Chapter 8
Motion of Particles

In this chapter, we will explore how to describe the position and momentum of a particle in quantum mechanics, and how we set up its Schrödinger equation. To this end, we need to work out how to describe the momentum and energy for a particle. We will conclude with a description of a bizarre phenomenon called quantum tunnelling, which is now widely used in advanced microscopes, and with a qualitative overview of the quantum mechanical foundations of chemistry.

8.1 A Particle in a Box

So far, we have looked at physics problems in quantum mechanics for which each possibility can be simply labelled: spin up or down, energy E_n, a photon coming from the left or from the top, etc. Our approach works extremely well for these cases, but what about the situation where a particle is moving continuously through space? This is a very common problem in physics, and we want to treat it quantum mechanically as well.

To solve this problem, we are going to extend the quantum theory we have developed so far to cover continuous properties such as position and momentum. Consider a particle sealed in a one-dimensional box—a long narrow tube—of length L. The position along the tube is given by x, with $0 \leq x \leq L$. We want to develop the mathematical theory for the state of a particle at a position x in the tube, but we will have to do this step by step.

First, we consider the very crude question whether the particle is in the left or the right side of the tube. Using the formalism of quantum mechanics we have developed so far, we can construct quantum states for this situation:

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$$|\text{left}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\text{right}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \tag{8.1}$$

Just like the states for the spin of an electron or the energy level of an atom, we can construct superpositions of these basis states:

$$|\psi\rangle = a|\text{left}\rangle + b|\text{right}\rangle = \begin{pmatrix} a \\ b \end{pmatrix} , \tag{8.2}$$

with $|a|^2 + |b|^2 = 1$. The probabilities of finding the particle in the left and right compartments of the tube are then given by

$$\Pr(\text{left}) = |\langle\text{left}|\psi\rangle|^2 = |a|^2 \quad \text{and} \quad \Pr(\text{right}) = |\langle\text{right}|\psi\rangle|^2 = |b|^2 , \tag{8.3}$$

exactly according to the rules of quantum mechanics we developed earlier. We can imagine that the tube can be taken apart into different compartments to see in which compartment the particle resides, for example by shaking and listening to the particle rattling inside. This would not give us any extra information about the exact position of the particle inside the compartment.

Instead of two compartments of length $L/2$, we can divide the tube into three smaller compartments with length $L/3$. The corresponding quantum states are then given by

$$|\text{left}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} , \qquad |\text{middle}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} , \qquad |\text{right}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} . \tag{8.4}$$

Note that this is now a three-dimensional vector, because there are three perfectly distinguishable measurement outcomes. The particle in the tube can again be in any superposition of these states, such as

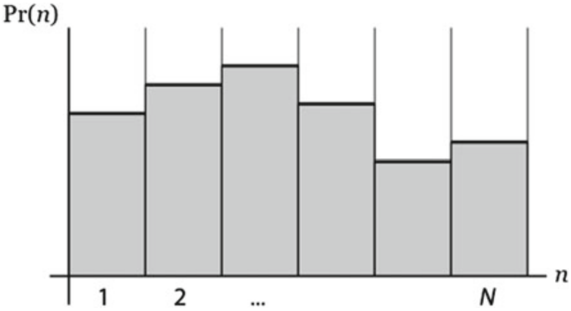
$$|\psi\rangle = a|\text{left}\rangle + b|\text{middle}\rangle + c|\text{right}\rangle = \begin{pmatrix} a \\ b \\ c \end{pmatrix} , \tag{8.5}$$

with $|a|^2 + |b|^2 + |c|^2 = 1$. The probabilities of finding the particle in the different compartments are then

$$\begin{aligned} \Pr(\text{left}) &= |\langle\text{left}\rangle|\psi\rangle|^2 = |a|^2 , \\ \Pr(\text{middle}) &= |\langle\text{middle}|\psi\rangle|^2 = |b|^2 , \\ \Pr(\text{right}) &= |\langle\text{right}|\psi\rangle|^2 = |c|^2 , \end{aligned} \tag{8.6}$$

The generalisation to N compartments should now be obvious. We can divide the tube into N compartments, each of length L/N. The corresponding quantum states $|n\rangle$ are labelled by a number n that indicates the compartment (running from 1 to N).

Fig. 8.1 Discrete position probabilities



The particle can be in any superposition of these states, so each $|n\rangle$ has an amplitude c_n (replacing the a, b, c, etc.). The state of a particle in a box of N compartments is therefore given by

$$|\psi\rangle = \sum_{n=1}^{N} c_n |n\rangle \quad \text{with} \quad \sum_{n=1}^{N} |c_n|^2 = 1 \,. \tag{8.7}$$

This is the generalisation of equation (8.5). Since N is very large, it is no longer convenient to write the states $|n\rangle$ in terms of vectors, so from now on we will have to rely on kets and bras.

The probability of finding the particle in the mth compartment is then given by

$$\Pr(m) = |\langle m|\psi\rangle|^2 = \left|\sum_{n=1}^{N} c_n \langle m|n\rangle\right|^2 = |c_m|^2 \,, \tag{8.8}$$

where we used that $\langle m|n\rangle = 0$ if $m \neq n$, and $\langle m|n\rangle = 1$ if $m = n$. The states $|n\rangle$ can be considered position states with a precision ℓ that is given by the size of the compartment $\ell = L/N$.

You may expect that we can make N arbitrarily large to get position states with arbitrary high precision. This is correct, but in order to get a true continuum of position states, we have to be very careful with the mathematics. We will go through it at a snail's pace, so we don't make any mistakes by relying on false intuitions. To derive the continuum of position states, we start with the normalisation condition that all probabilities defined by Eq. (8.8) must sum to one:

$$\sum_m \Pr(m) = \sum_m |c_m|^2 = 1 \,. \tag{8.9}$$

We can graphically place these probabilities next to each other in a histogram, where each bar has width (see Fig. 8.1). The normalisation condition means that the areas of all rectangles in the histogram must sum to one.

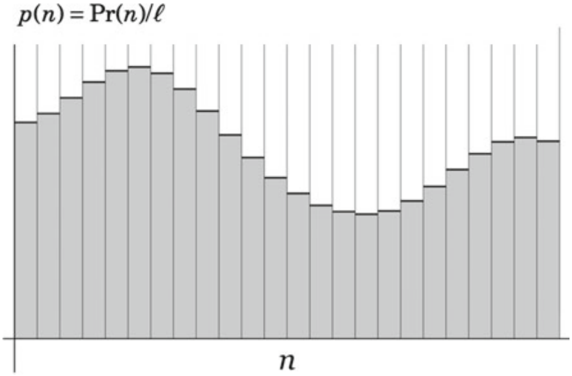


Fig. 8.2 Towards a continuum of probability densities. The interactive figure is available online (see supplementary material 1)

Next, we can identify the total horizontal length of the histogram with the length L of the box, which means that each bar in the histogram has a width ℓ. However, the area of each bar is the vertical height times the horizontal length, or $\Pr(n) \times \ell$ for the nth bar. The total area A of the bars in the histogram is then given by the sum over all the bars

$$A = \sum_{n=1}^{N} \Pr(n) \times \ell = \ell \left(\sum_{n=1}^{N} \Pr(n) \right) = \ell \,. \tag{8.10}$$

So $A = \ell$, instead of 1, and it has units of length! This means that we have broken the normalisation condition. We can fix this by dividing all probabilities by ℓ:

$$p(m) = \frac{\Pr(m)}{\ell} \,. \tag{8.11}$$

The $p(m)$ are no longer probabilities, because they are not dimensionless and do not take values between 0 and 1 (ℓ can be very small, pushing $p(m)$ beyond 1).

The $p(m)$ form a so-called *probability density function*. The name is explained by the fact that $p(m)$ is probability $\Pr(m)$ per length ℓ, just like a regular mass density is mass M per volume V. The normalisation condition can then be written in two ways:

$$\sum_{n=1}^{N} \Pr(n) = 1 \quad \text{and} \quad \sum_{n=1}^{N} p(n)\ell = 1 \,. \tag{8.12}$$

If we double the number of compartments while keeping the length of the box L constant, the width of each compartment halves: $\ell \to \ell/2$. Increasing N further will make ℓ increasingly smaller, and leads to a histogram shown in Fig. 8.2.

When we let $N \to \infty$, the width of each bar narrows to an infinitesimal length $\ell \to dx$, and the probability density $p(n)$ tends to a distribution $p(x)$ that depends on a continuous variable $x \in \mathbb{R}$ instead of an integer variable $n \in \mathbb{N}$. This is shown in Fig. 8.2. Because n and x belong to different types of numbers ($\mathbb{R}$ versus $\mathbb{N}$) we change the notation $n \to x$. In addition, while n runs from 1 to N, the position variable x runs from 0 to L.

The sum over the bars in a histogram gives the area under the curve $p(x)$ when we let $N \to \infty$. You may recall that this is exactly how integration is defined! So we can rewrite the right-hand side of Eq. (8.12) as

$$\int_0^L p(x)\, dx = 1\,. \tag{8.13}$$

The probability that the particle is found in the region between $x = a$ and $x = b$ is then given by the area under the curve between a and b:

$$\Pr([a,b]) = \int_a^b p(x)\, dx\,. \tag{8.14}$$

Now that we have constructed a continuous probability density function $p(x)$ from the discrete probabilities $\Pr(n)$, we need to extend the description of the discrete set of states $|n\rangle$ to a continuum set of states $|x\rangle$. We will see that this leads to a peculiarity in the normalisation of such states.

Since $\Pr(n) = |\langle n|\psi\rangle|^2$, we can write

$$p(n) = \frac{\Pr(n)}{\ell} = \left|\frac{\langle n|\psi\rangle}{\sqrt{\ell}}\right|^2 . \tag{8.15}$$

In other words, rather than considering the normalised states $|n\rangle$, we define a new (unnormalised) state

$$|x_n\rangle = \frac{|n\rangle}{\sqrt{\ell}}\,, \tag{8.16}$$

such that $p(n) = |\langle x_n|\psi\rangle|^2$. In the continuum limit $N \to \infty$, the nth compartment state $|n\rangle$ becomes the position eigenstate $|x\rangle$, where x becomes a real number. However, in this limit we have $\ell \to 0$, which means that the normalisation factor of $|x\rangle$ becomes $1/\sqrt{\ell}$, which goes to infinity as $\ell \to 0$. In other words, the state $|x\rangle$ cannot be normalised! This is something we have to live with, and luckily most of the time it will not cause any trouble. However, it does hint at difficulties when we are dealing with physics at increasingly smaller scales, for example when we want to combine quantum mechanics with general relativity.

Nevertheless, we still have an orthogonality relationship for position eigenstates. The inner product of two different position eigenstates $|x\rangle$ and $|x'\rangle$ must be zero.

$$\langle x|x'\rangle = \begin{cases} 0 & x \neq x' , \\ \infty & x = x' . \end{cases} \tag{8.17}$$

We can capture this behaviour with the Dirac delta function δ, such that

$$\langle x|x'\rangle = \delta(x - x') , \tag{8.18}$$

and δ is defined as $\delta(u) = 0$ if $u \neq 0$, and $\delta(u) = \infty$ if $u = 0$. Delta "function" is a bit of a misnomer, because technically it is not a function but a distribution. We cannot properly define it the way we just did, and instead we must define it via a limiting procedure. We will discuss this in more detail in the next mathematical intermezzo.

How do we use delta functions in a calculation? Nothing could be easier! Suppose you encounter the integral

$$\int f(x)\,\delta(x - a)\,dx . \tag{8.19}$$

When you see something like this, you don't have to evaluate the integral at all, just replace the argument x of the function f in the integrand with the value $x = a$ that makes the argument of the delta function zero. This works for any function where a lies in the domain of integration

$$\int f(x)\,\delta(x - a)\,dx = f(a) . \tag{8.20}$$

If a is outside the domain of integration, the integral is zero. This means that delta functions are your friend: they may look complicated, but they make integrals disappear without difficult or impossible calculations!

Let's see how this works for the state of a quantum particle. We can write the quantum state $|\psi\rangle$ as a superposition over position states:

$$|\psi\rangle = \int dx\, c(x)|x\rangle , \tag{8.21}$$

with $\int dx\, |c(x)|^2 = 1$ so that $|\psi\rangle$ is properly normalised. Notice how $|\psi\rangle$ can still be normalised, even if $|x\rangle$ cannot. Now, we calculate the inner product of $|\psi\rangle$ with some position eigenstate $|x'\rangle$, which gives

$$\begin{aligned} \langle x'|\psi\rangle &= \langle x'| \int dx\, c(x)|x\rangle \\ &= \int dx\, c(x)\langle x'|x\rangle = \int dx\, c(x)\,\delta(x - x') . \end{aligned} \tag{8.22}$$

This is an integral with a Dirac delta function, so we can evaluate it by choosing $x = x'$ for the integrand:

$$\langle x'|\psi\rangle = c(x')\,. \tag{8.23}$$

Traditionally, we choose the symbol ψ for the amplitudes $c(x)$ of a particle's position, so the label in the ket $|\psi\rangle$ matches the label of the amplitudes:

$$\langle x|\psi\rangle = \psi(x) \quad \text{and} \quad |\psi\rangle = \int dx\, \psi(x)|x\rangle\,. \tag{8.24}$$

We can also combine the two equations in Eq. (8.24) to obtain an expression for the identity operator in terms of the position eigenstates

$$|\psi\rangle = \int dx\, |x\rangle\, \psi(x) = \int dx\, |x\rangle\langle x|\psi\rangle = \left(\int dx\, |x\rangle\langle x|\right)|\psi\rangle\,, \tag{8.25}$$

and therefore

$$\int dx\, |x\rangle\langle x| = \mathbb{I}\,. \tag{8.26}$$

This is the completeness relation for the position of a particle. The symbol $\psi(x)$ is called the *wave function* of the particle, and it plays a central role in the quantum mechanical treatment of a particle, because it can be used to calculate everything we need. Notice that it is technically not the same as the state; it is the complex amplitude at position x.

How do we use the wave function in quantum mechanical calculations? As the simplest example, we can calculate the average position $\langle x\rangle$ of a particle. For any average, you multiply the value a_i with the probability p_i of that value, and then sum over all values:

$$\langle a\rangle = \sum_i a_i\, p_i\,. \tag{8.27}$$

For the position of a quantum mechanical particle, we multiply each possible infinitesimal position interval $[x, x+dx)$ by the probability $p(x)dx = |\psi(x)|^2 dx$ of finding the particle in that interval, and integrate ("sum") over all positions. This becomes

$$\langle x\rangle = \int_0^L x|\psi(x)|^2 dx\,. \tag{8.28}$$

Averages of other functions of position $f(x)$ can also be calculated according to the same rule:

$$\langle f(x)\rangle = \int_0^L f(x)|\psi(x)|^2 dx\,. \tag{8.29}$$

For example, we can calculate the square of the position of a particle by evaluating

$$\langle x^2 \rangle = \int_0^L x^2 |\psi(x)|^2 dx \,. \tag{8.30}$$

Next, we note that the position of a particle is an observable. It is a physical quantity that can be measured and yields real numbers as measurement outcomes. According to Chap. 5, this means there should be a Hermitian operator $\hat{x}$ associated with the position (technically, we should call this a self-adjoint operator). Indeed, we can derive the form of the operator by requiring the right measurement statistics:

$$\begin{aligned}\langle \hat{x} \rangle &= \int_{-\infty}^{+\infty} x\, p(x)\, dx = \int_{-\infty}^{+\infty} x |\langle x|\psi\rangle|^2\, dx \\ &= \int_{-\infty}^{+\infty} dx\, x \langle\psi|x\rangle\langle x|\psi\rangle = \langle\psi| \left(\int_{-\infty}^{+\infty} dx\, x |x\rangle\langle x| \right) |\psi\rangle \,. \end{aligned} \tag{8.31}$$

Since this must be true for any state $|\psi\rangle$, we find that

$$\hat{x} = \int_{-\infty}^{+\infty} dx\, x |x\rangle\langle x| \,. \tag{8.32}$$

This is the position operator. You can check yourself that it is self-adjoint: $\hat{x}^\dagger = \hat{x}$. By inspection you see that the states $|x\rangle$ are the (non-normalisable) eigenstates of $\hat{x}$ with eigenvalues x.

Let us consider now a specific example of a particle in a box of length L. Suppose that the wave function is given by

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \,. \tag{8.33}$$

You can check that the wave function is properly normalised by calculating the integral

$$\begin{aligned}\int_a^b |\psi(x)|^2\, dx &= \frac{2}{L} \int_a^b \sin^2\left(\frac{2\pi x}{L}\right) dx = \frac{1}{\pi} \int_{u=\frac{2\pi a}{L}}^{v=\frac{2\pi b}{L}} \sin^2 w\, dw \\ &= \frac{1}{2\pi} \int_u^v [1 - \cos(2w)]\, dw = \frac{1}{2\pi} \left[w - \frac{1}{2}\sin(2w) \right]_{w=u}^{w=v} \\ &= \frac{b}{L} - \frac{a}{L} - \frac{1}{4\pi} \sin\left(\frac{2\pi b}{L}\right) - \frac{1}{4\pi} \sin\left(\frac{2\pi a}{L}\right) \,. \end{aligned} \tag{8.34}$$

When $a = 0$ and $b = L$, we find

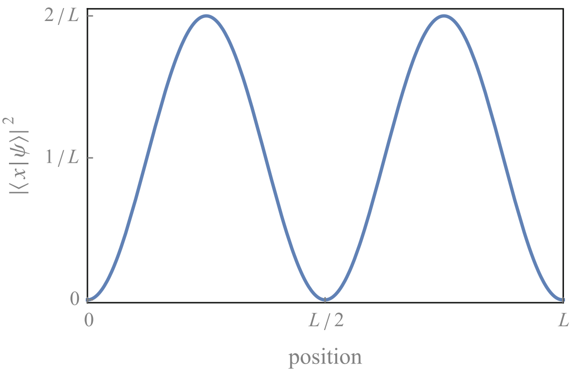


Fig. 8.3 The probability density $|\langle x|\psi\rangle|^2$ for the position of a particle in a box in the state $\psi(x)$ of Eq. (8.33)

$$\int_a^b |\psi(x)|^2\, dx = 1\,, \tag{8.35}$$

which means that the state is properly normalised. We can plot the probability density $p(x) = |\psi(x)|^2$ as a function of position, which is shown in Fig. 8.3.

The probability of finding the particle in the left-hand side of the box is given by the area under the curve between $x = 0$ and $x = L/2$. By symmetry, you can see immediately that this should be one half. Indeed, when we calculate the probability, we find

$$\int_0^{+\frac{1}{2}L} |\psi(x)|^2 dx = \frac{2}{L}\int_0^{+\frac{1}{2}L} \sin^2\left(\frac{2\pi x}{L}\right) dx = \frac{1}{2}\,. \tag{8.36}$$

You also see from the plot that the probability that we find the particle at the position $x = 0$ is zero. This raises the question: How does the particle get from the left-hand side of the box to the right-hand side if it has to go through a forbidden point? To answer this, remember that in Chap. 1 we could not say that the photon really went through one arm of the interferometer or the other, since extracting that information via a measurement destroyed the interference in the detectors. When a particle is in a quantum superposition of two states, you cannot say that it really is in one or the other of those two states.

Similarly, here the particle is in a quantum superposition of position states, so we cannot say that the quantum particle really has a position that we just don't know about. The particle does not have a position prior to a measurement! You can therefore not simply talk about the trajectory of a quantum particle in a meaningful way (without adding extra ingredients such as decoherence to make the particle behave more like a classical object). The answer to the question is thus that the question itself is ill-posed, because it mistakenly assumes that quantum particles have trajectories.

The general rule for calculating expectation values with a wave function can now be determined as follows: Suppose we have a state $|\psi\rangle$ and an operator A. Operating on the state produces a new state, which we can denote by $|A\psi\rangle = A|\psi\rangle$. Using the completeness relation, the expectation value of the operator A then becomes

$$\langle A\rangle = \langle\psi|A\psi\rangle = \int_{-\infty}^{+\infty} dx\ \langle\psi|x\rangle\langle x|A\psi\rangle = \int_{-\infty}^{+\infty} dx\ \psi^*(x)A\,\psi(x)\,. \tag{8.37}$$

The reason it works this way, and not using two instances of the completeness relation on either side of A, is that $|\psi\rangle$ lives in an infinite dimensional state space, and the rules become a bit more subtle there.

8.2 *Mathematical Intermezzo*: The Dirac Delta Function

The Dirac delta function plays an important role in quantum mechanics, so let's spend a little more time with it. You have already seen that the defining relation (8.20) can be used to effortlessly evaluate integrals. There is also a variety of other definitions that are very useful to know.

First, we need some kind of limiting procedure to give a precise meaning to infinity[1] (∞) in Eq. (8.17). Notice that if you plot $\delta(x-a)$ against the x-axis, you have zero everywhere, except at $x = a$ where you have a spike of infinite height. One way to approximate this is with a very tall, narrow rectangular function of height h and with w at position a, and zero everywhere else. Let's use this approximation of the Dirac delta function with the simplest possible function $f(x)$ in Eq. (8.20), namely the constant function $f(x) = c$. We then have

$$\int f(x)\,\delta(x-a)\,dx \approx \int_a^{a+w} ch\,dx = ch\,[x]_{x=a}^{x=a+w} = chw = c\,, \tag{8.38}$$

and we require $hw = 1$. This is true for all functions $f(x)$, so the area under the rectangle is 1. We can now define the Dirac delta function as the limit of a rectangle with width w and height $h = 1/w$ at $x = a$:

$$\delta(x-a) = \lim_{w\to 0}\begin{cases} 0 & x < a \quad \text{or} \quad x > a+w\,, \\ \frac{1}{w} & a \le x \le a+w\,. \end{cases} \tag{8.39}$$

Another useful definition is

$$\delta(a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{iax}\,dx\,. \tag{8.40}$$

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[1] There are many ways in which we can encounter infinity, and many different *types* of infinity. The symbol ∞ is a shorthand for how we ended up at infinity; you cannot use this symbol in regular arithmetic without paying attention to the context of how the infinity came about. This is why we have to introduce limiting procedures that provide this context.

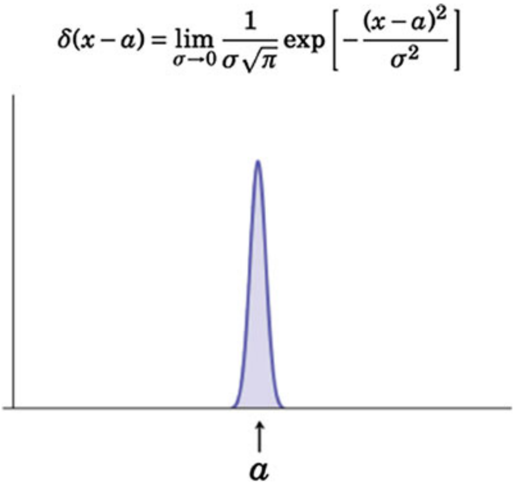


Fig. 8.4 The Dirac delta function. The interactive figure is available online (see supplementary material 2)

To get a feel for this definition, notice that for each value of e^{iax} there is another value $e^{iax+i\pi} = -e^{iax}$. So all factors cancel each other, except when $a = 0$. In that case all $e^{iax} = 1$, and add to infinity. Various constructions for the delta function are shown in Fig. 8.4.

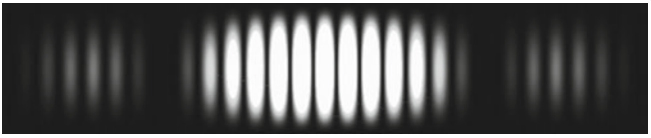
8.3 The Momentum of a Particle

We have spent quite some time exploring how to describe the position of a particle, and the obvious next question is: how do we describe its velocity v? Normally, we take the time derivative of the position of a particle to get the velocity:

$$v = \frac{dx}{dt}\,. \tag{8.41}$$

However, the position operator in Eq. (8.32) has no time dependence, and we therefore cannot use this traditional definition. Instead we must find another operator that captures the observable of velocity. We will find it more convenient to consider the momentum p instead, and use the relation $p = mv$ (where m is the mass of the particle) if we want to find the velocity. The reason for this is that the momentum is a more fundamental measure of the motion of a particle because it takes into account the inertial mass.

Before we consider the momentum of quantum particles, we briefly consider the famous double-slit experiment by Thomas Young, shown in Fig. 8.5. When we shine light of a specific wavelength onto a screen with two parallel narrow slits, the light behind the screen will give an interference pattern:



The width and fringe separation of the interference pattern depends on the width of the slit a and the distance d between the slits. Crucially, the interference pattern $I(x)$ also depends on the wavelength λ of the light:

$$I(x) = I_0 \cos^2\left(\frac{\pi d x}{\lambda R}\right) \operatorname{sinc}^2\left(\frac{\pi a x}{\lambda R}\right), \tag{8.42}$$

where x is the horizontal position on the screen, and R is the distance between the slits and the screen. The constant I_0 is related to the intensity of the light source.

What happens when we use electrons instead of photons? To find out, we prepare electrons with momentum p and send them through the slits and record the positions of the electrons on a screen behind the slits. We find exactly the same type of interference pattern that we obtained using light, shown in Fig. 8.6 (performed in 1989 by A. Tonomura and co-workers at the Central Research Laboratory, Hitachi, Ltd. Japan).

So electrons with momentum p behave in some way as waves with a wavelength λ that can be inferred from Eq. (8.42). When we compare the momentum p of the electrons with the wavelength λ inferred from the interference pattern, we experimentally find the relation

$$p = \frac{h}{\lambda}, \tag{8.43}$$

where h is Planck's constant. Does relation (8.43) hold also for photons? We know that light has a wavelength λ, but does it have momentum? Light can push objects

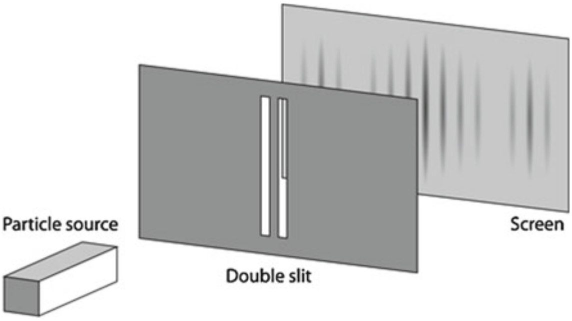


Fig. 8.5 The double slit experiment

Fig. 8.6 Building up the diffraction pattern with individual electrons. Courtesy of the Central Research Laboratory, Hitachi, Ltd. Japan. The interactive figure is available online (see supplementary material 3)

just by reflecting off their surface. This radiation pressure on the object causes a change in its momentum, and the conservation of the total momentum requires that the momentum change must be balanced by something. This implies that light has momentum too, even though photons are massless particles. Moreover, if we calculate the radiation pressure, the momentum of a photon with wavelength λ is exactly given by Eq. (8.43). We therefore extrapolate that Eq. (8.43) captures a fundamental truth about nature:

Particles with momentum p can behave as waves with wavelength $\lambda = h/p$.

This is a very profound result, which became known as the *wave-particle duality*. Each particle has characteristics of a wave, and vice versa. This correspondence between waves and particles was first proposed by Louis de Broglie (1925) and has so far held up for every type of particle and wave out there with this identification between particle momentum and wavelength. It is a direct manifestation of the fact that quantum mechanics describes objects as quanta. Notice also that this is a relation between wavelength and momentum, not velocity, which is why we prefer to work with momentum.

We will now explore the properties of the momentum states, and give an expression for the momentum operator. The state of an electron with momentum p is denoted as $|p\rangle$. Since the momentum p can take on any real value we expect that the momentum states behave similarly to the position eigenstates. We therefore take

$$\langle p|p'\rangle = \delta(p - p')\,. \tag{8.44}$$

We now wish to find the relationship between the position eigenstates $|x\rangle$ and the momentum states $|p\rangle$.

Since every state, including $|p\rangle$, can be written as a superposition of position states, we can write

$$|p\rangle = \int_{-\infty}^{+\infty} dx\ \psi_p(x)|x\rangle\,, \tag{8.45}$$

where the complex numbers $\psi_p(x) = \langle x|p\rangle$ encode the phases and amplitudes of the wave with momentum p at position x. Normally, the amplitudes and phases are written as $A\cos\phi$ or $A\sin\phi$, but because we work with complex phases we write $Ae^{i\phi}$. The phase ϕ in the interval $[0, 2\pi)$ indicates where we are along the wave, and can be written as

$$\phi = 2\pi\frac{x}{\lambda}\,. \tag{8.46}$$

We can then write

$$\psi_p(x) = A\,e^{i\phi} = A\,e^{2\pi ix/\lambda} = A\,e^{ipx/\hbar} = \langle x|p\rangle\,, \tag{8.47}$$

where the last equality follows directly from the definition in Eq. (8.45). We also used $\hbar = h/2\pi$. You can calculate the value for A by evaluating

$$\int dx\ \langle p'|x\rangle\langle x|p\rangle \tag{8.48}$$

using both Eqs. (8.44) and (8.47), and equating the results. This leads to the fundamental relationship

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\,. \tag{8.49}$$

Notice that this inner product is never zero, and has a constant modulus for all possible values of x and p. Only the phase ϕ depends on x and p.

Next, we want an expression for the momentum operator $\hat{p}$. We require that the momentum operator satisfies the eigenvalue equation

$$\hat{p}|p\rangle = p|p\rangle\,. \tag{8.50}$$

When we apply the completeness relation of Eq. (8.26) for position to both sides of this equation we obtain

$$\hat{p}\int dx\ |x\rangle\langle x|p\rangle = p\int dx\ |x\rangle\langle x|p\rangle \tag{8.51}$$

or

$$\hat{p}\int dx\ \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}|x\rangle = p\int dx\ \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}|x\rangle\,. \tag{8.52}$$

In other words, the operator $\hat{p}$ on the left brings the value p down from the exponential in the integral. The simplest mathematical operator that accomplishes this is the derivative:

$$\frac{d}{dx} e^{ipx/\hbar} = \frac{i}{\hbar}\, p\, e^{ipx/\hbar} \,. \tag{8.53}$$

We will have to correct for the factor $i/\hbar$ with a factor $-i\hbar$, which gives for the momentum operator

$$\hat{p} = -i\hbar \frac{d}{dx} \,. \tag{8.54}$$

A quick check of the units shows that the operator $\hat{p}$ has indeed dimensions of momentum.

In order to calculate the average momentum $\langle \hat{p} \rangle$ for a particle in the quantum state $\psi(x)$, we have to sandwich the operator $\hat{p}$ between $\psi^*(x)$ and $\psi(x)$, and integrate over x. The operator acts to the right on the wave function $\psi(x)$. We can do this for the wave function in Eq. (8.33) of a particle in a box:

$$\begin{aligned} \langle \hat{p} \rangle &= -i\hbar \int_0^L dx\, \psi^*(x) \frac{d}{dx} \psi(x) \\ &= -\frac{2i\hbar}{L} \int_0^L dx\, \sin\left(\frac{2\pi x}{L}\right) \frac{d}{dx} \sin\left(\frac{2\pi x}{L}\right) \\ &= -\frac{4\pi i\hbar}{L^2} \int_0^L dx\, \sin\left(\frac{2\pi x}{L}\right) \cos\left(\frac{2\pi x}{L}\right) \\ &= -\frac{2\pi i\hbar}{L^2} \int_0^L dx\, \sin\left(\frac{4\pi x}{L}\right) \\ &= -\frac{2\pi i\hbar}{L^2} \left[\frac{L}{4\pi} \cos\left(\frac{4\pi x}{L}\right) \right]_0^L = 0 \,. \end{aligned} \tag{8.55}$$

This makes sense, since a nonzero momentum would imply that the particle moves outside of the boundaries of the box after a long enough time.

You may have noticed that we now have two ways of calculating probabilities, namely via states (using kets and bras), and via wave functions (using integration over functions). Historically, these two approaches were developed side-by-side by Heisenberg (1925) and Schrödinger (1926), respectively (even though the ket and bra notation was due to Dirac). The relation between these two approaches is collected in Table 8.1.

Table 8.1 Comparison between matrix mechanics and wave mechanics

Matrix mechanics	Wave mechanics
quantum state $\lvert\psi\rangle$	wave function $\psi(x)$
position state $\lvert x_0\rangle$	$\psi(x) = \delta(x - x_0)$
momentum state $\lvert p_0\rangle$	$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ip_0x/\hbar}$
$\hat{x} = \int x\, \lvert x\rangle\langle x\rvert\, dx$	$\hat{x} = x$
$\hat{p} = \int p \lvert p\rangle\langle p\rvert\, dp$	$\hat{p} = -i\hbar\frac{d}{dx}$
$\langle A\rangle = \langle\psi\lvert A\rvert\psi\rangle$	$\langle A\rangle = \int \psi^*(x)\; A\; \psi(x)\; dx$

8.4 *Mathematical Intermezzo*: Fourier Transforms

Sometimes it is easier to solve a problem in quantum mechanics using the position operator, while at other times it is easier to solve them using the momentum operator. In general, when a system behaves in a wave-like manner, it is going to be easier to use momentum states, while systems that behave like particles are better described using position eigenstates. There is an important relationship between the states $|x\rangle$ in position space (which is infinite-dimensional, *not* three-dimensional!) and the states $|p\rangle$ in momentum space. This is given by the *Fourier transform*.

Suppose we have a quantum state $|\psi\rangle$, which can be expressed in terms of positions x via Eq. (8.24). But what if we want to express this state in terms of the momenta p? We can manipulate Eq. (8.24) as follows:

$$\begin{aligned} |\psi\rangle &= \int dx\; \psi(x)|x\rangle = \mathbb{I} \int dx\; \psi(x)|x\rangle \\ &= \left(\int dp\; |p\rangle\langle p|\right) \int dx\; \psi(x)|x\rangle = \int dp \int dx\; \psi(x)|p\rangle\langle p|x\rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int dp\; \int dx\; \psi(x)e^{-ipx/\hbar}|p\rangle \\ &= \int dp\; \Psi(p)|p\rangle\,, \end{aligned} \tag{8.56}$$

where we defined

$$\Psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\; \psi(x)e^{-ipx/\hbar}\,. \tag{8.57}$$

The complex function $\Psi(p)$ of the momentum variable p is the *Fourier transform* of the complex function $\psi(x)$ of the position variable x. We can also reverse this relation to obtain the inverse Fourier transform from momentum to position space

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\ \Psi(p) e^{ipx/\hbar} \,. \tag{8.58}$$

You can prove this yourself using the expression in Eq. (8.40) for the Dirac delta function. The Fourier transform allows us to quickly relate the quantum state in the position space to the quantum state in momentum space by evaluating the integrals in Eqs. (8.57) and (8.58). The Fourier transform is used in all of physics, but it is especially important in quantum mechanics.

8.5 The Energy of a Particle

Now that we know how to describe the position and momentum of a particle, we can finally derive what is arguably the most famous and important equation in quantum mechanics: the Schrödinger equation for a particle in a potential. As we have seen in Chap. 4, this is an equation that relates the time evolution of the quantum state to the energy. We therefore have to first construct the energy operator, or Hamiltonian.

You know already that the energy of a particle has two parts: kinetic energy and potential energy. The kinetic energy is the part of the energy that you get from movement, and can be written as

$$E_{\text{kinetic}} = \frac{1}{2} m v^2 = \frac{p^2}{2m} \,, \tag{8.59}$$

where m is the mass of the particle. In order to find the quantum mechanical equivalent, we just replace[2] the momentum p with the momentum operator $\hat{p}$. It is as simple as that:

$$p \to \hat{p} = -i\hbar \frac{d}{dx} \,. \tag{8.60}$$

The kinetic energy therefore becomes an operator as well:

$$E_{\text{kinetic}} \to H_0 = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \,. \tag{8.61}$$

To find the quantum mechanical description of the potential energy, we first recall that the quantum mechanical average of any function f of position x is just given by the integral

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[2] The procedure of replacing classical quantities with operators is called *quantisation*. Once you know which operators the classical quantities correspond to you can quantise nearly every problem in physics.

$$\langle f(x)\rangle = \int dx\, \psi^*(x)\, f(x)\, \psi(x)\,. \tag{8.62}$$

Therefore, the average potential energy is similarly given by

$$\langle V\rangle = \int dx\, \psi^*(x)\, V(x)\, \psi(x)\,, \tag{8.63}$$

and the quantum mechanical potential energy is just the function $V(x)$. The potential energy V is typically a function of position x, but not of momentum p. The potential does in general depend on the time t, for example when potentials are switched on for a finite period of time. We therefore write $V(x, t)$. The total energy operator H is then given by

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x, t)\,. \tag{8.64}$$

This is the Hamiltonian for a particle moving in a one-dimensional potential.

Finally, we use this Hamiltonian to get the full Schrödinger equation in one dimension:

$$i\hbar\frac{d}{dt}\psi(x, t) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x, t)\right]\psi(x, t)\,. \tag{8.65}$$

This is a differential equation for the wave function $\psi(x, t)$. For arbitrary potentials $V(x, t)$ such equations are typically difficult to solve, and must often be tackled numerically on a computer. If you want to go any further in your study of quantum mechanics, you must learn the mathematics of differential equations.

We will do one particularly simple example, where the potential is constant: $V(x, t) = V_0$. The Schrödinger equation in (8.65) can then be written as

$$i\hbar\frac{d\psi(x, t)}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi(x, t)}{dx^2} + V_0\,\psi(x, t)\,. \tag{8.66}$$

We can substitute a trial wave function

$$\psi(x, t) = A\exp\left(ikx - \frac{iEt}{\hbar}\right), \tag{8.67}$$

where k is a constant we can choose appropriately, E is the energy of the particle, and A the normalisation of the wave function. Taking the time and space derivatives of $\psi(x, t)$ gives

$$\frac{d\psi(x, t)}{dt} = -\frac{iE}{\hbar}\psi(x, t)\,, \tag{8.68}$$

and

$$\frac{d^2\psi(x,t)}{dx^2} = -k^2\psi(x,t)\,. \tag{8.69}$$

Putting this all back into Eq. (8.66) produces the equation

$$\left(E - \frac{\hbar^2 k^2}{2m} - V_0\right)\psi(x,t) = 0\,. \tag{8.70}$$

Since $\psi(x,t)$ is not zero in general, the term in brackets must be zero. This allows us to solve for k:

$$k = \pm\frac{\sqrt{2m(E - V_0)}}{\hbar}\,. \tag{8.71}$$

Notice that $\hbar k$ has units of momentum. We can therefore write $p = \pm\sqrt{2m(E - V_0)}$ and the wave function becomes[3]

$$\psi(x,t) = A \exp\left(\frac{ipx}{\hbar} - \frac{iEt}{\hbar}\right). \tag{8.72}$$

This is the solution for a particle in a constant potential V_0 with energy E and momentum p. The constant A depends on the size of the space, and we sometimes refer to it as the amplitude of the wave function in that part of space. The momentum p can be both positive and negative, corresponding to movement in the positive and the negative x-direction, respectively. When $E < V_0$, the momentum is imaginary! This is not a mistake in the theory. In the next section we will explore what this means.

8.6 ❧ The Scanning Tunnelling Microscope

We have seen already in Chap. 1 that quantum mechanical particles can behave rather strangely, and sometimes defy our classical way of thinking. Another counterintuitive and highly nonclassical consequence of quantum mechanics is quantum tunnelling.

Consider the following simple physical process: You throw a tennis ball against a wall. The ball will bounce back towards you. Now repeat this with a quantum mechanical "ball", for example an atom. Most of the time the atom will bounce right back to you, just like the tennis ball. Every once in a while, however, the atom ends up

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[3] If you have already taken a course on special relativity, you may recognise $px - Et$ as the product between the position and momentum four-vectors, even though our discussion has been completely non-relativistic. The quantity $px - Et$ is the accumulated phase of a wave, which is a Lorentz invariant scalar.

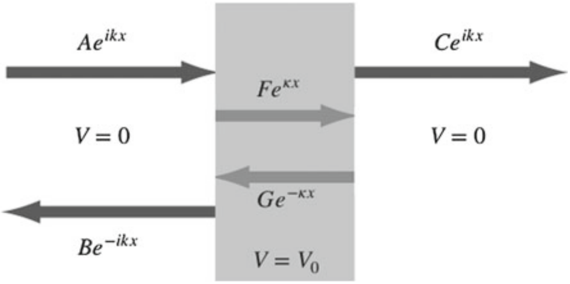


Fig. 8.7 Quantum tunnelling

behind the wall. Obviously, no classical ball can do this; the effect is purely quantum mechanical. To understand this, remember that the position of the atom is described by a wave function. The wall is described by a potential barrier. The potential is high at the location of the wall, and zero everywhere else. The atom bounces off the wall (most of the time) because its energy is lower than the potential barrier that is the wall.

The potential barrier determines the function $V(x)$ in the Hamiltonian in Eq. (8.65). Since the wall is there for the duration of the bouncing process, we can assume that V does not change in time. We therefore have for a wall of thickness a at position $x = 0$:

$$V(x) = \begin{cases} 0 & \text{if } x < 0 \text{ or } x > a\,, \\ V_0 & \text{if } 0 \leq x \leq a\,. \end{cases} \tag{8.73}$$

We calculated the the wave function of a particle with energy E and mass m in a constant potential V in the previous section, and when we set $t = 0$ in Eq. (8.72), we find

$$\psi(x) = A \exp\left(\frac{i}{\hbar}\sqrt{2m(E - V_0)}\, x\right)\,, \tag{8.74}$$

where, for brevity, we will write $k = \sqrt{2m(E - V_0)}/\hbar$. The situation is shown in Fig. 8.7.

On the left-hand side of the potential barrier we have $V = 0$, so the wave function is just a complex wave with amplitude A:

$$\psi(x < 0) = A \exp(ikx)\ . \tag{8.75}$$

However, since there may also be a reflected wave, we have to superpose another wave function (with a different amplitude B): $\psi(x < 0) = B \exp(-ikx)$, and the total wave function ψ_L on the left of the barrier is

$$\psi_L(x < 0) = Ae^{ikx} + Be^{-ikx}\ . \tag{8.76}$$

The minus sign indicates that the reflected particle is moving in the opposite direction. On the right-hand side of the wall, we have again a solution ψ_R of a very similar form, but possibly with a different amplitude:

$$\psi_R(x > a) = Ce^{ikx}\,. \tag{8.77}$$

There is no wave coming from the right in this example, so there is no contribution with $-k$ in the wave function in the region $x > a$.

Next, we wonder what the wave function looks like inside the barrier. Classically, this region is forbidden, so you might expect that $\psi(0 \leq x \leq a) = 0$. However, the Schrödinger equation says otherwise! Inside the wall the energy of the particle E is smaller than the potential barrier V_0. That makes the square root in Eq. (8.74) imaginary, and the argument of the exponential becomes real. If we define $\kappa = \sqrt{2m(V_0 - E)}/\hbar$, the wave function ψ_M inside the region becomes

$$\psi_M(0 \leq x \leq a) = Fe^{\kappa x} + Ge^{-\kappa x}\,, \tag{8.78}$$

again with both positive and negative solutions for κ. We now have to find how the amplitudes A, B, C, F, and G are related. The wave function must be continuous everywhere, which means that

$$\psi_L(0) = \psi_M(0) \qquad \text{and} \qquad \psi_M(a) = \psi_R(a)\,. \tag{8.79}$$

Similarly, the slopes of the wave functions in the different region must match at the boundaries, so that

$$\left.\frac{d\psi_L}{dx}\right|_{x=0} = \left.\frac{d\psi_M}{dx}\right|_{x=0} \quad \text{and} \quad \left.\frac{d\psi_M}{dx}\right|_{x=a} = \left.\frac{d\psi_R}{dx}\right|_{x=a}\,, \tag{8.80}$$

and we can solve this to get for the wave function at $x = 0$

$$A + B = F + G \quad \text{and} \quad ik(A - B) = \kappa(F - G), \tag{8.81}$$

and for the wave function at $x = a$

$$\begin{aligned} Ce^{ika} &= Fe^{\kappa a} + Ge^{-\kappa a} \\ ikCe^{ika} &= \kappa(Fe^{\kappa a} - Ge^{-\kappa a})\,. \end{aligned} \tag{8.82}$$

We can now solve for the variables A, B, C, F, and G using these equations and the normalisation to find the total wave function. However, it is more instructive to look at the ratios $R = |B|^2/|A|^2$ and $T = |C|^2/|A|^2$, because it tells us how much of the wave is reflected off the barrier, and how much is transmitted through the barrier. When we do this, after a fair amount of algebra we find that

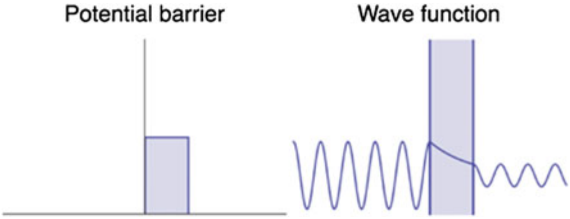


Fig. 8.8 The effect of the barrier on quantum tunnelling. The interactive figure is available online (see supplementary material 4)

$$R = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)}\right]^{-1}, \tag{8.83}$$

and

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}\right]^{-1}. \tag{8.84}$$

This means that even though the energy of the particle is lower than the potential of the barrier, it still has a small chance of being found behind the barrier. This is quantum tunnelling, shown in Fig. 8.8.

> *A similar phenomenon exists for classical electromagnetic waves that impinge on a conducting surface. When the conductivity is finite, the electromagnetic waves penetrate the conductor, and the amplitude will fall off exponentially with a characteristic length we call the skin depth. If the conducting material is thin enough, some of the wave will pass through. The remarkable thing in quantum mechanics is that this classical wave phenomenon also applies to particles due to the wave-particle duality.*

There is a very beautiful application of quantum tunnelling, namely scanning tunnelling microscopy (Binnig and Rohrer 1986). In this device, a very sharp needle (the tip of which is only a few atoms wide) is brought close to the surface of a material and given a positive electric potential. If the tip were to touch the surface, the electric potential would cause electrons to flow into the needle, creating a current. However, by keeping the needle slightly away from the surface, there is a small gap that acts as a potential barrier for the electrons on the surface. If the gap is big enough, the electrons will not have sufficient energy to jump the gap, and the only way to make it into the needle is via quantum tunnelling. The current measured in the needle is then directly proportional to the amount of tunnelling, given by T in Eq. (8.84). Since this depends on the separation a between the tip and the surface, we can scan the tip over the surface and obtain a current intensity profile. This is directly related to the profile of the surface, and can be used to "see" the surface of a material, for example silicon (shown in Fig. 8.9). This way, we can visualise features that are much too small to see with an optical microscope.

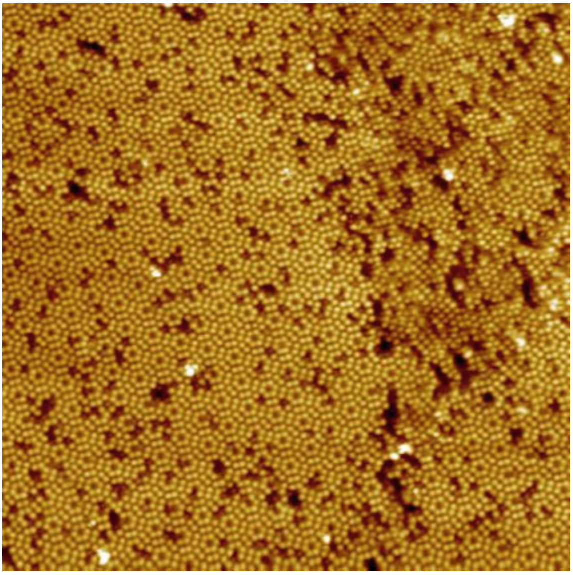


Fig. 8.9 An image of the surface of a silicon crystal from a scanning quantum tunnelling microscope. You can see the hexagonal crystal structure of silicon, as well as a lot of defects. Image taken by Dr. Ashley Cadby at the University of Sheffield

8.7 ❧ A Brief Glance at Chemistry

One of the great early triumphs of quantum mechanics is that it explains how chemistry works. While this requires a good working knowledge of how to solve partial differential equations, and is well beyond the scope of this book, we can still get a feel for how quantum mechanics explains the structure of atoms and how they can interact with each other. To see this, we need two ingredients: the quantum behaviour of electrons bound to the nucleus by the Coulomb force, and the Pauli Exclusion Principle (Pauli 1925). We have not encountered this principle before, since it does not follow directly from the theory we have developed so far. Instead, it is a very deep result that follows from a relativistic description of quantum mechanics, which goes far beyond our current level. Luckily for us, we can state the principle quite easily for our purposes:

Two electrons can not be in the same quantum state at the same time.

This means that if we want to put two electrons in a box, they cannot both have the same energy, spin, position and momentum. At least one of these must be different. While the Pauli Exclusion Principle is not an actual force, in some sense it has the effect that two electrons repel each other. This repulsion is different from the Coulomb force, which is true for all types of particles with like charge. The Pauli Exclusion Principle specifically holds for indistinguishable particles with half-integer spin ($S = \hbar/2$, $S = 3\hbar/2$, $S = 5\hbar/2$, etc.), regardless of any other forces on the particles.

We now discuss in broad strokes how quantum mechanics describes the structure of atoms. The simplest atom—the hydrogen atom—consists of a negatively charged electron bound to a positively charged proton. Since the proton is almost two thousand times heavier than the electron it will not move much under the Coulomb force of the electron, and we can assume that the proton sits at the centre of our coordinate system, and the electron orbits the proton. The Coulomb force F acting on the electron due to the proton can be written as

$$F = -\frac{e^2}{4\pi\epsilon_0 r^2}\,, \tag{8.85}$$

where e is the charge of the electron and the proton, r is the distance between the electron and the proton, and ϵ_0 is the permittivity of free space.

However, in quantum mechanics we do not really deal with forces, so unfortunately we cannot use Eq. (8.85) directly. Instead, we need the kinetic and potential energy of the electron, so we can construct the Hamiltonian for the Schrödinger equation. We need to translate the Coulomb force to the electrostatic potential $\Phi(r)$ created by the proton, as felt by the electron:

$$\Phi(r) = \frac{e}{4\pi\epsilon_0 r}\,. \tag{8.86}$$

The potential energy V of the electron in the electric field of the proton is the electron charge times the electrostatic potential of the proton: $V(r) = -e\,\Phi(r)$. The total Hamiltonian, including the kinetic energy of the electron, then becomes

$$H = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}\,, \tag{8.87}$$

with m the electron mass, and

$$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right). \tag{8.88}$$

The symbol $\partial/\partial x$ indicates (partial) differentiation in the x direction, and so on. The Schrödinger equation for the hydrogen atom then becomes

$$i\hbar\frac{d}{dt}\psi(\mathbf{r},t) = \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(\mathbf{r},t)\,. \tag{8.89}$$

Solving this equation is beyond the scope of this book, since it requires advanced knowledge of partial differential equations, and we have not developed this here.

Nevertheless, the Schrödinger equation can be solved, and in particular we can find the eigenstates ψ_n of the Hamiltonian from the eigenvalue equation

$$H\ \psi_n = E_n\ \psi_n\ , \tag{8.90}$$

where E_n are the energy eigenvalues for the electron.

When we solve for ψ_n in spherical coordinates r, θ, and ϕ, we find that it depends on two special functions, namely a radial function $R_{nl}(r)$ and the spherical harmonics $Y_{lm}(\theta, \phi)$ for the angular coordinates:

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)\ Y_{lm}(\theta, \phi). \tag{8.91}$$

We will not study these special functions here, but they play a central role in many branches of physics. The wave function depends not only on the energy label n, but also on two other numbers l and m. Together with the spin $s = \pm 1/2$, these are the quantum numbers of the electron in the hydrogen atom. The energy quantum number n is also called the *principal* quantum number.

The second quantum number l can take integer values from 0 to ∞, and denotes the angular momentum of the electron in the orbit around the proton. Angular momentum a quantity analogous to ordinary momentum $p = mv$, but for rotational motion instead of linear motion. It is conserved for the electron in the hydrogen atom.

Finally, the third quantum number m is the magnetic quantum number. This becomes important when we place the atom in a magnetic field. The value of the magnetic quantum number is bounded by l, such that $-l \leq m \leq l$. The three quantum numbers n, l, and m completely determine the spatial state of the electron (not taking into account its spin), and we can write it in shorthand as $|n, l, m\rangle$. They are orthogonal, in the sense that

$$\langle n', l', m' | n, l, m\rangle = \delta_{nn'}\ \delta_{ll'}\ \delta_{mm'}\ , \tag{8.92}$$

where δ_{nm} is zero when $n \neq m$, and one when $n = m$. This is the Kronecker delta, and it is the discrete version of the Dirac delta function. The spatial part of the wave function in spherical coordinates can then be found from $\psi_{nlm}(\mathbf{r}) = \langle r, \theta, \phi | n, l, m\rangle$, analogous to Eq. (8.24).

The energy eigenvalues of the electron in the hydrogen atom also follow from solving the eigenvalue equation (8.90), and are given by

$$E_{nls} \approx -\frac{mc^2\alpha^2}{2}\frac{1}{n^2}. \tag{8.93}$$

The number $\alpha \simeq 1/137$ is the fine structure constant. This is still not completely in agreement with experimental values, because there is another effect in play—the so-called *spin-orbit* coupling—which modifies the eigenvalues slightly. However, quantum mechanics has no problem including this effect.

Next, we want to know what the orbitals look like. To find the actual shapes of the electronic orbitals in hydrogen, we have to calculate the square of the wave function, since it is the probability (density) for finding the electron at position $\mathbf{r}$. Note that this is the best we can do in quantum mechanics: The electron does not orbit the nucleus

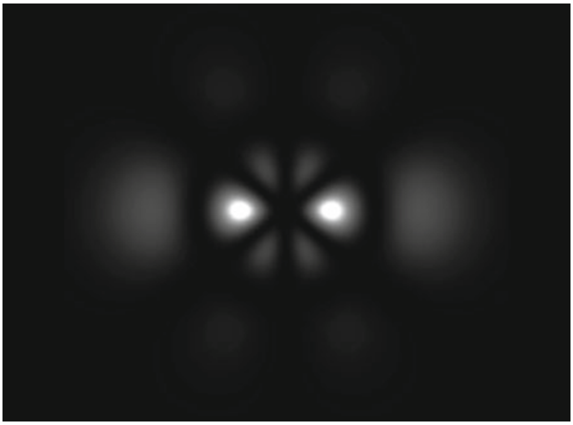


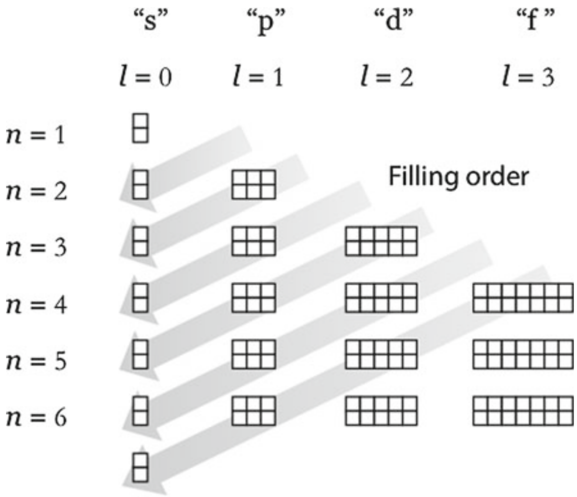
Fig. 8.10 Probability densities for the electron in hydrogen. The interactive figure is available online (see supplementary material 5)

in the same way a planet orbits the Sun. It does not have a path around the nucleus. We often speak of the electron "cloud", which is denser where it is more likely to find the electron. The probability densities for an electron in a hydrogen atom with the first five principal quantum numbers are plotted in Fig. 8.10. We restrict the plots to the electrons in the xz-plane for practical reasons.

So far, we have considered only a single electron in a bound state around a single proton. What about other atoms such as helium, carbon, and oxygen? If we treat the nucleus as a point at the centre of the atom (which is a very good approximation), then an atom with Z protons in the nucleus produces an electrostatic potential that is Z time stronger than the nucleus of hydrogen, which is a single proton. Any neutrons that may be present in the nucleus do not contribute to the electrostatic potential, since they are electrically neutral.

An atomic nucleus with Z protons can attract Z electrons before the atom becomes electrically neutral. Indeed, this is what tends to happen in ordinary matter: an atom captures Z electrons and will appear electrically neutral from a reasonably large distance (which in this case is only a few nanometers). However, all electrons have the same electrical charge $-e$, and like charges repel each other. As a crude approximation, we can assume that the electrons are so strongly attracted to the nucleus that they do not feel the repulsive Coulomb force of the other electrons. Of course, this is not true in reality, and the term in the Hamiltonian due to the electron-electron interaction will cause a shift in the energy levels of the atom. This can be observed in absorption and emission spectra (see Chap. 4 on how interactions change the energy eigenvalues of the Hamiltonian matrix). Here, we ignore this effect, because we merely seek a qualitative understanding of atoms and chemistry at this point. Nevertheless, quantum mechanics can deal with this complication too. So the electrons in an atom mostly ignore each other, and can be modelled approximately as individual electrons in a central potential of the form

Fig. 8.11 Atom energy shell filling order



$$V = -\frac{Ze}{4\pi\epsilon_0 r} . \tag{8.94}$$

Therefore, the solutions for the electrons in orbit around an atomic nucleus will look similar to the solutions we have found for the hydrogen atom. However, one crucial effect for electrons in atoms is far from negligible, and that is Pauli's Exclusion Principle.

If we want to put more than one electron in orbit around the nucleus, no two electrons can be in states that have equal n, l, m, and spin due to the Exclusion Principle. This means that the electrons with the same spin and principal quantum number n must have either different angular momentum l or a different magnetic quantum number m (or both). As we add electrons to orbits around the nucleus, they fill the accessible quantum states $|n, l, m\rangle$ and form a complex electronic structure.

The accessible quantum states are organised in "shells", corresponding to the different energy levels n. The angular momentum states are traditionally called "s" for $l = 0$, "p" for $l = 1$, "d" for $l = 2$, and "f" for $l = 3$. Larger values of l continue in alphabetical order ("g", "h", etc.). You may think that the electrons fill the shells one by one, but this is not the case. The energy eigenvalue in Eq. (8.93) depends on l as well as on the spin of the electron s, and this means that the filling order of the electron shells takes place as shown in Fig. 8.11. As a result, we first fill the lowest energy state $n = 1$, which can have only $l = 0$ and $m = 0$. We still have the spin value of the electron, $s = \pm 1/2$, so by choosing two electrons with opposite spin we can add two electrons to the lowest shell. We denote these electronic configurations by

$$1\text{s}^1 \qquad \text{and} \qquad 1\text{s}^2 , \tag{8.95}$$

where the superscript indicates how many electrons populate the level 1s. These are the electronic configurations of hydrogen (H) and helium (He).

Next, we put three electrons in orbit around a nucleus with three protons. The first shell is filled, which means that we must move to the next shell. According to the filling order shown in Fig. 8.11 this is the $n = 2$, $l = 0$ state, which in our new notation can be written as

$$\mathrm{Li}: \ 1\mathrm{s}^2\,2\mathrm{s}^1\,, \tag{8.96}$$

Similarly, we can write for beryllium

$$\mathrm{Be}: \ 1\mathrm{s}^2\,2\mathrm{s}^2\,, \tag{8.97}$$

and for boron

$$\mathrm{B}: \ 1\mathrm{s}^2\,2\mathrm{s}^2\,2\mathrm{p}^1\,. \tag{8.98}$$

Since for the heavier elements we end up with long strings of filled shells that do not change for subsequent elements, we often drop the specification of the lower filled shells. For example, we can denote the electronic structure of gold by

$$\mathrm{Au}: \ [\mathrm{Xe}]\,6\mathrm{s}^2\,4\mathrm{f}^{14}\,5\mathrm{d}^9\,, \tag{8.99}$$

where [Xe] is the electronic structure of the noble gas xenon:

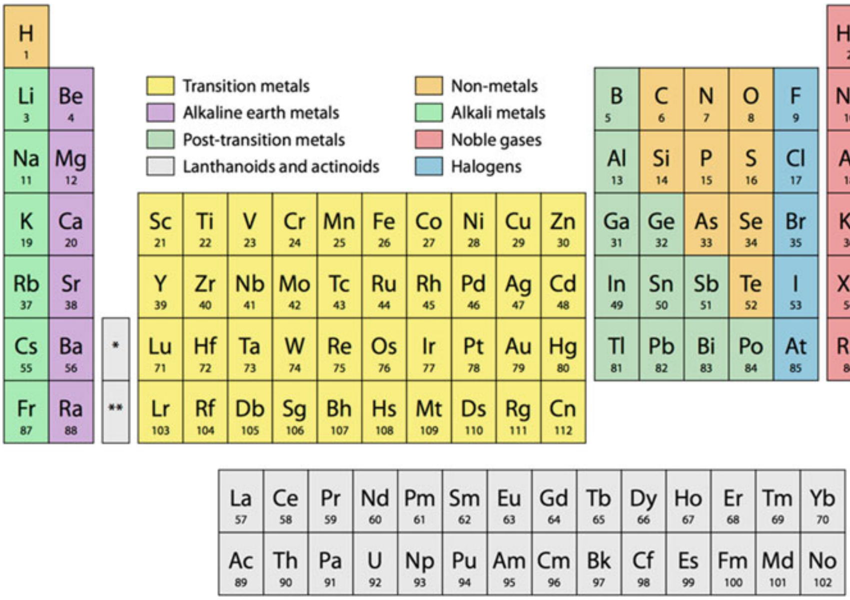
$$\mathrm{Xe}: \ 1\mathrm{s}^2\,2\mathrm{s}^2\,2\mathrm{p}^6\,3\mathrm{s}^2\,3\mathrm{p}^6\,4\mathrm{s}^2\,3\mathrm{d}^{10}\,4\mathrm{p}^6\,5\mathrm{s}^2\,4\mathrm{d}^{10}\,5\mathrm{p}^6\,. \tag{8.100}$$

Noble gases are elements that have a completely filled outer electronic shell (the p shell, except for helium), and are shown in the right-most column of the periodic table.

When atoms interact with other atoms, it is the outer electrons that determine their behaviour. These are the valence electrons. Atoms bond to each other when the valence electrons from one atom interact with the valence electrons from another atom. When the outer shell of an atom is full, there are no valence electrons, and the atom does not interact with other atoms much. Such an element is called inert, and these are the noble gases (Fig. 8.12).

The shape of the electronic clouds, shown in Fig. 8.10, determines how the atoms form into molecules. They explain why the angle of two hydrogen atoms with respect to an oxygen atom is 104.45° in a water molecule, and why diamonds have a tetrahedral crystal structure.

This has been merely a bird's eye overview of how quantum mechanics can explain the basic principles behind chemistry. The calculations that must be performed to obtain precise numbers corresponding to the results found in experiments are increasingly complex. For elements heavier than hydrogen we cannot even find general formulas that describe the atom, and we are forced to use approximation



🟨 Transition metals
🟪 Alkaline earth metals
🟩 Post-transition metals
⬜ Lanthanoids and actinoids
🟧 Non-metals
🟩 Alkali metals
🟥 Noble gases
🟦 Halogens

H 1																		He 2
Li 3	Be 4												B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12												Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20		Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38		Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	*	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	**	Lr 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112						

La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70
Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102

Fig. 8.12 The periodic table of elements. The interactive figure is available online (see supplementary material 6)

methods such as perturbation theory. This still allows us to make calculations to any required precision, and the agreement with experiments is remarkable. To date, we have not found any case where quantum mechanics cannot explain the results we see in experiments, except for the situation where the calculations become too big to run on a computer.

And all this we obtain from the basic theory we set out in this book. We can say with confidence that quantum mechanics is the most successful theory of nature that we have come up with so far, both in its scope of applicability and in its precision with which it predicts physical processes and quantities.

Exercises

1. A particle with mass m in a one-dimensional tube of length L has a Hamiltonian H that is given by

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

where $V(x) = 0$ when $0 \leq x \leq L$, and $V(x) = \infty$ otherwise (the value of ∞ means that the walls are impenetrable).

(a) Show that the wave functions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

are eigenfunctions of the Hamiltonian such that $H\psi_n = E_n\psi_n$, and $\psi_n = 0$ at the edges of the tube. Sketch the functions $\psi_n(x)$ for $n = 1, 2, 3, 4$.

(b) Show that the energy eigenvalues E_n are given by

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

(c) Are the wave functions $\psi_n(x)$ eigenfunctions of the *momentum* operator?

(d) Show that functions of the form $\phi_k(x) = \exp(\pm ikx)$ are solutions to the eigenvalue equation for momentum

$$-i\hbar\frac{d}{dx}\phi_k(x) = p\,\phi_k(x).$$

Determine the relationship between k and p.

(e) Construct the energy eigenfunctions $\psi_n(x)$ from the momentum eigenfunctions $\phi_k(x)$. What is the physical meaning of this relationship?

2. Rather than working out the energy eigenstates of a particle in a one-dimensional box, we may want to study more general time evolutions of the particle. A general wave function for the particle can be written as a superposition over all the energy eigenfunctions:
$$\psi(x) = \sum_n c_n\psi_n(x) .$$
Determine the state $\psi(x, t)$ after some time t has elapsed.
3. Calculate the position uncertainty Δx for a momentum eigenstate $|p\rangle$, and the momentum uncertainty Δp for a position eigenstate $|x\rangle$. Together with the De Broglie relation $p = h/\lambda$, this implies that wave behaviour is manifested when momentum states are prepared or measured, while particle behaviour is manifested when position states are prepared or measured. What happens when the position is measured for particles prepared in a momentum eigenstate?
4. By using the chain rule for differentiation, calculate an expression for the commutator $[\hat{x}, \hat{p}]$ between the position and momentum operator. You will have to consider how the commutator acts on an arbitrary wave function $\psi(x)$.
5. Find the normalisation constant in Eq. (8.49).
6. Consider the wave function

$$\psi(x) = \frac{1}{\sqrt[4]{\pi\sigma^2}} \exp\left[-\frac{(x - x_0)^2}{2\sigma^2}\right] ,$$

with σ a positive real number and the position x running from $-\infty$ to $+\infty$.

(a) What is the probability of finding a particle in the position interval $[x, x + dx)$? Sketch the probability density function $|\psi(x)|^2$.
(b) Calculate the Fourier transform $\Psi(p)$ of $\psi(x)$. What is the probability of finding a particle with momentum in the interval $[p, p + dp)$? Sketch the probability density function $|\Psi(p)|^2$.
(c) By varying σ, show how a sharper position will lead to a more uncertain momentum, and vice versa.

7. Derive the reflection and transmission coefficients for quantum tunnelling in equations (8.83) and (8.84). Show that these quantities behave appropriately when $V_0 \to 0$ and $V_0 \to \infty$. What happens when $a \to 0$?
8. The quantum state of a wave with momentum p is given in position space by

$$|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dx\; e^{ipx/\hbar} |x\rangle\,.$$

express this state in momentum space.

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