start from $\hbar\omega/2$ and are equally spaced by $\hbar\omega$. The general expression for the energy levels is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (8.20)$$

where n is an integer starting from 0 ($n = 0, 1, 2, 3\ldots$) – hence the ground state is

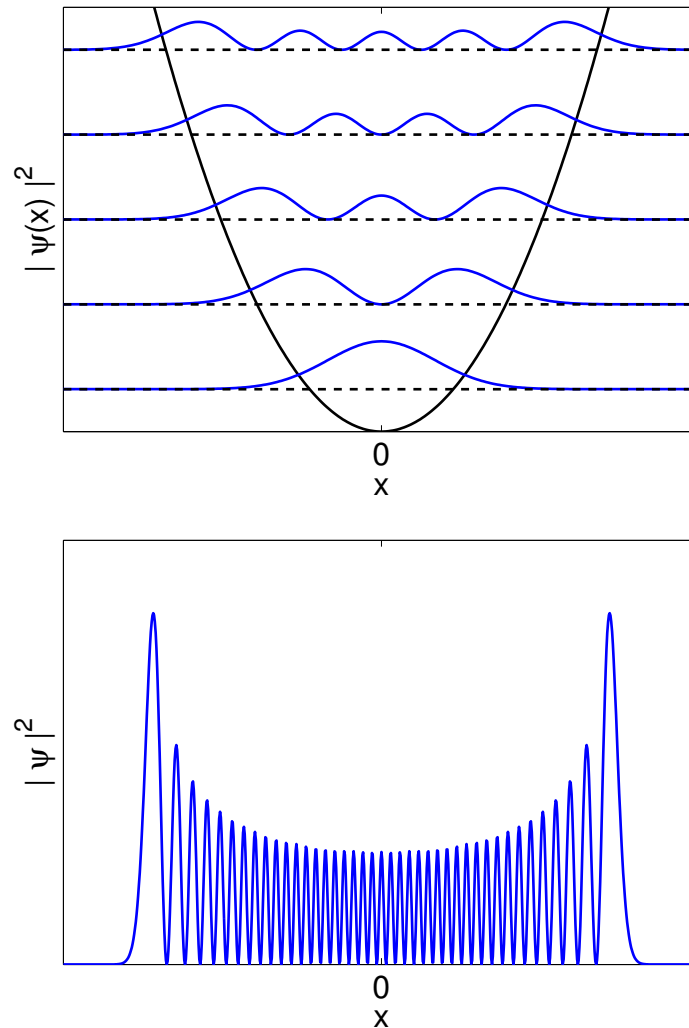labelled 0. There are an infinite number of bound states.

Figure 8.4 Probability density functions of the quantum harmonic oscillator.

The associated probability density functions are shown in Figure 8.4. Note that the ground state probability density is maximum at the centre of the potential; this is the opposite of the classical case. Excited-state solutions have two maxima in their probability density which move apart as the energy increases. In the limiting case, $E \gg \hbar\omega$ and the maxima in probability density are located at the edges of the harmonic well. This situation is shown for the $n = 40$ excited state in Figure 8.4. The oscillations eventually become so rapid that they cannot be resolved and we recover the classical probability distribution.

The zero-point energy of the quantum harmonic oscillator is incredibly important physically. Although somewhat beyond the scope of this unit, it relates to one of the first points that we mentioned in Section 1: the quantisation of electromag-

netic radiation. In the full quantum description of light (and how it interacts with atoms), electromagnetic fields are represented by excitations of a quantum harmonic oscillator and the zero-point energy is manifest as *vacuum fluctutations* – effectively photons popping in and out of existence. These zero-point fluctuations are required to kick-start all spontaneous emission processes.

Chapter 9

Dirac notation

So far we have looked at how solve the TISE in one dimension by writing down eigenfunctions that depend on one variable, x. Now we will look at an equivalent, but much more powerful, way to write quantum states as vectors rather than explicit functions. The formalism we will use is called *Dirac notation* after the British physicist and Nobel laureate Paul Dirac. Using the finite square well as an example, we will only scratch the surface of this incredibly powerful method; nevertheless we can begin to appreciate its capabilities.

9.1   Kets

We can write down a set of eigenfunctions that describe the bound states of an electron in a finite square well:

$$\{\psi_1, \psi_2, \psi_3, \psi_4\}. \tag{9.1}$$

In this case there are four bound states with associated quantum numbers $n = 1, 2, 3, 4$. The eigenfunctions are mutually orthogonal and are normalised.

Now we define a vector to represent the wavefunction of the electron. The vector is composed of complex amplitudes a_n describing the contribution from each of the eigenfunctions that the electron may inhabit:

$$|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix}. \tag{9.2}$$

This vector is called a *ket* or often a *state vector*. If we prepare the electron in the

first excited state, $n = 2$, the ket to describe it is:

$$|\psi\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \equiv |\psi_2\rangle \equiv |2\rangle. \tag{9.3}$$

We can recover the eigenfunction by premultiplying the state vector by a matrix containing the set of basis functions:

$$\psi = \begin{pmatrix} \psi_1 & \psi_2 & \psi_3 & \psi_4 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \psi_2. \tag{9.4}$$

So, if we know what the set of basis functions is (which we do – it's the set of eigenfunctions we found by solving the TISE) the the descriptions using ψ and $|\psi\rangle$ are equivalent.

So, for an electron in any eigenstate of the system with quantum number n we write

$$|\psi\rangle = |\psi_n\rangle \equiv |n\rangle. \tag{9.5}$$

Note that the quantum numbers required in the ket are specific to the particular system that we're describing (in this case, the finite square well); in the second half of the unit, you will see that it changes for other systems. To form a complete description, the ket must specify the value of all the quantum numbers required to describe the system, just as the eigenfunctions do.

9.2 Bras

We define a *bra* to be the complex conjugate of the transpose of a ket:

$$\langle\psi| = \begin{pmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{pmatrix}. \tag{9.6}$$

We can take the dot product (known as the inner product) between a bra and a ket to form a bracket. For our electron prepared in $n = 2$, $\langle\psi| = \langle 2|$ and

$$\langle 2|2\rangle = \begin{pmatrix} 0 & 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 1. \tag{9.7}$$

Exercise Find the inner product between the first and second excited states.

$$\langle 2|3 \rangle = \begin{pmatrix} 0 & 1 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = 0$$

So we see that inner products express the orthonormality or our eigenfunctions:

$$\langle \psi_i | \psi_j \rangle = \langle i|j \rangle = \delta_{ij} \tag{9.8}$$

and we define

$$\langle i|j \rangle = \int \psi_i^* \psi_j dx. \tag{9.9}$$

9.3 Operators

We know that operators acting on eigenfunctions return eigenvalues and eigenfunctions,

$$\hat{p}\psi_n = p_n \psi_n. \tag{9.10}$$

A similar expression can be written for our kets:

$$\hat{P}|n \rangle = p_n |n \rangle. \tag{9.11}$$

Note that operators must be matrices for this to work (matrix × vector = scalar × vector).

The most important operator is of course that for the total energy, known as the *Hamiltonian*, $\hat{H}$. It allows us to write the TISE in Dirac notation:

$$\hat{H}|n \rangle = E_n |n \rangle \tag{9.12}$$

which is equivalent to

$$\hat{H}\psi_n = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n(x)}{\mathrm{d}x^2} + V(x)\psi_n(x) = E_n \psi_n(x). \tag{9.13}$$

We can construct the expectation values of operators in the normal way,

$$\langle H \rangle = \langle n | \hat{H} | n \rangle = \int \psi_n^* \hat{H} \psi_n dx. \tag{9.14}$$

We know that $\hat{H} | n \rangle = E_n | n \rangle$, and E_n is just a number, so we see that

$$\langle H \rangle = \langle n | \hat{H} | n \rangle = E_n \langle n | n \rangle = E_n, \tag{9.15}$$

and we have recovered the expectation value for the energy in state n.

9.4   Superposition

At the end of Chapter 4, we looked at electrons that are not in a single eigenstate but are in a linear combination of more than one. These superposition states are described naturally in our new notation:

$$| \psi \rangle = a_1 | \psi_1 \rangle + a_2 | \psi_2 \rangle + a_3 | \psi_3 \rangle + \ldots . \tag{9.16}$$

The relative magnitudes of the $|a_i|^2$ describe the weighting of each eigenfunction within the superposition. Of course, we require our superposition state to satisfy a normalisation condition:

$$\langle \psi | \psi \rangle = 1. \tag{9.17}$$

It can be shown straightforwardly (see problems) that for any orthonormal set of eigenfunctions the normalisation condition reduces to

$$|a_1|^2 + |a_2|^2 + \ldots = 1. \tag{9.18}$$

Exercise Write in ket form and in vector notation a normalised superposition state in which the amplitude of the ground state is twice that of the first excited state and all others are zero.

$$a_1 = 2a_2, \quad \text{and } a_3 = a_4 = 0, \quad \text{and } |a_1|^2 + |a_2|^2 = 1$$

$$\therefore 4|a_2|^2 + |a_2|^2 = 1 \quad \rightarrow \quad |a_2|^2 = 1/5$$

$$\therefore a_2 = \frac{1}{\sqrt{5}}, a_1 = \frac{2}{\sqrt{5}}$$

$$|\psi\rangle = \frac{2}{\sqrt{5}}|1\rangle + \frac{1}{\sqrt{5}}|2\rangle = \frac{1}{\sqrt{5}}\begin{pmatrix} 2 \\ 1 \end{pmatrix}$$

What happens if we ask how much energy an electron in a superposition state has? We use our formalism to find the expectation value of the Hamiltonian.

Exercise Find the expectation value of the Hamiltonian on the state in the previous exercise.

$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle$$

$$= \left(\frac{2}{\sqrt{5}}\langle 1| + \frac{1}{\sqrt{5}}\langle 2| \right) \hat{H} \left(\frac{2}{\sqrt{5}}|1\rangle + \frac{1}{\sqrt{5}}|2\rangle \right)$$

$$= \frac{1}{5} \left(2\langle 1| + \langle 2| \right) \left(2E_1|1\rangle + E_2|2\rangle \right)$$

$$= \frac{1}{5} \left(4E_1 + E_2 \right)$$

$$= \frac{4}{5}E_1 + \frac{1}{5}E_2 = |a_1|^2 E_1 + |a_2|^2 E_2.$$

The value we have found, $\langle \hat{H} \rangle$, tells us the mean outcome of many measurements on identically-prepared systems, but as we saw at the end of Chapter 4, each individual measurement must find the electron in one of the energy eigenstates E_1 or E_2. Nevertheless, before the measurement is made, the electron exists in both states.

Once again we see that measurement changes the state of the system and causes the electron to be found in E_1 or E_2 with probability $|a_1|^2$ and $|a_2|^2$ respectively. How this occurs is not clear. In the *Copenhagen interpretation* of quantum mechanics, measurements induce *wavefunction collapse* into a particular eigenstate. However, their is no reasoning as to why the collapse should be triggered; this is known as the *measurement problem*. Alternative explanations have been sought, for example in the *many worlds* interpretation all possible measurement outcomes occur but the universe splits into different paths when measurements are made.