# QUANTUM PHYSICS
An Introduction to Quantum Theory

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Contents

Chapter 1

Introduction

1.1 What is Quantum Physics?

Quantum physics is a catch-all term for the ideas, devices and technologies made possible by the development of quantum mechanics in the early part of the 20th century. This course concentrates on the ideas behind quantum mechanics itself, but the broader field of quantum physics encompasses everything from the science of electronic devices and lasers to the philosophical mysteries of quantum measurement theory.

Quantum mechanics is our best current theory of matter and how it interacts. Matter in this context includes everything we normally think of as particles, waves, forces, and fields. In the quantum world, these are all (more or less) the same thing.

Given an experimental set-up, quantum mechanics tells you:

1. What can be measured.

2. The possible results of any measurement.

3. The probability of obtaining each of the possible results.

The rules used to calculate the probabilities, although abstract and mathematical, are precise and unambiguous. As a practical tool, quantum mechanics presents no difficulties and has been immensely successful.

1.2 Successes and Failures of Quantum Physics

To illustrate the extraordinary power and breadth of quantum theory, here are just a few of the phenomena it can explain:

Atomic structure and spectra	Radioactivity
Properties and interactions of elementary particles	Nucleosynthesis
Semiconductor physics & devices	Laser physics
Superconductivity and superfluidity	Chemical reactions
The periodic table	Density of matter
Conductivity of copper	Strength of steel
Hardness of diamond	Stability of matter
Properties of neutron stars and white dwarfs	Fisson/fusion
Magnetism	(The human brain?)

Some of the items in the list may strike you as classical, but if you ask one or two ''why'' questions you soon find yourself running in to quantum mechanics. Take the density of matter as an example: this depends on the size of an atom, which depends on the radius of an electron orbit and hence on quantum theory. We shall see later that the radius of a Hydrogen atom, known as the *Bohr radius*, a_0, is given by

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.529 \times 10^{-10}\,\text{m}, \tag{1.1}$$

where $\hbar := h/2\pi \approx 1.05 \times 10^{-34}$ Js is Planck's constant divided by 2π. The appearance of Planck's constant leaves no doubt that quantum theory is involved.

The version of quantum theory covered in this course neglects relativistic effects and is therefore an approximation, just as Newton's laws are an approximation to special relativity. The relativistic version of quantum mechanics, called quantum field theory, is very similar in outline but mathematically more difficult.

Quantum theory as a whole (including quantum field theory) has never been known to fail. Its applications have been limited by the difficulty of solving the equations, which are only tractable for rather simple systems, so there is no guarantee that problems will never be found; but even then quantum theory would remain useful, just as Newton's laws remained useful after the advent of special relativity. There is, as yet, no good quantised theory of gravity, but whether this indicates a fundamental problem with quantum mechanics or a failure of human ingenuity is unclear.

1.3 Quantum Weirdness

The most fascinating aspect of quantum mechanics is that it provides such a strange picture of the world. If you accept this picture — and given the practical successes of the theory it is difficult not to — you are left with no choice but to make fundamental changes to your idea of reality.

The first surprise is the *wave-particle duality* of the building blocks of matter. The world is not made of waves and particles, as in classical physics, but of peculiar hybrid objects with aspects of both. Suppose, for example, that you find an electron at $\mathbf{r}_1$ at time t_1 and then at $\mathbf{r}_2$ at a later time t_2. Since the electron is supposed to be a particle, you might imagine that it travelled along some specific path $\mathbf{r}(t)$ from $\mathbf{r}_1 = \mathbf{r}(t_1)$ to $\mathbf{r}_2 = \mathbf{r}(t_2)$. According to Feynman's path-integral formulation of quantum mechanics, however, this is wrong. In a precise mathematical sense (only hinted at in this course), the electron took all possible paths from $\mathbf{r}_1$ to $\mathbf{r}_2$ at once. Even worse, the components arriving along different paths interfered like waves.

Wave-particle duality is not the only strange aspect of quantum theory. The physical state of a quantum mechanical particle-wave is described by a *wave function*, $\psi(x,t)$, analogous to the amplitude of a classical wave. Unlike a classical wave, however, $\psi(x,t)$ does not evolve according to the classical wave equation,

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \psi(x,t)}{\partial t^2}, \tag{1.2}$$

where c is the phase velocity, but according to the time-dependent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar\frac{\partial \psi(x,t)}{\partial t}, \tag{1.3}$$

where m is the mass of the particle and $V(x)$ is the potential through which it moves. The most striking feature of Schrödinger's equation is that it has an i on the right-hand side, implying that the wave function is complex. Even if, by some fluke, $\psi(x,t)$ happened to be real at $t = 0$, it would not remain real. Complex waves are common in classical physics, of course, but the complex numbers are used only to simplify the mathematics and the physical waves remain real. In quantum theory, the wave function is *really* complex.

Perhaps the most puzzling aspect of quantum mechanics is that it predicts probabilities only. In classical physics, probabilities are used to describe our lack of knowledge of a physical system: if we know nothing about how a pack of cards has been shuffled, the probability of picking any particular card, say the three of spades, is 1/52; if we know where all the cards are in advance, we can find

the three of spades every time and there is no need for probability theory. Even for a complicated system such as the air in the Albert Hall, we could, in principle, measure the positions and velocities of all the molecules and predict the future evolution using Newton's laws; the probabilistic Maxwell-Boltzmann distribution is used only because the measurement is impractical and our knowledge incomplete.

It is tempting to imagine that the probabilistic nature of quantum theory arises in a similar way, and that quantum mechanics is just a rough statistical description of some more complicated underlying reality. As in the case of the air in the Albert Hall, we use a probabilistic description (there the Maxwell-Boltzmann equation; here quantum theory) only because our knowledge is incomplete. If we could discover the values of the *hidden variables* describing the underlying reality, we could dispense with probability theory altogether.

Hidden-variable theories are not completely impossible, but Bell's theorem shows that any such theory consistent with quantum mechanics must be non-local. This means, in effect, that every object in the universe has to be inter-dependent, and that we cannot interfere in one region without affecting everything else, no matter how far away. Most physicists find this idea so unsatisfactory that they prefer to think of nature as inherently probabilistic.

These ideas are fun, but the right time to think about them (if ever) is *after* you understand the workings of quantum theory. The aim of this course is to help you focus on the basics by making quantum mechanics as prosaic, straightforward and boring as possible! If you are unwilling to wait and want to find out more about the philosophical issues now, read *Speakable and Unspeakable in Quantum Mechanics: Collected Papers on Quantum Philosophy* by J.S. Bell. As well as inventing Bell's theorem and helping demystify the philosophical mess left by Bohr and friends, Bell (who was born in Belfast in 1928 and died in 1990) was a very good writer. His book is readable and quite accessible, requiring only a minimum of mathematics.

1.4   Course Content

This course covers the experimental evidence that led to the development of quantum mechanics and provides an introduction to quantum mechanical concepts and wave mechanics.

Concepts discussed include wave-particle duality, the wave function, the uncertainty principle, the Schrödinger equation, and the thorny question of measurement in quantum theory.

Schrödinger's wave mechanics is one of several equivalent formulations of non-relativistic quantum theory. The others, Heisenberg's matrix mechanics and Feynman's path-integral theory, look very different mathematically but describe the same physics and yield identical results.

To keep the mathematics as simple as possible, the introduction to wave mechanics in the second half of the course considers only a single non-relativistic particle in one dimension. The emphasis is on quantitative understanding and the practical application of physical principles rather than mathematical formalism (which is covered in detail in Fay Dowker's Quantum Mechanics course).

1.5 Some Useful Numbers

When does quantum mechanics matter? The conventional answer is at or below atomic/molecular length scales. This section discusses some of the most important length and energy scales associated with everyday matter.

[A less conventional answer, to which I subscribe, and which is supported by the long list of quantum phenomena in Sec. 1.2, is that almost everything is quantum mechanical.]

Units

SI plus Ångstroms (Å) and electron-volts (eV):

$$1 \, \text{nm} = 10^{-9} \, \text{m}$$
$$1 \, \text{Å} = 10^{-10} \, \text{m}$$
$$1 \, \text{ps} = 10^{-12} \, \text{s}$$
$$1 \, \text{fs} = 10^{-15} \, \text{s}$$
$$1 \, \text{eV} = 1.6 \times 10^{-19} \, \text{J}$$

The electron-volt

One eV is the kinetic energy gained by an electron falling through a potential difference of 1 V: $1 \, \text{eV} = qV = e$ Coulombs $\times$ 1 Joule per Coulomb $= 1.6 \times 10^{-19} \, \text{J}$.

Lengths

EM radiation

Radio: $\lambda \approx 1\,\text{m}$
Sunlight: $\lambda \approx 500\,\text{nm}$
X-rays: $\lambda \approx 0.1\,\text{nm}$

Distance between air molecules

The ideal gas law

$$PV = Nk_BT \qquad \Rightarrow \qquad \frac{V}{N} = \frac{k_BT}{P}. \qquad (1.4)$$

If, for simplicity, every molecule is assumed to occupy a cube of side a, so that $a^3 = V/N$, this gives

$$a^3 = \frac{k_BT}{P} \approx \frac{1.38 \times 10^{-23} \times 300}{1.01 \times 10^5}$$

and hence

$$a \approx 3.5\,\text{nm}.$$

Boltzmann's constant

The version of the ideal gas law taught in schools is

$$PV = n_mRT, \qquad (1.5)$$

where n_m is the number of moles and $R = 8.314\,\text{JK}^{-1}$ is the gas constant. Since $n_m = N/N_A$, where N is the total number of molecules and N_A is Avogadro's number, this can be rewritten

$$PV = \left(\frac{N}{N_A}\right)RT = N\left(\frac{R}{N_A}\right)T = Nk_BT. \qquad (1.6)$$

The new constant $k_B := (R/N_A) \approx 1.38 \times 10^{-23}\,\text{JK}^{-1}$ is known as Boltzmann's constant. On the whole, chemists prefer to work with moles and R, while physicists prefer molecules and k_B.

Distance between atoms in molecules/solids/liquids

A typical inter-atomic distance is a few Å.

Radius of an atom

A typical atomic radius is 1 Å.
(The radius of a Hydrogen atom, the Bohr radius a_0, is 0.529 Å.)

Radius of a nucleus

A typical nuclear radius is a few $\times 10^{-15}$ m.

Radius of a proton

$\approx 8.7 \times 10^{-16}$ m.

Radius of an electron

Zero!

Energies

Thermal energy at room temperature

$k_B T \approx 1.38 \times 10^{-23} \times 300 \approx 4.14 \times 10^{-21}$ J $\approx \frac{1}{40}$ eV.

Chemical bond

The energy of a typical covalent, ionic or metallic chemical bond is a few eV.
(The van der Waals bonds between closed-shell atoms are much weaker.)

Binding energies of electrons in atoms

The energy required to strip an electron from an atom ranges from a few eV for the outermost ''valence'' electrons to thousands of eV for the innermost ''core'' electrons of heavy atoms.

Chapter 2

Light is Waves

The waves with which we are most familiar — water waves, sound waves, the standing waves on a violin string — have several features in common.

Superposition and interference: If several waves overlap, the total displacement is the sum of the displacements of each.

Diffraction: Waves spread out after emerging from a narrow ($\lesssim \lambda$) opening.

Refraction: Waves change direction at boundaries between regions where the wave speed differs.

Light does all of these things, so light is a wave. The Schrödinger equation differs from the wave equation for light, but it is also a wave equation and quantum mechanics is also a theory of waves. To set the notation and establish a common starting point, the rest of this chapter revises material from your Vibrations and Waves course.

Historical note

Descartes and Newton, working in the 17th century, thought that light was a stream of particles, like bullets. It was not until the early 19th century that Thomas Young (born a Quaker in Somerset in 1773; learnt to read at 2; spoke a dozen languages; famous Egyptologist who helped decipher hieroglyphics; successful London physician) and others showed, apparently conclusively, that light was a kind of wave. For the next century or so, it was assumed that Newton and Descartes had been wrong. It is now clear that Newton, Descartes and Young were all correct: light is both a particle and a wave.

2.1 Light Waves in Vacuum

The wave equation

Light waves in vacuum satisfy the classical wave equation,

$$\frac{1}{c^2}\frac{\partial^2 \psi(x,t)}{\partial t^2} = \frac{\partial^2 \psi(x,t)}{\partial x^2}, \tag{2.1}$$

and travel at speed c. The constancy of the speed of light underlies special relativity but does not play an important role in this course. As far as we are concerned, light waves are much like any other waves.

Travelling waves

The mathematical representation of a travelling wave moving to the right is

$$\psi(x,t) = a\cos(kx - \omega t + \phi), \tag{2.2}$$

where $k = 2\pi/\lambda$ is the wave vector, $\omega = 2\pi f$ is the angular frequency, and ϕ is the phase shift. Since

$$\frac{1}{c^2}\frac{\partial^2\big(a\cos(kx - \omega t + \phi)\big)}{\partial t^2} = -\frac{\omega^2}{c^2}a\cos(kx - \omega t + \phi)$$

and

$$\frac{\partial^2\big(a\cos(kx - \omega t + \phi)\big)}{\partial x^2} = -k^2 a\cos(kx - \omega t + \phi),$$

the travelling wave satisfies the wave equation if and only if

$$\omega^2 = c^2 k^2 \qquad \Rightarrow \qquad \omega = \pm ck. \tag{2.3}$$

Any travelling wave with ω and k are linked in this way is a valid solution. Relationships such as $\omega = \pm ck$, which link the angular frequency of a wave to its wave vector, are called *dispersion relations*.

Phase velocity

Figure 2.1 shows the travelling wave from Eq. (2.2) at time $t = 0$. Note that

$$a\cos(kx - \omega t + \phi) = a\cos(k[x - (-\phi/k)] - \omega t),$$

so there is a crest at $x = -\phi/k$ when $t = 0$.
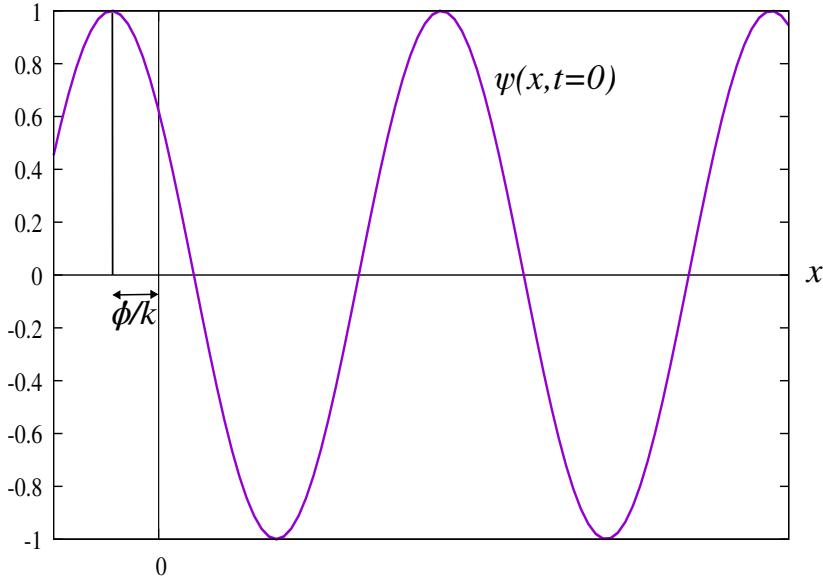
Figure 2.1: The travelling wave of Eq. 2.2 at time $t=0$.

At time t, the wave has a crest where

$$kx - \omega t + \phi = 0$$

and hence where

$$x = -\phi/k + (\omega/k)\, t.$$

This shows that the *phase velocity* v_p, which is the velocity of the wave crests, is

$$v_p = \frac{\omega}{k} = f\lambda. \tag{2.4}$$

Complex representation

Most of the time, we use the complex representation:

$$\begin{aligned}
a\cos(kx - \omega t + \phi) &= \mathrm{Re}\left(a^{i(kx-\omega t+\phi)} \right) \\
&= \mathrm{Re}\left(ae^{i\phi} e^{i(kx-\omega t)} \right) \\
&= \mathrm{Re}\left(Ae^{i(kx-\omega t)} \right),
\end{aligned} \tag{2.5}$$

where $A := ae^{i\phi}$ is known as the *complex amplitude* of the travelling wave. We usually omit the ''Re'' symbols, leaving them understood. In quantum theory, where the wave function $\psi(x,t)$ is genuinely complex, the ''Re'' symbols are not required anyway.

> **Sign conventions**
>
> In QM, a right-going travelling wave is written as $\psi(x,t) = a\cos(kx - \omega t + \phi)$. Why not $\psi(x,t) = a\cos(\omega t - kx + \phi')$ as in the Vibrations and Waves course? The two forms are equivalent if ϕ' is set equal to $-\phi$:
>
> $$a\cos(\omega t - kx + \phi') = a\cos(\omega t - kx - \phi) = a\cos(kx - \omega t + \phi).$$
>
> (The final step used the fact that $\cos\theta = \cos(-\theta)$). Why, then, do we use one form in V&W courses and another in QM courses? The reason is historical: the inventors of quantum theory *chose* to write the time dependence of the wave function as ''$-\omega t$'' and built their choice into the form of the Schrödinger equation. It would be too confusing to change this convention now.
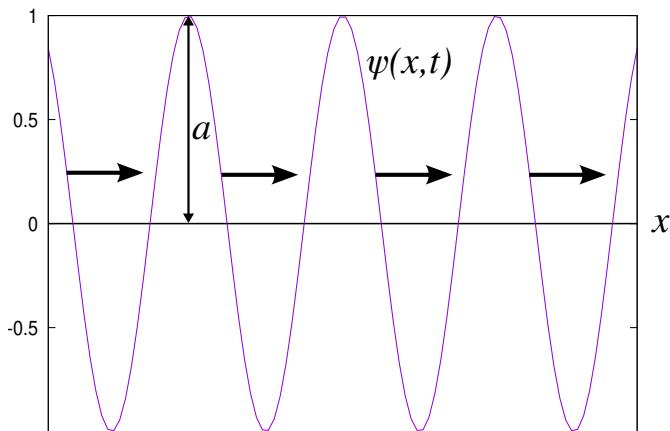
Figure 2.2: The crests of the travelling wave $\psi(x,t) = a\cos(kx - \omega t + \phi)$ move steadily to the right, so the maximum displacement is a at all points x.

Amplitude

The *amplitude* of a wave at a point x is the maximum displacement (of whatever it is that is waving) at that point. As shown in Fig. 2.2, the maximum displacement of a simple travelling wave,

$$\psi(x,t) = a\cos(kx - \omega t + \phi),$$

is equal to a at all points x.

Intensity

Waves transmit energy. The energy density (energy per unit volume) at x is proportional to the *intensity*, defined here as the square of the amplitude, at that point. For example, if

$$\psi = a \cos(kx - \omega t + \phi) = \text{Re}\left(A e^{i(kx-\omega t)}\right),$$

then
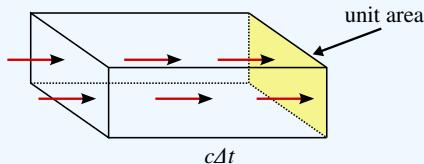
$$I = a^2 = a e^{i\phi} a e^{-i\phi} = A A^* = |A|^2. \tag{2.6}$$

The intensity of a simple travelling wave is therefore independent of position and time. For more complicated waves and interference patterns, this is no longer the case.

Eyes and most optical instruments are sensitive to I and do not detect the phase ϕ directly.

Other definitions of intensity

In other courses, you may see intensity defined as the energy striking a unit area (oriented perpendicular to the beam) per second, measured in Wm^{-2}. The diagram shows a beam of light passing through a unit area.

In time Δt, all of the light energy in the box of length $c\Delta t$ passes through the right-hand face of unit area. Hence, the energy striking a unit area in time Δt is $uc\Delta t$, where u is the energy per unit volume in the box. Dividing by the time interval Δt gives the energy striking a unit area per second, which is equal to uc. Since $u \propto a^2$ and c is a constant, both u and uc are proportional to a^2. In this course, and in quantum physics in general, intensity always means simply a^2.

Linearity

Perhaps the most important property of the wave equation (a property shared by the Schrödinger equation) is that it is linear: if $\psi_1(x, t)$ and $\psi_2(x, t)$ are solutions,

so is the linear combination $c_1\psi_1(x,t) + c_2\psi_2(x,t)$, where c_1 and c_2 are arbitrary constants. This is easy to prove by subsituting the linear combination into the wave equation and checking that it works.

Linearity is the mathematical statement of the superposition principle: if two (or more) waves evolving according to a linear wave equation move into the same region of space, they continue exactly as they would have done on their own. The total displacement (of whatever it is that is waving) is the sum of the displacements of the contributing waves, so you can see an interference pattern where the waves overlap, but they pass straight through each other unaltered.

We have already seen that a right-going travelling wave $\psi(x,t) = Ae^{i(kx-\omega(k)t)}$ is a solution of the wave equation as long as $\omega(k) = ck$. Because the wave equation is linear, an arbitrary superposition of N such travelling waves,

$$\psi(x,t) = \sum_{n=1}^{N} A_n e^{i(k_n x - \omega(k_n)t)}, \tag{2.7}$$

is also a solution. We can even generalize the sum to an integral, writing:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx-\omega(k)t)} dk. \tag{2.8}$$

The mysterious $1/\sqrt{2\pi}$ was added to make Eq. (2.8) look more like the Fourier transforms you met last year. If you wanted to, you could of course absorb the $1/\sqrt{2\pi}$ into the definition of $A(k)$.

To confirm that Eq. (2.8) is indeed a valid solution of the wave equation,

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right)\psi(x,t) = 0,$$

we plug it into the left-hand side and check if we get zero:

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right)\left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx-\omega(k)t)} dk\right)$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right) e^{i(kx-\omega(k)t)} dk$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \left(\frac{(-i\omega(k))^2}{c^2} - (ik)^2\right) e^{i(kx-\omega(k)t)} dk$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \left(-\frac{(\omega(k))^2}{c^2} + k^2\right) e^{i(kx-\omega(k)t)} dk.$$

Since $\omega(k) = ck$, the $-\frac{(\omega(k))^2}{c^2} + k^2$ factor in the integrand is always zero so the integral is also zero. The wave equation is satisfied.

If you set $t = 0$, Eq. (2.8) becomes

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k)e^{ikx} dk, \qquad (2.9)$$

which is *exactly* like the Fourier transforms you met last year. Inverting the Fourier transform gives

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x, 0)e^{-ikx} dx. \qquad (2.10)$$

This is very useful. Suppose that $\psi(x, t)$ is an arbitrary right-going complex solution of the wave equation. (We don't have to restrict its form in any other way.) From a snapshot at $t = 0$, we can use Eq. (2.10) to find the corresponding $A(k)$ and plug it into Eq. (2.8) to obtain an integral expression for $\psi(x, t)$ at any other time. This shows that any solution of the wave equation can be written as a superposition of travelling waves and provides a recipe for finding the expansion coefficients $A(k)$.

2.2 Interference

Because it is wave displacements that superpose, not intensities, the relative phases of the contributing waves matter:

pattern of relative phases (invisible) $\quad \Rightarrow \quad$ pattern of intensities (visible)

In fact, if intensities added, there would be no interference. Section 2.1 showed that the intensity of a simple travelling wave is uniform, so no matter how many travelling waves were superposed, adding their intensities would give a uniform result.

The fact that intensities, and thus energy densities, do not add is somewhat strange. You might wonder, for example, whether the total energy is conserved when two travelling waves overlap and an interference pattern is formed. Fortunately, it turns out (see question 6 on problem sheet 1 for an example) that the position average of the intensity is always equal to the sum of the intensities of the contributing waves. The total energy is therefore correct, even though the formation of the interference pattern redistributes that energy over space.
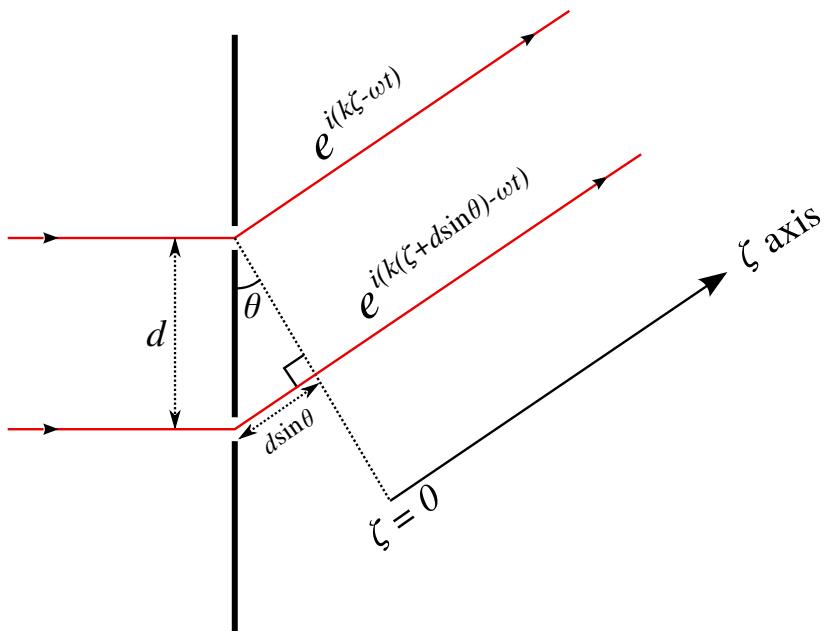
Figure 2.3: The two-slit experiment.

The phenomenon of interference becomes even stranger in quantum theory, where $I(x, t)dx$ is the probability that a measurement of the position of a particle with wave function $\psi(x, t)$ yields a result between x and $x + dx$.

Example: the two-slit experiment

The two-slit interference experiment is the standard example used to help understand the meaning of the quantum mechanical wave function and will play an important role later in this course. In fact, according to Feynman, the two-slit experiment contains ''the only mystery'' of quantum theory. (If you would like to read about this now, the first few pages of the *Feynman Lectures on Physics: Quantum Mechanics v.3* are excellent.) To prepare for the later discussion, this section reminds you of the mathematics of the two-slit interference experiment for classical waves.

The set-up is as illustrated in Fig. 2.3. Suppose that the wave emerging from the upper slit travels a distance $\zeta_t = \zeta$ before hitting a distant screen. The wave emerging from the lower slit and hitting the same point on the screen travels a slightly longer distance, $\zeta_b = \zeta + d\sin\theta$. (This formula assumes that we are interested in Fraunhofer diffraction, where the screen is so far away that the rays from the two slits are effectively parallel; if the screen is close to the slits, the assumption of parallel rays is no good, we are in the regime of Fresnel diffraction,
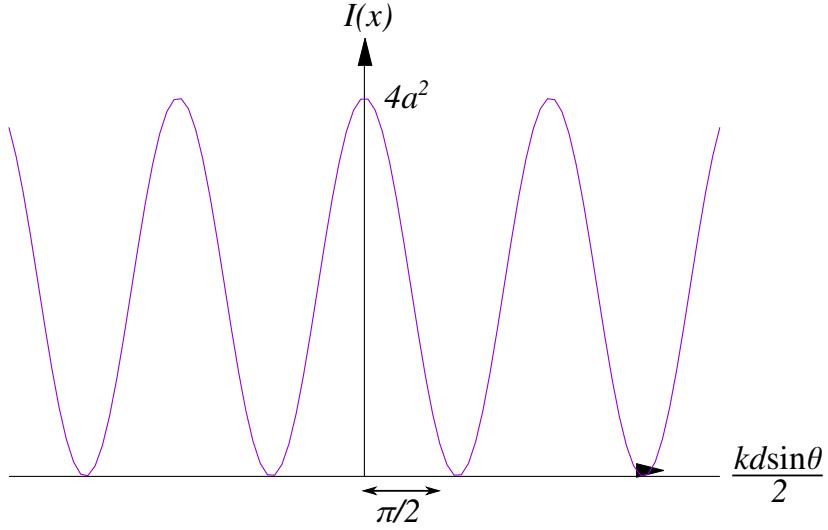
Figure 2.4: The two-slit diffraction pattern.

and the theory is harder.) Hence

$$
\begin{aligned}
\psi(\zeta, t) &= A e^{i(k\zeta_t - \omega t)} + A e^{i(k\zeta_b - \omega t)} \\
&= A e^{i(k\zeta - \omega t)} + A e^{i(k(\zeta + d\sin\theta) - \omega t)} \\
&= A \left(1 + e^{ikd\sin\theta}\right) e^{i(k\zeta - \omega t)}.
\end{aligned}
\tag{2.11}
$$

Introducing a new complex amplitude, $B = A \left(1 + e^{ikd\sin\theta}\right)$, this result becomes

$$
\psi(\zeta, t) = B e^{i(k\zeta - \omega t)}.
\tag{2.12}
$$

The intensity emerging in the ζ direction is

$$
\begin{aligned}
I = |B|^2 &= A \left(1 + e^{ikd\sin\theta}\right) A^* \left(1 + e^{-ikd\sin\theta}\right) \\
&= a^2 \left(2 + e^{ikd\sin\theta} + e^{-ikd\sin\theta}\right) && \text{(because } A = a e^{i\phi}) \\
&= 2a^2 \left(1 + \cos(kd\sin\theta)\right) && \text{(because } \cos\alpha = (e^{i\alpha} + e^{-i\alpha})/2) \\
&= 4a^2 \cos^2\left(\frac{kd\sin\theta}{2}\right) && \left(\text{because } 1 + \cos\alpha = 2\cos^2(\alpha/2)\right).
\end{aligned}
\tag{2.13}
$$

The diffraction pattern is as shown in Fig. 2.4. The first zero occurs where

$$
\frac{kd\sin\theta}{2} = \frac{\pi}{2}
\tag{2.14}
$$

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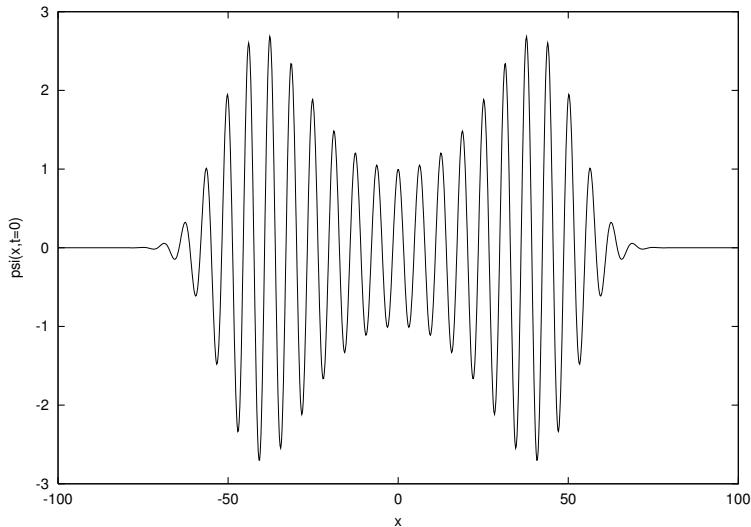
Figure 2.5: A wave packet with a clear carrier wave

and hence where

$$d \sin \theta = \frac{\pi}{k} = \frac{\lambda}{2}. \tag{2.15}$$

Since $d \sin \theta$ is the path-length difference, this is exactly what one might have expected: the zero of the interference pattern occurs when the waves from the two slits are $180°$ out of phase.

The interference pattern obtained in a real two-slit experiment is more complicated because the slits are not infinitesimally wide. The $\cos^2[(kd \sin \theta)/2]$ oscillation is still visible, but its amplitude is modulated by a relatively broad envelope, the shape of which corresponds to the diffraction pattern of a single slit of finite width.

2.3 Wave Packets

A wave packet is any group of waves. It does not have to be neat and symmetrical and centred on the origin — all that matters is that it dies away to zero far from some centre. The most interesting wave packets have a clearly distinguishable ''carrier'' wave, the amplitude of which is modulated by a much more slowly varying envelope. The wave packet in Fig. 2.5 is of this type. The short oscillations define the carrier wavelength λ_c and wave vector $k_c = 2\pi/\lambda_c$; the broader two-humped shape is the envelope. If Fig. 2.5 were the oscilloscope trace of a sound, the pitch would be the frequency of the carrier wave and the square of the envelope would give the volume as a function of time.
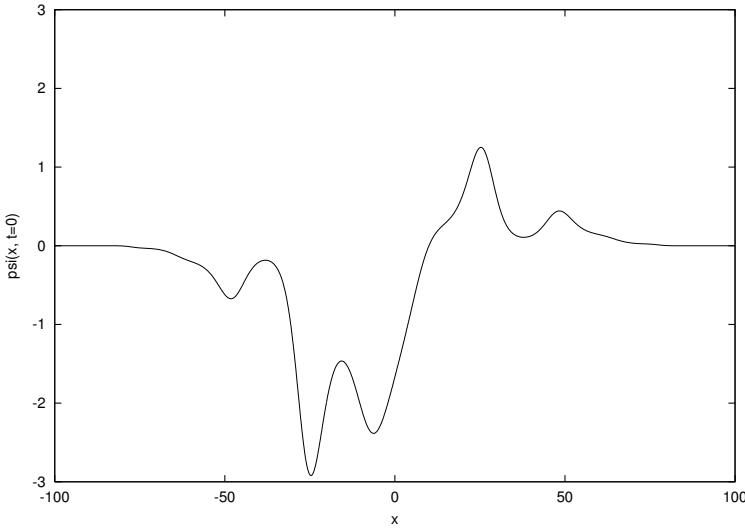
Figure 2.6: A wave packet without a clear carrier wave

Not all wave packets are so simple. Figure 2.6 shows a messier one without a clear carrier wave. A sound of this type would be a noise — a hand clap or a door closing — rather than a musical note with a clear pitch.

This observation has some interesting repercussions. Imagine, for example, that you want to make a wave packet that ''sounds like'' middle C, the frequency of which is approximately 262 Hz. If the wave packet is to have a clearly distinguishable pitch, it has to be long enough to contain many carrier-wave oscillations of this frequency. The exact number depends on how cleverly the human brain interprets sounds, but 25 might be a reasonable guess. Such a wave packet takes about $\frac{25}{262}$ s to pass by. Hence, no noise significantly shorter than 0.1 seconds can possibly sound like middle C. This is why most percussion instruments, which make very short sounds, have no discernible pitch.

As shown in Sec. 2.1, any right-going wave packet can be expressed as a superposition of right-going travelling waves:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx-\omega(k)t)} dk, \qquad (2.16)$$

where (for the classical wave equation) $\omega(k) = ck$.

Group velocity

Messy wave packets evolve in messy ways, but musical wave packets such as the one shown in Fig. 2.5 move along at a steady rate. In most cases (although not

when the waves are light in vacuum), they also spread out as they travel. It is the velocity of the envelope, not the velocity of the waves within it, that corresponds to the velocity of a QM particle represented as a packet of matter waves.

Suppose that the dispersion relation is $\omega = \omega(k)$. We have already seen that the crests inside a musical wave packet with carrier wave vector $k_c = 2\pi/\lambda_c$ move at the phase velocity $v_p = \omega_c/k_c$, where $\omega_c = \omega(k_c)$. The envelope of the wave packet moves at a different speed, known as the *group velocity*:

$$v_g = \left.\frac{d\omega}{dk}\right|_{k=k_c}. \tag{2.17}$$

You met this formula the Vibrations and Wave course last year, although it may not have been derived there. In case you are interested, a derivation is included below.

Before trying the derivation, however, let's look at some examples.

Light

Dispersion relation: $\omega = ck$.

$$v_p = \frac{\omega}{k} = c, \qquad\qquad v_g = \frac{d\omega}{dk} = c.$$

The crests within the packet move at the same speed as the envelope.

Quantum mechanical particle-waves

Dispersion relation: $\omega = \hbar k^2/(2m)$.

$$v_p = \frac{\omega}{k} = \frac{\hbar k}{2m}, \qquad\qquad v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m},$$

The crests within the wave packet move more slowly than the envelope.

Large, gravity-dominated, deep-ocean waves

Dispersion relation: $\omega = \sqrt{gk}$.

$$v_p = \frac{\omega}{k} = \sqrt{\frac{g}{k}}, \qquad\qquad v_g = \frac{d\omega}{dk} = \frac{1}{2}\sqrt{\frac{g}{k}}.$$

The crests within the wave packet move more quickly than the envelope.

Notice that the phase velocity may be larger or smaller than the group velocity. If the phase velocity is larger than the group velocity, the crests within a wave packet travel more quickly than the envelope, appearing at the back, growing as they move forward, and then dying away at the front; if the phase velocity is smaller than the group velocity, the crests travel more slowly than the envelope, appearing at the front and dying away at the back.

Derivation of the group velocity formula

You already know that the envelope of a ''musical'' wave packet (that is, a wave packet containing a narrow range of k vectors centred on the carrier wave vector k_c) travels at the group velocity $v_g = d\omega/dk|_{k_c}$ but may not have been told why. In case you are interested, a proof based on the idea of Fourier superposition is included below.

Consider a musical wave packet expressed as a superposition of travelling waves:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i[kx - \omega(k)t]} dk.$$

Since the wave packet is musical, the amplitude $A(k)$ is sharply peaked at k_c and very small when k is far from k_c. The value of the integral is therefore dominated by contributions from values of k close to k_c. This allows us to approximate $\omega(k)$ using the first two terms of a Taylor series about k_c:

$$\omega(k) \approx \omega(k_c) + \left.\frac{d\omega}{dk}\right|_{k=k_c} (k - k_c) = \omega_c + v_g(k - k_c),$$

where $v_g := d\omega/dk|_{k=k_c}$. The expression for $\psi(x,t)$ then becomes:

$$\begin{aligned}
\psi(x,t) &\approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i[kx - (\omega_c + v_g(k-k_c))t]} dk \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(k_c x - \omega_c t) + i(k-k_c)(x - v_g t)} dk \\
&= e^{i(k_c x - \omega_c t)} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(k-k_c)(x - v_g t)} dk.
\end{aligned}$$

The exponential prefactor is the carrier wave with wave vector k_c and angular frequency $\omega_c = \omega(k_c)$, while the integral gives the shape of the envelope. The important point is that the envelope is some function (which I shall call χ) of $x - v_g t$ only:

$$\psi(x,t) \approx e^{i(k_c x - \omega_c t)} \chi(x - v_g t).$$

This means that the envelope has the same shape — the shape of $\chi(x)$ — at all times. As t increases, this frozen shape simply moves along at velocity v_g.

The only approximation in the above derivation was the replacement of $\omega(k)$ by the first two terms of a Taylor series. This approximation is exact if the dispersion relation is linear (as it is for light waves, where $\omega = ck$) and good whenever the dispersion relation is close to linear over the range of wave vectors contributing to

the wave packet. If the dispersion relation is not quite linear, the neglected higher-order terms cause the wave packet to smear out as it moves along. The wider the spread of wavelengths in the wave packet, the more rapidly this smearing (called dispersion) occurs.

Chapter 3

Light is Particles

3.1   Detecting Individual Photons

Light always arrives in ''packets'' called photons, the detection of which is nowadays routine. The *quantum efficiency* of a detector is the fraction of incident photons registered.

Figure 3.1 helps illustrate how quantum efficiency can be measured. The six electronically-generated panels illustrate the gradual formation of an image as increasing numbers of photons are collected by an idealised camera in which every photon is detected and produces a bright spot. Because photons arrive one by one, images made with low photon numbers look like collections of dots, with the overall pattern emerging gradually as the number of dots increases.

By shining a known number of photons into a real camera and comparing the image formed to pictures like these, one can establish the fraction of photons detected. If, for example, the image created with 9.3×10^5 photons looks like image C, which an ideal camera would produce with only 9.3×10^4 photons, the quantum efficiency is about 10%.

Similar experiments can be managed with the human eye, by asking someone to look at a projector emitting a known number of photons per second. If one assumes that the eye forgets about photons that arrived more than, say, $0.2\,\mathrm{s}$ ago (which is about how long it takes for a human to register than an image has changed), one can convert the number of photons per second into a number of photons per image, and thus obtain a rough estimate of the quantum efficiency.

The results are quite surprising:

(i) The quantum efficiency of a human eye is about 5% at low light levels.
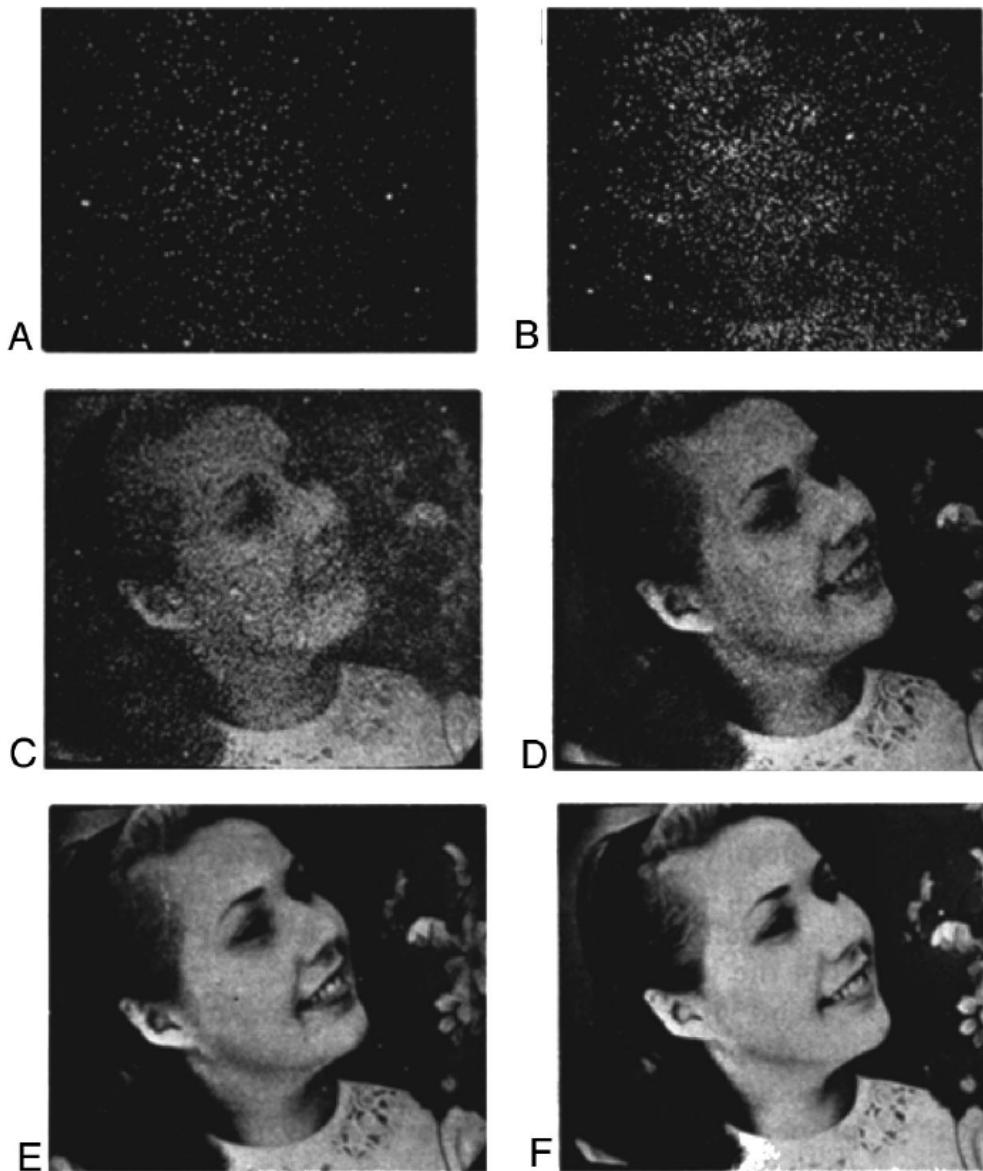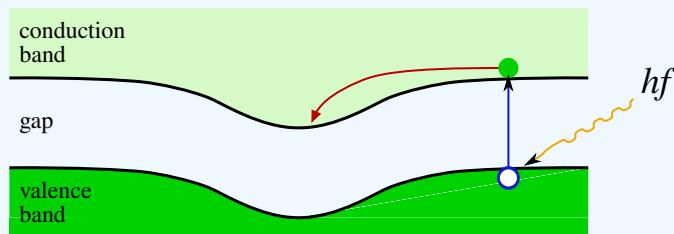
Figure 3.1: Images of a woman with flowers, as used by Rose in his article in *Physics Today* **42**, 24 (1989). The 6 images were made (electronically) using varying numbers of dots: A, 3×10^3; B, 1.2×10^4; C, 9.3×10^4; D, 7.6×10^5; E, 3.6×10^6; F, 2.8×10^7.

(ii) The quantum efficiency of photographic film is somewhat lower — typically less than 1%.

(iii) The quantum efficiency of a charge-coupled device (a ''CCD'', as found in a digital camera) ranges from 50–90%.

Charge-coupled devices

In a semiconductor, there is an energy gap between the filled electronic states, known as the valence band, and the empty electronic states, known as the conduction band. When a photon of sufficient energy is absorbed, it can excite an electron across this gap, out of the valence band and into the conduction band. In a CCD camera, voltages applied to conducting gates are used to apply a corrugated potential to the semiconductor, creating a huge array of tiny wells for electrons, several per pixel. As illustrated in the figure below, an electron excited by a photon falls into the nearest well, where it sits, perhaps for hours, until it is read out. The read out is accomplished by applying voltages to the gates to make the stored electrons ''click'' over, well by well, to the edge of the camera, where they are collected and counted. For inventing the CCD at AT&T Bell Laboratories in 1969, Boyle and Smith were awarded (part of) the 2009 Nobel Prize in Physics.

A photon of energy hf excites an electron from the valence band of a semiconductor to the conduction band. The electron then falls into the potential well to its left.

3.2 The Photoelectric Effect

The photoelectric effect is the emission of electrons when a beam of light strikes the surface of a solid. The photoelectric effect played an important role in the development of quantum mechanics and is still important today, although for
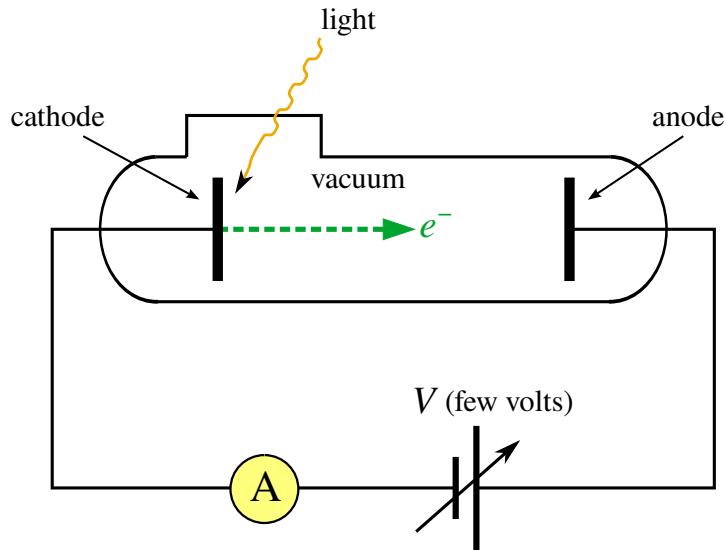
Figure 3.2: The apparatus used by Lenard in 1902 to observe the photoelectric effect.

different reasons. Photoemission is now used to investigate the nature of the electronic energy levels inside solids. Inverse photoemission, in which photons are emitted when a beam of electrons strikes the surface, is also used.

A diagram of the apparatus Lenard used to observe the photoelectric effect in 1902 is shown in Fig. 3.2. A beam of light shines through a window into a vacuum chamber, where it hits a metallic cathode. The photons kick electrons out of the cathode (a *cathode* is any electrode that emits electrons), some or all of which move through the vacuum chamber to the *anode* (any electrode that absorbs electrons), causing a current to flow through the ammeter. By applying a voltage V between the anode and the cathode, the fraction of electrons collected can be altered. For simplicity, we assume that the cathode and anode are made of the same metal (photoemission happens for non-metals also, but the cathode and anode must conduct electricity if a current is to be measured). The dependence of the current on V at fixed photon wavelength is shown in Fig. 3.3.

Observations

(a) When V is large and positive, the current I saturates at I_{max}:

$$I_{max} \propto \text{light intensity}.$$

The obvious interpretation is that the current saturates when the electric field due to the applied potential V is strong enough to guide all of the pho-
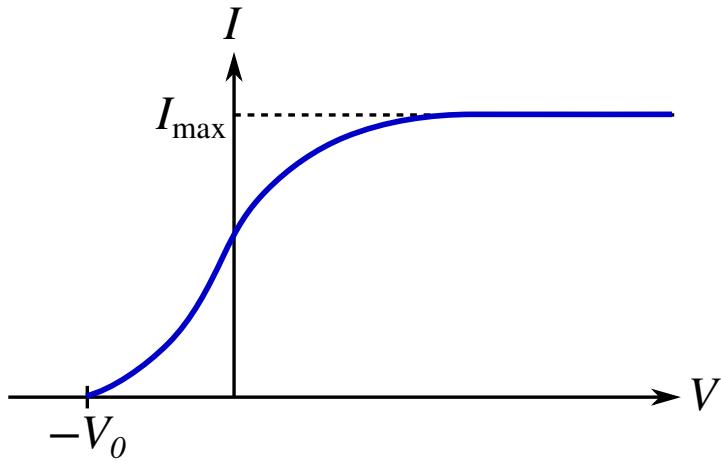
Figure 3.3: The current I measured by the ammeter as a function of the applied voltage V.

toemitted electrons to the anode, from where they flow back to the cathode through the ammeter. If every photoemitted electron is collected, increasing V cannot increase the current further.

(b) When $V < -V_0$, the current $I = 0$. The potential V_0 is known as the *stopping potential*.

The interpretation is that, at $V = -V_0$, only the most energetic photoemitted electrons are able to climb the potential barrier of height eV_0 to the anode.

$$\text{Maximum KE of emitted electrons} = \frac{1}{2}mv^2 = eV_0. \qquad (3.1)$$

Observations (a) and (b) have plausible classical explanations (although (b) is already strange: why such a sharp cut-off?). The following three observations are very hard to explain using classical physics.

(c) No delay is seen between the beginning of the illumination and the observation of the current.

The classical picture is that light energy arrives smoothly and the cathode warms up steadily until it becomes hot enough to emit electrons. One would not expect electron emission to begin immediately, especially when the light intensity is low.

(d) There is no light intensity threshold. The maximum current I_{max} is always proportional to the intensity, no matter how low the intensity.
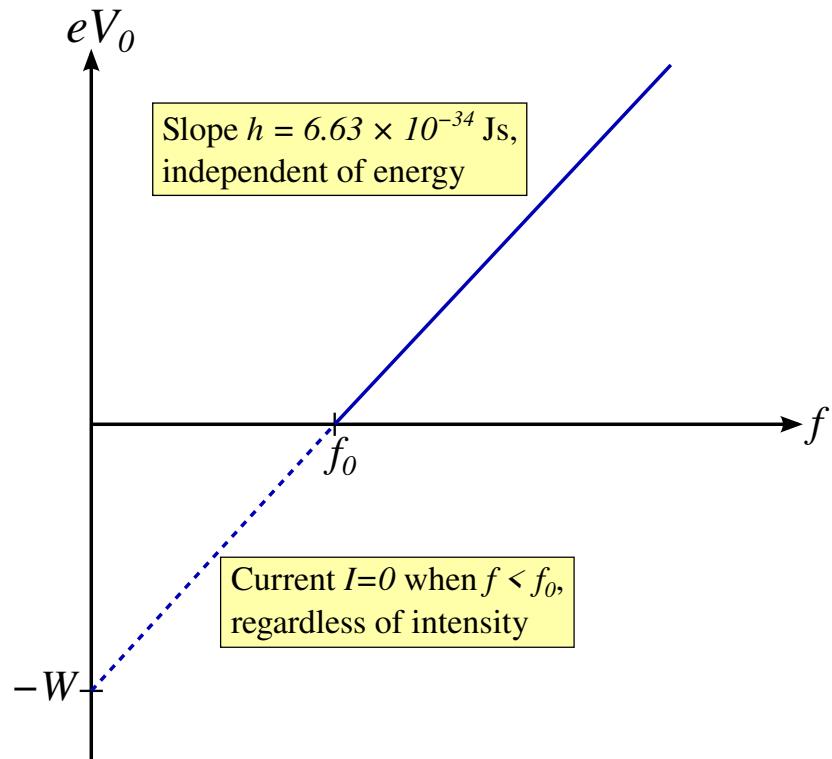
Figure 3.4: The relationship between the stopping potential V_0 and the photon frequency f.

In the classical picture, if the intensity were very low, one would not expect the cathode to warm up enough to emit electrons.

(e) The stopping potential V_0 depends on the metal and the photon frequency f, but *not* on the light intensity.

According to classical physics, if the intensity were to increase, the cathode would get hotter and the emitted electrons would have more kinetic energy. The stopping potential would therefore increase.

The measured relationship relation between V_0 and f is as shown in Fig. 3.4. The equation describing this graph is

$$eV_0 = hf - W. \tag{3.2}$$

The intercept $-W$ depends on the metal used for the cathode, but the slope $h \approx 6.63 \times 10^{-34}$ Js is universal, independent of cathode material and light intensity.
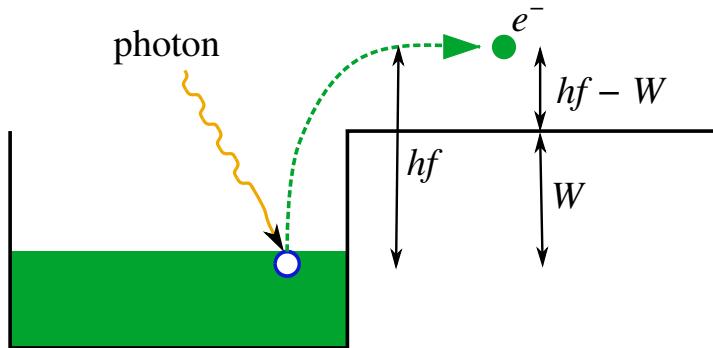
Figure 3.5: Einstein's explanation of the photoeletric effect.

Einstein's simple but revolutionary explanation

- W, the *work function*, which is typically a few eV, is the minimum energy required to kick an electron out of the metal.

- Light arrives as packets/photons/quanta of energy $hf = \hbar\omega$.

- There is no delay or threshold intensity because one photon can kick out one electron.

- Figure 3.5 illustrates Einstein's idea and shows how the principle of conservation of energy leads to

$$hf - W = \frac{1}{2}mv_{max}^2. \qquad (3.3)$$

Since, from Eq. (3.1), $\frac{1}{2}mv_{max}^2 = eV_0$, it follows that

$$eV_0 = hf - W,$$

which is Eq. (3.2).

3.3 The Production of X-Rays

X-rays, first observed by Röntgen in 1895, consist of penetrating electromagnetic radiation of wavelength $10^{-12} - 10^{-9}$ m. (For comparison, a typical visible photon has wavelength $\approx 500 \times 10^{-9}$ m.) X-rays are emitted when electrons of energy $10^3 - 10^5$ eV strike an anode made of atoms with a fairly high atomic number Z. The production of X-rays is the inverse of the photoemission process in which
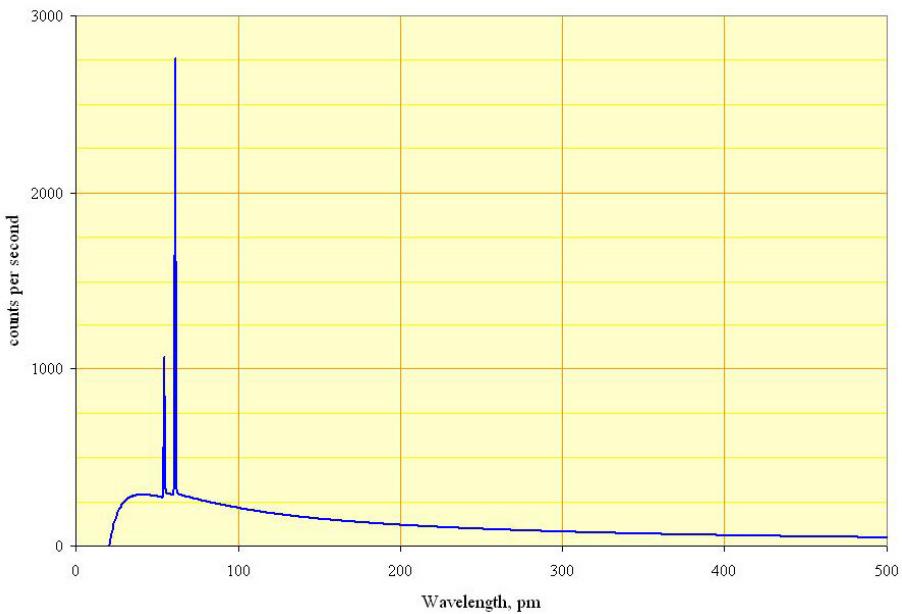
Figure 3.6: The spectrum of X-rays emitted when electrons of energy 60 keV strike a rhodium target (https://en.wikipedia.org/wiki/Bremsstrahlung).

photons strike a solid and electrons are emitted, although the photon energies involved are much higher than those used in photoemission experiments.

The intensity spectrum of the X-rays produced when electrons of energy 60 keV strike a rhodium target (rhodium is a transition metal with $Z = 45$) is shown in Fig. 3.6.

- The spikes depend on the anode material and correspond to transitions between atomic energy levels (which will be discussed later in this course). The incoming electron knocks an electron out of an atomic core state, leaving a hole that is later filled by an electron dropping down from a higher atomic energy level. The energy released, which is equal to the difference between the two atomic energy levels involved, is emitted as an X-ray photon.

- More interesting is the smooth background of bremsstrahlung (German for ''braking radiation'') emitted by the incoming electrons as they slow down after entering the anode. Maxwell's equations of electromagnetism predict that any accelerating/decelerating charge should emit radiation, so the existence of bremsstrahlung can be understood without invoking quantum

theory. What cannot be understood is the sharp *material-independent* cut-off wavelength λ_{min}, below which no radiation is emitted. Measurements show that λ_{min} is related to the energy E of the incoming electrons by

$$\lambda_{min} = \frac{hc}{E}, \tag{3.4}$$

where the constant $h \approx 6.63 \times 10^{-34}$ Js is exactly as in the photoelectric effect. For the experiment shown in Fig. 3.6, where $E = 60$ keV, this gives

$$\lambda_{min} = \frac{6.63 \times 10^{-34} \times 3.00 \times 10^8}{60 \times 10^3 \times 1.60 \times 10^{-19}} \approx 2.07 \times 10^{-11} \text{ m}.$$

Since $c = f\lambda$, the minimum wavelength implies a maximum frequency, f_{max}, given by

$$\frac{c}{f_{max}} = \frac{hc}{E}$$

and hence

$$hf_{max} = E. \tag{3.5}$$

The quantum mechanical explanation of the wavelength cut-off is obvious: an electron of energy E cannot produce a photon of energy $hf > E$. (The work function W is too small to be noticeable in these very high-energy experiments.)

3.4 Planck's Constant and Black-Body Radiation

(Not examinable)

Planck introduced his new constant h in 1900, before any of the experiments mentioned so far, as part of an attempt to understand black-body radiation (BBR). The theory of BBR is covered in detail in the statistical physics course later this year, but the subject is so interesting that I wanted to include a preview here.

What is black-body radiation?

Imagine a well-insulated oven with a very small hole from which electromagnetic radiation can leak out. The photons inside the oven make many collisions with the walls before escaping through the hole and have plenty of time to reach thermal equilibrium at the oven temperature T. Just as with the Maxwell-Boltzmann distribution of molecular speeds in a gas, the radiation in the oven (and hence the radiation emitted) is found to have a *universal* spectrum that depends only on the temperature of the oven. Expressed mathematically, this means that the energy
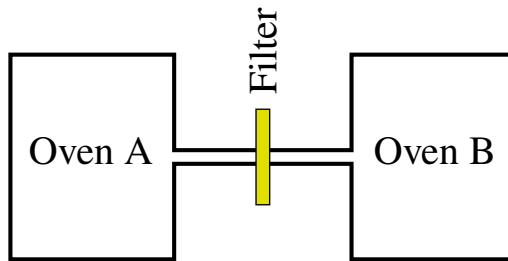
Figure 3.7: Two ovens joined by a narrow tube with a frequency selective filter.

per unit volume in the frequency range f to $f + df$ can be written as $U(f, T)df$, where the function $U(f, T)$ is independent of the material from which the oven is made or how it is constructed. To the extent that other hot objects act like black bodies (and many do), this explains why you can tell the temperature from the colour of the glow alone, without knowing what the object is made of.

Why is a glowing oven called a black body? Photons entering the oven via the tiny hole have to make so many collisions before re-emerging that they are almost certain to be absorbed first. The (hole in) the oven is therefore an ideal absorber as well as an ideal emitter.

Black-body radiation and the second law of thermodynamics

The fact that all black bodies of the same temperature emit identical radiation seems surprising at first. One way to see that it must be true is to use the second law of thermodynamics, which says, more or less, that there is no free lunch. More precisely, the Clausius formulation of the second law states that heat cannot flow spontaneously from a colder to a hotter object. If it did, the resulting temperature difference could be used to drive a heat engine and we could get unlimited energy for nothing.

How does the second law relate to BBR? Suppose that we were able to find two ovens, A and B, with different black-body spectra. We could then choose a frequency f and temperature T at which the energy density in A was greater than the energy density in B. If we connected the two ovens together via a filter that only passed electromagnetic radiation of that frequency, as shown in Fig. 3.7, there would be a net energy flow from oven A to oven B. A temperature difference would be generated spontaneously, heat would flow from the colder oven to the hotter oven, and the world's energy problems would be solved.
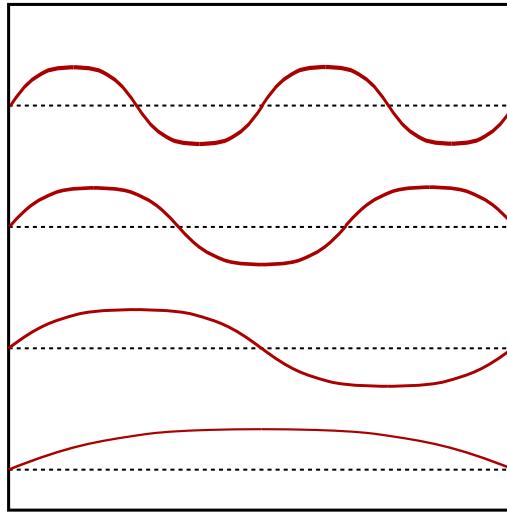
Figure 3.8: Electromagnetic standing waves in a cavity.

Examples of black-body radiation

- Heat from an oven or fridge open a crack.

- Photons created deep within the sun are scattered huge numbers of times and have plenty of opportunity to reach thermal equilibrium before emerging. The sun is an almost perfect black-body emitter at about 6000K.

- The cosmic microwave background is radiation left over after the decoupling of matter and radiation in the early universe. Although the cosmic microwave background has been cooled by the expansion of the universe since decoupling, its spectrum still has an almost perfect black-body form.

Theoretical difficulties

Physicists at the end of the 19th century thought they knew how to calculate the spectrum of BBR. As illustrated in Fig. 3.8, electromagnetic standing waves in a cavity can have various wavelengths (and hence frequencies $f = c/\lambda$), which are set by the cavity size. The possible standing waves can be listed and the number $N(f)df$ with frequencies in the range f to $f + df$ worked out. (You will go through the calculation in the statistical physics course.) For a large enough three-dimensional cavity, the result is that

$$N(f)df = \frac{8\pi f^2 df}{c^3} \tag{3.6}$$
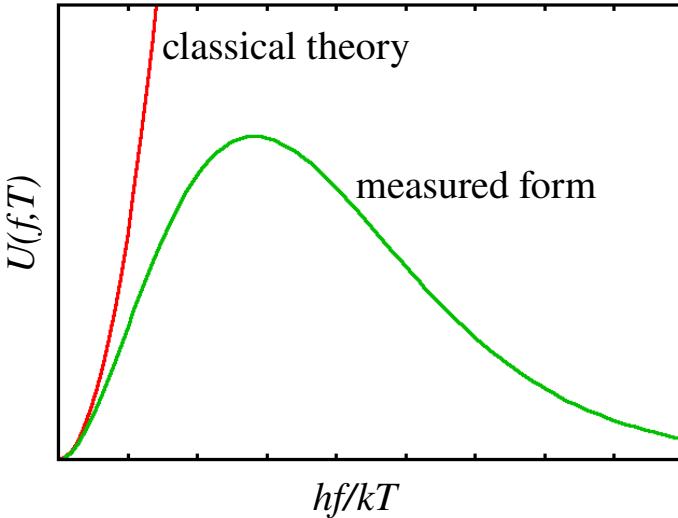
Figure 3.9: Comparison of the measured black-body spectrum and the classical Rayleigh-Jeans result, $U(f,T) = 8\pi f^2 kT/c^3$.

per unit volume of the cavity.

According to the classical theory of electromagnetism, every standing wave acts like a simple harmonic oscillator, and the mean energy of a classical harmonic oscillator at temperature T is known to be kT. Thus, the energy spectrum ought to be

$$U(f,T)df = kT \times \frac{8\pi f^2}{c^3} df. \tag{3.7}$$

This function, known as the Rayleigh-Jeans spectrum, is shown in Fig. 3.9, compared with the experimentally measured spectrum. The agreement is good at low frequencies, but the Rayleigh-Jeans formula predicts that the energy per unit frequency carries on rising as the frequency rises. Since there is no upper limit on the frequency (no lower limit on the wavelength of the waves that fit into the box), the total energy per unit volume is infinite! This theoretical disaster was christened the *ultra-violet catastrophe*.

Planck was able to fix the problem and reproduce the experimentally observed spectrum exactly by making the ad-hoc assumption that the walls of the cavity and the electromagnetic standing waves within the cavity could only exchange energy in chunks of size hf. (Nowadays, of course, we call these chunks photons.) If we accept this assumption, which much have seemed pretty wild at the time, the possible energies E of the standing wave of frequency f are

$$0, \quad hf, \quad 2hf, \quad 3hf, \quad \ldots.$$

Actually, this is slightly wrong: we now know that the allowed energies are $(n + \frac{1}{2})hf$, where $n = 0, 1, 2, \ldots$ and the extra $\frac{1}{2}hf$ is the *zero-point energy*. Fortunately, as you can check for yourself, the addition of the zero-point energy does not affect the form of the function $U(f, T)$ derived below.

Planck knew from classical statistical mechanics that the probability that a physical system at temperature T has energy E is $Ce^{-E/kT}$, where C is a constant. The value of C can be found from the condition that the system always has *some* energy, so the probabilities must add up to one:

$$1 = C \sum_{n=0}^{\infty} e^{-nhf/kT}.$$

The sum is a geometric series with first term $a = 1$ and ratio $r = e^{-hf/kT}$. Since $\sum_{n=0}^{\infty} ar^n = a/(1-r)$, it follows that $C = (1-r)/a = 1 - e^{-hf/kT}$. The probability p_n that the standing wave of frequency f has energy nhf is therefore

$$p_n = (1 - e^{-hf/kT}) e^{-nhf/kT}.$$

The *mean* energy $\langle E_f \rangle$ in the standing wave of frequency f is

$$\langle E_f \rangle = \sum_{n=0}^{\infty} (nhf) p_n = hf(1 - e^{-hf/kT}) \sum_{n=0}^{\infty} ne^{-nhf/kT}.$$

This series can also be evaluated (hint: $\sum_{n=0}^{\infty} ne^{-nx} = -\frac{d}{dx} \sum_{n=0}^{\infty} e^{-nx}$), giving

$$\langle E_f \rangle = hf(1 - e^{-hf/kT}) \times \frac{e^{-hf/kT}}{(1 - e^{-hf/kT})^2} = \frac{hf}{e^{hf/kT} - 1}.$$

Since the number of standing waves per unit volume is $8\pi f^2 df / c^3$ and the mean energy per standing wave is $\langle E_f \rangle$, the total energy in the frequency range f to $f + df$ per unit volume of the cavity must be

$$U(f, T)df = \frac{8\pi f^2 df}{c^3} \times \frac{hf}{e^{hf/kT} - 1}. \tag{3.8}$$

If h is set to 6.63×10^{-34} Js, this form fits the experimentally measured spectrum exactly.

If the photon energy hf is much smaller than the thermal energy kT, expanding the exponential in powers of the small parameter hf/kT gives

$$\frac{hf}{e^{hf/kT} - 1} \approx kT$$

and

$$U(f,T)df \approx \frac{8\pi f^2 kT df}{c^3},$$

as in the Rayleigh-Jeans law. At high frequencies, however, when $hf \gg kT$, the atoms in the walls do not have enough energy to make a photon of energy hf and the electromagnetic standing wave of frequency f is not excited. This explains why the Planck formula for the energy density drops to zero at high frequency, fixing the ultra-violet catastrophe.

(In the Structure of Matter course, you will learn that the vibrations of oxygen and nitrogen molecules do not contribute to the heat capacity of air at room temperature because the quantum of energy required to excite the vibrations is $\gg kT$. The similarity to Planck's explanation of BBR is obvious.)

Planck's achievement was remarkable, but it is not clear that he took the idea of quantisation as far as Einstein. He understood that the mechanism of energy exchange between the oven walls and the electromagnetic standing waves was chunky, but did not seem to realise that this might be because of the chunkiness of the electromagnetic field itself.

3.5   The Planck and De Broglie Equations

The last few sections of these notes were meant to convince you that photons are particles with energy

$$\boxed{E = hf = \hbar\omega \qquad \text{(Planck's equation)}} \tag{3.9}$$

Special relativity tells us that the energy and momentum of a relativistic particle are related by

$$E^2 = p^2 c^2 + m^2 c^4, \tag{3.10}$$

where m is the rest mass. Since photons have $m = 0$, it is reasonable to guess that their energy and momentum are related by

$$E^2 = p^2 c^2 \qquad \Rightarrow \qquad E = pc. \tag{3.11}$$

(Strictly, of course, this should be $E = |pc|$, since E is always positive but p is negative if the photon is moving in the $-x$ direction.)

Students sometimes argue that, since momentum is mv and photons have $m = 0$, photons cannot have momentum. This argument is wrong because the Newtonian

formula $p = mv$ only applies when $v \ll c$. For relativistic massive particles, the definition is

$$p = m\gamma v = \frac{mv}{\sqrt{1 - v^2/c^2}}.$$ (3.12)

Photons have $m = 0$ and $v = c$, so the numerator and denominator are both zero and the ratio is undefined. This leaves open the possibility that photons may have momentum even though they do not have rest mass. The formula $E = pc$ derived above from Planck's law can also be obtained directly from the classical theory of electromagnetism and was known long before the arrival of quantum theory.

Combining Eqs. (3.9) and (3.11) gives

$$hf = pc \qquad \Rightarrow \qquad p = \frac{hf}{c}$$ (3.13)

and hence

$$p = \frac{h}{\lambda} = \hbar k \qquad \text{(The de Broglie equation)}$$ (3.14)

In fact, as we shall see in Chapter 4, it turns out that Eqs. (3.9) and (3.14) apply to *all* particles, not just photons.

Some of the original experimental evidence in favour of the hypothesis that photons have momentum $p = h/\lambda$ is discussed in the next section of these notes. Compelling recent evidence is obtained every day at CERN, where the tracks of photons created in particle collisions are measured and the momentum conservation law does not work unless the photon momentum is taken into account. More generally, whenever photons are absorbed or reflected by an object, momentum is transferred and the object feels a force. Radiation therefore exerts a pressure, which is small but measureable.

3.6 Compton Scattering

In 1923, Compton decided to study the scattering of X-rays ($\lambda = 0.071\,\text{nm}$, $f = c/\lambda = 4.23 \times 10^{18}\,\text{Hz}$, $E = hf = 17.5\,\text{keV}$) from graphite. According to classical physics, X-rays are electromagnetic travelling waves of frequency $f = c/\lambda$. The fields associated with these waves exert forces on the electrons, causing them to vibrate at the same frequency. Since oscillating charges emit radiation, Compton expected to see scattered radiation at frequency f and perhaps also a few harmonics such as $2f$ or $3f$.

What he actually saw is illustrated in Fig. 3.10. As well as the scattered radiation
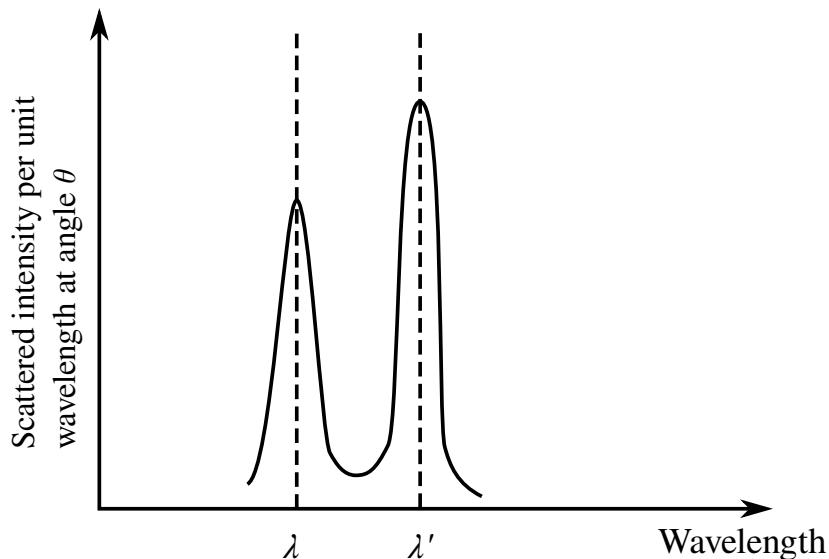
Figure 3.10: The intensity of Compton-scattered X-rays per unit wavelength as a function of wavelength.
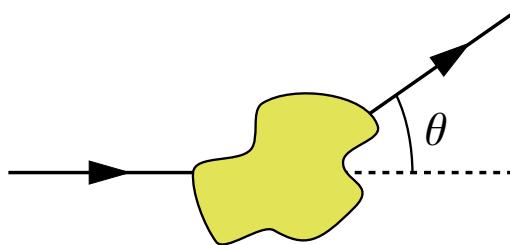
Figure 3.11: The Compton scattering angle.

of frequency f and wavelength λ predicted by classical theory, he also saw scattered X-rays of longer wavelength λ' (lower frequency f'). It was like shining a blue light at a mirror and seeing it come back red! The wavelength shift depended on the scattering angle θ illustrated in Fig. 3.11. In fact, careful measurements showed that

$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta),\qquad(3.15)$$

where m is the mass of an electron.

Compton found a simple and convincing explanation of his results based on the following assumptions:

- X-rays scatter from electrons (hence the appearance of the electron mass m in Eq. (3.15)).
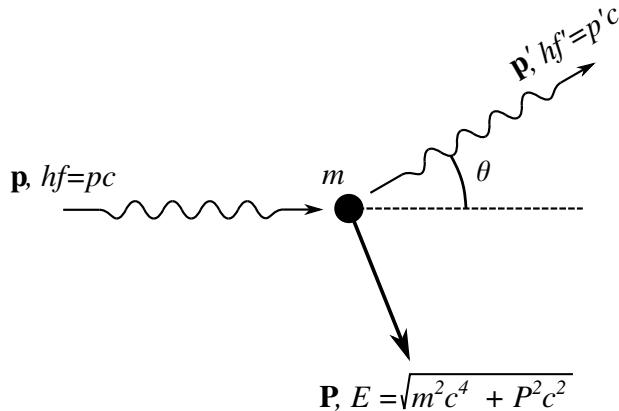
Figure 3.12: A photon of momentum **p** and energy $hf = pc$ hits a stationary electron of mass m. After the collision, the photon moves off with momentum **p'** and energy $hf' = p'c$ at angle θ, and the electron recoils with momentum **P** and energy $E = \sqrt{m^2c^4 + P^2c^2}$.

- Since the X-ray photon energy hf is much greater than the binding energy of an electron in a carbon atom, it suffices to consider scattering from a free electron.

- X-rays arrive as photons of energy $E = pc = hf$ (which was by then quite well established) and momentum $p = h/\lambda$ (which was still controversial).

A typical Compton scattering event is shown in Fig. 3.12. A photon of momentum **p** and energy $hf = pc$ hits a stationary electron of mass m. After the collision, the photon moves off with momentum **p'** and energy $hf' = p'c$ at angle θ, and the electron recoils with momentum **P** and energy $E = \sqrt{m^2c^4 + P^2c^2}$. Since the energy transferred to the electron may be large, the relativistic relationship between the electron energy and momentum has been used.

Applying the principle of energy conservation to the collision gives

$$pc + mc^2 = p'c + \sqrt{m^2c^4 + P^2c^2} \tag{3.16}$$

$$\Rightarrow \qquad \left[(p - p')c + mc^2\right]^2 = m^2c^4 + P^2c^2. \tag{3.17}$$

Momentum conservation gives

$$\mathbf{p} = \mathbf{p'} + \mathbf{P} \tag{3.18}$$

and hence

$$
\begin{aligned}
P^2 &= (\mathbf{p} - \mathbf{p}') \cdot (\mathbf{p} - \mathbf{p}') \\
&= p^2 - 2\mathbf{p} \cdot \mathbf{p}' + p'^2 \\
&= p^2 - 2pp' \cos\theta + p'^2 \\
&= (p - p')^2 + 2pp'(1 - \cos\theta).
\end{aligned}
\tag{3.19}
$$

Using Eq. (3.19) to eliminate P from Eq. (3.17) gives

$$
(p - p')^2 c^2 + 2mc^3(p - p') + m^2 c^4 = m^2 c^4 + (p - p')^2 c^2 + 2pp' c^2(1 - \cos\theta)
$$

and hence

$$
\begin{aligned}
& 2mc^3(p - p') = 2pp' c^2(1 - \cos\theta) \\
\Rightarrow \quad & \frac{1}{p'} - \frac{1}{p} = \frac{1}{mc}(1 - \cos\theta) \qquad \text{(dividing through by } 2mc^3 pp') \\
\Rightarrow \quad & \lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta) \qquad \text{(since } p = h/\lambda),
\end{aligned}
\tag{3.20}
$$

exactly as observed.

Compton's theory shows that an X-ray scattered from a free electron increases its wavelength from λ to λ', explaining the longer-wavelength peak in Fig. 3.10. Sometimes, however, the incoming X-ray fails to knock the target electron out of its atom and the momentum is transferred to the atom as a whole. Atoms are much more massive than electrons, so the energy transferred in such collisions is almost zero. This explains why some of the X-rays scatter without measurably changing in their wavelength λ.

Chapter 4

Particles are Waves

4.1 The Planck and De Broglie Equations Revisited

Louis de Broglie's 1924 hypothesis was much bolder than explained so far. He proposed, with essentially no supporting evidence, that *all* particles, not just photons, have wave-like properties and satisfy

$$p = h/\lambda = \hbar k \qquad \text{(The de Broglie equation)} \qquad (4.1)$$

$$E = hf = \hbar\omega \qquad \text{(The Planck equation)} \qquad (4.2)$$

Even more surprising is that he made this proposal in his PhD thesis! Few physicists, including his PhD examiner Paul Langevin, the inventor of Langevin dynamics and the Langevin equation (both of which I use in my own work), believed de Broglie's outlandish proposal at the time. Later, de Broglie said that Langevin was ''probably a little stunned by the novelty of my ideas.'' In fact, Langevin was so worried that he wrote to Einstein to ask whether de Broglie should be allowed to pass. Einstein seems to have had doubts too, but fortunately for his future reputation said yes. After some reflection, Einstein said: ''I believe it (de Broglie's work) is a first feeble ray of light on this the worst of our physics enigmas.'' Davisson and Germer demonstrated electron diffraction experimentally in 1927 and de Broglie won a Nobel Prize in 1929, only five years after finishing his PhD.
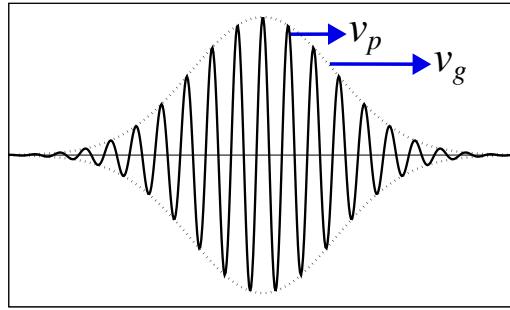
Figure 4.1: The phase and group velocities of a wave packet.

4.2 Dispersion Relation of Particle Waves

For the time being, let us simply assume that the Planck and de Broglie equations, $E = hf = \hbar\omega$ and $p = h\lambda = \hbar k$, apply to particles such as electrons as well as photons. (Some of the experimental evidence in favour of this assumption is discussed in Sec. 4.4.) For non-relativistic massive particles, we also know that

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}.$$

(4.3)

Hence, the dispersion relation of the de Broglie particle-waves must be

$$\hbar\omega = \frac{(\hbar k)^2}{2m} \quad \Rightarrow \quad \boxed{\omega = \frac{\hbar k^2}{2m}}$$

(4.4)

The phase velocity (the speed of the wave crests — see Fig. 4.1) is

$$v_p = \frac{\omega}{k} = \frac{\hbar k}{2m},$$

(4.5)

and the group velocity (the speed of the envelope of a wave packet — see Fig. 4.1 again) is

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m}.$$

(4.6)

This velocity p/m of the ''particle'' is the same as the group velocity of the wave packet, which makes sense.

4.3 Examples

An electron in an atom, molecule or solid has

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

and hence

$$\lambda = \frac{h}{\sqrt{2mE}}.$$ (4.7)

If $E = 5\,\text{eV} = 5 \times 1.60 \times 10^{-19}\,\text{J}$, which is typical for valence electrons in ordinary matter, then

$$\lambda \approx 5.5 \times 10^{-10}\,\text{m}.$$

This is larger than the radius of an atom and comparable to or larger than the spacing between atoms in molecules and solids, so the behaviour of the electrons is very wave-like. The electron waves diffract from the atoms, refract from changes in potential, and interfere just like light waves. The quantum theory of atomic bonding (and chemistry in general) is essentially a wave theory.

Electron energy scales

Why is the typical energy $E \approx 5\,\text{eV}$ of a valence electron in an atom, molecule or solid so much larger than kT (which is only about $1/40\,\text{eV}$ at room temperature)? One way to explain this is by analogy: the speeds at which planets orbit the sun have nothing to do with their temperature, but are determined by Newton's laws, $mv^2/r = GMm/r^2$. In a similar way, the speeds at which electrons ''orbit'' nuclei are determined by the quantum mechanical laws of motion. Thermal excitations increase the average speed a little, in metals at least, but the change is relatively tiny. Another contributing factor is the Pauli exclusion principle, which says that only one electron can occupy any quantum state. This makes it impossible to place all of the electrons in low-energy atomic orbitals.

An N_2 molecule in air at 300K has

$$m_{N_2} = 2 \times 14 \times 1.66 \times 10^{-27}\,\text{kg},$$

$$E = \frac{3}{2}kT \approx 0.039\,\text{eV},$$

$$\lambda = \frac{h}{\sqrt{2m_{N_2}E}} \approx 2.8 \times 10^{-11}\,\text{m}.$$

Since the wavelength is much smaller than the distance between molecules (which is $\approx 3.5 \times 10^{-9}\,\text{m}$ — see Sec. 1.5), it is easy to make N_2 wave packets much smaller than the inter-molecular separation. These tiny wave packets move around and collide almost like particles, explaining why it makes sense to view an air molecule (treated as a whole, ignoring the behaviour

of the electrons inside it) as a classical object in most cases. Quantum (wave-like) effects become more important when the temperature is very low and the de Broglie wavelength larger.

More surprising is that the de Broglie wavelength of an N_2 molecule is smaller than a single atom. This means that atoms and molecules (again regarded as whole objects) in solids can also be treated as classical particles in most cases.

How can the de Broglie wavelength of a molecule be smaller than the molecule itself? The answer is that the wavelength obtained by treating the molecule as a single entity (rather than a collection of electrons and nucleons, each of which has its own de Broglie wave) is associated with the molecule's centre of mass. The molecule itself can easily be larger than the uncertainty in its centre-of-mass position.

A person has

$$m \approx 60\,\text{kg},$$
$$v \approx 1\,\text{m s}^{-1},$$
$$\lambda = \frac{h}{p} \approx 1.1 \times 10^{-35}\,\text{m}!$$

The QM/wave-like properties of macroscopic objects are almost always undetectable.

4.4   Evidence that Particles are Waves

Electron diffraction

In 1927, Davisson and Germer showed that electrons can be diffracted by the regular array of atoms in a crystal, which acts much like a diffraction grating.

Because electrons are charged and not very massive, they are strongly scattered by solids and penetrate only very small distances. This makes electron diffraction a useful (and widely used) technique for studying how atoms are arranged at surfaces. It turns out that the 2D crystal structures of surfaces often have rather little to do with the 3D crystal structures inside solids.

Thermal neutron diffraction

A neutron ($m \approx 1.67 \times 10^{-27}$ kg) with energy $E = 3kT/2$ at $T = 300$ K has $\lambda = h/\sqrt{2mE} \approx 1.5 \times 10^{-10}$ m, which is comparable to the size of an atom. Just as with electrons, therefore, beams of neutrons are diffracted by the regular arrays of atoms in crystals.

Neutrons are much heavier than electrons and uncharged, so they penetrate deep inside solids and diffract from the bulk crystal structure, not the surface. This makes neutron diffraction a useful alternative to X-ray diffraction. Because neutrons have a magnetic moment, the diffraction pattern depends on the arrangement of magnetic moments in the target, making neutron diffraction especially useful for investigating magnetic solids.

He atom diffraction

The mass of a ^{4}He atom is about four times that of a neutron, so beams of low-energy He atoms also diffract from crystals. Unlike neutrons, however, low-energy He atoms are large enough to find it very difficult to penetrate solids. He diffraction, like electron diffraction, is a surface sensitive technique.

Scanning tunnelling microscopy

The scanning tunnelling microscope (STM) was invented by Gerd Binnig and Heinrich Rohrer at IBM Zürich in 1981. Although the invention was to some extent serendipitous (they were trying to build a microscope but had no idea they would achieve atomic resolution), their work was so obviously important that they were awarded the Nobel prize just a few years later, in 1986.

A schematic diagram of an STM is shown in Fig. 4.2. A tiny metallic tip (an atom or two across at its end) is scanned horizontally a few Å above a conducting surface. A small voltage is applied between the tip and the surface, causing electrons to jump across the gap. The jumping process, which is known as quantum mechanical tunnelling (and will be discussed later in this course), is exquisitely sensitive to distance, so the current rises and falls as the tip is scanned across the surface and approaches or moves away from the nearest surface atom.

Scanning tunnelling microscopes can measure the interference patterns of electron waves directly. The famous STM image reproduced in Fig. 4.3 shows the electron standing wave inside a quantum ''corral'' — a circle of 48 Fe atoms arranged using the STM tip itself on the surface of a piece of Cu [M.F. Crommie, C.P. Lutz, D.M. Eigler, *Science* **262**, 218 (1993)].
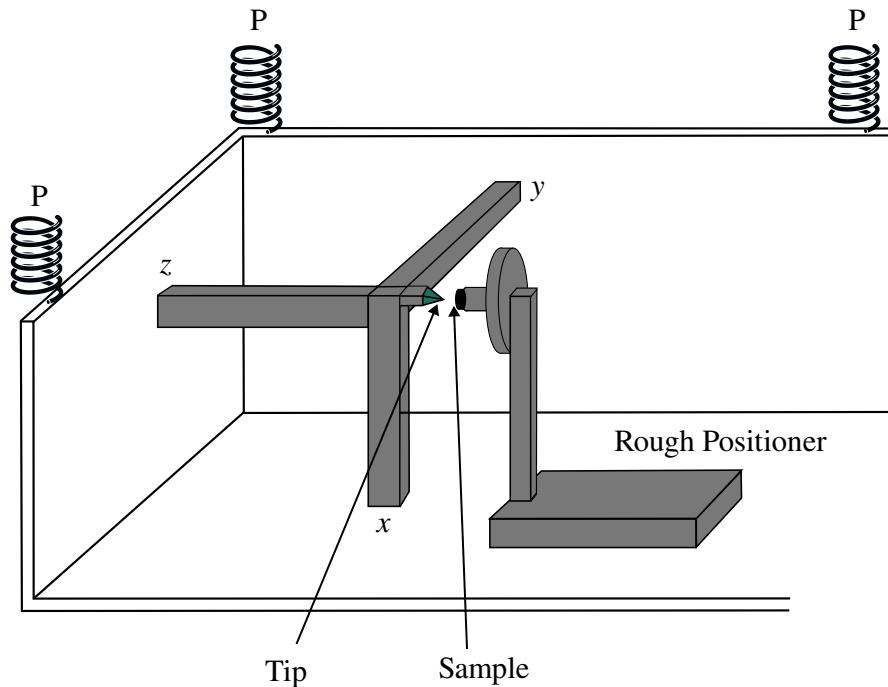
Figure 4.2: A (very) schematic diagram of a scanning tunnelling microscope. The piezoelectric drives x, y, and z are used to move the tip. The springs P represent a vibration filtering system.

The colours and 3D effect were created from the flat 2D current map using computer graphics, but the wave-like nature of the electron states is clear.

Two-slit interference

Two-slit interference patterns have been created using electrons, atoms and even C_{60} molecules [O. Nairz, M. Arndt, A. Zeilinger, Am. J. Phys. **71**, 319 (2003)].

Atomic energy levels

As will be explained Sec. 4.5, the quantised energy levels of atoms are a direct consequence of the wave-like properties of electrons.

4.5 Atomic Spectra

As illustrated in Fig. 4.4, hot solids emit/absorb a continuous spectrum of wavelengths/frequencies of electromagnetic radiation. Individual atoms and molecules, by contrast, only emit and absorb at specific wavelengths/frequencies. The sharp
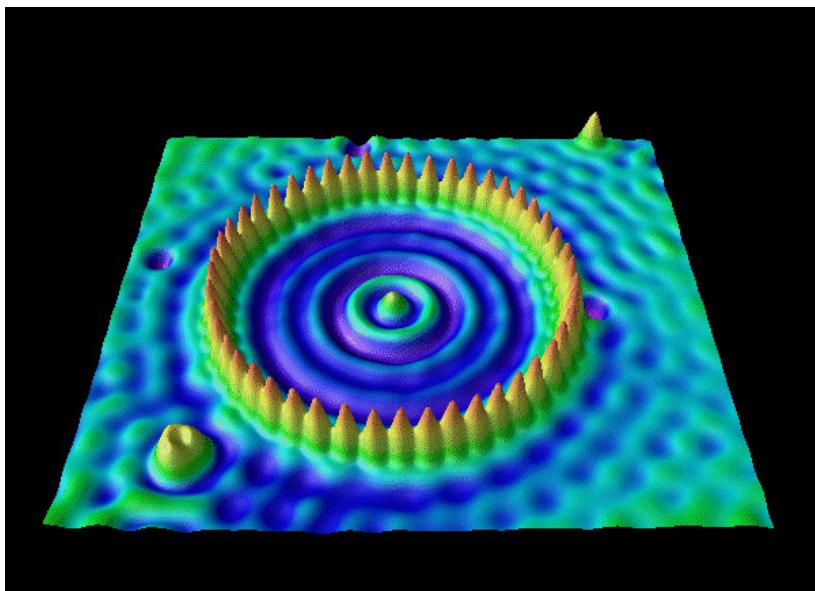
Figure 4.3: A ''corral'' of 48 Fe atoms on the surface of a piece of Cu. Before the image was taken, the STM tip was used to move the Fe atoms into position one by one. The potential due to the ring of Fe atoms is strong enough to trap an electron within the corral, producing a standing wave pattern.

absorption/emission lines can be seen by heating a gas, as when a volatile salt is thrown into a flame, or subjecting a gas to electrical discharges.

The absorption lines of atoms act as fingerprints and can be used to identify elements elsewhere in the universe. Helium, for example, was discovered on Earth only after it had been detected as dark lines in the black-body spectrum of the Sun. The dark lines are created when outgoing black-body photons are absorbed by cool He atoms in the Sun's outer layers. Atomic absorption lines also played an important role in the detection and measurement of the expansion of the universe: a red-shifted black-body spectrum is just a cooler black-body spectrum and does not tell you the recession velocity of a star unless the real temperature of the star is known; but a red-shifted He or H spectrum is characteristic.

The H atom has four clear spectral lines in the visible. These were first observed by Balmer in 1884 and fitted to a simple formula by Rydberg in 1890:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{m^2} \right), \qquad m = 3, 4, 5, \ldots, \qquad \text{(Balmer series)} \qquad (4.8)$$

where R_H, the Rydberg constant, is approximately $1.097 \times 10^7 \text{ m}^{-1}$. Using $1/\lambda =$
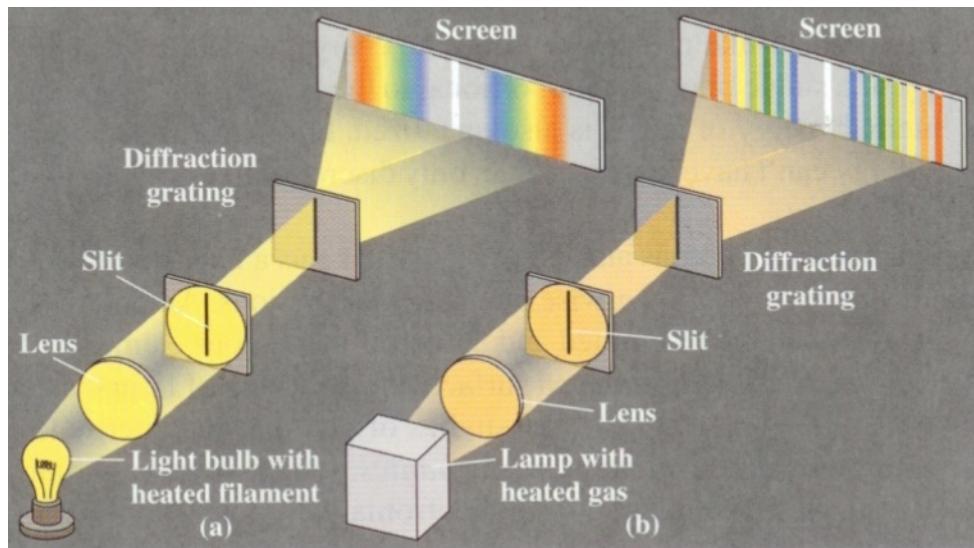
Figure 4.4: Comparison of the absorption spectra of a solid and a gas. [Fig. 38.1 from H.D. Young and R.A. Freedman, *University Physics with Modern Physics*, 11th Ed. (Addison Wesley, 2004).]

f/c, the Rydberg formula for the Balmer series becomes

$$hf = hcR_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{m^2}\right) \approx (13.6\,\mathrm{eV}) \times \left(\frac{1}{2^2} - \frac{1}{m^2}\right). \tag{4.9}$$

Replacing $1/2^2$ by $1/1^2$ gives the Lyman series, later observed in the ultraviolet. Replacing $1/2^2$ by $1/3^3$ gives the Paschen series, later observed in the infrared. In fact, spectral lines are found at all frequencies $f_{m \to n}$ for which

$$hf_{m \to n} \approx (13.6\,\mathrm{eV}) \times \left(\frac{1}{n^2} - \frac{1}{m^2}\right), \tag{4.10}$$

with m and n positive integers and $m > n$.

We can explain the spectrum by assuming that an H atom has quantised energy levels,

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2}, \qquad n = 1, 2, \ldots. \tag{4.11}$$

The energies are all negative because they correspond to bound electronic orbits; the total energies (kinetic + potential) of planets in orbit around the Sun are also negative, for the same reason. The lowest energy level, the *ground state*, has $n = 1$ and energy $-13.6\,\mathrm{eV}$. States with $n > 1$ are known as *excited states*. When

an atom makes a transition from a higher energy level m to a lower energy level n, it emits a photon of energy

$$hf_{m \to n} = E_m - E_n. \tag{4.12}$$

Similarly, when an atom starts in energy level E_n and absorbs a photon of energy $hf_{m \to n} = E_m - E_n$, it is excited to energy level E_m.

Other evidence for the quantisation of energy levels is seen in

- X-ray spectra (see Fig. 3.6).

- Vibrational and rotational spectra of molecules. The vibrational energy levels of molecules, such as the CO_2 molecules in the atmosphere, are also quantised and absorb light at specific frequencies only. Microwave ovens excite the rotational energy levels of water molecules.

- Absorption/emission spectra of point defects (such as vacancies, which are missing atoms, or interstitials, which are extra atoms jammed in to the crystal lattice) in solids.

4.6 Why Quantisation?

Quantisation is a natural consequence of confining waves. The harmonics of a violin string make a good example. If the string is bowed normally, the pitch you hear corresponds to the so-called fundamental mode, the wave pattern of which is shown in the top panel of Fig. 4.5. If you touch the string in the middle as you bow, you can excite the first harmonic, shown in the middle panel of Fig. 4.5. The wavelength of the first harmonic is half that of the fundamental, so the frequency is doubled and the note sounds an octave higher. If you touch the string a third of the way along, you can excite the second harmonic, which has a frequency three times higher than the fundamental and sounds an octave and a fifth higher.

The allowed frequencies of a violin string are proportional to n, with $n = 1$ for the fundamental, $n = 2$ for the first harmonic, and so on. This differs from the $1/n^2$ rule that seems to describe the energy levels of an H atom, but the idea is good:

> Confinement $\Rightarrow$ only certain standing waves allowed $\Rightarrow$ only certain frequencies allowed $\Rightarrow$ only certain energies allowed ($E = hf$).
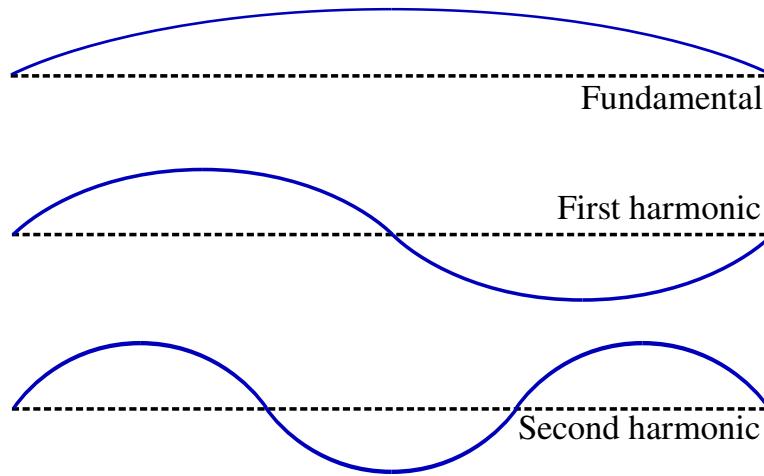
Figure 4.5:   The wave patterns of the fundamental, first and second harmonics of a violin string.

A solid is a huge box, so the allowed frequencies are very close together and a continuous absorption/emission spectrum is observed.

An atom is a tiny box, so the allowed frequencies are well separated and the absorption/emission spectrum consists of discrete lines.

4.7   The Bohr Atom

The Bohr model was the direct forerunner of modern quantum theory and gives the exact energy levels and rough sizes of one-electron atoms/ions (H, He$^+$, Li^{2+}, Be^{3+}, ...). It does not work for more complicated atoms, molecules or solids, and is probably better regarded as an interesting and useful curiosity than a valid description of nature.

The ideas underlying the Bohr model are simple:

(a) The electron moves around the nucleus in a circular Newtonian orbit.

(b) The de Broglie wavelength, $\lambda = h/p$, must ''fit in'' to the circumference of the orbit.

Consequences of (b)

The second of these ideas is illustrated in Fig. 4.6, which shows that the de Broglie

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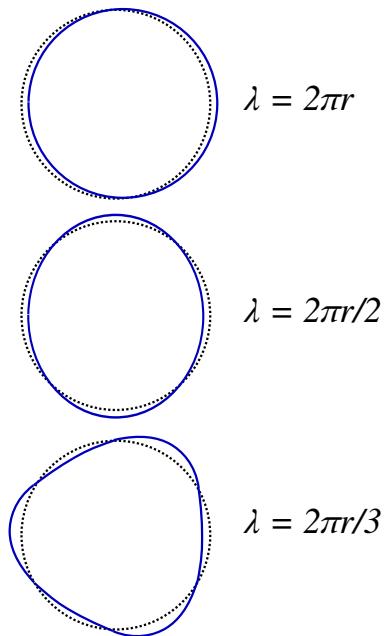
Figure 4.6: The first three Bohr orbits.

wavelength of the nth Bohr orbit is $2\pi r/n$. Since $p = h/\lambda$, this gives

$$p = \frac{hn}{2\pi r} = \frac{n\hbar}{r} \qquad \text{or} \qquad pr = n\hbar.$$

The angular momentum $L = mvr = pr$ is therefore quantised in units of $\hbar$:

$$L = mvr = n\hbar. \tag{4.13}$$

> **Angular momentum in real atoms**
>
> Although the Bohr theory is wrong about many things, this particular result is more or less right: the angular momentum of an atom is quantised and the unit is $\hbar$. Real atoms are more complicated because the orbits are three-dimensional (the angular momentum L is actually a vector) and because the electron has a *spin* — an intrinsic ''internal'' angular momentum of size $\hbar/2$. Furthermore, the quantum mechanical rules for adding the orbital and spin angular momenta differ from the simple vector addition rule used in classical mechanics.

Consequences of (a)

Applying Newton's second law in the form *Force = Centripetal Acceleration* gives

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r} = \frac{(mvr)^2}{mr^3}. \tag{4.14}$$

[Note: this derivation is for a hydrogen atom. The generalisation to a one-electron ion of atomic number Z will be set as a problem.] Since $L = mvr = n\hbar$, Eq. (4.14) becomes

$$\frac{e^2}{4\pi\epsilon_0 r_n^2} = \frac{(n\hbar)^2}{mr_n^3},$$

where r_n is the radius of the nth Bohr orbit. Solving for r_n yields

$$r_n = \frac{4\pi\epsilon_0(n\hbar)^2}{me^2}. \tag{4.15}$$

The smallest orbit has radius $r_1 \approx 0.53 \times 10^{-10}$ m. This distance is called a Bohr radius and denoted a_0. It is about the radius of a small atom.

The energy of the orbiting electron is given by

$$E = \text{KE} + \text{PE}$$

$$= \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$= \frac{1}{2}\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r},$$

where the last step used Eq. (4.14) again. The energy of the nth Bohr orbit is therefore

$$E_n = \frac{-e^2}{2(4\pi\epsilon_0)r_n} = \frac{-me^4}{2(4\pi\epsilon_0\hbar)^2 n^2} \approx \frac{-(13.6\,\text{eV})}{n^2}, \tag{4.16}$$

exactly as the spectroscopic evidence suggests.

Successes and failures of the Bohr Model

The Bohr model

✓ provides a partial explanation of the stability of atoms. Orbiting — and thus accelerating — electrons are unable to radiate away energy gradually, as classical physics suggests they should, because they can only have certain quantised energies.

✓ gives correct energy levels for the H atom and one-electron ions such as He^+ and Li^{2+}.

✓ predicts that angular momentum should be quantised in units of $\hbar$. This is more or less right.

✗ is no good for atoms with more than one electron.

✗ is no good for molecules or solids.

✗ relies on a misleading classical picture of orbiting electrons. The actual behaviour of electrons in atoms is more interesting than the Bohr model suggests.

✗ says nothing about how transitions between energy levels occur.

Chapter 5

The Wave Function

5.1 The Two-Slit Experiment Gets Weird

> We choose to examine a phenomenon which is impossible, absolutely impossible, to explain in any classical way, and which has in it the heart of quantum mechanics. In reality, it contains the only mystery. We cannot make the mystery go away by explaining how it works . . . In telling you how it works we will have told you about the basic peculiarities of all quantum mechanics.
>
> R.P. Feynman, *Lectures on Physics*, Vol. 3, Ch. 1.

To show the strangeness of the quantum world, and to help associate a meaning to the rather abstract wave that seems to be associated with quantum mechanical particles, we are going to analyse three versions of the two-slit experiment:

1. with classical particles

2. with classical waves

3. with quantum mechanical particles

The analysis will show that quantum mechanical ''particles'' such as electrons and photons are neither particles nor waves, but something wholly new with aspects of both. For want of a better word, they are sometimes called ''wavicles''.

In the two-slit experiment, a beam of particles or monochromatic waves passes through a screen containing two long narrow parallel slits. The number den-
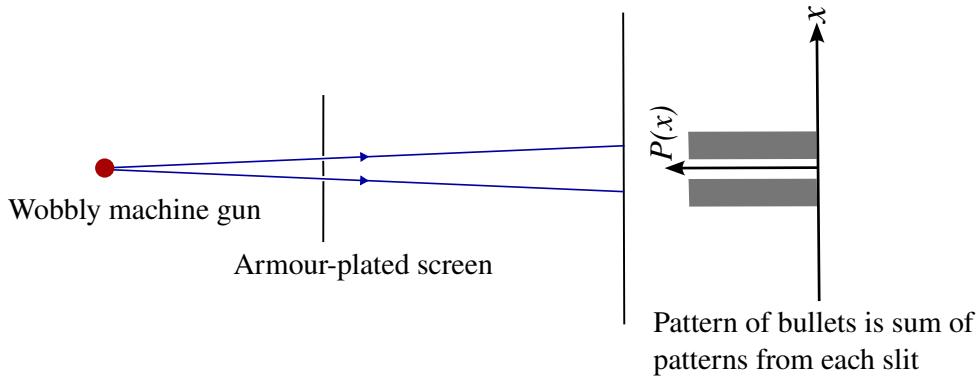
Figure 5.1: The two-slit experiment with classical particles.

sity/intensity of particles/waves hitting a detector a long way beyond the screen is measured.

1. **Classical particles:** Following Feynman, imagine that the incident particles are bullets fired from a wobbly machine gun and that the screen with the slits is armour plated (see Fig. 5.1). The detector consists of a sand trap which catches the bullets and allows us to see where each one lands. After the experiment, the sand trap is found to contain two groups of bullets, one centred on the ''shadow'' of each slit.

   If one slit is closed, the sand trap only collects the group of bullets passing through the open slit. Moreover, the pattern of bullets obtained with both slits open is exactly (to within statistical error) the sum of the patterns obtained with the upper slit closed and with the lower slit closed. If $P_t(x)$ is the probability density that a randomly chosen bullet fired from the gun arrives at x when only the top slit is open, $P_b(x)$ is the probability density that it arrives at x when only the bottom slit is open, and $P_{tb}(x)$ is the probability density that it arrives at x when both slits are open, then

$$P_{tb}(x) = P_t(x) + P_b(x).$$

2. **Classical waves:** In this case, the machine gun is replaced by a source of waves and the detector by any device that measures the wave intensity (*i.e.*, the arriving energy density) as a function of position. If the classical waves are sound waves, for example, the detector might be an array of microphones. The signal arrives smoothly, not in ''lumps'' as with classical particles.

   The measured intensity is an interference pattern, which may be calculated by adding the complex amplitudes of the waves emerging from the two slits
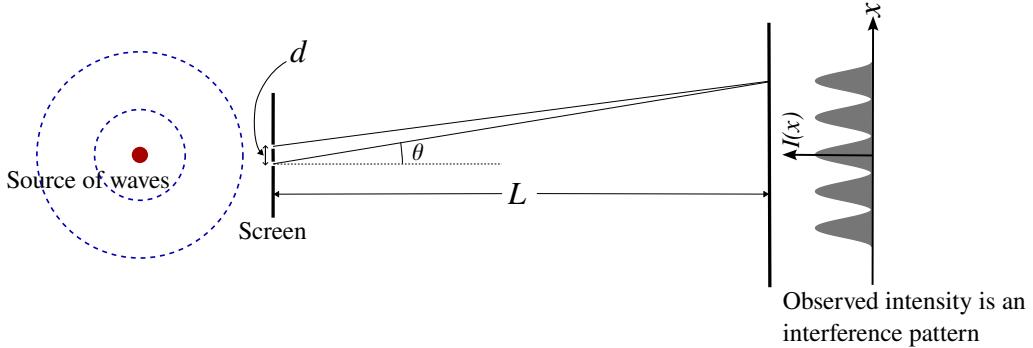
Figure 5.2: The two-slit experiment with classical waves.

and taking the square modulus of the sum. The form of this interference pattern (in the case when the slits are much narrower than the wavelength and the source and screen are far from the slits, so that the curvature of the wave fronts can be ignored) is shown in Fig. 5.2.

The wave theory that leads to this pattern was covered in Sec. 2.2. Starting from the observation that the amplitudes of the waves emerging from the two slits add, it was shown that the wave $\psi_{tb}(\zeta, t)$ a distance ζ from the top slit in the θ direction is

$$\psi_{tb}(\zeta, t) = \psi_t(\zeta, t) + \psi_b(\zeta, t) = Ae^{i(k\zeta - \omega t)} + Ae^{i(k(\zeta + d\sin\theta) - \omega t)}$$
$$= A_t e^{i(k\zeta - \omega t)} + A_b e^{i(k\zeta - \omega t)} = A_{tb} e^{i(k\zeta - \omega t)},$$

where $A_t = A$, $A_b = Ae^{ikd\sin\theta}$, and $A_{tb} = A_t + A_b$. As usual with waves, the strength of the signal measured by a detector (placed far from the slits in the θ direction) is proportional to the *intensity*:

$$I_{tb} \propto \text{wave intensity in } \theta \text{ direction}$$
$$= |A_{tb}|^2$$
$$= (A_t^* + A_b^*)(A_t + A_b)$$
$$= |A_t|^2 + |A_b|^2 + A_t^* A_b + A_b^* A_t$$
$$= I_t + I_b + (\text{interference terms}).$$

Because the waves from the two slits interfere, the pattern of intensities $I_{tb}(\theta)$ obtained with both slits open is *not* the sum of the pattern $I_t(\theta)$ obtained when only the top slit is open and the pattern $I_b(\theta)$ obtained when only the bottom slit is open.

In fact, if one slit is closed, the interference pattern of the two parallel narrow slits is replaced by the diffraction pattern a single slit. Assuming

that the width of the slit is much narrower than the wavelength, the single-slit diffraction pattern is very broad and varies slowly as a function of angle. In places where the intensity of the two-slit interference pattern is zero or very small, closing one slit may actually *increase* the measured intensity.

3. **Quantum mechanical particles:** In this case, the machine gun is replaced by a source of quantum mechanical particles, perhaps photons from a laser or electrons from an electron gun. The detector is some device (e.g., a CCD camera) able to measure the arrival position of a single photon or electron.

   By stopping down the source until only one quantum particle is in the apparatus at any one time, one can establish that each particle causes a single detector at a single point in space to fire, exactly as for classical particles. However, the distribution of quantum mechanical particles is nothing like the distribution of classical particles; instead, it looks *exactly* like the interference pattern observed for classical waves.

   When one slit is closed, the observed particle distribution changes from the rapidly varying (in space) two-slit interference-pattern to the smooth broad interference pattern of a single narrow slit. As with classical waves, closing one slit causes the wave intensity (which is now proportional to the number of arriving particles) to *increase* at some points. The only way to reconcile this observation with the classical picture of particles as bullets is to allow the paths of the particles passing through one slit to depend on whether the other slit is open or closed. If the paths through one slit are assumed to be independent of the state of the other, closing one slit can only decrease the number of particles hitting the detector at x.

   Theories of this correlated type (in which the paths taken through one part of the system depend on what happens far away) can be constructed and made consistent with quantum theory. In the de Broglie-Bohm theory, for example, the paths of the particles are affected by a separate wave, the form of which depends on the state of both slits. Unfortunately, such theories are highly non-local: you cannot in general predict the path of a particle without knowing the position of more or less every other particle in the universe. The wave interference picture used in standard quantum theory is simpler and more physical.

Conclusions

The quantum mechanical two-slit experiment suggests that quantum mechanical objects are associated with waves, the amplitudes of which add linearly. Just as in classical physics, the superposition of the waves emerging from the two slits yields an interference pattern.

The two-slit experiment also shows that quantum mechanical objects be-have like particles. The detectors that measure the arrival positions of these quantum particles always find them at one place or another — their energy is localised, not smeared out as for a wave.

The link between the particle and wave pictures is provided by the wave intensity: the probability that a position measurement finds a particle at point **r** is proportional to the wave intensity at that point. This is typical of quantum theory: although it provides precise predictions of probabilities, it cannot predict where a particular particle will end up.

The interference pattern of arrival probabilities does not depend on the number of particles passing through the apparatus per second. If the par-ticle flux is very low, very few dots appear on the screen per second, but the distribution of dots is unaltered. The interference pattern persists even when the flux is so low that there is no significant chance of finding more than one particle in the apparatus at a time. This shows that the interfer-ence cannot be the result of many particles ''colluding'' — one is all you need.

5.2   What is an Electron?

An electron is . . .

- *not* a particle (although it has some particle-like properties);

- *not* a wave (although it has some wave-like properties).

It is something new — a ''wavicle''.

- In between measurements, wavicles propagate like waves, diffracting, re-fracting, interfering, and so on. The Schrödinger equation that describes how these waves propagate is not the same as the classical wave equation, but both describe waves.

- Some types of detectors respond to wavicles by producing particle-like ''spikes'' at sharply defined positions. After such a measurement, the wave packet of the wavicle is very small (but it soon begins to spread out again — as wave packets do).

Questions quantum theory cannot answer:

- Where is the particle between measurements?

- How did the particle get from A to B?

Probabilities in quantum theory:

- Quantum mechanics allows you to work out the possible values (known as *eigenvalues*) of any observable (measurable quantity). A few important observables are position, momentum, velocity, and energy.

- It you know the wave function $\psi(x, t)$, you can also work out the probabilities of measuring each of these allowed values.

- The wave function $\psi(x, t)$ is central to quantum theory but is not itself an observable. The intensity $|\psi(x, t)|^2$ is the probability density observed in position measurements.

The phenomenon of radioactive decay provides some evidence in favour of the idea that the world may really be probabilistic at the atomic scale. Suppose, for example, that you start with a large number $N(t{=}0)$ of radioactive nuclei. Instead of all decaying together a fixed time after they were created, as might be expected, the number $N(t)$ remaining at time t decreases exponentially: $N(t) = N(0)e^{-\alpha t}$, where α is a constant. This observation can be explained if one assumes that the nuclei decay at random, with a fixed fraction α decaying per second:

$$dN = -\alpha N dt$$

$$\Rightarrow \qquad \int \frac{dN}{N} = -\alpha \int dt$$

$$\Rightarrow \qquad \ln N(t) = C - \alpha t.$$

Setting $t = 0$ shows that $C = \ln(N(0))$ and hence

$$N(t) = N(0)e^{-\alpha t}.$$

5.3 Probability Densities

Because quantum mechanics only predicts probabilities, concepts from probability theory play a central role in the rest of this course. This section provides a brief review of the idea of a probability density.

Imagine that you measure the heights of N people. The probability that anybody in your sample is exactly 1.8 m tall is zero. Some people may be roughly 1.8 m
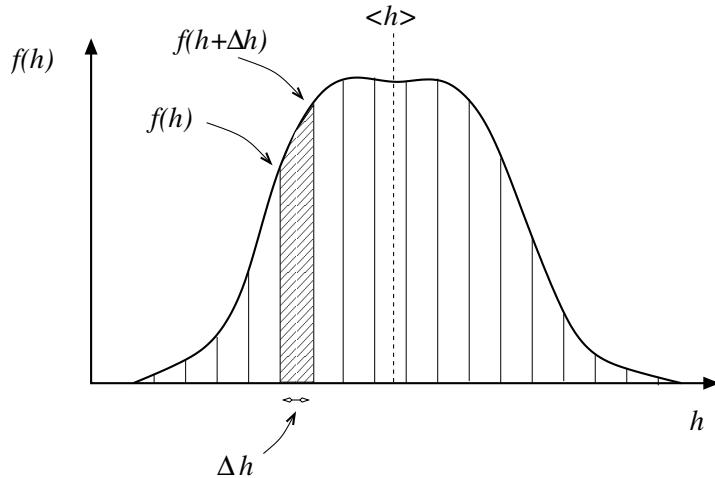
Figure 5.3: Probability density function of the heights of people.

tall, and a few may be very close to 1.8 m tall, but there is no chance of finding someone who is *exactly* 1.8 m tall (plus or minus nothing).

We can, however, ask about the number of people $n(h, h + \Delta h)$ with heights between h and $h+\Delta h$, where Δh is finite. Given a large enough sample of people, the ratio $n(h, h + \Delta h)/N$ is independent of the sample size N and we can define the corresponding probability

$$p(h, h + \Delta h) = \lim_{N \to \infty} \frac{n(h, h + \Delta h)}{N}.$$

If Δh is small enough, the number of people with heights between h and $h + \Delta h$ ought to be proportional to Δh. (For example, one would expect the number of people with heights between 1.8000 m and 1.8002 m to be roughly twice the number with heights between 1.8000 m and 1.8001 m.) This suggests defining a *probability density function* (pdf) $f(h)$ via:

$$p(h, h + \Delta h) = f(h)\,\Delta h.$$

As long as Δh is small enough, $f(h)$ should be independent of the value of Δh. The pdf is the central quantity in all applications of probability theory to continuous random variables.

Figure 5.3 shows an example pdf. The probability that the height of a randomly chosen person lies between h and $h + \Delta h$ is equal to the shaded area, which is approximately $f(h)\Delta h$ if Δh is small enough. The probability that the height lies between h_{low} and h_{high} (where h_{low} and h_{high} need not be close) is the area under

the curve from h_{low} to h_{high}:

$$p(h_{\text{low}}, h_{\text{high}}) = \int_{h_{\text{low}}}^{h_{\text{high}}} f(h)\, dh.$$

Since the probability that h lies somewhere between zero and infinity is equal to 1, it follows that

$$\int_0^\infty f(h)\, dh = 1.$$

The expected height $\langle h \rangle$ is defined via:

$$\begin{aligned}
\langle h \rangle \approx\ & (0 \times \text{Prob. height is between } 0 \text{ and } \Delta h) \\
& + (\Delta h \times \text{Prob. height is between } \Delta h \text{ and } 2\Delta h) \\
& + \ldots \\
& + (n\Delta h \times \text{Prob. height is between } n\Delta h \text{ and } (n+1)\Delta h) \\
& + \ldots \\
\approx\ & \sum_{n=0}^\infty n\Delta h\, f(n\Delta h)\, \Delta h \\
=\ & \sum_{n=0}^\infty h_n f(h_n)\, \Delta h,
\end{aligned}$$

where $h_n := n\Delta h$ is the value of the height h at the left-hand edge of the nth strip of width Δh. In the limit as $\Delta h \to 0$, the summation turns into an integral and the $\approx$ signs become $=$ signs:

$$\langle h \rangle = \int_0^\infty h f(h)\, dh.$$

Similarly, the expected value of any function $g(h)$ of the height h is given by:

$$\langle g(h) \rangle = \int_0^\infty g(h) f(h)\, dh.$$

The variance σ^2 of the pdf $f(h)$ is defined by:

$$\begin{aligned}
\sigma^2 &= \left\langle (h - \langle h \rangle)^2 \right\rangle \\
&= \left\langle h^2 - 2\langle h \rangle h + \langle h \rangle^2 \right\rangle \\
&= \langle h^2 \rangle - 2\langle h \rangle \langle h \rangle + \langle h \rangle^2 \\
&= \langle h^2 \rangle - \langle h \rangle^2.
\end{aligned}$$

Since expected values are integrals, this may also be written

$$\sigma^2 = \int_0^\infty (h - \langle h \rangle)^2 f(h)\, dh$$

$$= \int_0^\infty h^2 f(h)\, dh - \left(\int_0^\infty h f(h)\, dh \right)^2.$$

The square root of the variance, known as the standard deviation, provides a useful measure of the spread of people's heights around the mean.

5.4 Working with Wave Functions

Suppose that a particle (wavicle) has wave function $\psi(x)$ at some fixed time t (suppressed to simplify the notation). Our analysis of the two-slit experiment suggested that

$$|\psi(x)|^2 dx \propto \begin{cases} \text{probability that a measurement of position gives} \\ \text{a result between } x \text{ and } x + dx \end{cases}$$

A wave function is said to be *normalised* if

$$\int_{-\infty}^\infty |\psi(x)|^2 dx = 1. \tag{5.1}$$

If $\psi(x)$ is normalised, the ''$\propto$'' sign can be replaced by an ''$=$'' sign,

$$|\psi(x)|^2 dx = \begin{cases} \text{probability that a measurement of position gives} \\ \text{a result between } x \text{ and } x + dx \end{cases} \tag{5.2}$$

and $|\psi(x)|^2$ is a probability density.

Given an unnormalised wave function $\psi_u(x)$, for which

$$\int_{-\infty}^\infty |\psi_u(x)|^2 dx = C \qquad (C \neq 1),$$

we can find the corresponding normalised wave function $\psi_n(x)$ by dividing through by $\sqrt{C}$:

$$\psi_n(x) = \frac{\psi_u(x)}{\sqrt{C}}.$$

It is usually easiest to work with normalised wave functions.

Most of the examples in this course assume that the world is one-dimensional, but three-dimensional wave functions are only a little more difficult to deal with. A three-dimensional wave function $\psi(\mathbf{r})$ is normalised if

$$\int_{\text{all space}} |\psi(\mathbf{r})|^2\, d^3r = 1. \tag{5.3}$$
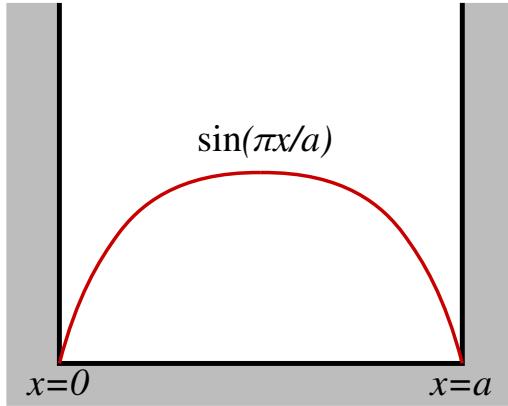
Figure 5.4: The unnormalised ground-state wave function of a particle confined in a box.

As in one dimension, if $\psi(\mathbf{r})$ is normalised then $|\psi(\mathbf{r})|^2$ is a probability density:

$$|\psi(\mathbf{r})|^2 \, d^3r = \begin{cases} \text{probability that a measurement of position gives} \\ \text{a result in the volume element } d^3r \text{ at position } \mathbf{r}. \end{cases} \quad (5.4)$$

Example: Particle in a Box

We shall see later in the course that a particle in the box-like potential well

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

has the (unnormalised) ground-state wave function

$$\psi_u(x) = \begin{cases} \sin(\pi x / a) & 0 < x < a, \\ 0 & \text{otherwise.} \end{cases}$$

(a) Normalise ψ_u:

$$\int_{-\infty}^{\infty} |\psi_u(x)|^2 dx = \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{1}{2}a,$$

so the normalised wave function is

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) & 0 < x < a, \\ 0 & \text{otherwise.} \end{cases}$$

(b) Find the mean position of the particle:

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

$$= \int_0^a x \, \frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) dx$$

$$= \text{lots of algebra (try it!)}$$

$$= \frac{a}{2}.$$

This makes sense.

(c) Find the rms uncertainty in the position of the particle:

$$(\Delta x)^2 = \sigma^2 = \left\langle (x - \langle x \rangle)^2 \right\rangle$$

$$= \int_0^a (x - \langle x \rangle)^2 \, \frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) dx$$

$$= \int_0^a \left(x - \frac{a}{2}\right)^2 \frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) dx$$

$$= \text{even more algebra (try it again!)}$$

$$= a^2 \left(\frac{1}{12} - \frac{1}{2\pi^2}\right).$$

Hence

$$\Delta x \approx 0.18a.$$

Chapter 6

The Uncertainty Principle

6.1 Physical Interpretation of $A(k)$

Suppose we allow a superposition of two matter waves,

$$\psi(x) = A_1 e^{ik_1 x} + A_2 e^{ik_2 x},$$

to pass through the diffraction grating shown in Fig. 6.1. The time dependence of $\psi(x,t)$ is not important here, so I have suppressed it. You can imagine, if you want, that I have chosen a fixed time t_0 and defined $\psi(x) := \psi(x, t_0)$.

Both components of $\psi(x)$ interfere constructively at $\theta = 0$, but their first off-centre diffraction peaks are at different angles:

$$\sin \theta_1 = \frac{\lambda_1}{d} = \frac{2\pi}{k_1 d}, \qquad \sin \theta_2 = \frac{\lambda_2}{d} = \frac{2\pi}{k_2 d}.$$

Unlike the incident wave, which contained components with two different wave vectors and so had an uncertain momentum, an outgoing particle found in a particular diffracted beam has a precisely known wavelength λ and momentum $p = h/\lambda = \hbar k$. In essence, the grating is a momentum measuring device.

Since the intensities of the diffraction patterns corresponding to wave vectors k_1 and k_2 are proportional to $|A_1|^2$ and $|A_2|^2$, respectively, the probability that the momentum measurement yields the result $\hbar k_1$ is proportional to $|A_1|^2$ and the probability that it yields $\hbar k_2$ is proportional to $|A_2|^2$.

This is just a plausibility argument — I haven't proved anything mathematically because I don't yet have a mathematical framework for quantum theory — but it seems fairly convincing. Let us accept it and think about the continuous superposition of plane waves required to make an arbitrary wave packet:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dk.$$
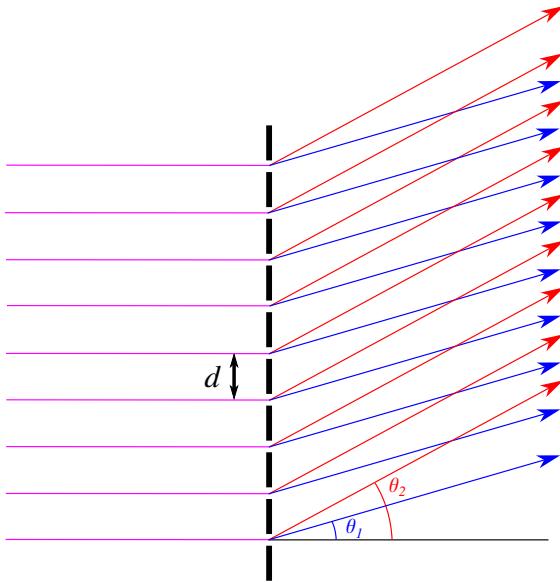
Figure 6.1: A diffraction grating can be used to separate the components of a superposition of plane waves.

In this case, the obvious interpretation is that $A(k)$ is a ''wave function for k'':

> The probability that a measurement of k yields a result in the interval from k to $k + dk$ is proportional to $|A(k)|^2 dk$.

Since $p = \hbar k$, this is physically equivalent to saying that $A(k)$ is a ''wave function for momentum.''

Parseval's identity, which you met last year (but which I re-derive below to remind you where it comes from), says that

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} |A(k)|^2 dk. \tag{6.1}$$

Hence, if the position wave function $\psi(x)$ is properly normalised, so is the corresponding momentum wave function $A(k)$.

Derivation of Parseval's Identity

Suppose that $\psi(x)$ and $A(k)$ are a Fourier transform pair:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dk, \qquad A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx.$$

Then

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = \int_{-\infty}^{\infty} \psi^*(x)\left(\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} A(k)e^{ikx}dk\right)dx$$

$$= \int_{-\infty}^{\infty}\left(\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{ikx}\psi^*(x)dx\right)A(k)\,dk$$

$$= \int_{-\infty}^{\infty}\left(\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-ikx}\psi(x)dx\right)^* A(k)\,dk$$

$$= \int_{-\infty}^{\infty} A^*(k)A(k)\,dk.$$

The re-ordering of the integrations in the second line is OK if $\psi(x)$ satisfies the Dirichlet conditions, and hence whenever $A(k)$ exists.

6.2 Momentum and Position Uncertainties

Given the interpretation of $|A(k)|^2$ as a probability density for k, we can write down expressions for the expected value (also known as the expectation value or, in statistics, the mean) and variance of the wavevector k:

$$\langle k \rangle = \int_{-\infty}^{\infty} k\,|A(k)|^2\,dk, \tag{6.2}$$

$$\sigma_k^2 = \left\langle (k - \langle k \rangle)^2 \right\rangle = \int (k - \langle k \rangle)^2\,|A(k)|^2\,dk. \tag{6.3}$$

In quantum theory, the standard deviation σ_k is known as the ''uncertainty in k'' and written Δk. We will adopt this notation and terminology from now on.

Since $p = \hbar k$, the expressions for the expected value $\langle p \rangle$ and uncertainty Δp of the momentum are almost the same:

$$\langle p \rangle = \int_{-\infty}^{\infty} \hbar k\,|A(k)|^2\,dk, \tag{6.4}$$

$$(\Delta p)^2 = \left\langle (\hbar k - \langle \hbar k \rangle)^2 \right\rangle = \int (\hbar k - \langle \hbar k \rangle)^2\,|A(k)|^2\,dk. \tag{6.5}$$

These definitions are of course analogous to the definitions of $\langle x \rangle$ and Δx introduced via an example in Sec. 5.4:

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\psi(x)|^2\,dx, \tag{6.6}$$

$$(\Delta x)^2 = \left\langle (x - \langle x \rangle)^2 \right\rangle = \int (x - \langle x \rangle)^2\,|\psi(x)|^2\,dx. \tag{6.7}$$

Given a wave function $\psi(x)$ and its Fourier transform $A(k)$, we are now in a position to state the momentum-position version of the Heisenberg uncertainty principle precisely:

$$\Delta p\,\Delta x \geq \frac{\hbar}{2}, \tag{6.8}$$

where Δx and Δp are root-mean square uncertainties as defined above. We will derive this inequality mathematically in Chapter 7. Before attempting a mathematical derivation, however, let us take a rough and ready intuitive approach.

6.3 The Bandwidth Theorem

What is the minimum possible size of a wave packet constructed using waves with wave vectors in a narrow range $\langle k \rangle \pm \Delta k$ centred on $\langle k \rangle$?

Two-wave example

For simplicity, start by considering an example with just two component cosine waves, $\psi_1(x)$ and $\psi_2(x)$, which have equal amplitudes and interfere constructively at $x = 0$:

$$\psi_1(x) = \cos(k_1 x), \qquad\qquad \psi_2(x) = \cos(k_2 x).$$

Figure 6.2 shows the two components and their sum,

$$\psi(x) = \psi_1(x) + \psi_2(x) = \cos(k_1 x) + \cos(k_2 x),$$

in the case when $k_1 = 0.95\,\text{m}^{-1}$ and $k_2 = 1.05\,\text{m}^{-1}$. The short carrier wave and the slowly varying interference envelope of the beats are clear.

How wide are the beats? The first zero of the envelope function occurs at the point marked by the dashed vertical lines in Fig. 6.2. The functions $\cos(k_1 x)$ and $\cos(k_2 x)$ are equal and opposite at this point, and hence the phases $k_1 x$ and $k_2 x$ differ by π. This gives

$$k_2 x = k_1 x + \pi,$$

or, equivalently,

$$\Delta x \approx \text{half-width of beat envelope} = \frac{\pi}{|k_2 - k_1|} \approx \frac{\pi}{2\Delta k}.$$

The smaller the difference $\Delta k = |k_2 - k_1|/2$ between the wave vectors of the two cosine waves, the larger the half-width Δx of the ''wave packet'':

$$\Delta x \Delta k \approx \frac{\pi}{2}.$$
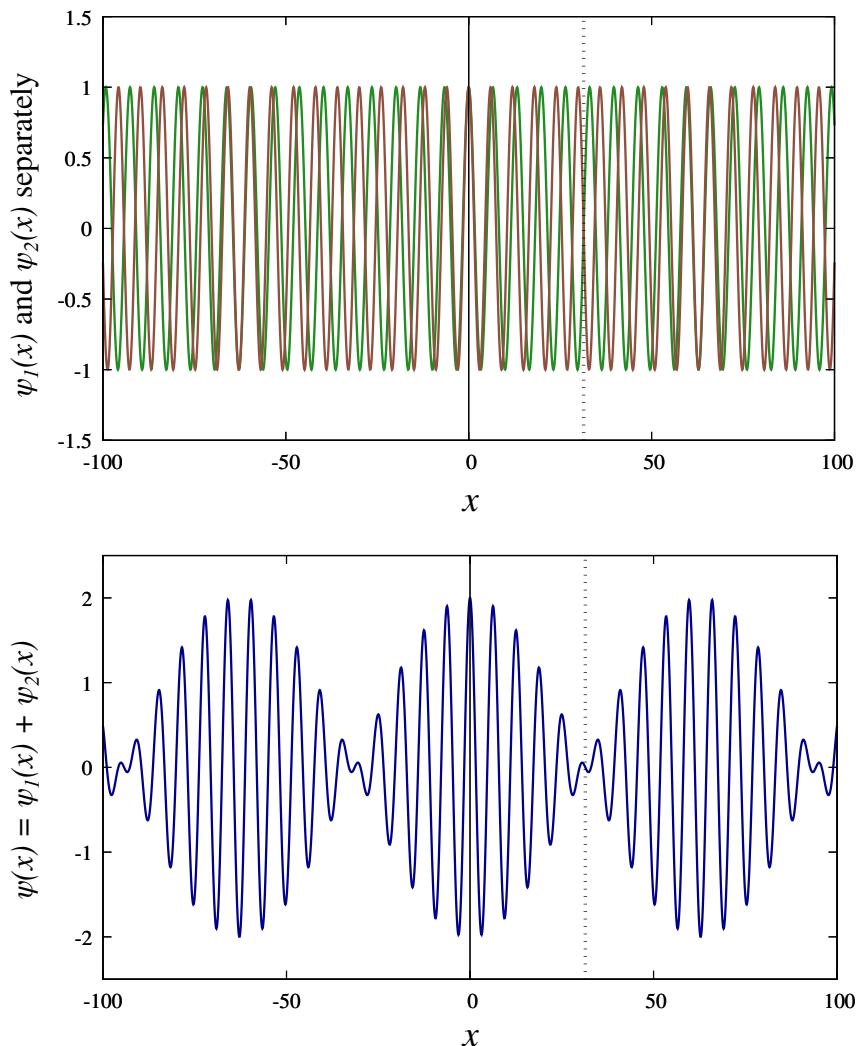
Figure 6.2: Two cosine waves with similar wavelengths and their interference pattern. The vertical dashed lines mark the point where $1.05x = 0.95x + \pi$.

General case

Let us now consider a general wave packet in the form

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int A(k)e^{ikx}\, dk,$$

constructed using an $A(k)$ centred on

$$\langle k \rangle = \int_{-\infty}^{\infty} k\, |A(k)|^2\, dk$$

with squared uncertainty

$$(\Delta k)^2 = \int_{-\infty}^{\infty} (k - \langle k \rangle)^2\, |A(k)|^2\, dk.$$

The mathematics is harder in this case, but the physical principle is the same: in order to shift from the constructive interference that occurs at the centre of the wave packet to the perfect destructive interference that occurs everywhere outside the wave packet, the relative phases of the components have to change by something close to π. This allows us to estimate the rms width of the wave packet, Δx, from the rms spread of wave vectors, Δk.

The distance Δx over which the components with wave vectors $\langle k \rangle - \Delta k$ and $\langle k \rangle + \Delta k$ accumulate a phase difference of π satisfies

$$(\langle k \rangle + \Delta k)\Delta x = (\langle k \rangle - \Delta k)\Delta x + \pi,$$

and hence

$$\Delta x \approx \frac{\pi}{2\Delta k}.$$

The rms width of the wave packet cannot be very much smaller than this, no matter how cleverly the phases and amplitudes are chosen.

This reasoning is imprecise (you might quibble about factors of 2 or π), but the conclusion is simple and correct. If $\psi(x)$ is normalised and $\langle x \rangle$ and Δx are defined via

$$\langle x \rangle = \int x\, |\psi(x)|^2\, dx$$

and

$$(\Delta x)^2 = \int (x - \langle x \rangle)^2\, |\psi(x)|^2\, dx,$$

the values of Δx and Δk are related by a strict inequality,

$$\boxed{\Delta k\, \Delta x \geq \frac{1}{2}} \tag{6.9}$$

This is known as the bandwidth theorem. It is important to understand that no quantum mechanics is involved here: the bandwidth theorem is a general result and applies to all sorts of waves.

Note that nothing has been said about the *maximum* size of the wave packet. It is always possible to choose the phases and amplitudes of the components such that they interfere constructively at any number of arbitrary places, so the maximum size is unbounded.

Real wave packets move around and change shape, so they are functions of x and t, not just x. However, given a time-dependent wave packet $\psi(x,t)$, you can always create a snapshot $\psi(x)$ by choosing a time t_0 and defining $\psi(x) := \psi(x,t_0)$. The shape of $\psi(x)$ depends on the choice of t_0, but the bandwidth theorem holds for *any* function of x and thus for any snapshot of the wave packet.

We might equally well have chosen a specific position x_0 and measured the time-dependent amplitude $\psi(x_0,t)$ to obtain a function of time only: $\psi(t) := \psi(x_0,t)$. Just as $\psi(x)$ can be written as a superposition of waves, so can $\psi(t)$:

$$\psi(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} G(\omega)\, e^{-i\omega t}\, d\omega.$$

The name of the dummy variable of integration has been changed from k to ω in honour of its physical interpretation as an angular frequency, and the Fourier transform of $\psi(t)$ with respect to t has been called $G(\omega)$, but the mathematics is otherwise identical and everything we said about functions of x applies equally well to functions of t. In particular, the bandwidth theorem takes the form

$$\Delta\omega\, \Delta t \geq \frac{1}{2} \tag{6.10}$$

This version of the bandwidth theorem provides a fundamental limit on the information carrying capacity of any communications system: in order to transmit B bits per second, implying a wavepacket duration $\Delta t \approx 1/B$, you need a bandwidth of at least $\Delta\omega = 1/(2\Delta t) = B/2$. This explains why governments can raise billions by auctioning off regions of the electromagnetic spectrum to communications companies.

6.4 Heisenberg's Uncertainty Principle

In quantum theory, where $p = \hbar k$ and $E = \hbar\omega$, the two versions of the bandwidth theorem translate into two versions of the Heisenberg uncertainty principle:

> **The position-momentum uncertainty principle**
>
> $$\Delta p \, \Delta x \geq \frac{\hbar}{2} \qquad\qquad (6.11)$$

> **The energy-time uncertainty principle**
>
> $$\Delta E \, \Delta t \geq \frac{\hbar}{2} \qquad\qquad (6.12)$$

The uncertainty principle is easy to misinterpret and many of the explanations on the internet are confusing and/or confused. One way to cut through the gobbledegook is to focus on an experiment that could be used to test it.

Start with a large number (say $2N$) of identical quantum mechanical systems, each containing a single quantum mechanical particle with the same wave function. You might, for example, start with $2N$ hydrogen atoms, each containing a single electron in its ground state.

> In N of the systems, measure the particle's position: $\{x_i, \ i = 1, N\}$
> In the *other* N, measure the particle's momentum: $\{p_i, \ i = 1, N\}$

From the measurements of position, evaluate

$$\langle x \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i \quad \text{and} \quad (\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} (x_i - \langle x \rangle)^2.$$

From the measurements of momentum, evaluate

$$\langle p \rangle = \frac{1}{N} \sum_{j=1}^{N} p_j \quad \text{and} \quad (\Delta p)^2 = \langle (p - \langle p \rangle)^2 \rangle = \frac{1}{N} \sum_{j=1}^{N} (p_j - \langle p \rangle)^2.$$

Then, for large enough N, one always finds that

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

This result has interesting consequences.

- The more precisely you can predict the outcome of a measurement of x (or p), the less precisely you can predict the outcome of a measurement of p (or x). This is very unlike classical physics, where you can know enough about the system to predict the precise values of both x and p.
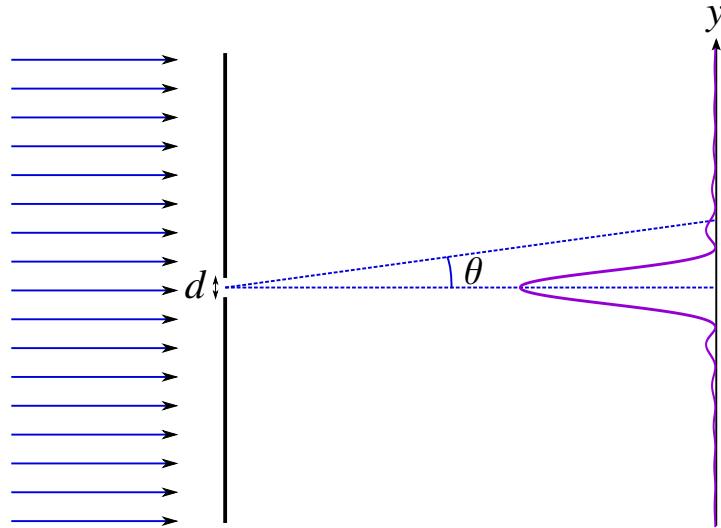
Figure 6.3: Single-slit diffraction.

- Immediately after a measurement of x (or p), the value of Δx (or Δp) must be very small and hence Δp (or Δx) must be very large. This means that you cannot improve your knowledge of (and thus ability to predict the outcome of a measurement of) one of the two without simultaneously decreasing the precision of your knowledge of the other.
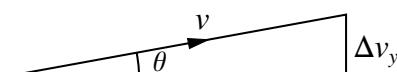
6.5 Consequences of the Uncertainty Principle

Diffraction

Why do particles diffract as illustrated in Fig. 6.3? One way to understand is via the uncertainty principle. On emerging from the slit, the uncertainty Δy in the vertical position of the particle is of order $d/2$. Combining this with the Heisenberg uncertainty principle gives

$$\Delta p_y \geq \frac{\hbar}{2\Delta y} \approx \frac{\hbar}{d}.$$

Assuming that the deviation angle θ is small, so that $\sin\theta = \Delta v_y / v \approx \theta$,

this gives

$$\theta \approx \frac{\Delta v_y}{v} = \frac{\Delta p_y}{p} \gtrsim \frac{\hbar}{d\hbar k} = \frac{1}{kd}.$$

75

From Problem Sheet 1, Q7, the first zero of the diffraction pattern occurs where

$$\frac{kd \sin \theta}{2} = \pi \qquad \Rightarrow \qquad \theta \approx \frac{2\pi}{kd} \quad \text{(since } \theta \text{ is small).}$$

The estimate from the uncertainty principle is smaller — as it should be.

Zero-point energy

A particle confined in a ''box'' of size ℓ has

$$\Delta x \approx \frac{\ell}{2}.$$

(We are only after an order of magnitude estimate here; it would have been equally acceptable to use ℓ or $\ell/3$ or ...) Hence

$$\Delta p \geq \frac{\hbar}{2\Delta x} \approx \frac{\hbar}{\ell}.$$

Since $\langle p \rangle = 0$ (the particle is confined in the box, so its average momentum must be zero), $(\Delta p)^2 = \langle (p - \langle p \rangle)^2 \rangle = \langle p^2 \rangle$. Hence

$$\langle \text{KE} \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{(\Delta p)^2}{2m} \gtrsim \frac{\hbar^2}{2m\ell^2}.$$

Decreasing ℓ increases this ''zero-point'' kinetic energy.

The existence of zero-point energy explains:

- Why the electrons in atoms do not spiral into the nucleus. When ℓ is as small as a nucleus, the zero-point energy cost of confining the electron, which is proportional to $1/\ell^2$, outweighs the Coulomb potential energy gain, which is proportional to $1/\ell$. The kinetic energy cost of confining protons and neutrons is much smaller because they are much heavier than electrons; the forces binding them together (the strong interaction) are also much stronger.

- Why the motion of electrons in atoms and atoms in molecules and solids does not cease as $T \to 0$.

- Why quantum mechanical particles suddenly released from boxes such as atomic traps spread out.

$$\Delta p \gtrsim \frac{\hbar}{\ell} \qquad \Rightarrow \qquad \Delta v \gtrsim \frac{\hbar}{m\ell} \quad \text{(typical spreading speed).}$$
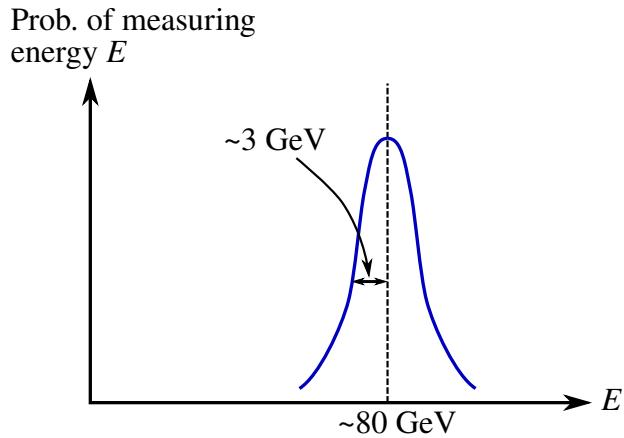
Figure 6.4: The width of the W.

Short-lived quantum states

Because of the energy-time version of the uncertainty principle, $\Delta E \, \Delta t \geq \hbar/2$, the wave packets associated with short-lived quantum states have uncertain energies.

For example, the W particle (the charged intermediate vector boson responsible, with the Z, for the weak interaction) has a mass of order $80 \, \text{GeV}/c^2$ and a lifetime of order 10^{-25}s. How precisely can its energy be specified?

$$\Delta E \gtrsim \frac{\hbar}{2\Delta t} = \frac{1.05 \times 10^{-34}}{2 \times 10^{-25}} \approx 5.25 \times 10^{-10} \, \text{J} \approx 3.3 \, \text{GeV}.$$

This is known as the width of the W.

Another consequence of the time-energy uncertainty principle is that things with very short lifetime do not have to conserve energy exactly. ''Virtual'' particles can appear out of the vacuum briefly before disappearing again (and they do!).

Chapter 7

The Time-Dependent Schrödinger Equation

7.1 Starting Points

> Once at the end of a colloquium I head Debye saying something like: ''Schödinger, you are not working right now on very important problems anyway. Why don't you tell us some time about that thesis of de Broglie, which seems to have attracted some attention?'' So, in one of the next colloquia, Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle and how he could obtain the quantization rules of Neils Bohr and Sommerfeld by demanding that an integer number of waves should be fitted along a stationary orbit. When he had finished, Debye casually remarked that he thought this way of talking was rather childish. As a student of Sommerfeld he had learned that, to deal properly with waves, one had to have a wave equation. It sounded quite trivial and did not seem to make a great impression, but Schödinger evidently thought a bit more about the idea afterwards.
>
> F. Bloch, ''Reminiscences of Heisenberg and the early days of quantum mechanics'', *Physics Today* **29** (12), pp. 23–27 (1976).

Some books try to derive Schrödinger's wave equation by starting from Newton's second law and applying mysterious quantisation rules. In my view this is philosophical nonsense. Quantum theory provides a more fundamental and

widely applicable description of the world than Newton's laws (which do not work at the atomic scale) and cannot be "derived" from classical mechanics. If anything, Newton's second law ought to be regarded as an approximation to the Schrödinger equation — an approximation that works very well when applied to large objects but fails on the atomic scale.

Although it is not possible to derive the Schrödinger equation (or any other fundamental law of nature), the experimental evidence discussed earlier in this course suggests that it ought to have the following properties:

(a) Linearity

> If $\psi_1(x, t)$ and $\psi_2(x, t)$ are solutions, then $b_1\psi_1(x, t) + b_2\psi_2(x, t)$ must also be a solution for any choice of the constants b_1 and b_2.

This reflects our understanding that quantum mechanical waves superpose like "normal" waves; their amplitudes add when they overlap, but they pass through each other unaltered, evolving as if the other overlapping waves were not there. The linearity condition also implies that the normalisation of the wave function is not a property of the Schrödinger equation itself: if $\psi(x, t)$ is a solution then so is $b\psi(x, t)$ for any constant b. The normalistion has to be imposed "by hand".

(b) Dispersion relation

> For a free particle (one that experiences no forces or potentials), the wave function $e^{i(kx-\omega t)}$ ought to be a solution of the Schrödinger equation if and only if
>
> $$\hbar\omega = \frac{\hbar^2 k^2}{2m} \qquad \left(E = \frac{p^2}{2m}\right)$$

Solutions of the ordinary wave equation,

$$\frac{\partial^2 \psi}{\partial t^2} = c^2 \frac{\partial^2 \psi}{\partial x^2},$$

satisfy (a) but not (b).

- To verify that (a) is satisfied, suppose that ψ_1 and ψ_2 are two solutions of the ordinary wave equation:

$$\frac{\partial^2 \psi_1}{\partial t^2} = c^2 \frac{\partial^2 \psi_1}{\partial x^2}, \qquad\qquad \frac{\partial^2 \psi_2}{\partial t^2} = c^2 \frac{\partial^2 \psi_2}{\partial x^2}.$$

Adding b_1 times the first equation to b_2 times the second gives

$$b_1 \frac{\partial^2 \psi_1}{\partial t^2} + b_2 \frac{\partial^2 \psi_2}{\partial t^2} = b_1 c^2 \frac{\partial^2 \psi_1}{\partial x^2} + b_2 c^2 \frac{\partial^2 \psi_2}{\partial x^2},$$

and hence

$$\frac{\partial^2 (b_1 \psi_1 + b_2 \psi_2)}{\partial t^2} = c^2 \frac{\partial^2 (b_1 \psi_1 + b_2 \psi_2)}{\partial x^2}.$$

This shows that $b_1 \psi_1 + b_2 \psi_2$ also satisfies the ordinary wave equation.

- To verify that (b) is *not* satisfied, note that

$$\frac{\partial^2 e^{i(kx - \omega t)}}{\partial t^2} = -\omega^2 e^{i(kx - \omega t)} \quad \text{and} \quad c^2 \frac{\partial^2 e^{i(kx - \omega t)}}{\partial x^2} = -c^2 k^2 e^{i(kx - \omega t)}.$$

Hence, $e^{i(kx - \omega t)}$ satisfies the ordinary wave equation if and only if

$$\omega^2 = c^2 k^2 \qquad \Rightarrow \qquad \omega = \pm c k.$$

This is the correct dispersion relation for light waves or waves on a violin string, but no good for wavicles with $\hbar \omega = \hbar^2 k^2 / 2m$.

7.2 (Re-)Discovering the Time-Dependent Schrödinger Equation

The ordinary wave equation may not produce the correct dispersion relation for wavicles, but its analysis suggests how to write down an equation that does.

Assume that the Schrödinger equation for a free particle involves partial derivatives with respect to t and x and has solutions of the form $\psi(x, t) = e^{i(kx - \omega t)}$. Differentiating $e^{i(kx - \omega t)}$ with respect to time pulls down a factor of $-i\omega$, whilst differentiating it with respect to position pulls down a factor of ik. Equivalently, every application of $i\hbar \partial / \partial t$ multiplies $e^{i(kx - \omega t)}$ by $\hbar \omega$ and every application of $-i\hbar \partial / \partial x$ multiplies $e^{i(kx - \omega t)}$ by $\hbar k$:

$$i\hbar \frac{\partial}{\partial t} \longrightarrow \hbar \omega, \tag{7.1}$$

$$-i\hbar \frac{\partial}{\partial x} \longrightarrow \hbar k. \tag{7.2}$$

It follows that the differential equation

$$\left(i\hbar\frac{\partial}{\partial t}\right)\psi(x,t) = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2\psi$$

has solutions of the form $e^{i(kx-\omega t)}$ with $\hbar\omega = \hbar^2 k^2/2m$. This is the correct dispersion relation for free non-relativistic massive particles. Combining the derivatives on the right-hand side gives the time-dependent Schrödinger equation for a free particle:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} \tag{7.3}$$

Like the ordinary wave equation, the Schrödinger equation is linear.

Equation (7.3) works for free particles (particles on which no forces act), but not for particles moving through a potential $V(x)$ and experiencing forces $F(x) = -dV(x)/dx$. In classical mechanics, the total energy of such a particle is $p^2/2m + V(x)$, suggesting the dispersion relation

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x).$$

A dispersion relation is supposed to give ω as a function of k and ought not to involve x, so this is fishy — but it might make sense in a system where $V(x)$ varies so slowly with x that it can be approximated as a constant over a region containing many de Broglie wavelengths. At any rate, the fishy manoeuvre suggests trying the differential equation

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi \tag{7.4}$$

(A ψ factor has to be included in the potential energy term to keep the equation linear.) Equation (7.4) is the general form of the *time-dependent Schrödinger equation* for one particle in one dimension.

In three dimensions, the wave function $\psi(\mathbf{r},t)$ depends on the particle's position vector $\mathbf{r}$ and the time t. The three-dimensional generalisation of the time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi \tag{7.5}$$

> **Aside: Potentials in Physics**
>
> In electricity and magnetism courses, the ''potential at x'' is the potential energy of a unit test charge placed at x. In classical and quantum mechanics, a slightly different definition is used: the ''potential at x'' is not the potential energy of a test charge but the potential energy of the physical particle being studied at x. For example, in an E&M course, the potential a distance r from a nucleus of charge Ze would be $Ze/4\pi\epsilon_0 r$; in a QM or classical mechanics course, the potential of an electron (charge $-e$) a distance r from the nucleus would be $-Ze^2/4\pi\epsilon_0 r$.

Notes

- We note again that we have not *derived* Eqs. (7.3), (7.4) or (7.5); we merely *guessed* them as the simplest differential equations we could think of consistent with the experimental results. That our guesses were good is confirmed only by their practical success.

- Because of the i's in Eqs. (7.3) and (7.4), the quantum mechanical wave function $\psi(x,t)$ is *necessarily* complex. Even if $\psi(x,t)$ starts off real, the time evolution described by Eq. (7.4) soon makes it complex.

- Although travelling waves such as $e^{i(kx-\omega(k)t)}$ with $\hbar\omega = \hbar^2 k^2/2m$ satisfy the Schrödinger equation for a free particle, they do not satisfy the Schrödinger equation for a particle moving through a position-dependent potential $V(x)$. It is still possible to find solutions with a simple $e^{-i\omega t}$ time dependence, and hence a well-defined energy $E = \hbar\omega$, but their spatial parts are more complicated. This will be explained in Chapter 9.

- Since, for small enough Δt,

$$\frac{\partial \psi(x,t)}{\partial t} \approx \frac{\psi(x,t+\Delta t) - \psi(x,t)}{\Delta t},$$

we can approximate Eq. (7.4) as a finite difference equation:

$$i\hbar\psi(x,t+\Delta t) \approx i\hbar\psi(x,t) + \Delta t\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t)\right).$$

Given the wave function $\psi(x,0)$ at time $t{=}0$, this equation allows you to step forward to find $\psi(x,\Delta t)$, then $\psi(x,2\Delta t)$, and so on. The mathematical evolution described by the Schrödinger equation is therefore entirely deterministic: given the wave function at time $t{=}0$, you can predict it at all future

times. In this sense (ignoring the complications of the poorly understood measurement process), Schrödinger's universe is just as ''clockwork'' as Newton's. The difference is that Schrödinger's clockwork evolution predicts the *probability densities* for the outcomes of measurements and does not in general allow you to make certain predictions about the future.

Chapter 8

Operators and Observables

8.1 Operators in Quantum Mechanics

In the process of (re-)discovering the Schrödinger equation, we associated the momentum $p = \hbar k$ with the differential operator $-i\hbar\partial/\partial x$. To save writing in future, we make this official by defining the *momentum operator*:

$$\hat{p} := -i\hbar\frac{\partial}{\partial x} \qquad (8.1)$$

We also associated the energy $E = \hbar\omega$ with the operator $i\hbar\partial/\partial t$. This operator is not usually named, but we can call it the *energy operator*:

$$\hat{E} := i\hbar\frac{\partial}{\partial t} \qquad (8.2)$$

The Schrödinger equation was ''derived'' by using these associations to turn the classical expression for the energy of a particle, $E = p^2/2m + V(x)$, into a differential equation

$$
\begin{aligned}
i\hbar\frac{\partial\psi}{\partial t} &= \left(\frac{\hat{p}^2}{2m} + V(x)\right)\psi \\
&= \left(\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + V(x)\right)\psi \\
&= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi.
\end{aligned}
\qquad (8.3)
$$

Following the operator theme, Eq. (8.3) is often written as

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi,\qquad(8.4)$$

where

$$\hat{H} := -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\qquad(8.5)$$

is known as the *Hamiltonian operator* or simply the *Hamiltonian*.

The time-dependent Schrodinger equation, Eq. (8.4), tells us that the energy and Hamiltonian operators, $\hat{E}$ and $\hat{H}$, have the same effect on the time-dependent wavefunction $\psi(x,t)$. Both operators can be used to represent the energy, but the Hamiltonian operator turns out to be more useful.

It is an axiom (''*A self-evident principle or one that is accepted as true without proof as the basis for argument; a postulate*'') of QM that any observable — any property that you might in principle be able to measure — is associated with an operator. For example, the position operator, $\hat{x}$, is defined by the equation:

$$\hat{x}\psi(x,t) = x\psi(x,t)\qquad(8.6)$$

In other words, the action of the operator $\hat{x}$ is to multiply the wave function $\psi(x,t)$ to which it is applied by the position coordinate x, producing a new function $x\psi(x,t)$. This definition looks pointless at first, but operators are so deeply embedded in quantum theory that it turns out to be quite useful.

In many cases, you can guess the QM operator for an observable from your knowledge of classical physics. The classical angular momentum, for example, is $\mathbf{r}\times\mathbf{p}$, so you might guess that the quantum mechanical angular momentum operator is $\hat{\mathbf{r}}\times\hat{\mathbf{p}}$. This turns out to be right.

8.2   Commutation Relations

It is important to understand that operators such as $\hat{x}$, $\hat{p}$ and $\hat{H}$ do not necessarily commute with each other: if you apply two operators to a state, one after another, the result you get may depend on the order of application. The most famous example concerns $\hat{p}$ and $\hat{x}$.

Start with an arbitrary wave function $\psi(x)$ and consider the result of first applying $\hat{p}$ to get the function $\hat{p}\psi$ and then applying $\hat{x}$:

$$\hat{x}\big(\hat{p}\psi(x)\big) = \hat{x}\left(-i\hbar\frac{\partial\psi(x)}{\partial x}\right) = -i\hbar x\frac{\partial\psi(x)}{\partial x}.$$

Now see what happens if you apply $\hat{x}$ first and then $\hat{p}$:

$$\hat{p}\big(\hat{x}\psi(x)\big) = -i\hbar\frac{\partial}{\partial x}\big(x\psi(x)\big) = -i\hbar\psi(x) - i\hbar x\frac{\partial\psi(x)}{\partial x}.$$

The two results are not the same! In fact, we have discovered that:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\,\psi(x) = i\hbar\psi(x).$$

Since this holds regardless of the state ψ, it is actually an operator identity:

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar. \tag{8.7}$$

This is an example of what is known as a commutation relation, and expressions such as $\hat{A}\hat{B} - \hat{B}\hat{A}$ are called commutators. They crop up so often that they have been given a special notation:

$$\big[\hat{A}, \hat{B}\big] := \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{8.8}$$

8.3 Hermitian Operators

All of the quantum mechanical operators associated with observables are *Hermitian* operators. You may also see the term *self-adjoint*, which you can take as equivalent to Hermitian.

> **Definition of a Hermitian Operator**
>
> An operator $\hat{O}$ is said to be Hermitian if, given any two wave functions $\psi(x)$ and $\phi(x)$:
>
> $$\int_{-\infty}^{\infty} \phi^*(x)\left(\hat{O}\psi(x)\right)dx = \int_{-\infty}^{\infty}\left(\hat{O}\phi(x)\right)^*\psi(x)\,dx. \quad (8.9)$$

[Strictly, it is also necessary to specify the function space from which the arbitrary functions $\psi(x)$ and $\phi(x)$ are chosen. For example, to make sure that the integrals are finite, $\phi(x)$ and $\psi(x)$ must die off fast enough as $x \to \pm\infty$. Physicists are lazy and often ignore mathematical issues such as this, but those of you who are mathematicians at heart might like to know that the type of function space used in QM is called a Hilbert space.]

Showing that $\hat{x}$ is Hermitian is easy:

$$\int_{-\infty}^{\infty} \phi^*(x)\,(\hat{x}\psi(x))\; dx = \int_{-\infty}^{\infty} \phi^*(x)\,x\psi(x)\,dx$$

$$= \int_{-\infty}^{\infty} (x\phi(x))^*\,\psi(x)\,dx$$

$$= \int_{-\infty}^{\infty} (\hat{x}\phi(x))^*\,\psi(x)\,dx. \qquad \checkmark$$

To show that $\hat{p} = -i\hbar\partial/\partial x$ is Hermitian, all we need to do is integrate by parts:

$$\int_{-\infty}^{\infty} \phi^*\,(\hat{p}\psi)\; dx = \int_{-\infty}^{\infty} \phi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right) dx$$

$$= -i\hbar \int_{-\infty}^{\infty} \left(\frac{\partial(\phi^*\psi)}{\partial x} - \frac{\partial\phi^*}{\partial x}\psi\right) dx$$

$$= -i\hbar\left[\phi^*\psi\right]_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \frac{\partial\phi^*}{\partial x}\psi\,dx$$

$$= \int_{-\infty}^{\infty} \left(-i\hbar\frac{\partial\phi}{\partial x}\right)^*\psi\,dx$$

$$= \int_{-\infty}^{\infty} (\hat{p}\phi)^*\,\psi\,dx. \qquad \checkmark$$

The boundary term vanished because we assumed that $\phi^*(x)\psi(x)$ tends to zero as $x \to \pm\infty$. This assumption is valid because physical wave functions are probability amplitudes and must be normalisable, implying that $\int_{-\infty}^{\infty} |\psi(x)|^2 dx$ must be finite and hence that $|\psi(x)| \to 0$ as $x \to \pm\infty$.

> **Aside: Hemitian Matrices**
>
> You might already have met the idea of a Hermitian matrix, **O**, which is one for which $O_{ij} = (O_{ji})^*$. If you rewrite the definition of a Hermitian operator as
>
> $$\int_{-\infty}^{\infty} \phi^*(x)\hat{O}\psi(x)\,dx = \left(\int_{-\infty}^{\infty} \psi^*(x)\hat{O}\phi(x)\,dx\right)^*, \qquad (8.10)$$
>
> the analogy between the two definitions becomes clear. The indices i and j labelling the elements of the matrix **O** are analogous to the functions ϕ and ψ sandwiching the operator $\hat{O}$.

It follows that $\hat{p}^2$ is also Hermitian.

$$\int_{-\infty}^{\infty} \phi^*(x)\hat{p}^2\psi(x)\,dx = \int_{\infty}^{\infty} (\hat{p}\phi(x))^*\,\hat{p}\psi(x)\,dx = \int_{\infty}^{\infty} \left(\hat{p}^2\phi(x)\right)^*\psi(x)\,dx.$$

To understand the final step, imagine re-naming the state $\hat{p}\phi(x)$ as, say, $\chi(x)$, and applying the Hermitian property in the form:

$$\int_{-\infty}^{\infty} \chi^*(x)\hat{p}\psi(x)\,dx = \int_{-\infty}^{\infty} (\hat{p}\chi(x))^*\,\psi(x)\,dx,$$

which is valid as long as $\chi^*(x)\psi(x) \to 0$ as $x \to \pm\infty$.

An even simpler argument shows that the potential energy operator $V(\hat{x})$ is Hermitian. Hence so is the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}). \tag{8.11}$$

Hermitian operators have all sorts of convenient and interesting mathematical properties, which you will learn about on the next problem sheet, in the Quantum Mechanics course that follows this one, and in the Sturm-Liouville theory part of your Differential Equations course.

8.4 Momentum Uncertainty Revisited

So far, we have found the momentum uncertainty $(\Delta p)^2 := \langle p^2 \rangle - \langle p \rangle^2$ using the equations

$$\langle p \rangle = \int_{-\infty}^{\infty} \hbar k |A(k)|^2\,dk \quad \text{and} \quad \langle p^2 \rangle = \int_{-\infty}^{\infty} (\hbar k)^2 |A(k)|^2\,dk.$$

This approach is conceptually clear but we have to find $A(k)$ by Fourier transforming the wave function $\psi(x)$ before we can use it. In this section, as an example of the use of the momentum operator and a step on the way to deriving the uncertainty principle, we will see how to work out $\langle p \rangle$ and $\langle p^2 \rangle$ without Fourier transforming.

Let us start with the expression for $\langle p \rangle$, which we write in the form

$$\langle p \rangle = \int_{-\infty}^{\infty} A^*(k)\,\hbar k\,A(k)\,dk.$$

Remembering that $A(k)$ and $\psi(x)$ are a Fourier transform pair:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k)e^{ikx}dk, \qquad A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x)e^{-ikx}dx,$$

we can express $A(k)$ in terms of $\psi(x)$:

$$\langle p \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A^*(k)\, \hbar k \left(\int_{-\infty}^{\infty} e^{-ikx} \psi(x)\, dx \right) dk$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A^*(k) \left(\int_{-\infty}^{\infty} \left(\hat{p} e^{ikx} \right)^* \psi(x)\, dx \right) dk,$$

where the last step followed because $\hat{p} e^{ikx} = \hbar k e^{ikx}$. Using the Hermitian property of $\hat{p}$ to rearrange the inner integral gives

$$\langle p \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A^*(k) \left(\int_{-\infty}^{\infty} \left(e^{ikx} \right)^* \hat{p} \psi(x)\, dx \right) dk,$$

and changing the order of integration turns this into

$$\langle p \rangle = \int_{-\infty}^{\infty} \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A^*(k) e^{-ikx}\, dk \right) \hat{p} \psi(x)\, dx.$$

The new inner integral is the complex conjugate of the Fourier integral for $\psi(x)$, so we reach a very nice result:

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{p} \psi(x)\, dx \qquad (8.12)$$

A very similar derivation starting from

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} A^*(k)\, (\hbar k)^2\, A(k)\, dk$$

and using two applications of $\hat{p}$ and two uses of the Hermitian property leads to

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{p}^2 \psi(x)\, dx \qquad (8.13)$$

Putting everything together, we have shown that

$$(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2 = \int_{-\infty}^{\infty} \psi^*(x) \hat{p}^2 \psi(x)\, dx - \left(\int_{-\infty}^{\infty} \psi^*(x) \hat{p} \psi(x)\, dx \right)^2.$$

The reasons for calling $\hat{p}$ the momentum operator should be becoming clearer.

8.5   Dirac Notation

Writing out all of these integrals is tedious, so from now on we are going to use Dirac's shorthand notation:

$$\int_{-\infty}^{\infty} \phi^*(x)\,\psi(x)\,dx \quad \longrightarrow \quad \langle \phi, \psi \rangle, \tag{8.14}$$

$$\int_{-\infty}^{\infty} \phi^*(x)\,(\hat{O}\psi(x))\,dx \quad \longrightarrow \quad \langle \phi, \hat{O}\psi \rangle, \tag{8.15}$$

$$\int_{-\infty}^{\infty} \left(\hat{O}\phi(x)\right)^* \psi(x)\,dx \quad \longrightarrow \quad \langle \hat{O}\phi, \psi \rangle. \tag{8.16}$$

Equations (8.15) and (8.16) are just special cases of Eq. (8.14). To obtain Eq. (8.15), for example, all you have to do is take Eq. (8.14) and replace the function $\psi(x)$ by the function $\hat{O}\psi(x)$.

> **Aside: Alternative Notations**
>
> Most books use a slightly different form of Dirac notation, replacing the commas between what Dirac called the ''bra'' and the ''ket'' by vertical lines: $\langle \phi, \psi \rangle \longrightarrow \langle \phi | \psi \rangle$ and $\langle \phi, \hat{O}\psi \rangle \longrightarrow \langle \phi | \hat{O}\psi \rangle$. Another vertical line is sometimes placed after the operator, so that $\langle \phi | \hat{O}\psi \rangle$ becomes $\langle \phi | \hat{O} | \psi \rangle$. We will stick with the comma version here.

The following rules follow directly from the definition of the bra-ket:

$$\langle \phi, \psi \rangle = \langle \psi, \phi \rangle^* \tag{8.17}$$

$$\langle \phi, \hat{O}\psi \rangle = \langle \hat{O}\psi, \phi \rangle^* \tag{8.18}$$

$$\langle \phi, a_1\psi_1 + a_2\psi_2 \rangle = a_1 \langle \phi, \psi_1 \rangle + a_2 \langle \phi, \psi_2 \rangle \tag{8.19}$$

$$\langle a_1\phi_1 + a_2\phi_2, \psi \rangle = a_1^* \langle \phi_1, \psi \rangle + a_2^* \langle \phi_2, \psi \rangle \tag{8.20}$$

where a_1 and a_2 are arbitrary complex numbers. A normalised wave function ψ satisfies $\langle \psi, \psi \rangle = 1$.

The definition of a Hermitian operator looks much simpler (and is easier to remember) in Dirac notation:

$$\langle \phi, \hat{O}\psi \rangle = \langle \hat{O}\phi, \psi \rangle. \tag{8.21}$$

Note how this differs from Eq. (8.18). In fact, if we apply Eq. (8.18) to Eq. (8.21), we get

$$\langle \phi, \hat{O}\psi \rangle = \langle \psi, \hat{O}\phi \rangle^*. \tag{8.22}$$

This is the Dirac notation equivalent of the alternative definition of Hermiticity from Eq. (8.10).

8.6 Conservation of Normalisation

As a first example of the use of Dirac notation, we are going to show that the time-dependent Schrödinger equation conserves (but, because it is linear, does not fix) the value of

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

This guarantees that the total probability of finding the particle somewhere never changes. Particles are not created or destroyed in non-relativistic quantum theory.

To prove that the normalisation integral is independent of time, we simply evaluate its time derivative:

$$
\begin{aligned}
\frac{\partial}{\partial t} \langle \psi, \psi \rangle &= \left\langle \frac{\partial \psi}{\partial t}, \psi \right\rangle + \left\langle \psi, \frac{\partial \psi}{\partial t} \right\rangle && \text{moving } \tfrac{\partial}{\partial t} \text{ into integral over } x \\
&= \left\langle \frac{-i\hat{H}\psi}{\hbar}, \psi \right\rangle + \left\langle \psi, \frac{-i\hat{H}\psi}{\hbar} \right\rangle && \text{because } \tfrac{\partial \psi}{\partial t} = \tfrac{-i\hat{H}\psi}{\hbar} \\
&= \frac{i}{\hbar} \langle \hat{H}\psi, \psi \rangle - \frac{i}{\hbar} \langle \psi, \hat{H}\psi \rangle && \text{using Eqs. (8.20) and (8.19)} \\
&= 0. && \text{because } \hat{H} \text{ is Hermitian}
\end{aligned}
$$

The second line used the time-dependent Schrödinger equation, $i\hbar \partial \psi / \partial t = \hat{H}\psi$, rearranged into the form $\partial \psi / \partial t = -i\hat{H}\psi / \hbar$.

8.7 Derivation of the Uncertainty Principle

We now have everything we need to derive the uncertainty principle. Given an arbitrary normalised wave function $\psi(x)$, the squared uncertainties are

$$(\Delta x)^2 = \langle \psi, (\hat{x} - \langle x \rangle)^2 \psi \rangle, \qquad (\Delta p)^2 = \langle \psi, (\hat{p} - \langle p \rangle)^2 \psi \rangle,$$

where $\langle x \rangle = \langle \psi, \hat{x}\psi \rangle$ and $\langle p \rangle = \langle \psi, \hat{p}\psi \rangle$. Writing $\hat{x} - \langle x \rangle$ and $\hat{p} - \langle p \rangle$ again and again is boring, so define

$$\hat{X} := \hat{x} - \langle x \rangle, \qquad\qquad \hat{P} := \hat{p} - \langle p \rangle,$$

and rewrite the position and momentum uncertainties as

$$(\Delta x)^2 = \langle \psi, \hat{X}^2 \psi \rangle, \qquad\qquad (\Delta p)^2 = \langle \psi, \hat{P}^2 \psi \rangle \, .$$

Note also that the subtraction of the expected values has no effect on the value of the commutator:

$$[\hat{X}, \hat{P}] = \hat{X}\hat{P} - \hat{P}\hat{X} = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar.$$

Now consider the wavefunction

$$\phi(x) = (\hat{X} + i\lambda\hat{P})\psi(x),$$

where λ is a constant to be determined. This is a peculiar definition, but $\phi(x)$ is just some complex function of position, so

$$\langle\phi, \phi\rangle = \int_{-\infty}^{\infty} |\phi(x)|^2 \, dx \geq 0.$$

This is the inequality that will lead to the uncertainty principle.

The tricky step is to relate $\langle\phi, \phi\rangle$ to $(\Delta x)^2$ and $(\Delta p)^2$:

$$
\begin{aligned}
\langle\phi, \phi\rangle &= \langle(\hat{X} + i\lambda\hat{P})\psi, \phi\rangle \\
&= \langle\hat{X}\psi, \phi\rangle - i\lambda\langle\hat{P}\psi, \phi\rangle && \text{using Eq. (8.20)} \\
&= \langle\psi, \hat{X}\phi\rangle - i\lambda\langle\psi, \hat{P}\phi\rangle && \hat{X}, \hat{P} \text{ Hermitian} \\
&= \langle\psi, (\hat{X} - i\lambda\hat{P})\phi\rangle && \text{recombining terms} \\
&= \langle\psi, (\hat{X} - i\lambda\hat{P})(\hat{X} + i\lambda\hat{P})\psi\rangle && \phi := (\hat{X} + i\lambda\hat{P})\psi \\
&= \langle\psi, \left(\hat{X}^2 + \lambda^2\hat{P}^2 + i\lambda(\hat{X}\hat{P} - \hat{P}\hat{X})\right)\psi\rangle && \text{expanding} \\
&= \langle\psi, \left(\hat{X}^2 + \lambda^2\hat{P}^2 - \hbar\lambda\right)\psi\rangle && \hat{X}\hat{P} - \hat{P}\hat{X} = i\hbar \\
&= (\Delta x)^2 + \lambda^2(\Delta p)^2 - \hbar\lambda. && \psi \text{ normalised}
\end{aligned}
$$

Since the left-hand side is ≥ 0, the right-hand side must also be ≥ 0:

$$(\Delta p)^2\lambda^2 - \hbar\lambda + (\Delta x)^2 \geq 0,$$

for all values of λ. This quadratic function of λ has a single minimum where

$$\frac{d}{d\lambda}\left((\Delta p)^2\lambda^2 - \hbar\lambda + (\Delta x)^2\right) = 2(\Delta p)^2\lambda - \hbar = 0,$$

and hence where

$$\lambda = \frac{\hbar}{2(\Delta p)^2}.$$

Plugging this back into the quadratic inequality gives

$$(\Delta p)^2\left(\frac{\hbar}{2(\Delta p)^2}\right)^2 - \hbar\left(\frac{\hbar}{2(\Delta p)^2}\right) + (\Delta x)^2 \geq 0,$$

which rearranges to

$$(\Delta x)^2 \geq \frac{\hbar^2}{4(\Delta p)^2}.$$

Finally, taking the square root (remembering that Δx and Δp are positive) and multiplying through by Δp, we obtain the position-momentum version of the uncertainty principle:

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

Chapter 9

Energy Levels

The time-dependent Schrödinger equation allows you to work out $\psi(x,t)$ if you know $\psi(x,0)$, but that is all it does; it is an *equation of motion* and does not say anything (directly) about quantisation or energy levels. This chapter explains how to go about computing *energy eigenvalues* (also known as energy levels or quantised energies) and *energy eigenfunctions* (the corresponding wave functions).

9.1 Energy Eigenfunctions

Our intuition is that states of a precise energy (which are equivalent to states of a precise angular frequency because $E = \hbar\omega$) are solutions of the time-dependent Schrödinger equation in which only one angular frequency appears. They are the quantum mechanical equivalents of pure sine-wave sounds or laser light of a specific frequency. Because only one angular frequency is present, all measurements of the frequency, and thus of the energy of the particle, must give the same result.

This idea prompts us to look for solutions of the time-dependent Schrödinger equation of the form:

$$\psi(x,t) = u(x)e^{-i\omega t}, \tag{9.1}$$

where $u(x)$ is some spatial function yet to be determined. If we plug this trial solution into the time-dependent Schrödinger equation, Eq. (7.4), we get:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(ue^{-i\omega t}\right) + V\left(ue^{-i\omega t}\right) = i\hbar\frac{\partial}{\partial t}\left(ue^{-i\omega t}\right).$$

Since u depends only on x and $e^{-i\omega t}$ depends only on t, this simplifies to

$$e^{-i\omega t}\left(-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2}\right) + e^{-i\omega t}Vu = e^{-i\omega t}\hbar\omega u.$$

Cancelling the common $e^{-i\omega t}$ factor (which can never be zero) gives the *time-independent Schrödinger equation*,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x) = Eu(x) \tag{9.2}$$

where $E = \hbar\omega$. This may also be written in terms of the Hamiltonian operator defined in Eq. (8.5):

$$\hat{H}u(x) = Eu(x) \tag{9.3}$$

Notes

- You may have noticed that the technique used to derive the time-independent Schrödinger equation is very like the separation of variables method from your Differential Equations course. The only difference is that, instead of looking for solutions of the form $u(x)f(t)$, where $u(x)$ and $f(t)$ are functions to be determined, we set $f(t) = e^{-i\omega t}$ because we already knew the form of the time dependence. We could equally well have assumed only that $\psi(x,t) = u(x)f(t)$, derived the ordinary differential equation satisfied by $f(t)$, and shown that it has solutions of the form $e^{-i\omega t}$.

- For confined or bound particles such as electrons in atoms, Eq. (9.3) only has solutions for specific energies, which can be labelled using integers:

$$\left.\begin{array}{r} u_n(x) \\ E_n \end{array}\right\} \qquad n = 1, 2, 3, \ldots$$

The eigenvalues E_n are the quantised energy levels observed in experiments. The eigenfunctions $u_n(x)$ are direct mathematical and physical analogues of the standing waves on a violin string.

- For free or unbound particles, such as protons in the solar wind or electrons moving through a semiconductor, it is possible to find solutions of Eq. (9.3) for all values of the energy E within specific ranges ($E \geq 0$ for a free particle). The solutions of Eq. (9.3) are then labelled using a continuous variable (such as the wave vector k) instead of an integer.

- As pointed out in Chapter 8, there is a close analogy between Hermitian operators such as $\hat{H}$ and Hermitian matrices. There is an equally close analogy between Eq. (9.3) and a matrix eigenvalue equation such as

$$\mathbf{Hv} = \lambda\mathbf{v},$$

where $\mathbf{H}$ is a Hermitian matrix, λ an eigenvalue, and $\mathbf{v}$ an eigenvector. This explains why E is called an energy eigenvalue and $u(x)$ an energy eigenfunction.

- In Question 6 of Problem Sheet 5, you showed that the eigenvalues of any Hermitian operator are real. (The same holds for Hermitian matrices.) Since the eigenvalues of $\hat{H}$ are supposed to be energy levels, this is reassuring.

- The three-dimensional version of the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2 u(\mathbf{r}) + V(\mathbf{r})u(\mathbf{r}) = Eu(\mathbf{r}) \qquad (9.4)$$

where $V(\mathbf{r})$ is the potential experienced by the particle. For an electron in a hydrogen atom, this becomes

$$-\frac{\hbar^2}{2m}\nabla^2 u(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0 r}u(\mathbf{r}) = Eu(\mathbf{r}). \qquad (9.5)$$

You will learn how to solve this differential equation later in the module and will discover that its energy eigenvalues match the energy levels of the hydrogen atom exactly (barring tiny relativistic corrections, which can also be calculated).

- The time-independent Schrödinger equation predicts the shell structure of atoms and thus the periodic table of the elements. It also works for molecules and solids. In principle, at least, it explains almost all of the chemistry and physics of everyday matter.

9.2 Example: Energy Eigenfunctions of a Free Particle

We learnt earlier in the course that the time-dependent Schrödinger equation for a free particle,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial^2 x} = i\hbar\frac{\partial\psi(x,t)}{\partial t}, \qquad (9.6)$$

has solutions of the form

$$\psi(x,t) = e^{i(kx-\omega t)} = e^{ikx}e^{-i\omega t}, \qquad (9.7)$$

with $\omega = \hbar k^2/2m$. These already look like $u(x)e^{-i\omega t}$ with $u(x) = e^{ikx}$, so the energy eigenfunctions (which are labelled by the continuous variable k) are

$$u(k, x) = e^{ikx}. \tag{9.8}$$

(Note: as the eigenfunctions extend to $\pm\infty$, they are not normalisable.)

Let's check this by solving the time-independent Schrödinger equation. Since $V(x) = 0$ for a free particle, we need to solve:

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

Rearranging gives

$$\frac{d^2u(x)}{dx^2} = -\frac{2mE}{\hbar^2}u(x) = -k^2u(x),$$

where I have defined $k^2 := 2mE/\hbar^2$. This is the same differential equation obeyed by a classical simple harmonic oscillator (with t replaced by x), so you already know the solutions:

$$u(k, x) = e^{\pm ikx}.$$

(Note: until now we have always always chosen the plus sign, writing $u(k, x) = e^{ikx}$, but this is not a restriction as we did not insist that k had to be positive.) Furthermore, rearranging the definition $k^2 = 2mE/\hbar^2$ gives

$$E(k) = \frac{\hbar^2 k^2}{2m},$$

which is the correct expression for the energy of the particle.

For a free particle, we have seen that solutions of a precise energy, $E = \hbar^2 k^2/2m$, also have a precise momentum, $\hbar k$. In other words, the energy eigenfunctions are also momentum eigenfunctions. If the potential $V(x)$ varies with position, however, the energy eigenfunctions are not just plane waves and can only be found by solving Eq. (9.3). In most cases, this requires the use of a computer.

Any function can be Fourier transformed, of course, so all eigenfunctions can be viewed as superpositions of plane waves, but these superpositions contain a range of values of momentum if $V(x)$ depends on position. Physically, this is because the potential exerts forces on the particle: $F(x) = -dV(x)/dx$. As in classical mechanics, the conservative forces changes the particle's momentum whilst leaving its total energy invariant. The energy eigenfunctions therefore contain contributions with a range of different momenta and are no longer simple sine or cosine waves or complex exponentials.

Figure 9.1: A square well of width a, showing the first three energy eigenfunctions and the corresponding energy eigenvalues.

9.3 Example: Energy Eigenfunctions of a Particle in an Infinite Square Well

A more interesting example is the particle in a box introduced in Sec. 5.4. The box and the first three energy eigenfunctions are shown in Fig. 9.1.

The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2 u(x)}{dx^2} + V(x)u(x) = Eu(x),$$

where

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a, \\ \infty & \text{otherwise.} \end{cases}$$

There is no chance of finding the particle outside the box, so the wave function must be zero unless $0 \leq x \leq a$. Assuming that it is also continuous at $x = 0$ and $x = a$, the boundary conditions are

$$u(x = 0) = u(x = a) = 0.$$

The assumption that the wave function must be continuous will be revisited and justified more carefully when we consider scattering from a potential step in Sec. 9.7.

In the region $0 \leq x \leq a$, where $V(x) = 0$, the Schrödinger equation reads

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

This is a second-order ordinary differential equation (ODE), so we expect two independent solutions. To find them, substitute the trial solution $u(x) = e^{bx}$ into the left-hand side of the ODE:

$$-\frac{\hbar^2}{2m}\frac{d^2\left(e^{bx}\right)}{dx^2} = -\frac{\hbar^2 b^2}{2m}e^{bx}.$$

[Note: using $u(x) = e^{bx}$ as a trial solution is not very smart — we are expecting wave-like behaviour, so using $u(x) = e^{ikx}$ would have been more sensible — but it is interesting to see how it works out.] The left-hand side of the ODE equals the right-hand side if $b = \pm\sqrt{-2mE/\hbar^2}$, so the general solution is

$$u(x) = Ae^{bx} + Be^{-bx}, \qquad b = \sqrt{-2mE/\hbar^2}.$$

To pin down the values of the integration constants A and B, impose the boundary conditions, $u(0) = u(a) = 0$, to get:

$$A + B = Ae^{ba} + Be^{-ba} = 0.$$

The first equation says that $A = -B$, in which case the second equation reads $A(e^{ba} - e^{-ba}) = 2A\sinh(ba) = 0$. Since the sinh function is only zero at the origin, this implies either: (i) that $b = 0$, implying $u(x) = Ae^{bx} + Be^{-bx} = A + B = 0$; or (ii) that $A = 0$, implying $B = -A = 0$ and thus $u(x) = 0$ again. It looks as if the simultaneous equations have no solutions!

The escape route is to notice that b does not have to be real. In fact, if you look at the equation $b = \sqrt{-2mE/\hbar^2}$ and remember that we expect the energy to be positive on physical grounds (the potential energy within the box is zero and the kinetic energy is positive), it seems much more likely that b is imaginary. Let us therefore write $b = ik$ and re-express the general solution as

$$u(x) = Ae^{ikx} + Be^{-ikx}, \qquad k = \sqrt{\frac{2mE}{\hbar^2}}.$$

This still satisfies the time-independent Schrödinger equation within the box, but the boundary conditions now give

$$A + B = Ae^{ika} + Be^{-ika} = 0.$$

The boundary condition at $x = 0$ again implies that $A = -B$. Now, however, when we substitute this back into the boundary condition at $x = a$, we get

$$A(e^{ika} - e^{-ika}) = 2iA\sin(ka) = 0.$$

Since we do not want to lose the solution by setting A to zero, this forces ka to be a multiple of π, leaving us with eigenfunctions of the form

$$u_n(x) = 2iA_n \sin\left(\frac{n\pi x}{a}\right) = C_n \sin\left(\frac{n\pi x}{a}\right), \qquad n = 1, 2, \ldots,$$

where we have defined $C_n := 2iA_n$. Remembering that $k = \sqrt{2mE/\hbar^2}$, and hence that $E = \hbar^2 k^2/2m$, the corresponding energy eigenvalues are

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}, \qquad n = 1, 2, \ldots.$$

The energy levels are quantised because of the effect of the boundary conditions, which express the physical idea that the waves have to fit into the box.

Note that solving the Schrödinger equation did not fix the value of the constant C_n. We already know that it cannot because the Schrödinger equation is linear: if $u_n(x)$ is a solution, so is any multiple of $u_n(x)$. To find C_n, it is necessary to normalise $u_n(x)$ as described in Sec. 5.4. In other words, we choose C_n such that

$$\int_0^a |u_n(x)|^2 \, dx = \int_0^a |C_n|^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1.$$

After evaluating the integral, one finds that

$$C_n = \sqrt{\frac{2}{a}}.$$

Although the value of C_n came out to be independent of n, this is just a fluke. In most examples, different eigenfunctions require different normalisation constants.

To summarise, the energy eigenvalues and normalised energy eigenfunctions of a particle of mass m in an infinite square well of width a are:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}, \qquad u_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \qquad n = 1, 2, 3, \ldots.$$

9.4 Energy Eigenfunctions and General Solutions

It is important to understand that wave functions of the form $u(x)e^{-i\omega t}$ are very special solutions of the time-dependent Schrödinger equation. Unless you have just measured the energy, forcing the system into an energy eigenfunction, the wave function of a free particle is unlikely to take the form $u(x)e^{-i\omega t}$.

As discussed earlier in the course, however, any wave packet that satisfies the time-dependent Schrödinger equation for a free particle can be written as a linear combination of time-dependent plane waves:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega(k)t)} dk, \tag{9.9}$$

where $\omega(k) = \hbar k^2/2m = E(k)/\hbar$. The general solution of the time-dependent Schrödinger equation for a free particle can thus be written as a linear combination of energy eigenfunctions $u(k,x) = e^{ikx}$, each of which evolves with its own special time dependence $e^{-i\omega(k)t}$.

This result is not restricted to free particles. The energy eigenfunctions of a bound particle, prevented from escaping to infinity by the forces from a potential $V(x)$, are labelled using integers, not continuous variables such as k, but the general result still holds. Any solution of the time-dependent Schrödinger equation can be written as a linear combination of energy eigenfunctions, each of which evolves in time at its own rate:

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n u_n(x) e^{-i\omega_n t}, \tag{9.10}$$

where $\omega_n = E_n/\hbar$. The energy eigenfunctions $u_n(x)$ are now more complicated (they are no longer plane waves), the integral in Eq. (9.9) has been replaced by the sum in Eq. (9.10), the function $A(k)$ has been replaced by the coefficients c_n, and $\omega_n = E_n/\hbar$ is no longer equal to $\hbar k^2/2m$, but the basic idea is the same.

9.5 Eigenfunction Expansions, Probabilities, and Expectation Values

Suppose that the normalised wave function at some fixed time t is $\psi(x)$. We are planning to measure the energy. Here are the steps you need to take to work out the possible results and the probabilities of obtaining them.

1. Solve the time-independent Schrödinger equation,

$$\hat{H} u_n(x) = E_n u_n(x), \tag{9.11}$$

   to find the energy eigenvalues E_n and the corresponding energy eigenfunctions $u_n(x)$. For simplicity, I am assuming that you are interested in bound states to which you can assign integer labels, $n = 1, 2, \ldots$.

2. One you have found the energy eigenfunctions, write $\psi(x)$ as a superposition of them:

$$\psi(x) = \sum_{n=1}^{\infty} c_n u_n(x). \tag{9.12}$$

It is a theorem (not proved here) that the eigenfunctions of any Hermitian operator form a complete set, so expressing $\psi(x)$ as a superposition of eigenfunctions is always possible.

3. Working out the expansion coefficients c_n looks difficult but is actually quite easy. As you showed in part (b) of Question 6 on Problem Sheet 5, eigenfunctions corresponding to different eigenvalues are orthogonal:

$$\langle u_m, u_n \rangle = \int_{-\infty}^{\infty} u_m^*(x)\, u_n(x)\, dx = 0 \qquad \text{if} \qquad E_m \neq E_n.$$

If you also choose to normalise the eigenfunctions,

$$\langle u_m, u_m \rangle = \int_{-\infty}^{\infty} u_m^*(x)\, u_m(x)\, dx = 1,$$

they form what is called a complete (because you can use them to expand any wave function), orthonormal (because they are both orthogonal and normalised) set:

$$\langle u_m, u_n \rangle = \int_{-\infty}^{\infty} u_m^*(x)\, u_n(x)\, dx = \delta_{mn}. \tag{9.13}$$

To find a specific expansion coefficient c_m, all you have to do is multiply Eq. (9.12) by $u_m^*(x)$ and integrate both sides. In Dirac notation,

$$\langle u_m, \psi \rangle = \left\langle u_m, \sum_{n=1}^{\infty} c_n u_n \right\rangle = \sum_{n=1}^{\infty} c_n \langle u_m, u_n \rangle = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m,$$

or, in integral notation,

$$\int_{-\infty}^{\infty} u_m^*(x)\, \psi(x)\, dx = \int_{-\infty}^{\infty} u_m^*(x) \left(\sum_{n=1}^{\infty} c_n u_n(x) \right) dx$$

$$= \sum_{n=1}^{\infty} c_n \int_{-\infty}^{\infty} u_m^*(x)\, u_n(x)\, dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m.$$

In other words, to work out c_m, all you have to do is evaluate an integral:

$$c_m = \langle u_m, \psi \rangle = \int_{-\infty}^{\infty} u_m^*(x)\, \psi(x)\, dx. \tag{9.14}$$

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4. You will probably not be surprised to hear that the probability p_m of measuring energy level E_m is equal to $|c_m|^2$:

$$p_m = \text{prob. of measuring energy } E_m = |c_m|^2. \qquad (9.15)$$

This is another axiom of quantum theory.

Notes

- The procedure for finding the expansion coefficients c_n may remind you of the procedure used to find the coefficients of a Fourier series. If you solve the time-independent Schrödinger equation with $V(x) = 0$, subject to what are called periodic boundary conditions, $\psi(x+a) = \psi(x)$, which are appropriate for describing functions with a repeat length of a, the (unnormalised) energy eigenfunctions you obtain are just $e^{2\pi inx/a}$, $n = 0, \pm 1, \pm 2, \dots$. The eigenfunction expansion, Eq. (9.12), then becomes a Fourier series:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{2\pi inx/a}.$$

It is convenient in this case to label the eigenfunctions using positive and negative integers instead of natural numbers (although you could use natural numbers if you wanted to), but otherwise a Fourier expansion is just a special case of an eigenfunction expansion.

- Since

$$\langle \psi, \psi \rangle = \left\langle \sum_{m=1}^{\infty} c_m u_m, \sum_{n=1}^{\infty} c_n u_n \right\rangle = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \langle c_m u_m, c_n u_n \rangle$$

$$= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \langle u_m, u_n \rangle = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \delta_{mn}$$

$$= \sum_{m=1}^{\infty} |c_m|^2$$

and $\langle \psi, \psi \rangle = 1$, it follows that $\sum_{m=1}^{\infty} |c_m|^2 = 1$. This is reassuringly consistent with the interpretation of $|c_m|^2$ as a probability.

- We have already seen that $\langle x \rangle = \langle \psi, \hat{x}\psi \rangle$ is the expected value of x and $\langle p \rangle = \langle \psi, \hat{p}\psi \rangle$ is the expected value of p. Is it also the case that $\langle \psi, \hat{H}\psi \rangle$

is the expected value of E? Let's check:

$$\langle \psi, \hat{H}\psi \rangle = \left\langle \sum_{m=1}^{\infty} c_m u_m, \hat{H}\left(\sum_{n=1}^{\infty} c_n u_n\right) \right\rangle = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \langle u_m, \hat{H}u_n \rangle$$

$$= \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n \langle u_m, E_n u_n \rangle = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n E_n \langle u_m, u_n \rangle$$

$$= \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} c_m^* c_n E_n \delta_{mn} = \sum_{m=1}^{\infty} |c_m|^2 E_m.$$

Since $|c_m|^2 = p_m$ is the probability of measuring energy level E_m, the expected value of the energy, averaged over a large enough number of measurements, ought to be $\sum_{n=1}^{\infty} p_m E_m = \sum_{n=1}^{\infty} |c_m|^2 E_m$, so this looks right. The expected value of the energy is indeed equal to $\langle \psi, \hat{H}\psi \rangle$.

9.6 The Quantum Mechanical Simple Harmonic Oscillator

The potential energy and force law for a classical simple harmonic oscillator are

$$V(x) = \frac{1}{2}sx^2, \qquad\qquad F(x) = -\frac{dV}{dx} = -sx,$$

where x is the displacement of the particle from its equilibrium position and s is the spring constant. The motion of the classical particle is determined by Newton's laws.

A quantum mechanical simple harmonic oscillator is any system in which a quantum mechanical particle feels a potential of the form $\frac{1}{2}sx^2$. For small displacements, the potential energy of an atom vibrating about its equilibrium position in a molecule or solid is well approximated by a quadratic of this type. Atoms are small enough for quantum effects to be important under some circumstances, so their vibrations are often treated quantum mechanically.

The energy levels E_n and eigenfunctions $u_n(x)$ of the oscillating particle satisfy the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2 u_n(x)}{dx^2} + \frac{1}{2}sx^2 u_n(x) = E_n u_n(x).$$

You will learn how to solve this using a clever operator method later in the quanutm physics module. (It can also be solved in terms of Gaussians and Hermite polynomials.) For now, all you need to know is the result,

$$E = \left(n + \tfrac{1}{2}\right)\hbar\omega_{\text{cl}}, \qquad n = 0, 1, 2, ...,$$
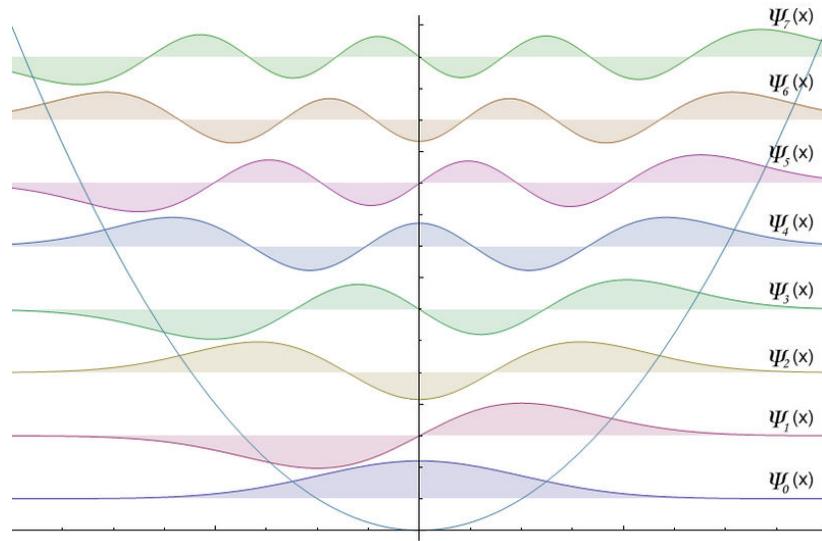
Figure 9.2: The first few energy eigenfunctions of a quantum mechanical simple harmonic oscillator.

where $\omega_{\text{cl}} = \sqrt{s/m}$ is the angular frequency of a classical oscillator with spring constant s and mass m. The lowest few energy levels are

$$E_0 = \tfrac{1}{2}\hbar\omega_{\text{cl}} \qquad\qquad \text{(ground state)}$$
$$E_1 = \tfrac{3}{2}\hbar\omega_{\text{cl}} \qquad\qquad \text{(first excited state)}$$
$$E_2 = \tfrac{5}{2}\hbar\omega_{\text{cl}} \qquad\qquad \text{(second excited state)}$$
$$\cdot \quad \cdots \qquad\qquad\qquad\qquad \cdots$$

The eigenfunctions shown in Fig. 9.2 look similar to those of a particle in a box, although the formulae that describe them turn out to be considerably more complicated. Since the potential rises smoothly as x increases, there are no ''hard wall'' boundary conditions forcing the eigenfunctions to zero at specific points. Rather, the eigenfunctions tend smoothly to zero as $|x|$ increases, satisfying the boundary conditions $u_n(x) \to 0$ as $x \to \pm\infty$.

It is a special feature of the quantum mechanical simple harmonic oscillator that adjacent energy levels are always separated by the same energy difference $\hbar\omega_{\text{cl}}$. When molecules switch between adjacent vibrational energy levels, they emit or absorb photons of this energy. Since the frequencies of the modes of oscillation are characteristic of the vibrating molecule, measurements of the energies of the photons emitted and absorbed can be used as a ''fingerprint'' to identify different molecules. The photons are normally in the infra-red.

The ground state (lowest possible energy state) of a *classical* simple harmonic oscillator has the particle sitting stationary at $x = 0$; this state has zero kinetic energy, zero potential energy, and zero total energy. In a quantum mechanical oscillator, the ground state $u_0(x)$ has energy $E_0 = \frac{1}{2}\hbar\omega_{\mathrm{cl}}$. The zero-point energy is therefore $\frac{1}{2}\hbar\omega_{\mathrm{cl}}$.

9.7 Scattering from a Potential Step

What happens when a particle of kinetic energy E encounters a potential step of height $V_0 > E$?
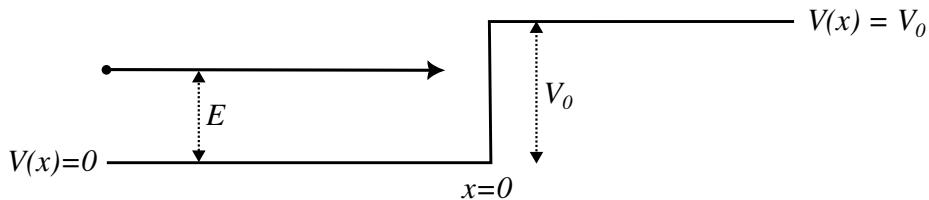

Figure 9.3: A potential step.

Since the kinetic energy of the arriving particle is smaller than the potential energy V_0 required to climb the step, classical physics says that the particle will always bounce back. In quantum mechanics, by contrast, there is a small chance of finding the particle *beyond* the edge of the step; the probability density dies off exponentially with distance into the classical forbidden region, but it is not zero.

If the step is actually one edge of a barrier with a finite width, it is even possible for the particle to tunnel through the classically forbidden region and emerge on the other side. In the Sun, pairs of positively charged nuclei have to tunnel through the Coulomb potential energy barrier that separates them before fusing to release the energy that powers the Earth. In a scanning tunnelling microscope, measurements of the tiny current that flows as electrons tunnel across the gap between a sharp tip and the surface of a solid are used to build up an atomic-scale relief map of the surface. The astonishing STM image shown in Fig. 9.4 shows what can be done.

The Schrödinger Equation

The wave function of a particle with a precise energy $E = \hbar\omega$ has the form $\psi(x,t) = u(x)e^{-i\omega t}$. As usual, the spatial part of this wave function satisfies the
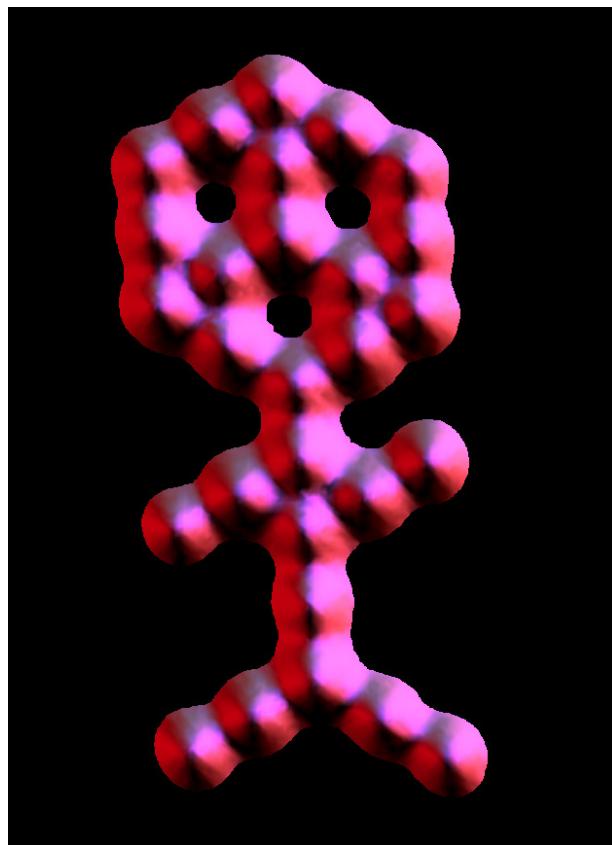
Figure 9.4: A sculpture made by using an STM tip to arrange individual CO molecules on a Pt surface. The STM tip used to move the molecules was also used to image them. (Image from IBM Corporation, originally downloaded from http://www.almaden.ibm.com/vis/stm/gallery.html.)

time-independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]u(x) = Eu(x).$$

Since $V(x) = 0$ if $x < 0$ and $V(x) = V_0$ if $x > 0$, we can rewrite this equation as:

$$\begin{cases} -\dfrac{\hbar^2}{2m}\dfrac{d^2u(x)}{dx^2} = Eu(x) & x < 0, \\[2ex] -\dfrac{\hbar^2}{2m}\dfrac{d^2u(x)}{dx^2} = (E - V_0)u(x) & x > 0. \end{cases}$$

These are second-order ordinary differential equations with constant coefficients, so the two independent solutions of each equation are easy to guess.

Solutions for $x < 0$

If we substitute the trial solution $e^{\pm ikx}$ into the left-hand side of the Schrödinger equation for $x < 0$, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2 e^{\pm ikx}}{dx^2} = \frac{\hbar^2 k^2}{2m}e^{\pm ikx}.$$

Thus, the trial solution satisfies the Schrödinger equation if and only if

$$E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm\sqrt{\frac{2mE}{\hbar^2}}.$$

The general solution in this region is

$$u(x) = Ae^{ikx} + Be^{-ikx},$$

where A and B are arbitrary (complex) constants. In physical terms, A and B are the complex amplitudes of the incident and reflected waves.

Solutions for $x > 0$

If we substitute the $e^{\pm ikx}$ trial solution into the Schrödinger equation for $x > 0$, we obtain

$$\frac{\hbar^2 k^2}{2m}e^{\pm ikx} = (E - V_0)e^{\pm ikx},$$

and hence

$$k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}.$$

So far, this looks very like the $x < 0$ case. However, because $E - V_0 < 0$, the constant k must now be imaginary:

$$k = \pm i\gamma \quad \text{with} \quad \gamma = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}.$$

The general solution in the $x > 0$ region is thus

$$u(x) = Ce^{-\gamma x} + De^{\gamma x},$$

where C and D are arbitrary (complex) constants.

The wave function $|u(x)|^2$ should not tend to infinity as $x \to \infty$, so D must be zero. (If we replace the potential step by a potential barrier of finite width, the wave function to the right of the barrier is oscillatory again and D, which is the coefficient of the $e^{\gamma x}$ solution within the barrier, does not have to be exactly zero.

Nevertheless, the wave function decreases so rapidly within the barrier that the $De^{\gamma x}$ term produced when some of the arriving $Ce^{-\gamma x}$ term reflects back from the potential step at the right-hand side of the barrier can often be ignored.) The constant A is the amplitude of the incident wave and depends on the experimental setup. Once A has been chosen, the values of B and C can be found by matching the $x < 0$ and $x > 0$ solutions at their meeting point, $x = 0$.

Use of Boundary Conditions

The boundary conditions at $x = 0$ are:

$$u(x = 0^-) = u(x = 0^+), \qquad (u \text{ is continuous at } x = 0)$$

$$\left.\frac{du}{dx}\right|_{x=0^-} = \left.\frac{du}{dx}\right|_{x=0^+}, \qquad \left(\frac{du}{dx} \text{ is continuous at } x = 0\right)$$

Origin of Boundary Conditions

To understand where these boundary conditions come from, remember that $u(x)$ satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u(x)}{dx^2} + (V(x) - E)u(x) = 0.$$

Integrating this equation from $x = -\delta$ to $x = +\delta$ gives

$$\int_{-\delta}^{\delta}\left(-\frac{\hbar^2}{2m}\frac{d^2u(x)}{dx^2} + (V(x) - E)u(x)\right) dx = 0,$$

and hence

$$\left[\frac{du}{dx}\right]_{-\delta}^{\delta} = \frac{2m}{\hbar^2}\int_{-\delta}^{\delta}(V(x) - E)u(x)\, dx.$$

Since $V(x)$, E and $u(x)$ are finite, the right-hand side tends to zero as $\delta \to 0$. Hence

$$\left.\frac{du}{dx}\right|_{x=\delta} - \left.\frac{du}{dx}\right|_{x=-\delta} \to 0 \quad \text{as} \quad \delta \to 0.$$

This shows that du/dx is continous at $x = 0$. Integrating once more shows that $u(x)$ is also continuous.

Continuity of $u(x)$ gives

$$\lim_{x\to0^-}\left(Ae^{ikx} + Be^{-ikx}\right) = \lim_{x\to0^+}Ce^{-\gamma x},$$

and hence
$$A + B = C.$$

Continuity of du/dx gives
$$\lim_{x \to 0^-} \left(ikAe^{ikx} - ikBe^{-ikx}\right) = \lim_{x \to 0^+} \left(-\gamma Ce^{-\gamma x}\right),$$

and hence
$$ik(A - B) = -\gamma C.$$

Solving the simultaneous equations,
$$A + B = C, \qquad\qquad ik(A - B) = -\gamma C,$$

gives B and C in terms of A:
$$B = \frac{k - i\gamma}{k + i\gamma}A, \qquad\qquad C = \frac{2k}{k + i\gamma}A.$$

Interpreting the Results

As already explained, A and B are the complex amplitudes of the incident and reflected waves. The intensity of the reflected wave is
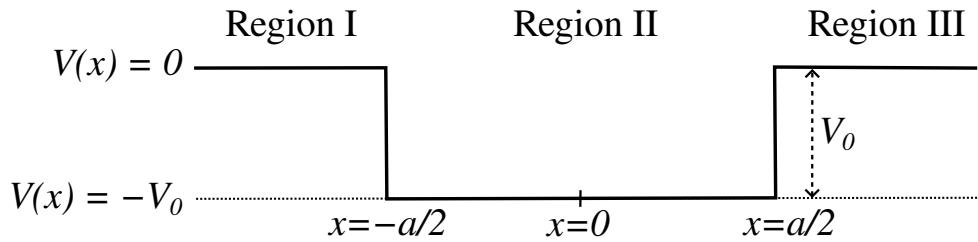
$$|B|^2 = \left(\frac{k - i\gamma}{k + i\gamma}A\right)^* \left(\frac{k - i\gamma}{k + i\gamma}A\right) = \left(\frac{k + i\gamma}{k - i\gamma}A^*\right)\left(\frac{k - i\gamma}{k + i\gamma}A\right) = |A|^2.$$

Since the intensity at point x is proportional to the probability density of finding the particle at x, this shows that every particle that strikes the barrier is eventually reflected.

More interesting is the fact that C is not equal to zero. This implies that there is a non-zero probability density,

$$|Ce^{-\gamma x}|^2 = \frac{4k^2}{k^2 + \gamma^2}|A^2|e^{-2\gamma x},$$

of finding the particle at a position x inside the barrier. The exponential decrease with x implies it is very unlikely that the particle will be found far inside the barrier, but even this is not ruled out. If the barrier has a finite width w, the particle can ''tunnel'' through it and emerge on the other side. The probability of tunnelling is approximately proportional to $e^{-2\gamma w}$. (The result is approximate because we have not actually solved the Schrödinger equation for a barrier of finite width; we solved for a step — a barrier of infinite width — and then waffled. Treating a barrier of finite width is straightforward in principle but requires more algebra. See Question 7 of Problem Sheet 6.)

Figure 9.5: Finite square well of width a.

9.8 The Finite Square Well

The next interesting example is a square well of finite depth, as shown in Fig. 9.5. The potential outside the well is zero and the potential within the well is $-V_0$, where V_0 is a positive constant. The potential step example suggests that the bound state eigenfunctions will extend a little beyond the edges of the well.

When studying the infinite square well in Sec. 9.3, we placed the origin at one side of the well. This made sure that the energy eigenfunctions were sine waves and simplified the algebra. Here it turns out to be easier to place the origin in the middle of the well, which now extends from $x = -a/2$ to $x = a/2$. Since we chose to set the potential outside the well to zero, the potential inside the well is negative: $V(x) = -V_0$. We are interested in bound states, for which $-V_0 < E < 0$. If $E > 0$, it is possible to find unbound/extended eigenfunctions at all energies.

The general form of the solution in Regions I, II and III is:

Region I	$(x < -a/2)$	$u(x) = Ae^{-\gamma x} + Be^{\gamma x}$
Region II	$(-a/2 \leq x \leq a/2)$	$u(x) = Ce^{ikx} + De^{-ikx}$
Region III	$(a/2 < x)$	$u(x) = Fe^{-\gamma x} + Ge^{\gamma x}$

with

$$k = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}, \qquad \gamma = \sqrt{\frac{-2mE}{\hbar^2}}.$$

Remember that $-V_0 < E < 0$ here, so k and γ are real. We are looking for normalisable bound solutions that tend to zero as $x \to \pm\infty$, so we set $A = G = 0$. This leaves us with four unknowns: B, C, D and F.

Region I	$(x < -a/2)$	$u(x) = Be^{\gamma x}$
Region II	$(-a/2 \leq x \leq a/2)$	$u(x) = Ce^{ikx} + De^{-ikx}$
Region III	$(a/2 < x)$	$u(x) = Fe^{-\gamma x}$

The matching conditions state that u and du/dx must be continuous at $x = -a/2$ and $x = +a/2$, producing four equations:

$$Be^{-\gamma a/2} = Ce^{-ika/2} + De^{ika/2}, \qquad Ce^{ika/2} + De^{-ika/2} = Fe^{-\gamma a/2},$$

$$\gamma Be^{-\gamma a/2} = ikCe^{-ika/2} - ikDe^{ika/2}, \quad ikCe^{ika/2} - ikDe^{-ika/2} = -\gamma Fe^{-\gamma a/2}.$$

We could probably solve these if we tried hard enough, but it is a forbidding job. To make things easier, we are going to use symmetry.

Use of Symmetry

The function $u(x)$ satisfies the Schrödinger equation:

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

Introducing a new variable, $y := -x$, this can be written

$$-\frac{\hbar^2}{2m} \frac{d^2u(-y)}{dy^2} + V(-y)u(-y) = Eu(-y),$$

where we used the chain rule,

$$\frac{d}{dx} = \frac{dy}{dx}\frac{d}{dy} = -\frac{d}{dy},$$

to deduce that

$$\frac{d^2}{dx^2} = \frac{d^2}{dy^2}.$$

Because $V(y)$ is even about the point $y = 0$, which is in the middle of the potential well, we know that $V(-y) = V(y)$. This allows the transformed Schrödinger equation to be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2u(-y)}{dy^2} + V(y)u(-y) = Eu(-y).$$

The function $u(-y)$ satisfies this transformed ODE whenever $u(x)$ satisfies the Schrödinger equation. But the transformed ODE is exactly the same in form as the original Schrödinger equation! Hence, if $u(x)$ satisfies the Schrödinger equation, so does $u(-x)$. Furthermore, since the Schrödinger equation is linear, the even and odd linear combinations,

$$u_{\mathrm{e}}(x) = u(x) + u(-x) \quad \text{and} \quad u_{\mathrm{o}}(x) = u(x) - u(-x),$$

are also solutions. Even if we find solutions that do not look even or odd at first, we can always take linear combinations to obtain even or odd solutions.

> If the potential $V(x)$ is even, all solutions of the Schrödinger equation are (or can be chosen to be) even or odd.

Even Solutions

Let us look for the even solutions first. These have $F = B$ and $D = C$, so that:

Region I $\quad(x < -a/2)$ $\qquad u(x) = Be^{\gamma x}$

Region II $\quad(-a/2 \leq x \leq a/2)$ $\qquad u(x) = C(e^{ikx} + e^{-ikx}) = 2C\cos(kx)$

Region III $\quad(a/2 < x)$ $\qquad u(x) = Be^{-\gamma x}$

The matching conditions at $x = -a/2$ state that u and du/dx must be continuous there:

$$Be^{-\gamma a/2} = 2C\cos(-ka/2) = 2C\cos(ka/2),$$
$$\gamma Be^{-\gamma a/2} = -2kC\sin(-ka/2) = 2kC\sin(ka/2).$$

(Because of the symmetry of the even solution, the matching conditions at $x = a/2$ give the same equations and tell us nothing new.) Dividing one of these equations by the other then gives

$$\gamma = k\tan(ka/2).$$

The values of γ and k both depend on E, so this equation determines the energy eigenvalues. Unfortunately, it does so in an inconveniently indirect way. To make a more direct link, start from the definitions of γ and k,

$$k = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}, \qquad \gamma = \sqrt{\frac{-2mE}{\hbar^2}},$$

and combine them to eliminate the terms that involve E explicitly:

$$k^2 + \gamma^2 = \frac{2mV_0}{\hbar^2}.$$

This allows us to express γ/k in terms of k alone,

$$\frac{\gamma}{k} = \sqrt{\frac{2mV_0}{\hbar^2 k^2} - 1},$$

and hence in terms of $ka/2$ alone,

$$\frac{\gamma}{k} = \sqrt{\frac{ma^2V_0/2\hbar^2}{(ka/2)^2} - 1} = \sqrt{\frac{\mu^2}{(ka/2)^2} - 1},$$

where $\mu^2 := ma^2V_0/2\hbar^2$. The relationship $\gamma/k = \tan(ka/2)$ that fixes the energy eigenfunctions then becomes

$$\tan(ka/2) = \sqrt{\frac{\mu^2}{(ka/2)^2} - 1}. \tag{9.16}$$

Equation (9.16) determines the values of $ka/2$ consistent with the matching conditions and thus the allowed values of k, γ and E. Once you have found these, either of the two matching conditions can be used to express C in terms of B. The final step is to normalise the eigenfunction to find B.

The most interesting of these steps, and the only one we will work through in detail, is to solve Eq. (9.16) to find the allowed values of $ka/2$. You might think it would be easy to rearrange to express $ka/2$ in terms of μ, but the equation is transcendental and cannot be solved analytically. A more successful approach, illustrated in Fig. 9.6, is to plot both sides of Eq. (9.16) as functions of $ka/2$. The solutions of the equation are the values of $ka/2$ at which the two curve cross.

Odd Solutions

This time we have $D = -C$ and $F = -B$, so that:

Region I	$(x < -a/2)$	$u(x) = Be^{\gamma x}$
Region II	$(-a/2 \le x \le a/2)$	$u(x) = C(e^{ikx} - e^{-ikx}) = 2iC\sin(kx)$
Region III	$(a/2 < x)$	$u(x) = -Be^{-\gamma x}$

The matching conditions at $x = -a/2$ become

$$Be^{-\gamma a/2} = 2iC\sin(-ka/2) = -2iC\sin(ka/2),$$
$$\gamma Be^{-\gamma a/2} = 2ikC\cos(-ka/2) = 2ikC\cos(ka/2),$$

and dividing one equation by the other gives

$$\gamma = -k\cot(ka/2).$$

As in the even case, the next step is to express γ in terms of k to get

$$\cot(ka/2) = -\sqrt{\frac{\mu^2}{(ka/2)^2} - 1}.$$

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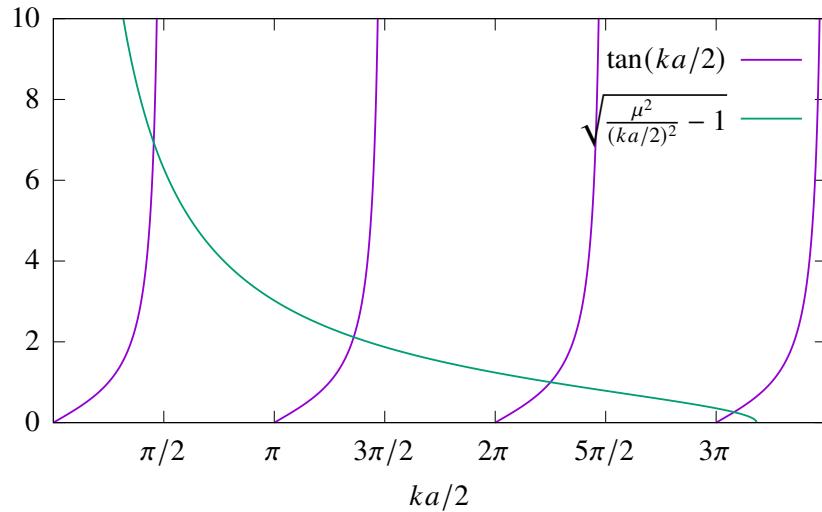
Figure 9.6:   Both sides of the equation $\tan(ka/2) = \sqrt{\frac{\mu^2}{(ka/2)^2} - 1}$ in the case when $\mu = 10$. Solutions occur where the two curves cross. The square root is imaginary if $ka/2 > \mu$, so there are only four even bound states when $\mu = 10$.
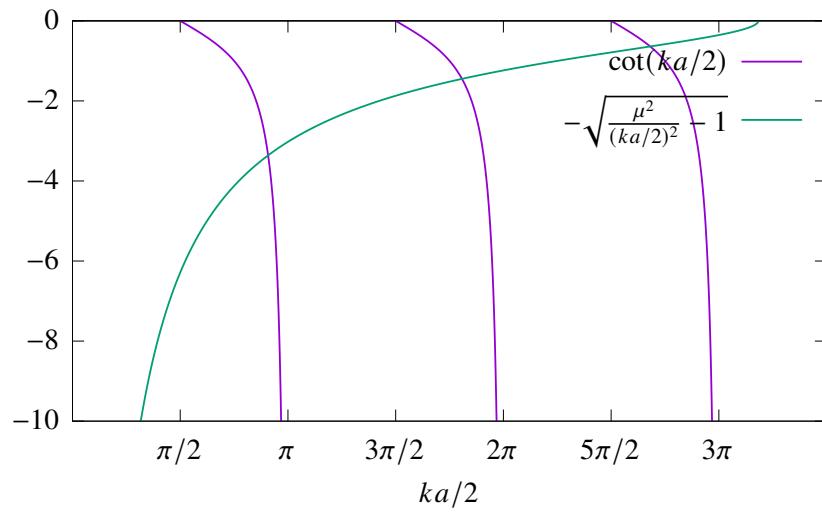

Figure 9.7:   Both sides of the equation $\cot(ka/2) = -\sqrt{\frac{\mu^2}{(ka/2)^2} - 1}$ in the case when $\mu = 10$. Solutions occur where the two curves cross. The square root is imaginary if $ka/2 > \mu$, so there are only three odd bound states when $\mu = 10$.
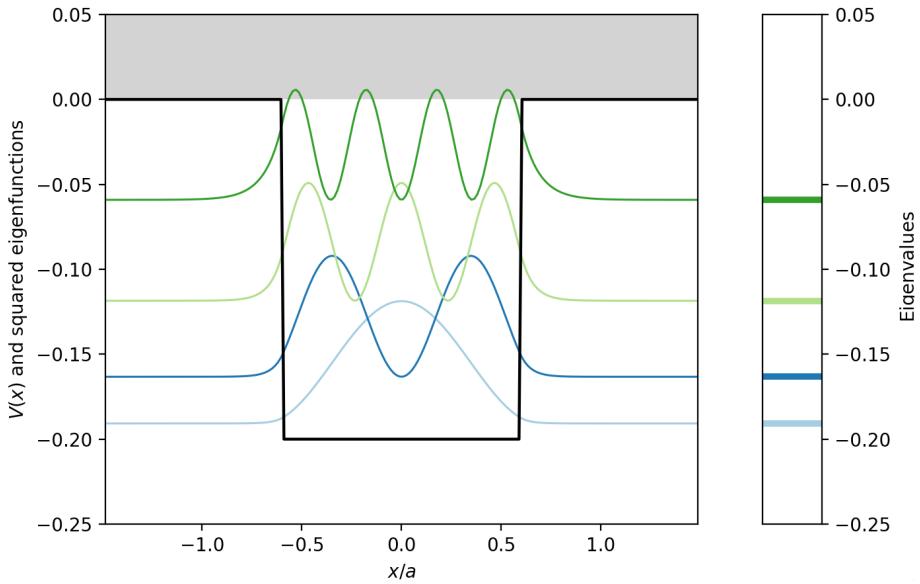
Figure 9.8: The probability densities $|u_n(x)|^2$ for the first four eigenfunctions of a finite square well, calculated numerically. (Figure from https://www.osscar.org/courses/quantum_mechanics.html).

The graphical solution of this equation is illustrated in Fig. 9.7.

The results of numerical calculations of the particle probability densities $|u_n(x)|^2$ for the first few energy eigenfunctions are shown in Fig. 9.8. Because the wave functions have been squared, even the odd ones look even.