Quantum Mechanics

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Recommended Books and Resources

There is no shortage of excellent textbooks on quantum mechanics. Two good introductory books, at a similar level to this course, are:

- David. J. Griffiths, "*Introduction to Quantum Mechanics*"
- Alasdair Rae, "*Quantum Mechanics*"

Both books excel in providing clear and straightforward explanations and if you're struggling with the basics are good places to turn. They don't however do anything sophisticated and won't help much for later courses.

If you want a book to last a lifetime, rather than just one year, there are also many options. Here are some that I like.

- Shankar, "*Principles of Quantum Mechanics*"

A long and detailed book, but one where the author takes you by the hand and leads you gently through some challenging calculations.

- Landau and Lifshitz Volume 3 "*Quantum Mechanics: Non-Relativistic Theory*"

There's no hand holding in Landau's theoretical minimum, just encyclopedic information, explained without fuss. It is, however, remarkably readable.

- Steven Weinberg, "*Lectures on Quantum Mechanics*"

Weinberg is always worth listening to.

Contents

1 Introduction

Without wishing to overstate the case, the discovery of quantum mechanics is the single greatest achievement in the history of human civilisation.

Quantum mechanics is an outrageous departure from our classical, comforting, common sense view of the world. It is more baffling and disturbing than anything dreamt up by science fiction writers. And yet it is undoubtably the correct description of the universe we inhabit, providing insights into many aspects of the world around us.

Among the many successes of quantum mechanics are answers to old and very basic questions. Like why is matter stable? And why does the sun shine and why is it yellow? And why are all solids either conductors or insulators? But quantum mechanics also opens up vistas that we didn't previously know existed, from novel states of matter where the constituent particles become so entangled that they can be coaxed to perform seemingly impossible tasks, to the subatomic world of fluctuating ethereal fields, to a revised understanding of the meaning of information and what one can achieve with it.

Although quantum mechanics gives the right answers to all questions, it does so at a price. The answers are always statistical in nature. There are few certainties in the quantum world. Of course, there are few certainties in the classical world too, but we can always strive to eliminate them. In classical physics, knowledge is power: the more you know, the better off and less uncertain you are. This is because classical probabilities are always about our ignorance and any classical system that appears random does so because it is somehow difficult, but never impossible, for us to know what's going on inside.

This is is not the way of the quantum world. The randomness is real, the unpredictability inherent. There is no way to game the system or gain some illicit knowledge of underlying quantum properties that would reduce the uncertainty. If, for example, a particle has probability $\frac{1}{2}$ to be in one place and probability $\frac{1}{2}$ to be elsewhere, this may well be because the particle really is in both places at the same time. Any attempt to eliminate the quantum uncertainty will simply shift it, like a bubble in wallpaper, elsewhere. As we will see, quantum particles are fragile objects and the very act of looking changes them, disturbing many of the other delicate properties that they possess.

The purpose of these lectures is to begin to get to grips with the quantum world and understand some of the strange behaviour that it exhibits. As should be clear already, this is something of a step into the unknown and our classical intuition will not be a great guide in the quantum realm. Fortunately we have a better guide because, for reasons that we do not fully understand, the quantum world is described astonishingly well by the language of mathematics. Our strategy in these lectures, and later ones, will be to embrace this mathematical description and leverage it to build a new intuition for how the universe really works.

1.1 The Wavefunction

The difference between quantum and classical mechanics does not involve just a small tweak. Instead it is a root and branch overhaul of the entire framework.

This is manifest from the very beginning as we can see by comparing how we describe the *state* of a system in the two frameworks. The state is the information that tells us all we need to know about the system at a fixed time, with the idea that the laws of physics will then dictate how the state evolves at all later times. Throughout these lectures we will deal only with the dynamics of a single particle. For the present discussion, we'll think about a particle moving in $\mathbf{R}^3$.

In the classical world, the state of the particle is determined by its position $\mathbf{x}$ and its velocity $\mathbf{v} = \dot{\mathbf{x}}$. If you specify both bits of information at some time t_0 then you can use the equation of motion $\mathbf{F} = m\ddot{\mathbf{x}}$ to determine $\mathbf{x}(t)$ and $\mathbf{v}(t)$ for all time. Importantly, it's not enough to just know only, say, the position of the particle at $t = t_0$. You need both $\mathbf{x}(t_0)$ and $\dot{\mathbf{x}}(t_0)$. Mathematically, this is because the equation of motion is a second order differential equation and so you need to specify two integration constants to get a unique solution.

In the quantum world, the state of a particle is determined by its *wavefunction*. This is a complex valued function

$$\psi(\mathbf{x}, t)$$

As we will see, if you know the wavefunction at some time, say t_0, then you have all the information that you need to determine the state at all other times.

The description in terms of the wavefunction is not a small amendment to classical mechanics. We've replaced the three position coordinates $\mathbf{x} \in \mathbf{R}^3$ with an infinite amount of information, a functions worth of information. Moreover, we haven't specified anything about the particle's velocity; that information must also be contained, in some manner, in the wavefunction $\psi(\mathbf{x}, t)$.

The wavefunction has a very simple interpretation. Or, more precisely, the mod-square of the wavefunction has a very simple interpretation. It tells us the probability that we will find a particle at a given position. The probability density P for a particle to sit at point $\mathbf{x}$ is

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

This is known as the *Born rule*, after Max Born who first understood that quantum mechanics is a theory of probability rather than certainty.

From the probability density, you can compute actual probabilities by multiplying by a volume: the probability that the particle sits in some small volume dV centred around point $\mathbf{x}$ is $P(\mathbf{x},t)dV$.

In all other realms of science, probability arises because of our ignorance. If you throw a classical dice, and know its initial state with complete precision, then there is no doubt about what will happen. Once the dice leaves your hand, the probability that you will roll a six is either 0 or 1. If you were really good at solving differential equations, you could just figure out the answer and impress your friends. But, in most circumstances we don't have a good knowledge of the initial state of the dice and, besides, differential equations are hard. So we just give up, admit that we don't know what will happen, and say that the probability of rolling a six is $\frac{1}{6}$. Crucially, however, the introduction of probability is entirely due to our lack of knowledge; it is not an inherent property of the dice.

This is not the case in quantum mechanics. The state $\psi(\mathbf{x},t)$ contains all the information about a particle and the probabilistic interpretation is not because of any failing on our part, but instead due to an inherent randomness in the quantum world. This is, to put it mildly, something of a departure from the Newtonian way of thinking.

The novelty in the wavefunction description of the particle might suggest other interpretations of the function $\psi(\mathbf{x},t)$. You might, for example, wonder if perhaps we shouldn't think of a particle at all, but rather some fluid-like object, spread out over space. Such objects are commonplace in physics and are known as *fields*. The electric and magnetic fields are familiar examples. But that's *not* the right way to think about the wavefunction. This is because we never observe a fragmented particle, one that's lost its particle form and starts spreading jell-o like throughout space. Any measuring device that will allow you to determine whether a particle is in some designated region of space will return the answer yes or no. It won't tell you "well, the particle's a little bit here but mostly somewhere over there to the left". The wavefunction doesn't describe some real fluid; it is more nebulous. It is a wave only of probability.

Figure 1. In any particular experiment, you only detect particles with very definite trajectories and no hint of the more nebulous underlying wavefunction.

This is illustrated in Figure 1 which shows the tracks left by electrons and positrons as they pass through a detector known as a bubble chamber. The fast travelling particles move in approximately straight lines, while those that are slower spiral in circles due to an applied magnetic field. The electrons bend one way, the positrons the other, giving the back-to-back spirals that you can see. For our purposes, the key point is that when the particles entered the detector, they were described by a wavefunction that was spread out over a large part of space. Yet, the particles don't appear as fluffy, insubstantial clouds of probability. Instead, they leave clear tracks, with a definite trajectory.

The introduction of probability at such a fundamental level means that we must abandon the idea of predicting, with certainty, what will happen in a given experiment. There is no way to say when and where the spirals will appear in the picture above. We can only compute the likelihood for this to happen. Clearly this is retrograde step from the Newtonian (strictly, Laplacian) dream of knowing everything that will happen, from the beginning to the end of time.

One might wonder if perhaps it's possible to restore this dream at some deeper level. Maybe the wavefunction $\psi(\mathbf{x},t)$ is just some coarse-grained description of something finer and more subtle that's going on underneath. Maybe another layer of reality awaits discovery, one that allows us to bring back our comfortable deterministic, Newtonian way of thinking. There is good reason to think that this is not the case. Reality is, at heart, probabilistic. We'll mention some of the arguments for this in Section 3.5 where we touch upon some of the interpretations of quantum mechanics. A fuller description of why a deterministic world is incompatible with experiment will be given in the lectures on Topics in Quantum Mechanics (see, in particular, the section on

Quantum Foundations). For now, you'll just have to accept that the world in which we live is not the one our forefathers grew up believing in. It is random and uncertain. It is also, as we will see, considerably more interesting because of it.

1.1.1 Normalisation

The probabilistic interpretation means that the wavefunction can't just be any old function. The particle has to be somewhere, and this translates to the requirement

$$\int d^3x \; P(\mathbf{x},t) = \int d^3x \; |\psi(\mathbf{x},t)|^2 = 1$$

Wavefunctions that have this property are said to be *normalised*.

In practice, this isn't such a big deal. Suppose that we have a wavefunction $\Psi(\mathbf{x},t)$ that isn't normalised but instead obeys

$$\int d^3x \; |\Psi(\mathbf{x},t)|^2 = N < \infty$$

If N is finite we say that the wavefunction is *normalisable*. Clearly a wavefunction is normalisable only if $\psi(\mathbf{x},t) \rightarrow 0$ sufficiently fast as $|\mathbf{x}| \rightarrow \infty$. In this case, we can always construct a normalised wavefunction

$$\psi(\mathbf{x},t) = \frac{1}{\sqrt{N}}\Psi(\mathbf{x},t)$$

Quite often in these lectures, it will turn out to be useful to work with un-normalised wavefunctions Ψ and then remember to include the normalisation factor only at the end when computing probabilities.

From the discussion above, it should be clear that we will have little use for wavefunctions that cannot be normalised because

$$\int d^3x \; |\psi(\mathbf{x},t)|^2 = \infty$$

These have no probabilistic interpretation and should be discarded. They do not describe quantum states. (I should warn you that this statement, while mostly true, comes with small and annoying caveat that will rear its head fairly soon. We will address this in Section 2.1.)

There is one other relation between wavefunctions that is important: two wavefunctions that differ by a constant, complex phase should actually be viewed as describing equivalent states

$$\psi(\mathbf{x},t) \equiv e^{i\alpha}\psi(\mathbf{x},t)$$

for any constant, real α. Note, in particular, that this doesn't change the probability distribution $P = |\psi|^2$. Nor, it will turn out, does it change anything else either. (The "anything else" argument is important here. As we'll see later, if you multiplied the wavefunction by a spatially varying phase $e^{i\alpha(\mathbf{x})}$ then it doesn't change the probability distribution $P = |\psi|^2$ but it does change other observable quantities and so multiplying by such a factor does not give back the same state.)

Combining the need for normalisation, together with the phase ambiguity, it is sometimes useful think of states as the collection of normalisable, complex functions with the equivalence relation

$$\psi(\mathbf{x},t) \equiv \lambda\psi(\mathbf{x},t)$$

for any complex $\lambda \in \mathbf{C}$ with $\lambda \neq 0$. The wavefunctions ψ and $\lambda\psi$ should be viewed as describing the same physical state.

1.1.2 Superposition

The set of wavefunctions form a *vector space*. This means that if $\psi_1(\mathbf{x},t)$ and $\psi_2(\mathbf{x},t)$ are both possible states of the system, then so too is

$$\psi_3(\mathbf{x},t) = \alpha\psi_1(\mathbf{x},t) + \beta\psi_2(\mathbf{x},t)$$

for any $\alpha, \beta \in \mathbf{C}$. This is known as the *principle of superposition.*

The mathematics underlying this statement is simple. If ψ_1 and ψ_2 are states of the system then both must be normalisable. They may, indeed, be normalised but for now let's just assume that

$$\int d^3x \; |\psi_i(\mathbf{x},t)|^2 = N_i < \infty \qquad \text{for } i = 1, 2$$

Then ψ_3 is also a possible state of the system provided that it too is normalisable. But it is straightforward to show that it has this property. First we have

$$\int d^3x \;\; |\psi_3|^2 = \int d^3x \;\; |\alpha\psi_1 + \beta\psi_2|^2 \leq \int d^3x \; \Big(|\alpha\psi_1| + |\beta\psi_2|\Big)^2$$

where we've used the triangle inequality $|z_1 + z_2| \leq |z_1| + |z_2|$ for any $z_1, z_2 \in \mathbf{C}$. Continuing, we have

$$\int d^3x \ |\psi_3|^2 \leq \int d^3x \ \Big(|\alpha\psi_1|^2 + |\beta\psi_2|^2 + 2|\alpha\psi_1||\beta\psi_2|\Big) \leq \int d^3x \ \Big(2|\alpha\psi_1|^2 + 2|\beta\psi_2|^2\Big)$$

where, now, in the last step we've used the fact that $(|z_1|-|z_2|)^2 \geq 0$ which, rearranging, gives $2|z_1||z_2| \leq |z_1|^2 + |z_2|^2$. So, finally, we get the result we wanted

$$\int d^3x \ |\psi_3|^2 \leq 2|\alpha|^2 N_1 + 2|\beta|^2 N_2 < \infty$$

We learn that ψ_3 is normalisable, and hence also an allowed state of the system.

The idea that functions form a vector space might be novel. There is a simple notational trick that should help convince you that it's not too far from things you've seen already. If we have some n-dimensional vector $\vec{y}$, then we often use subscript notation and write it as y_i with $i = 1, \ldots, N$. We could equally well write it as $y(i)$ with $i = 1, \ldots, N$. A function $y(x)$ is a similar kind of object, but now with a continuous label $x \in \mathbf{R}$ rather than the discrete label $i = 1, \ldots, N$.

Of course, the big difference is that we're now dealing with an infinite dimensional vector space rather than a finite dimensional vector space, and I would be lying if I told you that this doesn't bring new issues to the table. Indeed, we've already met one of them above: we don't consider any old function $\psi(\mathbf{x})$ to be in our vector space, but rather only normalisable functions. There are many further subtleties in store but we will be best served by simply ignoring them at this point. We'll return to some issues in Section 3.

The principle of superposition has profound physical consequences. Suppose that you have a particle that, at some time t_0, you know is localised somewhere near the point $\mathbf{X}$. For example, we could describe it by the Gaussian wavefunction

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{N}} \, e^{-a(\mathbf{x}-\mathbf{X})^2}$$

for some choice of a that tells you how spread out the wavefunction is. Here N is a normalisation factor that won't concern us. (For what it's worth, we should take $N = (\pi/2a)^{3/2}$ if we want to ensure that ψ is normalised.) This is a state in which you might imagine that the particle still retains something of its classical particle nature, at least in the sense that the probability distribution is not spread out over long distances.

However, the superposition principle tells us that we should also entertain the idea that the particle can sit in a state

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{N'}}\left(e^{-a(\mathbf{x}-\mathbf{X}_1)^2} + e^{-a(\mathbf{x}-\mathbf{X}_2)^2}\right)$$

for arbitrary positions $\mathbf{X}_1$ and $\mathbf{X}_2$. But now the cat is really out of the bag! The interpretation of this state is that the particle has somehow split and now sits both near $\mathbf{X}_1$ and near $\mathbf{X}_2$. Indeed, we'll shortly see clear experimental consequences of states like the one above, where elementary particles – which are, as far as we can tell, indivisible – are coaxed into travelling along two or more different paths simultaneously. Taken to the logical extreme, it is states like the one above that lead us to seemingly paradoxical situations with cats that are both alive and dead.

1.2 The Schrödinger Equation

The wavefunction gives us a description of the state of the system. The next step is to understand how these states evolve in time. This is described by the *Schrödinger equation*,

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \tag{1.1}$$

Here $\hbar$ is *Planck's constant*, a fundamental constant of nature. Its value is

$$\hbar \approx 1.05 \times 10^{-34}\ \text{Js}$$

In the quantum world, the energy unit of choice is the electronvolt, defined by the kinetic energy that an electron picks up when accelerated over a potential difference of 1 volt. It is related to the Joule as 1 eV $\approx 1.6 \times 10^{-19}$ J. In these units, we have

$$\hbar = 6.58 \times 10^{-16}\ \text{eV s}$$

The numerical value of $\hbar$ is important for specific applications. But, conceptually, the units that $\hbar$ carries are more important. It has dimension of energy × time. This is the same dimension as angular momentum $\mathbf{L} = m\dot{\mathbf{x}} \times \mathbf{x}$. It is also the same dimension as the action in classical mechanics, $S = \int dt\ \frac{1}{2}m\dot{\mathbf{x}}^2 - V$.

A slightly old-fashioned convention is to define Planck's constant to be $h = 2\pi\hbar$. This is bad practice. First, $\hbar$ appears in equations much more often than the combination $2\pi\hbar$. But, more importantly, the quantity $\hbar$ is used exclusively for Planck's constant and its appearance in any equation is jumping up and down and screaming at you that quantum mechanics is at play. Meanwhile, h can mean many things in physics, from "height" to "magnetic field density". In these lectures we'll use only $\hbar$.

1.2.1 The Hamiltonian

The next object in the Schrödinger equation that needs explanation is $\hat{H}$. This is known as the *Hamiltonian*. Different choices of Hamiltonian describe different laws of physics. In these lectures, we will restrict ourselves to non-relativistic particles moving in three dimensions in the presence of a potential energy $V(\mathbf{x})$. For such a system, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}) \tag{1.2}$$

This is an example of a *differential operator*. It takes a function $\psi(\mathbf{x})$ and gives you back a new function, but only after differentiating by the Laplacian

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For much of these lectures, we will denote operators with a hat, like $\hat{H}$. I should mention, however, that this notation is a little like training wheels on a bike and in future lecture courses hats will be discarded and you just have to remember what objects are operators.

A few comments are in order about the Schrödinger equation and Hamiltonian. First, the Schrödinger equation replaces the venerable $\mathbf{F} = m\mathbf{a}$ in classical mechanics. Importantly, the Schrödinger equation is first order in time, rather than second order. This, ultimately, is why the state of a quantum system is described by $\psi(\mathbf{x})$ and not both $\psi(\mathbf{x})$ and $\dot{\psi}(\mathbf{x})$.

Next, the "Hamiltonian" is not something entirely novel to quantum physics. It is actually a concept that arises in more sophisticated presentations of Newtonian physics. You can read about this approach in the lectures on Classical Dynamics. In the classical world, the Hamiltonian is closely related to the energy of the system which, for us, is

$$E = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{x}) \tag{1.3}$$

where $\mathbf{p} = m\dot{\mathbf{x}}$ is the momentum of the particle. As these lectures proceed, we will also see the connection between the operator Hamiltonian $\hat{H}$ and energy. For now, we can just note that there is clearly a similarity in structure between the equations (1.2) and (1.3). If we wanted to push this analogy further, we might postulate some relationship in which momentum is replaced by a derivative operator,

$$\mathbf{p} \rightarrow \pm i\hbar\nabla \quad ?$$

where it's not clear whether we should take + or − since the energy depends only on $\mathbf{p}^2$. More importantly, it's not at all clear what a relationship of this kind would mean! How could the momentum of a particle – which, after all, is just a number — possibly be related to something as abstract as taking a derivative? As these lectures proceed, we'll see the connection between momentum and derivatives more clearly. (We'll also see that we should actually take the minus sign!)

It turns out that not all classical theories can be written using a Hamiltonian. Roughly speaking, only those theories that have conservation of energy can be formulated in this way. Importantly, the same is true of quantum mechanics. This means, in particular, that there is no Schrödinger equation for theories with friction. In many ways that's no big loss. The friction forces that dominate our world are not fundamental, but the result of interactions between many (say 10^{23}) atoms. There are no such friction forces in the atomic and subatomic worlds and, moreover, the formalism of quantum mechanics does not allow us to easily incorporate such forces.

(If, for some reason, you really do want to consider quantum friction then you're obliged to include the direct coupling to the 10^{23} other atoms and track what happens. There are interesting applications of this, not least an idea known as *decoherence*.)

One final comment: as we proceed to more advanced physical theories, whether relativistic quantum field theory or even more speculative endeavours like string theory, the Schrödinger equation (1.1) remains the correct description for the evolution of the quantum state. All that changes is the Hamiltonian (1.2), which is replaced by something more complicated, as too are the wavefunctions on which the Hamiltonian acts.

1.2.2 Conservation of Probability

We made a big deal about insisting that our wavefunctions are normalised so that they have a probability interpretation. But now we have the Schrödinger equation that tells us how the wavefunction evolves in time and we should make sure that this does not mess up a previously normalised wavefunction.

To this end, let's look at how the probability density changes in time. We have $P = |\psi|^2$ and so,

$$\frac{\partial P}{\partial t} = \psi^\star \frac{\partial \psi}{\partial t} + \frac{\partial \psi^\star}{\partial t}\psi \tag{1.4}$$

The Schrödinger equation (1.1) and its complex conjugate give

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right) \quad \text{and} \quad \frac{\partial \psi^\star}{\partial t} = \frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi^\star + V\psi^\star\right)$$

We see that the terms with the potential V cancel out when inserted in (1.4) and we're left with

$$\begin{aligned}\frac{\partial P}{\partial t} &= \frac{i\hbar}{2m}\left(\psi^\star\nabla^2\psi - \psi\nabla^2\psi^\star\right)\\ &= \frac{i\hbar}{2m}\nabla\cdot\left(\psi^\star\nabla\psi - \psi\nabla\psi^\star\right)\end{aligned}$$

We write this as

$$\frac{\partial P}{\partial t} + \nabla\cdot\mathbf{J} = 0 \tag{1.5}$$

where $\mathbf{J}$ is known as the *probability current* and is given by

$$\mathbf{J} = -\frac{i\hbar}{2m}\left(\psi^\star\nabla\psi - \psi\nabla\psi^\star\right) \tag{1.6}$$

Equations of the form (1.5) have a special place in the laws of physics. They are known as *continuity equations* and arises whenever there is a conserved quantity. (For example, the same equation appears in Electromagnetism where it relates the charge density to the electric current and ensures the conservation of electric charge.)

To see that the continuity equation implies a conservation law, consider some region $V \subset \mathbf{R}^3$ with boundary S. We then integrate to get the probability P_V that the particle lies somewhere in this region.

$$P_V(t) = \int_V d^3x\ P(\mathbf{x},t)$$

The continuity equation tells us that this probability changes as

$$\frac{\partial P_V}{\partial t} = -\int_V d^3x\ \nabla\cdot\mathbf{J} = -\int_S d\mathbf{S}\cdot\mathbf{J} \tag{1.7}$$

where, in the final step, we have used the divergence theorem. We see that the probability that the particle lies in V can change, but only if there is a flow of probability through the surface S that bounds V. If we know for sure that $\mathbf{J} = 0$ everywhere on the surface S, then the probability that the particle is in the region V doesn't change: $\partial P_V/\partial t = 0$.

The importance of the continuity equation is that it doesn't just tell us that some quantity is conserved: it tells us that the object is conserved *locally*. In the present context, this quantity is probability. The probability density can't just vanish in one region of space, to reappear in some far flung region of the universe. Instead, the evolution of the probability density is local. If it does change in some region of space then it's because it has moved into a neighbouring region. The current $\mathbf{J}$ tells you how it does this.

As a special case, if we take the region V to be all of space, so $V = \mathbf{R}^3$, then

$$P_{\text{anywhere}} = \int d^3x \; |\psi(\mathbf{x},t)|^2$$

As we've already seen, $P_{\text{anywhere}} = 1$. The change in the probability is, using (1.7),

$$\frac{\partial P_{\text{anywhere}}}{\partial t} = -\int_{S^2_\infty} d\mathbf{S}\cdot\mathbf{J}$$

where S^2_∞ is the asymptotic 2-sphere at the infinity of $\mathbf{R}^3$. Any normalised wavefunction must have $\psi \to 0$ as $|\mathbf{x}| \to \infty$ and, for all but the most pathological wavefunctions, this ensures that the current (1.6) also decays suitably quickly, $\mathbf{J} \to 0$ as $|\mathbf{x}| \to \infty$, so that

$$\frac{\partial P_{\text{anywhere}}}{\partial t} = 0$$

This is the statement that if the wavefunction is normalised at some time, then it remains normalised for all time.

1.2.3 The Collapse of the Wavefunction

There is one situation where the Schrödinger equation (1.1) does not describe the evolution of a quantum state. This occurs when we do a measurement.

As an example, suppose that at time t_0 we have a particle sitting in a superposition of two well-separated positions, $\mathbf{X}_1$ and $\mathbf{X}_2$, something like

$$\psi(\mathbf{x},t_0) = \frac{1}{\sqrt{N'}}\left(e^{-a(\mathbf{x}-\mathbf{X}_1)^2} + e^{-a(\mathbf{x}-\mathbf{X}_2)^2}\right)$$

Left to its own devices, this state will evolve through the Schrödinger equation. But suppose instead that we chose to do a measurement of the particle. For example, we can put a detector in the vicinity of $\mathbf{X}_1$ and see if it registers.

Suppose that the detector does indeed see the particle. Then we know for sure that the particle is sitting near $\mathbf{X}_1$ and that means that it can't possibly be elsewhere. The probability that it sits near $\mathbf{X}_2$ must then vanish! Correspondingly, after the measurement, the wavefunction can't have any support near $\mathbf{X}_2$. Instead, at time t_+ immediately after the measurement the wavefunction must jump to something localised near $\mathbf{X}_1$, like

$$\psi(\mathbf{x},t_+) = \frac{1}{\sqrt{N}}\,e^{-a(\mathbf{x}-\mathbf{X}_1)^2}$$

This is known as the *collapse of the wavefunction*.

There is something more than a little disconcerting about this aspect of quantum mechanics. Just a few pages ago, I told you that the probability in the wavefunction was not due to our ignorance, but instead to an inherent randomness of the system. Yet now we see that once we gain additional knowledge about the system – like where the particle actually is – the wavefunction necessarily changes. Which makes it sound like the wavefunction is describing some aspect of what we know after all!

The collapse of the wavefunction also demonstrates that our gain in knowledge is far from innocent. There is no way to learn something about a quantum system without perturbing that system, sometimes violently so. In the discussion above, it may appear that the collapse of the wavefunction only increases knowledge since we now have a better understanding of the particle's position. However, the wavefunction contains other, more subtle information and this too has been disturbed by the collapse which, typically, will lead to an increase of uncertainty in other properties.

Furthermore, the collapse of the wavefunction doesn't happen locally. Now the probability density really does just vanish from one region of space and re-emerge in the region where we detected the particle. You might worry that this will lead to contradiction with causality or with special relativity. It turns out that it doesn't but we won't get to fully understand why until later lectures. (See, for example, the section on Bell's inequality in the lectures on Topics in Quantum Mechanics.)

The fact that the wavefunction can evolve in two very different ways – the first through the smooth development of the Schrödinger equation, the second from the abrupt collapse after measurement – is one of the most unsettling aspects of quantum mechanics. It has led to much handwringing and philosophising and gnashing of teeth and mumbling of words like "ontic" and "epistemic", none of which seems to be quite enough to calm the nerves. We'll say more about these issues in Section 3.5 when we discuss the different interpretations of quantum mechanics.

1.3 The Double Slit Experiment

The double slit set-up is a simple but iconic experiment that vividly demonstrates some of the stranger aspects of quantum mechanics.

To set the scene, we first describe two experiments from classical physics. The set-up in both is the same: there is a wall, with two openings in it. These are the eponymous double slits. Behind the wall is a detector. You stand in front of the wall and throw things. The only difference between the two experiments lies in what you throw.

First, we throw particles. These are boring classical particles, like tennis balls. You throw randomly in the direction of the wall. Some simply bounce off the wall, while others get lucky and go through the slits. Then you measure the distribution of balls seen in the detector.

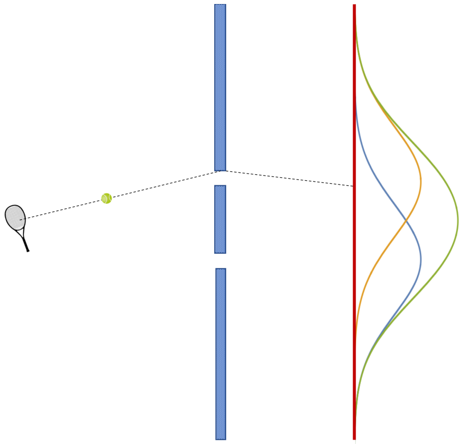


Figure 2. The distribution for classical particles.

In this case, things are nice and simple. Suppose that you close the bottom slit, keeping only the top slit open, and then measure the distribution of balls reaching the detector. The resulting distribution looks something like the yellow curve shown in Figure 2. Call this P_1. Similarly, if you close the top slit, but keep the bottom slit open then you measure the same distribution just shifted downwards. This is the blue curve in the figure. Now open both slits. What you see is the sum of the previous distributions,

$$P_{12} = P_1 + P_2$$

This is the green curve in the figure. So far, so good.

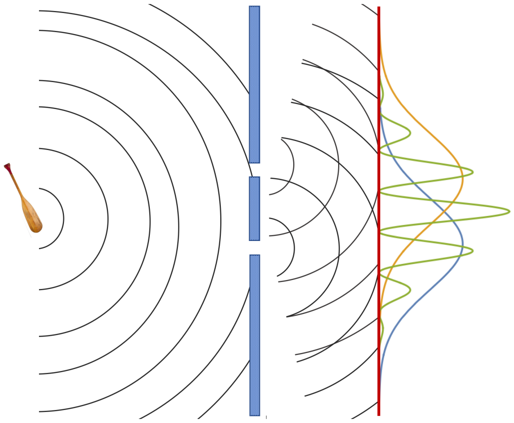


Figure 3. The distribution for classical waves.

Our second experiment is the same, but now with waves rather than particles. For our purposes, these can be water waves, sound waves or light waves. For any kind of wave, there is a new ingredient that dramatically changes the outcome: this is interference. Here we give a broad brush description of the physics.

First, we open one slit and not the other. The waves are diffracted at the slit and propagate out radially towards the detector where we can measure their intensity. The end result is very similar to that of a particle: a distribution spread out, peaked around the position of the first slit. This is shown in the yellow

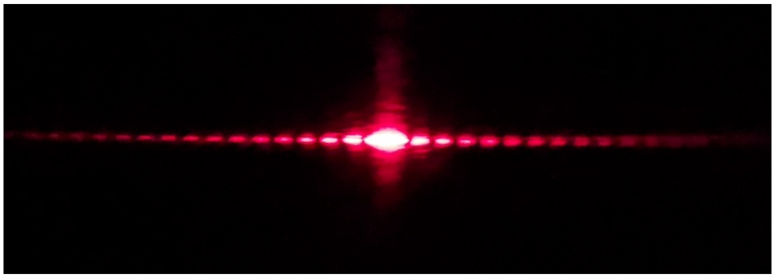


Figure 4. The interference of light waves through a double slit taken from this website.

and blue curves in Figure 3, corresponding to keeping only the top, or only the bottom, slit open respectively.

The real difference comes when we open both slits. The waves pass through along two paths and, when they recombine on the other side, add constructively or destructively. The result is the distinctive interference pattern shown in the green curve. Crucially, at some positions the intensity when both slits are open can be less than when any single slit is open. This happens, for example, at positions where the two waves cancel themselves out completely so the intensity on the screen vanishes. An interference pattern of this kind can be seen vividly using lasers, as shown in Figure 4.

With this classical intuition in place, we now turn to the quantum world. We will perform the double slit experiment one last time, now with quantum particles, say electrons. For appropriately sized slits, the result is a combination of the two classical experiments described above. First, when we detect an electron it appears just like a classical particle would appear. That means that each time we play the game, the electron appears as a point on the detector, rather than something continuous and smeared out like a wave. However, after playing the game many times, the probability distribution seen on the screen agrees with that of a classical wave, exhibiting an interference pattern. An example is shown in Figure 5.

Perhaps the most striking aspect of this result is that there are certain places on the screen where fewer electrons are detected when both slits are open than when any one slit is open. There's no way to explain this from a classical worldview where the particle follows a trajectory that goes *either* through the first slit *or* through the second. It must be that each particle somehow knows about the presence of both slits.

We can understand this behaviour from what little we know about quantum mechanics. First, when one slit is open, the particle is described by a wavefunction $\psi_1(\mathbf{x})$ and

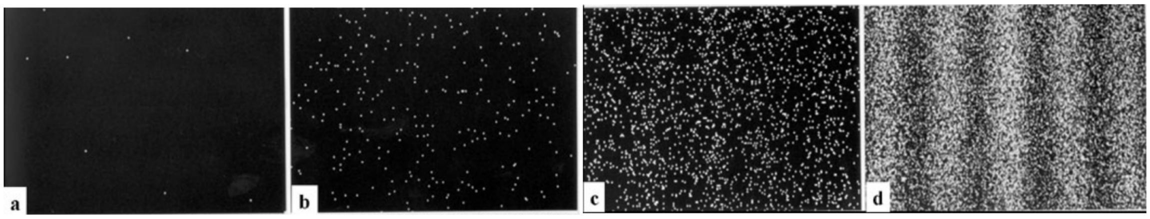


Figure 5. The double slit experiment, performed by Hitachi. The results show the build up the interference pattern from 8 electrons, to 270 electrons, to 2000 electrons and, finally, to 160,000 electrons where the interference fringes are clearly visible.

the probability distribution that we see on the screen is

$$P_1(\mathbf{x}) = |\psi_1(\mathbf{x})|^2$$

Similarly, with the second slit open and the first closed, we have $P_2(\mathbf{x}) = |\psi_2(\mathbf{x})|^2$. But when both slits are open, the principle of superposition tells us that it is the wavefunctions that add, not the probabilities. This means that we have $\psi_{12}(\mathbf{x}) = \psi_1(\mathbf{x}) + \psi_2(\mathbf{x})$ and so the new probability distribution is

$$P_{12}(\mathbf{x}) = |\psi_1(\mathbf{x}) + \psi_2(\mathbf{x})|^2 = P_1 + P_2 + \psi_1^\star(\mathbf{x})\psi_2(x) + \psi_2^\star(\mathbf{x})\psi_1(\mathbf{x})$$

We see that the cross-terms mean that $P_{12} \neq P_1 + P_2$. These cross-terms are responsible for the interference pattern.

The conclusion that each electron necessarily passes through both slits is, to say the least, a little surprising. One could try to find a clever way to evade it, perhaps by setting up some ingenious apparatus near one of the slits that will tell us for sure which slit the particle travelled through. It turns out that any attempt to do this will necessarily disturb the state of the particle. For example, if you know for sure that the particle passed through slit 1 (or, equivalently, that it did not pass through slit 2) then the wavefunction collapses to

$$\psi_{12}(\mathbf{x}) \longrightarrow \psi_1(\mathbf{x})$$

and the interference pattern disappears. There are general principles – notably the Heisenberg uncertainty relation that we will meet in Section 3 – that say that any apparatus that can determine through which slit the particle passed will necessarily also disturb the state of particle enough to destroy the interference fringes.

Quantum mysteries are often phrased as the question of whether an electron is a particle or a wave. The answer that is usually given is: both. A much better answer is: neither. Electrons, like all quantum objects, exist in a regime where our everyday experience is of little use. The idea that such objects can be described in terms of things that we can find on the beach is, to put it mildly, a little immature. A quantum particle is, instead, described by a wavefunction. The right way to proceed is not to search for some classical metaphor that will capture some aspect of the quantum particle, but instead to better understand the rules that govern these wavefunctions.

2 A Quantum Particle in One Dimension

There is much more to say about the basic postulates of quantum mechanics. However, rather than presenting the full mathematical framework up front, we're instead going to explore a few simple examples of the Schrödinger equation. In doing so, we'll build some intuition for how to think about the wavefunction and the various pieces of information that it encodes. Along the way, we'll motivate how to think about physics in the quantum world.

A few of the steps in this section will involve something of a leap of faith as we try to elucidate the meaning of the wavefunction. In Section 3, we will return to the basic formulation of quantum mechanics where we will state the rules of the game more precisely and present a more complete description of the theory.

We will cut our teeth on quantum mechanical systems that involve a single particle moving in one spatial dimension. This means that the wavefunction $\psi(x,t)$ depends on just a single variable x (in addition to time) and the Schrödinger equation becomes

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

We will solve this equation for various choices of $V(x)$ and interpret the results.

The Time Independent Schrödinger Equation

At first glance, the Schrödinger equation looks fairly daunting because it is a partial differential equation. In fact, there is a straightforward way to deal with the time variable. The idea is to look for separable solutions of the form

$$\psi(x,t) = e^{-i\omega t}\psi(x) \tag{2.1}$$

for some choice of frequency ω. Note that we have indulged in a slight abuse of notation, denoting both $\psi(x,t)$ and $\psi(x)$ with the same variable. In what follows, it will hopefully be clear which one we are talking about in any given circumstance. Where there is a possibility for confusion, we'll keep the arguments explicit.

Because this is the way that we will solve all Schrödinger equations in these lectures, let us briefly return to the general case with

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\psi(x,t) \tag{2.2}$$

Plugging in the ansatz (2.1), we find ourselves having to solve

$$\hat{H}\psi(x) = E\psi(x) \qquad \text{where } E = \hbar\omega \tag{2.3}$$

This is known as the *time independent Schrödinger equation*. If you really want to make a distinction, the original Schrödinger equation (2.2) is, of course, known as the *time dependent Schrödinger equation*. Here we'll usually just refer to both as the Schrödinger equation unless there's likely to be some confusion about which one we're talking about.

The Schrödinger equation in the form (2.3) looks very much like the eigenvalue equations that we meet when working with matrices and this is a very good analogy to have in mind as we proceed. In all the examples that we study, we'll see that there are solutions to (2.3) only for very specific values of E. Furthermore, these special values of E will have the interpretation of the possible energies of the system.

Separable solutions of the form (2.1) are sometimes referred to as *stationary states* and sometimes as *energy eigenstates*. They play a special role in quantum mechanics. One might worry that restricting attention to solutions of this kind is too restrictive, and that we are missing a whole bunch of other interesting solutions. In fact, as we go on we will see that all solutions can be expressed as linear combinations of different stationary states.

2.1 The Free Particle

Our first example is the simplest. We take a particle moving in one dimension in the absence of a potential

$$V(x) = 0$$

In this case, the time independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.4}$$

All we have to do is solve this. The solutions are straightforward to write down: there is a different solution for every $k \in \mathbf{R}$, given by

$$\psi(x) = e^{ikx} \tag{2.5}$$

The eigenvalue E in (2.4) is then given by

$$E = \frac{\hbar^2 k^2}{2m} \tag{2.6}$$

As we mentioned above, the value E has the interpretation of the energy of the state e^{ikx}. For now, take this as just one more postulate of quantum mechanics, perhaps one that has some justification given our earlier comments about the relationship between the energy and the Hamiltonian. We'll revisit these postulates in Section 3.

If we do interpret (2.6) as the energy of the particle, we should probably compare it to our classical expectations. In the absence of a potential energy, there is only kinetic energy and this is given by

$$E_{\text{classical}} = \frac{p^2}{2m}$$

where $p = m\dot{x}$ is the momentum of the particle. Clearly this suggests that the momentum of the state (2.5) should be identified with

$$p = \hbar k \tag{2.7}$$

This is the correct interpretation. We will later see that (2.5) is a "momentum eigenstate", which means that it is a state with definite momentum.

The wavefunction (2.5) can be viewed as a sum of sin and cos functions and describes a complex-valued wave of wavelength

$$\lambda = \frac{2\pi}{|k|} \tag{2.8}$$

Here the $|k|$ is needed because k can have either sign, while the wavelength is always positive. The relationship (2.7) between the momentum p and wavelength λ then becomes

$$|p| = \frac{2\pi\hbar}{\lambda}$$

In this context, λ is called the *de Broglie wavelength* of the particle. Any non-relativistic particle, with momentum p, has an associated wavelength λ and, as we will see, in certain situations will exhibit wavelike properties. The more grown-up version of the de Broglie relation is (2.7) where k is referred to as the *wavenumber*. However, it's not unusual for physicists in general (and me in particular) to be sloppy and refer to k as the momentum.

There is, however, an annoying subtlety that arises in this simplest example of quantum mechanics. The wavefunction (2.5) is *not* normalisable! If you integrate it you get

$$\int_{-\infty}^{+\infty} dx\ |\psi|^2 = \int_{-\infty}^{+\infty} dx\ 1 = \infty$$

That's bad! It means that we can't actually think of $\psi = e^{ikx}$ as a state of our particle. What should we make of this?

This is a slippery issue, and one that doesn't arise in many other situations. We will, ultimately, address this issue head on in Section 2.4 where wavefunctions like (2.5) will be too useful to ignore. But we will be best served if we first sidestep the problem and look at situations where it doesn't arise.

2.1.1 A Particle on a Circle

One simple fix is to consider a particle moving on a circle of radius R. The Schrödinger equation is still (2.3) and its solutions are still (2.5), but now there is the additional requirement that the wavefunction should be periodic, so that

$$\psi(x + 2\pi R) = \psi(x)$$

Not all solutions (2.5) obey this requirement. We must have

$$e^{ik(x+2\pi R)} = e^{ikx} \quad \Rightarrow \quad e^{2\pi ikR} = 1$$

This holds only for k of the form

$$k = \frac{n}{R} \quad \text{with } n \in \mathbf{Z}$$

This is our first sign of the *quantum* in quantum mechanics. This word refers to the fact that certain quantities, which are always continuous variables in the classical world, can only take certain discrete values in this new framework. For the particle on a circle, we see that the momentum is *quantised*

$$p = \frac{\hbar n}{R} \quad \text{with} \quad n \in \mathbf{Z} \tag{2.9}$$

as is the energy

$$E = \frac{\hbar^2 n^2}{2mR^2} \quad \text{with} \quad n \in \mathbf{Z}$$

The possible values of the momentum are split by $\hbar/R$. As the circle gets larger, the gap between the allowed momentum states becomes smaller. At some point, this will be experimentally indistinguishable from momentum p taking arbitrary real values. Similar comments hold for the energy. The collection of all possible energies is known as the *spectrum* of the Hamiltonian.

As an extreme example, we don't know if our universe is infinite or if it is finite, with a radius $R \gtrsim 20$ billion light years. If the latter is true, then you wouldn't be able to travel with arbitrary momentum, but only very specific values finely graded by $\sim 1/R$. Needless to say, we have no way of measuring momentum to an accuracy which can distinguish these two options.

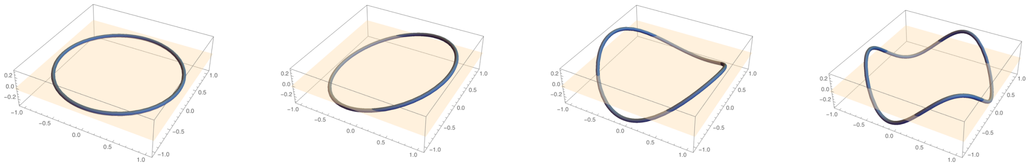

n=0 n=1 n=2 n=3

Figure 6. The (real part of the) wavefunction, plotted around the circle for the lowest energy states. These rotate in time with frequency $\omega = E/\hbar$.

Conversely, suppose that there are spatial dimensions in our universe beyond the obvious three that we see. If such dimensions exist, we need a reason why we've not observed them. One obvious possibility is that they wrap around to form a circle or some other compact space. In this case, the lowest energy wavefunctions simply spread uniformly around the extra dimension. If you want to move in the extra dimension, then you need a minimum amount of momentum $p = \hbar/R$ and, correspondingly, a minimum amount of energy $\hbar^2/2mR^2$. If we can't muster this minimum energy then we are unaware of these extra dimensions. But, ironically, we're unaware of them because we inhabit them uniformly, rather than because we're stuck at one point.

There are no pressing reasons to believe that extra dimension exist in our universe. Our best particle accelerators reach energies of around 10^{12} eV, also known as a TeV, and there is no sign of them knocking particles into the next dimension. This puts a limit on the size of these putative small extra dimensions of $R < 10^{-19}$ m or so. (To give you the fuller story, you really need relativistic dynamics by the time we get to these energies. The result is that the minimum momentum in the extra dimension requires energy $E = \hbar c/R$, but the general conclusion remains unchanged.)

The discreteness in quantities like momentum and energy is one of the characteristic features of quantum mechanics. However, as the example above illustrates, there is no discreteness in the fundamental equations. Instead, the discreteness is an emergent phenomenon. The integers n arise only when you solve these equations. In the current example, there is a nice intuitive explanation for how this arises: the only states that are allowed are those for which an integer number n of de Broglie wavelengths fits nicely around the circle. Indeed, the quantisation condition (2.9) becomes

$$\lambda = \frac{2\pi R}{|n|} \quad \text{with} \quad n \in \mathbf{Z}$$

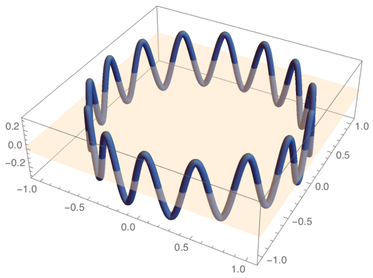


Figure 7. The (real part of the) wavefunction for $n = 15$.

The wavefunctions for $n = 0, 1, 2$ and 3 are plotted in Figure 6. The $n = 0$ wavefunction is simply a constant. It's not so obvious that the $n = 1$ wavefunction oscillates once as we go around the circle, but this becomes increasingly easy to visualise as n increases. The $n = 15$ wavefunction is shown in Figure 7.

Finally, we can return to the normalisability issue that plagued our earlier example of a particle on a line. The wavefunction (2.5) is not normalised but, when viewed on a circle, it is at least normalisable. We have

$$\int_0^{2\pi R} dx\ |\psi|^2 = 2\pi R$$

which tells us that the correctly normalised wavefunction is

$$\psi(x) = \frac{e^{ikx}}{\sqrt{2\pi R}}$$

You can see that this doesn't fare well if we try to return to a particle on the real line by taking $R \to \infty$. In this limit, the wavefunction becomes smaller and smaller in its attempt to remain normalised, until it vanishes completely.

2.1.2 The Infinite Potential Well

We get very similar physics by looking at a particle trapped in an infinite potential well of width L. We can achieve this by setting

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

You may think that we're no longer dealing with a free particle now that we're subjecting it to an infinite potential energy. However, the effect of an infinite $V(x)$ is very easy to deal with. The Schrödinger equation equation is

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

and if we're looking for states with finite energy E, then we must have $\psi = 0$ in any region where $V(x) = \infty$. Intuitively this is obvious: the infinite potential is just a plot device that allows us to insist that the particle is restricted to lie in the region $0 < x < L$. Within this region, we again have our free Schrödinger equation

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

but now with the restriction that $\psi(x) = 0$ at the two ends of the interval $x = 0$ and $x = L$. The solutions are, once more, a restricted class of the e^{ikx} wavefunctions.

To see the restriction in more detail, first recall that in our previous example the wavevector k can take either sign. Moreover, in that case e^{+ikx} and e^{-ikx} describe two different states since, from (2.7), they correspond to a particle with positive or negative momentum. For the particle in the interval, we will consider the more general ansatz

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

now with $k > 0$. The requirement that $\psi(x = 0) = 0$ tells us that $B = -A$, so the wavefunction must be of the form

$$\psi(x) = A\left(e^{ikx} - e^{-ikx}\right) = 2iA\sin kx$$

The factor of $2iA$ in front simply changes the normalisation of the wavefunction and doesn't affect the physics. Now we have to impose the requirement that the wavefunction vanishes at the other end of the integral, $\psi(x = L) = 0$, or

$$\sin kL = 0 \quad \Rightarrow \quad k = \frac{\pi n}{L} \quad \text{with } n \in \mathbf{Z}^+$$

Finally, if we want the wavefunction to be normalised correctly, we should take

$$\psi(x) = \sqrt{\frac{2}{L}}\sin kx \tag{2.10}$$

The wavefunctions for the $n = 1, 2, 3$ and 4 states are shown in Figure 8.

There is one slightly subtle difference from our previous example: in the current case n should be a positive integer, while for the particle on the circle it could have either sign. This is because reversing the sign of k in (2.10) merely flips the overall sign of the wavefunction which, as we have seen, does not give a different state. This means that the $+n$ and $-n$ states are the same. Meanwhile, if you set $n = 0$, the wavefunction simply vanishes and so the upshot is that we restrict n to be a positive integer.

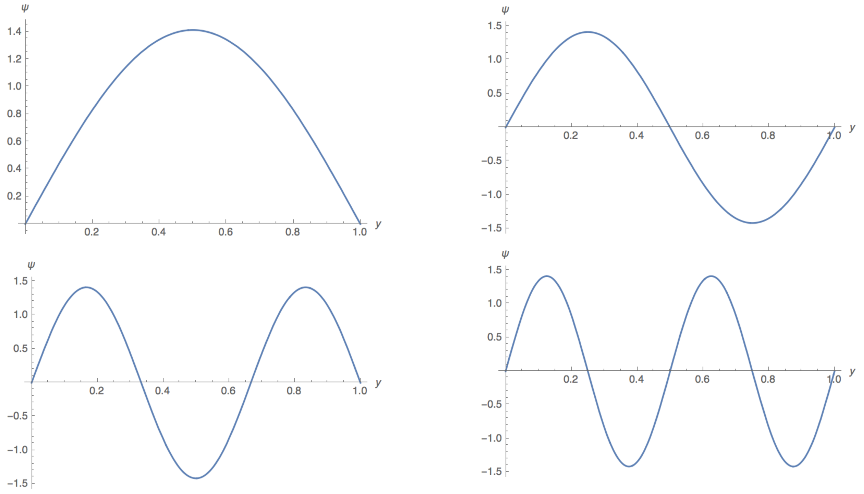


Figure 8. The ground state wavefunction for an infinite potential well in the top left, followed by the first three excited states.

In this example, we again see that energy is quantised, taking values

$$E = \frac{\hbar^2\pi^2 n^2}{2mL^2} \tag{2.11}$$

This is very similar to the result of a particle on a circle.

What about the momentum? Recall our previous discussion: the state e^{ikx} has momentum $p = \hbar k$. But for the current example, we have (ignoring the normalisation) $\psi = e^{ikx} - e^{-ikx}$. This is the superposition of two states, one with momentum $p = +\hbar k$ and the other with momentum $p = -\hbar k$. This means that these states do *not* have a well defined momentum. This shouldn't be a surprise because a classical particle in a box bounces back and forth and doesn't have a well defined sign of the the momentum either. Similarly, you can think of the wavefunctions as standing waves, bouncing backwards and forwards between the two walls but not going anywhere. We'll become more precise about how to identify the momentum of a state as we go on.

The discreteness of energy levels in the infinite well has an important application, similar in spirit to the "extra dimension" story that we told above, but significantly less science fiction. Consider particles moving, as particles do, in three spatial dimensions. Suppose that you trap them in a well in one dimension, but still allow them to wander in the other two. Then, provided that you can restrict their energies to be small enough, the particles will act, to all intents and purposes, as if they're really two-dimensional objects.

This is in sharp distinction to what happens in classical mechanics where the particles would move *approximately* in two dimensions but there would always be small oscillations in the well that can't be ignored. In contrast, the discreteness of quantum mechanics turns an approximate statement into an exact one: if the particle doesn't have enough energy to jump to the $n = 2$ state then it really should be thought of as a 2d particle. Of course, we can also restrict its motion once more and make it a 1d particle.

This may not seem like a big deal at this stage but, as we will learn in later courses, interesting things can happen in low dimensions that don't happen in our 3d world. But these things aren't mere mathematical curiosities: they can be constructed in the lab using the method above. (If you want an example, in 2d — but not in 1d or in 3d — it's possible for an electron to split into N objects each carrying fractional electric charge $1/N$. And this can be seen in experiments!)

2.1.3 The Gaussian Wavepacket

Let's now return to the problem of a free particle moving on a line, with $x \in \mathbf{R}$. Recall that the time dependent Schrödinger equation is

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

This is solved by the separable solution

$$\psi_k(x,t) = e^{-iE_k\, t/\hbar}e^{ikx}$$

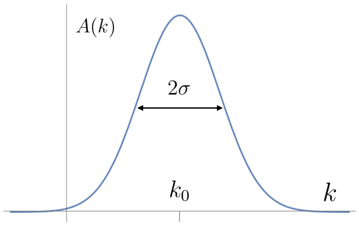
for any choice of $k \in \mathbf{R}$. In anticipation of what's coming next, we've changed the notation to make it clear that both the wavefunction ψ_k and the energy E_k depend on the wavenumber k, with the latter given by

$$E_k = \frac{\hbar^2 k^2}{2m}$$

The problem, as we've seen, is that ψ_k is not a normalisable wavefunction on $\mathbf{R}$ and therefore is an illegal state. However, that doesn't stop us from taking superpositions of ψ_k to build states that are normalisable. The most general superposition takes the form

$$\psi(x,t) = \int_{-\infty}^{+\infty} dk\ A(k)\,\psi_k(x,t) \tag{2.12}$$

for some function $A(k)$. Moreover, for each choice of $A(k)$, this wavefunction will solve the time dependent Schrödinger equation . This follows from a simple, yet important, observation about the general time dependent Schrödinger equation (1.1): it is linear. This means that if you find two solutions ψ_1 and ψ_2 that solve the Schrödinger equation, then their sum is guaranteed to solve it as well. This linearity of quantum mechanics is, like the Schrödinger equation itself, something that persists as we move on to more advanced topics. It is one of the very few ways in which quantum mechanics is simpler than classical mechanics.



For our purposes, let's consider a wavefunction built by taking

$$A(k) = \exp\left(-\frac{(k-k_0)^2}{2\sigma} + \frac{k_0^2}{2\sigma}\right)$$

This is a Gaussian distribution over momentum states ψ_k, centred around the wavenumber $k = k_0$, with width $\sigma > 0$. A sketch is shown to the right. The additional factor of $e^{k_0^2/2\sigma}$ is just a constant and only affects the normalisation of the wavefunction; we've included it so that things look simpler below.

When used to construct the linear superposition (2.12), the Gaussian distribution means, roughly speaking, that we include significant contributions only from wavenumbers that lie more or less within the window

$$(k-k_0)^2 \lesssim \text{a few times } \sigma \tag{2.13}$$

Outside of this window, the coefficients $A(k)$ drop off very quickly. What does the resulting wavefunction look like? We have

$$\begin{aligned}\psi(x,t) &= \int_{-\infty}^{+\infty} dk\ \exp\left(-\frac{k^2-2kk_0}{2\sigma} - i\frac{\hbar t k^2}{2m} + ikx\right)\\ &= \int_{-\infty}^{+\infty} dk\ \exp\left(-\frac{\alpha}{2}\left(k-\frac{\beta}{\alpha}\right)^2 + \frac{\beta^2}{2\alpha}\right)\end{aligned}$$

where, in the second line, we have simply completed the square and the various parameters are given by

$$\alpha = \frac{1}{\sigma} + \frac{i\hbar t}{m}\ , \quad \beta = \frac{k_0}{\sigma} + ix \tag{2.14}$$

At this stage, we have an integral to do. This is well-known Gaussian integral, with

$$\int_{-\infty}^{+\infty} dk\ e^{-\alpha(k-\gamma)^2/2} = \sqrt{\frac{2\pi}{\alpha}}$$

This result holds for any γ and for any α with $\mathrm{Re}(\alpha) > 0$. A quick look at the α defined above confirms that we're in business, and the final result for the wavefunction is

$$\psi(x,t) = \sqrt{\frac{2\pi}{\alpha(t)}} \exp\left(-\frac{1}{2\alpha(t)}\left(x - \frac{ik_0}{\sigma}\right)^2\right) \tag{2.15}$$

where the function $\alpha(t)$ is defined in (2.14). We see that the wavefunction also takes the form of a Gaussian, now in space, and with a time dependent width $\alpha(t)$.

There's a lot to unpack in this formula. First, note that the wavefunction is normalisable. (Although, as we shall see shortly, not actually normalised.) This follows from the fact that $\psi(x,t)$ decays exponentially quickly as $x \to \pm\infty$. So although we built the wavefunction from the non-normalisable, and hence illegal, waves (2.5) there's nothing wrong with the end product. This is the first sign that we shouldn't be so hasty in simply discarding the e^{ikx} wavefunctions on the line. They may not be genuine states of the system, but they're still useful.

The state described by (2.15) has neither definite momentum nor energy nor, indeed, position. This is actually the lot of most states. Moreover, the state does not take the simple separable form (2.1) of the stationary states that we've discussed until now. Indeed, the time dependence is fairly complicated. It turns out that one can construct all solutions of the Schrödinger equation through similar linear superpositions of stationary states. When, as in the present case, the stationary states are simply e^{ikx}, the linear superposition is just the Fourier transform of a function. But it also holds in more complicated cases. This is why its sensible to solve the time dependent Schrödinger equation by first looking for solutions to the simpler time independent Schrödinger equation. We'll address this further in Section 3.

Next, we can try to extract some physics from the state (2.15) which goes by the name of the *Gaussian wavepacket*. Clearly it describes a state that is fairly well localised in space. But, as time goes on, it becomes more and more spread out[1]. This is what happens to quantum probability if it is not trapped by some potential: it disperses. It is only the stationary states that have a definite energy and, correspondingly, the simple $e^{-iEt/\hbar}$ time dependence that stick in one place.

There is also something interesting in the size of the dispersion. Recall that we built the state by integrating over momentum modes in the window (2.13). We can think of this in terms of the variance, or *uncertainty*, of the wavenumber which we write as

$$\Delta k^2 \sim \sigma$$

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[1] The Mathematica website has a nice demonstration of an evolving Gaussian wavepacket.

where $\sim$ is an important mathematical symbol that means the thing of the left is roughly like the thing on the right. It's useful in physics when trying to tease out some relation without bothering about all the details like annoying numerical coefficients. Meanwhile, the spread in position is determined by the function $\alpha(t)$ given in (2.14). It is at its minimum when $t = 0$, so we have

$$\Delta x^2 \sim \alpha(t) \geq \alpha(t=0) = \frac{1}{\sigma}$$

We see that the spread of the wavefunction in position space is inversely proportional to its spread in wavenumber or, equivalently, its spread in momentum $p = \hbar k$. Multiplying these together, we get

$$\Delta x^2 \, \Delta p^2 \gtrsim \hbar^2$$

This is our first glimpse at the famous *Heisenberg uncertainty relation*. You can localise a particle in space only at the expense of having a broad range of momenta, and vice versa. We'll derive the proper mathematical expression of the Heisenberg uncertainty relation in Section 3.4.1.

This also gives us a new perspective on our original attempt at writing states as $\psi = e^{ikx}$. These wavefunctions have a definite momentum, $p = \hbar k$. But they are also spread out everywhere in space and this is what resulted in their non-normalisable downfall.

2.1.4 A First Look at Expectation Values

There is one thing that might still seem puzzling about our wavefunction

$$\psi(x,t) = \sqrt{\frac{2\pi}{\alpha(t)}} \exp\left(-\frac{1}{2\alpha(t)}\left(x - \frac{ik_0}{\sigma}\right)^2\right)$$

We constructed it by summing over states with different wavenumbers, but they were peaked around $k = k_0$. And one might think that this should result in a particle moving with some average momentum $p = \hbar k_0$. But it's not obvious that our wavefunction is moving to the left or right in any way. In fact, pinning down its location is a little bit confusing because there's the imaginary piece $-ik_0/\sigma$ sitting in the exponent. How should we think of this?

To get a better sense of what's going on, we should compute the probability density $P \propto |\psi|^2$. At this point we should be more careful about the overall normalisation, so we introduce a constant C that we'll figure out later and write $P = C|\psi|^2$. We then have

$$P(x,t) = \frac{2\pi C}{|\alpha|}\exp\left(-\frac{1}{2\alpha}(x - ik_0/\sigma)^2 - \frac{1}{2\alpha^\star}(x + ik_0/\sigma)^2\right)$$
$$= \frac{2\pi C e^{k_0^2/\sigma}}{|\alpha|}\exp\left(-\frac{1}{\sigma|\alpha|^2}\left(x - \frac{\hbar k_0 t}{m}\right)^2\right) \tag{2.16}$$

where you need a little bit of algebra to get to the second line. You can check that the probability is correctly normalised if we take $C = e^{-k_0^2/\sigma}/\sqrt{4\sigma\pi^3}$. Importantly, the normalisation factor itself doesn't depend on time. This had to be the case because we've constructed this wavefunction to obey the time dependent Schrödinger equation and, as we saw in Section 1.2.2, if you normalise the wavefunction at one time then it stays normalised for all times.

From the form of the probability (2.16), you can clearly see the growing width of the distribution, with

$$|\alpha|^2 = \frac{1}{\sigma^2} + \frac{\hbar^2 t^2}{m^2}$$

However, it is now also clear that the probability distribution doesn't just sit at the origin and spread out, but instead moves. This follows because the x dependence takes the form $x - vt$ where the velocity is

$$v = \frac{\hbar k_0}{m}$$

If we think in classical terms, and define the momentum to be $p = mv$, then we have $p = \hbar k_0$ as expected.

There should be a more systematic way to extract this information about the momentum of a state, one that doesn't involve staring at complicated formulae to figure out what's going on. And there is. Our equation (2.16) is a probability distribution for the position of the particle. As with any probability distribution, we can use it to compute averages and variances and so on.

Given a probability distribution $P(x)$, with $x \in \mathbf{R}$, the average of any function $f(x)$ is given by

$$\langle f(x)\rangle = \int_{-\infty}^{+\infty} dx\; f(x)\, P(x)$$

In quantum mechanics the average is usually called the *expectation value* and, as above, is denoted by angular brackets $\langle \cdot \rangle$. We can then ask: what is the average position of the particle given the probability distribution (2.16)? We simply need to compute the integral

$$\begin{aligned}\langle x\rangle &= \frac{1}{\sqrt{\pi\sigma|\alpha|^2}}\int_{-\infty}^{+\infty} dx\; x\, \exp\left(-\frac{1}{\sigma|\alpha|^2}\left(x-\frac{\hbar k_0 t}{m}\right)^2\right)\\ &= \frac{1}{\sqrt{\pi\sigma|\alpha|^2}}\int_{-\infty}^{+\infty} d\tilde{x}\;\left(\tilde{x}+\frac{\hbar k_0 t}{m}\right)\,\exp\left(-\frac{\tilde{x}^2}{\sigma|\alpha|^2}\right)\end{aligned}$$

where, in the second line, we've shifted the integration variable to $\tilde{x} = x - \hbar k_0 t/m$. We can now use the general result for Gaussian integrals,

$$\int_{-\infty}^{+\infty} dx\; e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad \text{and} \quad \int_{-\infty}^{+\infty} dx\; x\, e^{-ax^2} = 0 \tag{2.17}$$

where the second equality follows because the integrand is odd (and suitably well behaved at infinity). Using these, we get

$$\langle x\rangle = \frac{\hbar k_0 t}{m}$$

showing, once again, that the wavepacket travels with velocity $v = \hbar k_0/m$.

We could do further calculations to compute the average of any other function $f(x)$. But instead we're going to pause and ask a different question. How do we compute the average momentum of the wavepacket?

At first glance, this might seem like an odd question. After all, we've just computed the velocity v and so the average momentum is surely $p = mv$. However, in later examples things won't be so straightforward and this is a useful place to pause and see what's going on.

One reason this is an interesting question is because it gets to the heart of the difference between classical and quantum mechanics. In classical mechanics, the state of the system is determined by both x and p. But in quantum mechanics we have only the wavefunction, $\psi(x)$ and this has to contain information about both position and momentum. So how is this encoded? This is one of the steps in this section that involves a leap of faith and no small amount of creativity.

In fact, we saw a hint of how to proceed back in the introduction. Recall that our Hamiltonian for a one-dimensional particle is

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

while, in classical mechanics, the energy of a particle is

$$E_{\text{classical}} = \frac{p^2}{2m} + V(x)$$

This suggests a relationship between momentum p and the act of taking a derivative

$$p \ \longleftrightarrow \ -i\hbar\frac{d}{dx}$$

where I've picked the minus sign, as opposed to plus sign, because I've studied this course before. This is the clue that we need. Given a wavefunction $\psi(x)$, the momentum is encoded in how fast it varies in space. We can see this in the simple non-normalisable states $\psi = e^{ikx}$ where $\psi' = ike^{ikx}$ and is clearly bigger for higher momentum. In general, the correct relationship between momentum and the derivative manifests itself in the following formula

$$\langle p\rangle = -i\hbar\int_{-\infty}^{+\infty} dx\ \psi^\star\frac{d\psi}{dx} \tag{2.18}$$

We'll have a lot more to say about this in Section 3. For now, let's just see what it gives for our Gaussian wavepacket. We have

$$\begin{aligned}\langle p\rangle &= \frac{1}{\sqrt{\pi\sigma|\alpha|^2}}e^{-k_0^2/\sigma}\int_{-\infty}^{+\infty} dx\ e^{-(x+ik_0/\sigma)^2/2\alpha^\star} \times -i\hbar\frac{d}{dx}\,e^{-(x-ik_0/\sigma)^2/2\alpha} \\ &= \frac{1}{\sqrt{\pi\sigma|\alpha|^2}}\int_{-\infty}^{+\infty} dx\ \frac{i\hbar}{\alpha}\left(x-\frac{ik_0}{\sigma}\right)\exp\left(-\frac{1}{\sigma|\alpha|^2}\left(x-\frac{\hbar k_0 t}{m}\right)^2\right)\end{aligned}$$

where, after taking the derivative, the algebra needed to go from the first to the second line is identical to that in (2.16). Again shifting the integration variable to $\tilde{x} = x - \hbar k_0 t/m$, we have

$$\langle p\rangle = \frac{1}{\sqrt{\pi\sigma|\alpha|^2}}\int_{-\infty}^{+\infty} d\tilde{x}\ \frac{i\hbar k_0}{\alpha}\left(\frac{\tilde{x}}{k_0}+\frac{\hbar t}{m}-\frac{i}{\sigma}\right)\exp\left(-\frac{\tilde{x}^2}{\sigma|\alpha|^2}\right) = \hbar k_0$$

where, to get the final equality, we did the Gaussian integrals (2.17) and then used the expression for α given in (2.14).

That was a fair bit of work just to get the answer that we expected all along: $\langle p\rangle = \hbar k_0$. As we go on, we'll see that the expression (2.18) is the right way to think about the average momentum of any state.

2.2 The Harmonic Oscillator

The harmonic oscillator is the name given to a particle moving in a quadratic potential. In classical mechanics, the energy is

$$E_{\text{classical}} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 \tag{2.19}$$

The classical equation of motion follows from the fact that energy is conserved, which means that $\dot{E}_{\text{classical}} = 0$ or, equivalently,

$$\ddot{x} = -\omega^2 x$$

The most general solution has the form $x(t) = A\cos(\omega(t - t_0))$ and describes a particle bouncing backwards and forwards with frequency ω.

In this section we will look at the quantum harmonic oscillator. This means that we want to solve the Schrödinger equation with Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{2.20}$$

It's difficult to overstate the importance of the harmonic oscillator in quantum mechanics. It is, by some margin, the single most important example that we will study. The reasons for this are twofold. The first is Taylor's theorem: if you take any potential $V(x)$ and expand close to a minimum then, at leading order, you will most likely find the harmonic oscillator. This means that small perturbations of more or less any system in Nature are described by the Hamiltonian (2.20). (There are exceptions. Very occasionally, you might find a potential where the quadratic term vanishes, so $\omega = 0$, and you have to look at the next term in the Taylor expansion. This situation is rare but interesting.)

The second reason for the utility of the harmonic oscillator is more practical. Human beings are not particularly good at solving equations. This isn't so apparent when you first learn theoretical physics because, quite reasonably, your teachers don't want to stand up in front a classroom and continually repeat "yeah, we don't know how to solve this one either". Instead we shine a light on our successes. But as theoretical physics gets more advanced, these successes become harder and harder to find. At some point the only system that we can actually solve is the harmonic oscillator. Or, more precisely, things that can be made to look like the harmonic oscillator. The art of theoretical physics is then to make everything look like a harmonic oscillator. Take whatever you think is the coolest result in physics – maybe the Higgs boson, or some new material like topological insulators, or maybe gravitational waves or Hawking radiation. For all of them, the underlying theory is primarily to do with harmonic oscillators.

There are, it turns out, a number of different ways to solve the harmonic oscillator. In these lectures we won't do anything fancy and just go ahead and solve the Schrödinger equation viewed as a differential equation.

2.2.1 The Energy Spectrum

Our goal is to find solutions to the time independent Schrödinger equation ,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}m\omega^2x^2\psi=E\psi \tag{2.21}$$

Here the word "solution" means finding all normalisable $\psi(x)$ that satisfy the Schrödinger equation and, for each one, the accompanying energy E.

There are a bunch of constants sitting in (2.21) and life is simpler if we can just get rid of them. To this end, define

$$y=\sqrt{\frac{m\omega}{\hbar}}x \quad \text{and} \quad \tilde{E}=\frac{2E}{\hbar\omega} \tag{2.22}$$

Then the Schrödinger equation takes the cleaner form

$$\frac{d^2\psi}{dy^2}-y^2\psi=-\tilde{E}\psi \tag{2.23}$$

Before we get going, we can find one solution just by staring. This is the Gaussian wavefunction

$$\psi(y)=e^{-y^2/2} \tag{2.24}$$

The derivatives are $\psi'=-y\psi$ and $\psi''=y^2\psi-\psi$, so we see that this obeys the Schrödinger equation with (rescaled) energy $\tilde{E}=1$.

Furthermore, it's simple to see that all normalisable solutions should fall off in the same exponential fashion, with $\psi\sim e^{-y^2/2}$ as $y\to\pm\infty$. This follows from looking at the large y behaviour of (2.23), where the $\tilde{E}\psi$ term is necessarily negligible compared to the $y^2\psi$. This motivates the general ansatz

$$\psi(y)=h(y)\,e^{-y^2/2} \tag{2.25}$$

where we will shortly take $h(y)$ to be a polynomial. Taking derivatives of this wavefunction gives $\psi' = (h' - hy)e^{-y^2/2}$ and $\psi'' = (h'' - 2h'y + hy^2 - h)e^{-y^2/2}$ so the Schrödinger equation (2.23) becomes

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (\tilde{E} - 1)h = 0 \tag{2.26}$$

You can check that this is indeed satisfied by our earlier solution (2.24) with $h = 1$. To find the general solution, we take the polynomial ansatz

$$h(y) = \sum_{p=0}^{\infty} a_p y^p$$

Here p is just a dummy summation index; do not confuse it with momentum! Plugging this ansatz into (2.26) gives a relation between the coefficients,

$$\begin{aligned} (p+2)(p+1)a_{p+2} - 2pa_p - (\tilde{E} - 1)a_p = 0 \\ \Rightarrow \quad a_{p+2} = \frac{2p - \tilde{E} + 1}{(p+2)(p+1)} a_p \end{aligned} \tag{2.27}$$

All we have to do is solve this simple recurrence relation.

First note, that the recurrence relation involves two independent sets of coefficients: a_p with p even, and a_p with p odd. These two sets don't talk to each other and so we have two classes of solutions. We'll see the interpretation of this shortly.

Next, let's look at what happens for large p. There are two options: either the recurrence relation terminates, so that $a_p = 0$ for all $p > n$ for some n. Or the recurrence relation doesn't terminate and $a_p \neq 0$ for all p. We're going to argue that only the first option is allowed. If the recurrence relation keeps going forever, the resulting wavefunction will be non-normalisable.

Why is this? If the recurrence relation doesn't terminate then, for very large p, we have $a_{p+2} \approx 2a_p/p$. But this is the kind of expansion that we get from an exponentially growing function. To see this, look at

$$e^{y^2} = \sum_{p=0}^{\infty} \frac{y^{2p}}{p!} = \sum_{p=0}^{\infty} b_p y^p \quad \text{with} \quad b_p = \begin{cases} \frac{1}{(p/2)!} & \text{if } p \text{ is even} \\ 0 & \text{if } p \text{ is odd} \end{cases}$$

The appropriate recurrence relation for this exponential function is then

$$b_{p+2} = \frac{(p/2)!}{(p/2+1)!} b_n = \frac{1}{p/2+1} b_p \longrightarrow \frac{2}{p} b_p \quad \text{as } p \to \infty$$

The upshot of this argument is that, if the recurrence relation (2.27) fails to terminate then, for large $|y|$, the wavefunction actually looks like $\psi(y) = h(y)e^{-y^2/2} \rightarrow e^{+y^2}e^{-y^2/2} = e^{+y^2/2}$

The emergence of such solutions isn't entirely unexpected. We know that, at large y, both $e^{-y^2/2}$ and $e^{+y^2/2}$ are equally valid solutions. Our preference for the former over the latter is for physical reasons, but the power-law ansatz that we're playing with has no knowledge of this preference. Therefore it's no surprise that it offers up the $e^{+y^2/2}$ solution as an option. Nonetheless, this doesn't change the fact that it's not an option we want to make use of. The $e^{+y^2/2}$ wavefunctions are non-normalisable and therefore illegal. Moreover, unlike the more straightforward $\psi = e^{ikx}$ wavefunctions that we met in the last section, there's no redemption for wavefunctions that grow exponentially quickly. They are not of interest and should be discarded.

All of which is to say that we should be looking for solutions to (2.27) for which the sequence a_p terminates. This means that there must be some positive integer n for which

$$2n - \tilde{E} + 1 = 0 \tag{2.28}$$

But this is the spectrum of the theory that we were looking for! The allowed energy states of the harmonic oscillator take the form

$$\tilde{E}_n = 1 + 2n \quad \text{ with } n = 0, 1, 2, \ldots$$

Recalling the scaling (2.22), the energies are

$$E_n = \hbar\omega\left(\frac{1}{2} + n\right) \quad \text{ with } n = 0, 1, 2, \ldots \tag{2.29}$$

All energies are proportional to $\hbar\omega$, with ω the frequency of the harmonic oscillator. Furthermore the states are equally spaced, with

$$E_{n+1} - E_n = \hbar\omega$$

2.2.2 The Wavefunctions

It is not hard to get the wavefunctions. We simply work backwards from the result (2.28) to figure out all the earlier coefficients in the polynomial. We learn that the Gaussian wavefunction (2.24) that we guessed earlier is actually the lowest energy state of the system,

$$\psi = e^{-y^2/2} \quad \Rightarrow \quad E_0 = \frac{1}{2}\hbar\omega \tag{2.30}$$

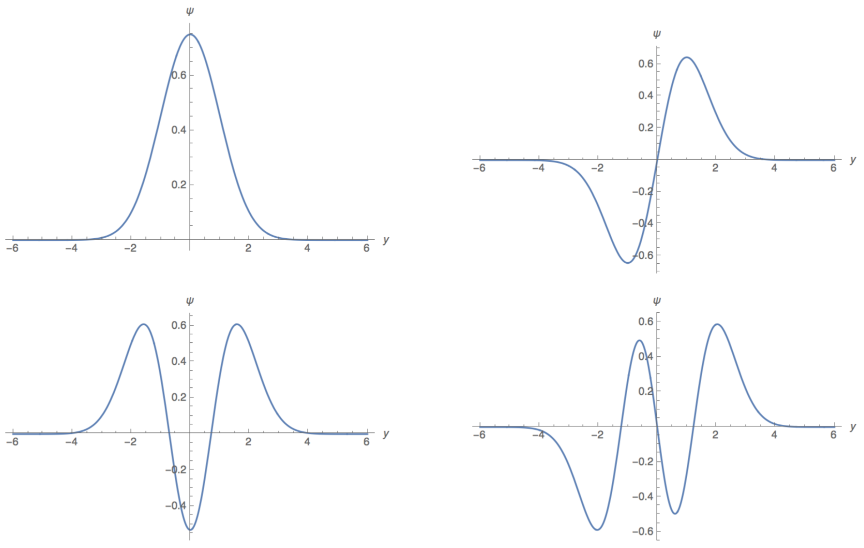


Figure 9. The normalised wavefunctions for the harmonic oscillator ground state and the first three excited states. The n^{th} excited state crosses the x-axis n times.

The lowest energy state in any system is called the *ground state*. Note that we also came across Gaussian wavefunctions (2.15) when discussing the free particle. In that context, they spread out over time. Not so here. The fact that the Gaussian is an energy eigenstate of the harmonic oscillator means that it has the simple time dependence $e^{-iE_0 t/\hbar}$ of any stationary state. You can think of the wavefunction as pinned in place by the rising potential.

The next few (unnormalised) wavefunctions are

$$\begin{aligned} \psi = 2ye^{-y^2/2} \quad &\Rightarrow \quad E_1 = \frac{3}{2}\hbar\omega \\ \psi = (-2+4y^2)e^{-y^2/2} \quad &\Rightarrow \quad E_2 = \frac{5}{2}\hbar\omega \\ \psi = (-12y+8y^3)e^{-y^2/2} \quad &\Rightarrow \quad E_3 = \frac{7}{2}\hbar\omega \end{aligned}$$

These, together with the Gaussian, are shown in Figure 9. In general, the functions $h(y)$ are known as *Hermite polynomials* and have a number of nice properties.

We can now return to one issue that we left hanging. The recurrence relation (2.27) does not relate a_p with p even to those with p odd. This manifests itself in the solutions above where the polynomials contain only even powers of y or only odd powers of y. Correspondingly, the two classes of solutions that we anticipated earlier are simply even or odd functions, with

$$\begin{aligned} &\psi(y) = \psi(-y) \quad \text{when } a_p \neq 0 \text{ for } p \text{ even} \\ \text{and} \quad &\psi(y) = -\psi(-y) \quad \text{when } a_p \neq 0 \text{ for } p \text{ odd} \end{aligned}$$

There is a general lesson here. Whenever the potential is an even function, meaning $V(x) = V(-x)$, then the energy eigenstates will arrange themselves into even and odd functions. Underlying this is the concept of *parity symmetry*, which is the statement that the physics is unchanged under $x \to -x$. We'll make use of this idea of parity symmetry later in these lectures.

At first glance, the wavefunctions that we've found don't seem to capture much of the familiar classical physics of a particle bouncing back and forth in a potential. Because they're all stationary states, the time dependence is simply an overall phase $e^{-iEt/\hbar}$ in front of the wavefunction. You can compute the average position and momentum in any of the states above and you will find $\langle x \rangle = \langle p \rangle = 0$. In some sense, this is what you expect because it is also the average behaviour of the classical solution! Still, it would reassuring if we could see some remnant of our classical intuition in these wavefunctions.

A general property of quantum systems is that they tend to look more classical as you go to higher energies. For example, the discretisation effects may be less noticeable if they're small compared to the overall energy of the system. For the harmonic oscillator, the wavefunctions for the 20th and 60th excited states are shown in Figure 10. Although it may not be obvious, some key elements of the classical trajectories can be seen hiding in these wavefunctions.

First, look at the way the wavefunction oscillates. We know that a free particle with definite momentum $p = \hbar k$ is associated to e^{ikx}. The bigger k, the smaller the wavelength, and the higher the momentum. In the wavefunctions shown in Figure 10, you can see that the wavelength of oscillations is much smaller near the bottom of the potential and then gets stretched towards the edges. This coincides with the classical expectation, where the particle is travelling much faster at the bottom of the potential and slows as it rises.

The way to quantify this idea uses a technique known as the *WKB approximation*. We'll discuss this in more detail in the lectures on Topics in Quantum Mechanics, but here we just describe the basic idea which is enough to extract the physics that we care about. We write the Schrödinger equation as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \left(E - \frac{1}{2}m\omega^2 x^2\right)\psi$$

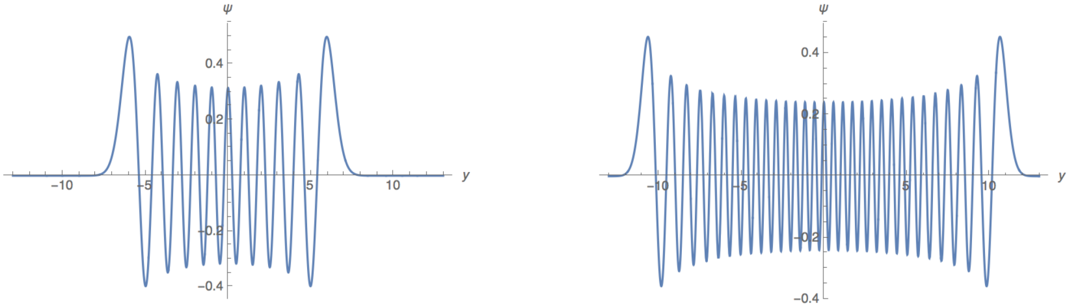


Figure 10. Harmonic oscillator wavefunctions for the 20th excited state on the left, and the 60th excited state on the right.

The idea is that, for large E, we might be able to think of the $E - \frac{1}{2}m\omega^2 x^2$ as roughly constant over some small region of x. We then get two different kinds of behaviour: if $x^2 < 2E/m\omega^2$ then the wavefunction oscillates, approximately as e^{ikx} for some k. Alternatively, when $x^2 > 2E/m\omega^2$, the wavefunction drops off as $e^{-k|x|}$ for some k. The WKB approximation builds on this intuition by looking for solutions where k itself varies with x, so $k = k(x)$. This, of course, is what's seen in the wavefunctions plotted in Figure 10.

One consequence of this is that we expect that, as E increases, the wavefunctions extend further out. Indeed, the $n = 60$ wavefunction extends out further than the $n = 20$ wavefunction. Mathematically this follows simply because there are higher powers of y in the polynomial $h(y)$. The kind of ideas sketched above can be used to show that, for large E, the final turning point of the wavefunction occurs at

$$x^2_{\text{max}} \approx \frac{2E}{m\omega^2}$$

This is precisely the turning point of the classical particle, where the kinetic energy in (2.19) vanishes.

Finally, look at the overall envelope of the wavefunction, a curve that peaks at the edges and dips in the middle. This is telling us that if you do a measurement of a particle in this high energy state, you're more likely to find it near the edges than near the origin. But this, too, is the same as the classical picture. If you take a photograph of a ball oscillating in a harmonic potential, you're most likely to catch it sitting towards the end of its trajectory, simply because it's going slower and so spends more time in those regions. Conversely, the ball is less likely to be caught as it whizzes past the origin. This is, again, captured by the form of the wavefunction. We see that the quantum world is not completely disconnected from the classical. You just have to know where to look.

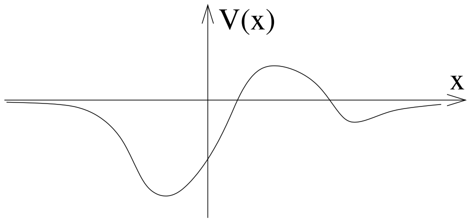
2.3 Bound States

Any potential that rises indefinitely at infinity will, like the harmonic oscillator, have an infinite collection of discrete allowed energies. In this section (and the next) we will look at a slightly different class of potentials, those which asymptote to some constant value

$$V(x) \;\rightarrow\; \text{constant} \quad \text{as } x \;\rightarrow \pm\infty$$

The value of the constant doesn't matter; it just shifts the overall energies. For this reason, we may as well just set it to zero and consider potentials that asymptote to $V(x) \;\rightarrow 0$ as $|x| \rightarrow \infty$. An example of such a potential is shown in the figure.

In fact there are a whole bunch of subtleties here to entrap the unwary. These relate to the question of how *fast* the potential asymptotes to zero. At this stage these subtleties are just an annoyance so we'll assume that the potential falls off suitably quickly (for example, an exponential decay will certainly be fine).



Now we want to ask: what are the solutions to the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{2.31}$$

We can start to address this by looking at the form of the solutions as $x \rightarrow \pm\infty$ where the Schrödinger equation reduces to that of a free particle:

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

There are two qualitatively different kinds of solution to this equation:

- Scattering States: The solutions with energy $E > 0$ are characterised by $k \in \mathbf{R}$ and take the form

  $$\psi = e^{ikx} \quad \text{with} \quad E = \frac{\hbar^2 k^2}{2m}$$

  As we saw in Section 2.1 these states are non-normalisable and this remains true here. We'll see what role they play in the next section where we will learn about scattering.

- Bound States: The solutions with energy $E < 0$ are characterised by $\eta \in \mathbf{R}$ and take the form

  $$\psi = Ae^{-\eta x} + Be^{+\eta x} \quad \text{with} \quad E = -\frac{\hbar^2\eta^2}{2m}$$

  We didn't even consider such wavefunctions when we discussed the free particle because they're obviously badly non-normalisable. For example, we could set $B = 0$ so that the wavefunction $\psi = e^{-\eta x}$ decays nicely as $x \to +\infty$, but then it will blow up at $x \to -\infty$.

  However, it's possible that we may be able to find good wavefunctions with this asymptotic form when we solve the full Schrödinger equation (2.31). For the state to be normalisable we would require that it decays at both ends, with

  $$\psi \sim \begin{cases} e^{-\eta x} & \text{as } x \to +\infty \\ e^{+\eta x} & \text{as } x \to -\infty \end{cases}$$

  Note that to solve the Schrödinger equation we must have the same value of η in the exponent on both sides to ensure that the solution has constant E. Such wavefunctions are called *bound states* because they are necessarily trapped somewhere in the potential. As we will see, they occur only for very specific values of η.

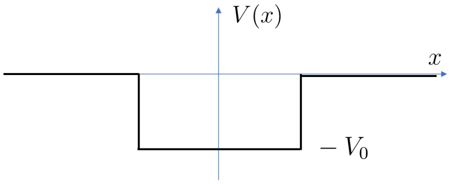
In the rest of this section, we will study a couple of simple potentials to get some intuition for how and when bound states occur. This will also provide an opportunity to address a couple of technical mathematical points that arise when solving the Schrödinger equation.

2.3.1 A Finite Potential Well

Our first example is the potential well of the form

$$V(x) = \begin{cases} -V_0 & -a < 0 < a \\ 0 & \text{otherwise} \end{cases} \qquad (2.32)$$

It's not difficult to see that there are no bound states if $V_0 < 0$. We will take $V_0 > 0$, so the potential is a dip as shown in the figure.



Clearly the potential is discontinuous at $x = \pm a$ and this raises the question of what kind of wavefunction $\psi(x)$ we should be looking for. The answer is that $\psi(x)$ itself should be continuous, as too should $\psi'(x)$. But $\psi''(x)$ inherits the discontinuity of the potential.

To see the statements above, first integrate the Schrödinger equation (2.31) over a small interval at $x = a$,

$$-\frac{\hbar^2}{2m}\int_{a-\epsilon}^{a+\epsilon} dx\ \frac{d^2\psi}{dx^2} = \int_{a-\epsilon}^{a+\epsilon} dx\ (E - V(x))\psi$$

$$\Rightarrow \qquad \left.\frac{d\psi}{dx}\right|_{a+\epsilon} - \left.\frac{d\psi}{dx}\right|_{a-\epsilon} = -\frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon} dx\ (E - V(x))\psi$$

Although $V(x)$ is discontinuous at $x = a$, it is finite. This means that the integral on the right-hand side vanishes as we take limit $\epsilon \to 0$, telling us that ψ' is continuous at $x = a$. But if $\psi'(x)$ is continuous then so too is $\psi(x)$ itself. Returning to the Schrödinger equation (2.31), we then see that the discontinuity in $V(x)$ can only show up in the second derivative $\psi''(a)$.

Now our strategy for solving the Schrödinger equation is clear: we find solutions inside and outside the well and then patch them together, making sure that both ψ and ψ' are continuous at the join.

Before we proceed, there is one last idea that will make our life easier. This is the idea of parity, which comes from the observation that the potential is an even function with $V(x) = V(-x)$. This means that all solutions to the Schrödinger equation will be either even functions or odd functions. (We saw this in the example of the harmonic oscillator.) To see why this is necessarily the case, first note that if $\psi(x)$ solves the Schrödinger equation for some value of E, then so too does $\psi(-x)$. Under the assumption that there aren't two different wavefunction with the same energy (a so-called non-degenerate spectrum), we must have

$$\psi(x) = \alpha\psi(-x)$$

for some $\alpha \in \mathbf{C}$. But we have

$$\psi(x) = \psi(-(-x)) = \alpha\psi(-x) = \alpha^2\psi(x)$$

which tells us that $\alpha = \pm 1$, corresponding to either odd or even wavefunctions. (It's possible to extend this proof even in the case of degenerate spectra but this won't be needed for the examples that we'll consider here.)

As we'll now see, knowing in advance that we're looking for even or odd solutions to the Schrödinger equation greatly simplifies our task of finding solutions. We'll look for each in turn.

Even Parity Wavefunctions

Let's start by taking the even parity case. We're looking for bound state solutions which, outside the potential well, must take the form

$$\psi(x) = \begin{cases} Ae^{-\eta x} & x > a \\ Ae^{+\eta x} & x < -a \end{cases} \tag{2.33}$$

Here A is simply a normalisation constant. Our real interest is in the possible values of η since these will determine the energy of the bound state $E = -\hbar^2\eta^2/2m$.

Inside the potential well, the Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E + V_0)\psi \qquad -a < x < a$$

This is, of course, once again the Schrödinger equation for a free particle, just with shifted energy. As before, there are two kinds of solutions:

- Solutions with $E > -V_0$ have wavefunctions $e^{\pm ikx}$.
- Solutions with $E < -V_0$ have wavefunctions $e^{\pm\eta' x}$.

It turns out that the former solutions are the ones of interest and all our bound states will have energies $-V_0 < E < 0$. This is perhaps not surprising give that $-V_0$ is the lowest value of the potential.

Because we're looking for parity even solutions, we should consider $\psi = e^{+ikx} + e^{-ikx}$ or,

$$\psi(x) = B\cos kx \qquad |x| < a \tag{2.34}$$

where B is again a normalisation constant and k is, like η, related to the energy, now with

$$E = -\frac{\hbar^2\eta^2}{2m} = \frac{\hbar^2k^2}{2m} - V_0 \tag{2.35}$$

Our next step is to patch the exponentially decaying solutions (2.33) outside the well with the oscillatory solution (2.34) inside the well. Because both solutions are even functions, we only have to do this patching once at $x = +a$; the solution will then be automatically patched at $x = -a$ as well. We have

$$\begin{aligned} \psi(x) \text{ cts at } x = a \Rightarrow \quad & B\cos ka = Ae^{-\eta a} \\ \psi'(x) \text{ cts at } x = a \Rightarrow \quad & -kB\sin ka = -\eta Ae^{-\eta a} \end{aligned}$$

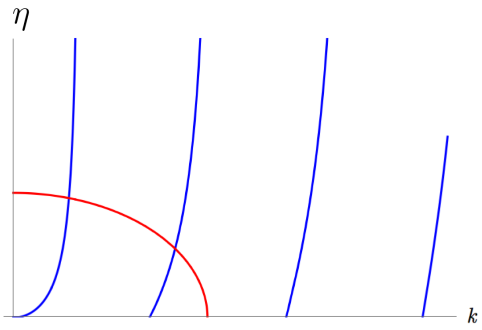


Figure 11. A graphical solutions for even parity, bound state energies in a finite well.

Dividing the second condition by the first gives us the requirement

$$k \tan ka = \eta \tag{2.36}$$

But k and η are not independent; they are related by the condition (2.35). Our task, therefore, is to solve (2.36) in conjunction with (2.35).

There is no simple solution to this transcendental equation, but it's not difficult to understand the property of the solutions using graphical methods. In Figure 11 we first plot the graph $\eta = k \tan ka$ in blue, and then superpose this with the circle

$$k^2 + \eta^2 = \frac{2mV_0}{\hbar^2}$$

shown in red. We restrict to the range $\eta \geq 0$ as befits our normalisable wavefunction. We get a solution whenever the red curve intersects the blue one. As expected, there are only discrete solutions, happening for specific values of η. Moreover, there are also only a finite number of them.

We see that the first solution is guaranteed: no matter how small the radius of the circle, it will always intersect the first blue line. However, the number of subsequent solutions depends on the parameters in the game. We can see that the number of solutions will grow as we increase V_0, the depth of the well, since this increases the radius of the red circle. The number of solutions will also grow as we increase the width of the well; this is because the separation between the blue lines is determined by the divergence of the tan function and so occurs when $k \approx \pi/2a$. As we increase a, keeping V_0 fixed, the blue lines get closer together while the red circle stays the same size.

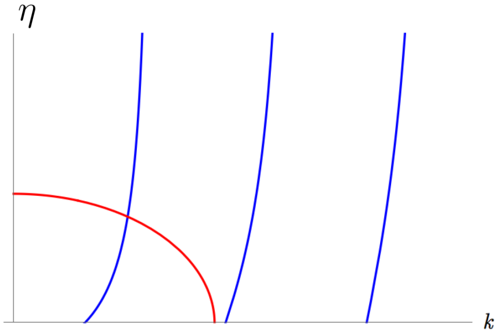


Figure 12. A graphical solutions for odd parity, bound state energies in a finite well.

We can be more precise about this. From the graph, the $n^{\rm th}$ crossing occurs somewhere in the region

$$(n-1)\pi < k_n a < \left(n - \frac{1}{2}\right)\pi$$

giving an estimate of energy of the $n^{\rm th}$

$$E_n = \frac{\hbar^2 k_n^2}{2m} - V_0$$

In the limit of an infinite well, we have $V_0 \to \infty$ so the red circle becomes infinitely large, intersecting the blue lines only asymptotically where $k_n a = (n - 1/2)\pi$. Clearly all energies descend to $-\infty$ in this limit, but we can instead measure energies with respect to the floor of the potential. We then get

$$E + V_0 \to \frac{\hbar^2\pi^2(2n-1)^2}{8ma^2}$$

But we've met this result before: it coincides with the energy spectrum (2.11) of a particle in an infinite well. (To see the agreement, we have to note that $L = 2a$ and, furthermore, remember that we have restricted to even parity states only which is why we've got only odd integers $(2n-1)$ in the numerator.)

There is one last mild surprise in our analysis. All our bound states have energy

$$-V_0 < E < 0$$

This is what we would expect for a classical particle, trapped inside the well. The quantum novelty is that the wavefunction itself is not restricted only to the well: it leaks out into the surrounding region $|x| > a$, albeit with an exponentially suppressed wavefunction (2.33). This means that there is some finite probability to find the particle outside the well, in a region that would be classically inaccessible.

Odd Parity Wavefunctions

We can easily repeat this analysis in the case of odd parity wavefunctions. We're now looking for bound state solutions which, outside the potential well, takes the form

$$\psi(x) = \begin{cases} Ae^{-\eta x} & x > a \\ -Ae^{+\eta x} & x < -a \end{cases}$$

Meanwhile, the odd parity wavefunction inside the well is

$$\psi(x) = B \sin kx \qquad |x| < a$$

Patching these two solutions at $x = a$ gives

$$\begin{aligned} \psi(x) \text{ cts at } x = a \Rightarrow & \quad B \sin ka = Ae^{-\eta a} \\ \psi'(x) \text{ cts at } x = a \Rightarrow & \quad kB \cos ka = -\eta Ae^{-\eta a} \end{aligned}$$

which now gives us

$$\frac{k}{\tan ka} = -\eta \tag{2.37}$$

Once again this should be solved in conjunction with (2.35). Once again, graphs are our friend. The graph of (2.37) is shown in blue in Figure 12, while the circle corresponding to (2.35) is shown in red.

This time we see that there is no guarantee that a solution exists. The first blue line emerges from the $\eta = 0$ axis at $ka = \pi/2$. The red circle intersects this first line only if

$$\frac{2mV_0}{\hbar^2} > \frac{\pi^2}{4a^2} \quad \Rightarrow \quad \frac{8mV_0}{\hbar^2\pi^2} > \frac{1}{a^2} \tag{2.38}$$

This means that the first parity odd solution exists only if the potential is deep enough or wide enough.

We can also see the solutions that were previously missing as we take $V_0 \to \infty$. The divergences in the blue lines now occur at $ka = n\pi$ for any $n \in \mathbf{Z}$. Measured above the floor of the potential, the energies then become

$$E + V_0 \to \frac{\hbar^2\pi^2(2n)^2}{8ma^2}$$

where now we see that there are only even integers $2n$ in the numerator.

2.3.2 A Delta Function Potential

As our second example, we will consider a potential that is, at first glance, slightly odd: a delta function sitting at the origin

$$V(x) = -V_0\,\delta(x)$$

for some constant V_0. Recall that the delta function isn't a real function, but a distribution satisfying

$$\delta(x) = 0 \text{ unless } x = 0 \quad\text{and}\quad \int_{-\infty}^{+\infty} \delta(x) = 1$$

You can think of as an infinitely narrow, but infinitely long spike localised at the origin. You might think that it's not particularly realistic as a potential, and there is some merit to that. But there are situations – such as impurities in solids – where the exact form of the potential is complicated and most likely unknown and it is useful to have a simple toy model that can be easily solved. This is what the delta function offers.

The discontinuity in the delta function is significantly more extreme than that of the finite potential well and, once again, we're going to have to understand how to deal with it. Our strategy is the same as before: we take the Schrödinger equation as the starting point and see what the potential means for the wavefunction. To start, we integrate the Schrödinger equation over a small region around the origin

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon} dx\ \frac{d^2\psi}{dx^2} = \int_{-\epsilon}^{+\epsilon} dx\ (E + V_0\delta(x))\psi$$

This time the right-hand side isn't so innocent. While the E term simply vanishes in the limit $\epsilon \to 0$, the delta function doesn't. We then find

$$\lim_{\epsilon\to 0}\left(\left.\frac{d\psi}{dx}\right|_{+\epsilon} - \left.\frac{d\psi}{dx}\right|_{-\epsilon}\right) = -\frac{2mV_0}{\hbar^2}\psi(0) \tag{2.39}$$

We learn that the delta function leaves its imprint in the derivative of the wavefunction, and ψ' must now be discontinuous at the origin. The wavefunction itself, however, should be continuous.

This is all the information that we need to find a bound state. Away from the origin, the negative energy, normalisable solutions of the Schrödinger equation are simply

$$\psi(x) = \begin{cases} Ae^{-\eta x} & x > 0 \\ Ae^{+\eta x} & x < 0 \end{cases}$$

for some $\eta > 0$. Note that we've chosen normalisation factors that ensure the wavefunction is continuous,

$$\lim_{x\to 0^+} \psi(x) = \lim_{x\to 0^-} \psi(x) = A$$

However, the presence of the delta function means that the two solutions must be patched together with a discontinuity in the derivative

$$\lim_{x\to 0^+} \psi'(x) - \lim_{x\to 0^-} \psi'(x) = -A\eta\left(\lim_{x\to 0^+} e^{-\eta x} + \lim_{x\to 0^-} e^{+\eta x}\right) = -2A\eta$$

This should be identified with the discontinuity (2.39) giving the result that we need.

$$\eta = \frac{mV_0}{\hbar^2}$$

We learn that the negative-valued delta function has just a single bound state with energy

$$E = -\frac{\hbar^2\eta^2}{2m} = -\frac{V_0^2 m}{2\hbar^2} \tag{2.40}$$

This calculation also makes it clear how the presence of a potential can change the asymptotic behaviour from $e^{\eta x}$ as $x \to -\infty$ to $e^{-\eta x}$ as $x \to +\infty$. The delta function does this all in one go, but can only achieve the feat for a very specific value of η. More general potentials flip the sign of the exponent more gradually, but again can only do so for specific values of η, leading to a (typically finite) discrete collection of bound states.

2.3.3 Some General Results

There are a number of simple, but useful, statements that we can prove for bound states in any 1d potential $V(x)$. These results hold for the two different kinds of potentials that we've discussed so far, namely

- Potentials, like the harmonic oscillator, that diverge asymptotically so that $V(x) \to \infty$ as $|x| \to \pm\infty$. These will have an infinite number of normalisable states that decay exponentially quickly as $|x| \to \infty$. In this case, we usually take $V(x) > 0$ and the states have energy $E > 0$.

- Potentials, like the finite well, that asymptote to some constant which we can take to be $V(x) \to 0$ as $|x| \to \infty$. As we've seen, these will have a finite number of bound states that decay exponentially, all of which have $E < 0$.

In what follows, we'll refer to both kinds of states as bound states.

Claim: The spectrum of bound states is *non-degenerate*. This means that there aren't two distinct wavefunctions with the same energy.

Proof: Suppose the converse is true, meaning that both $\psi(x)$ and $\phi(x)$ have the same energy so that

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad \text{and} \quad -\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V(x)\phi = E\phi$$

Consider the *Wronskian*,

$$W(\psi,\phi) = \psi\frac{d\phi}{dx} - \frac{d\psi}{dx}\phi$$

This has the property that it is constant in space, as we can see by taking a derivative and using the Schrödinger equation

$$\frac{dW}{dx} = \psi\frac{d^2\phi}{dx^2} - \frac{d^2\psi}{dx^2}\phi = \frac{2m}{\hbar^2}\left(\psi(V-E)\phi - \psi(V-E)\phi\right) = 0$$

For normalisable states, we know the value of the Wronskian as $|x| \to \infty$: there we have $\psi = \phi = 0$, and so $W = 0$. Hence we must have $W = 0$ everywhere. This means that, at any finite x with $\psi(x)$, $\phi(x) \neq 0$, we have

$$\frac{1}{\psi}\frac{d\psi}{dx} = \frac{1}{\phi}\frac{d\phi}{dx} \quad \Rightarrow \quad \psi(x) = \alpha\phi(x)$$

for some constant $\alpha \in \mathbf{C}$. But any two wavefunctions related by a constant α correspond to the same state. This means that the spectrum is non-degenerate. □

Note that the argument above fails for the non-normalisable momentum states e^{ikx} since these are nowhere vanishing. And, indeed, such states are typically degenerate with e^{ikx} and e^{-ikx} having the same energy.

Claim: The bound state wavefunctions can always be taken to be real.

Proof: If $\psi(x)$ obeys the Schrödinger equation then so too does $\psi^\star(x)$. We can then invoke the proof above to find $\psi(x) = \alpha\psi^\star(x)$ for some constant $\alpha \in \mathbf{C}$. Taking the modulus square tells us that $|\psi|^2 = |\alpha|^2|\psi|^2$, so α is a phase: $\alpha = e^{i\chi}$. Now we can define $\psi_{\text{real}} = e^{-i\chi/2}\psi$ and, as the name suggests, this is real. To check this, look at $\psi^\star_{\text{real}} = e^{+i\chi/2}\psi^\star = e^{+i\chi/2}(e^{-i\chi}\psi) = \psi_{\text{real}}$. □

Claim: The ground state has no nodes. This means that $\psi(x) \neq 0$ except when $|x| \to \infty$.

Semi Proof: We're running very slightly ahead of ourselves in attempting to prove this statement, but we've got just enough in place to give the gist of the proof, if not the full rigorous version. Suppose that you have a guess at the ground state wavefunction $\psi(x)$, but where $\psi(x) = 0$, for some finite x. We're going to show that it's always possible to construct a new state with lower energy.

In fact, that last statement is almost true. What we're actually going to show is that it's always possible to construct a new state with lower *average* energy. Following our discussion in Section 2.1.4, the average energy of any normalised, real state ψ is

$$\begin{aligned}\langle E\rangle &= \int_{-\infty}^{+\infty} dx\ \left(-\frac{\hbar^2}{2m}\psi\frac{d^2\psi}{dx} + V(x)\psi^2\right)\\ &= \int_{-\infty}^{+\infty} dx\ \left(\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\right)^2 + V(x)\psi^2\right)\end{aligned}$$

where, in the second line, we've integrated by parts and thrown away the boundary term because we're dealing with normalisable states. The expression for the average energy should be plausible given our earlier result (2.18) for the average momentum. We will make it more precise in Section 3.3 when we discuss more about expectation values. For now, we will take it as given.

Now consider the state $|\psi|$. The derivative is ill-defined any point where $\psi(x) = 0$, but this doesn't affect the average energy since it happens at a set of measure zero in the integral. This means that $|\psi|$ has the same average energy as ψ. But now we can smooth out the cusp so that the derivative is smooth everywhere. Furthermore, in the region near the cusp, the derivative will be smaller after smoothing, which means that $\langle E\rangle$ will also be smaller. This is how we lower the energy of the state.

Some fiddly mathematical analysis issues aside, there is one statement that we need to complete the proof. If the true ground state energy of the system is E_0, then the average energy of any state is $\langle E\rangle \geq E_0$, with equality only for the ground state. This is intuitive and not too difficult to prove. It's known as the *variational principle* in quantum mechanics and has quite a few applications. You can read more about this in the lectures on Topics in Quantum Mechanics. This variational principle now ensures that the initial guess $\psi(x)$ with a node cannot be the true ground state of the system.

$\square$

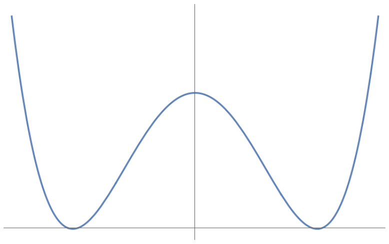


Figure 13. A double well potential, with two degenerate minima.

Claim: The n^{th} excited state has n nodes, i.e. n distinct places where $\psi(x) = 0$.

No Proof: This is harder to prove and we won't do it here. Note, however, that you can see the pattern of increasing nodes in both the infinite well potential and the harmonic oscillator (and, if you work harder, the finite well potential). $\square$

2.3.4 The Double Well Potential

There is a particularly interesting system that we can't solve exactly but can use the results above to get a feeling for the qualitative physics. This is the *double well potential*, which is the name given to any function that takes the shape shown in Figure 13.

Classically, the system has two ground states, corresponding to the two minima of the potential. The question is: what happens to a quantum particle placed in this potential?

We could focus attention near one of the minima, say the one on the right $x = x_{\text{min}}$. If we expand the potential about this point, we have

$$V(x) \approx V''(x_{\text{min}})\,(x - x_{\text{min}})^2 + \mathcal{O}(x^4)$$

For small x, this looks just like the harmonic oscillator that we discussed in Section 2.2. Indeed, as we stressed back then, one of the reasons that the harmonic oscillator is so important is that it is the first approximation to almost all potentials when expanded about their minima.

We might reasonably think that we can import our understanding of the harmonic oscillator to understand what's going on in this case. In particular, the ground state of the harmonic oscillator is a Gaussian (2.30),

$$\psi_{\text{right}}(x) = \exp\left(-\frac{1}{2a^2}(x - x_{\text{min}})^2\right)$$

where a is a length scale determined by the mass of the particle and $V''(x_{\text{min}})$. The wavefunction is sketched in orange in the figure below. A first guess might be that this provides a good approximation to the ground state of the double well potential.

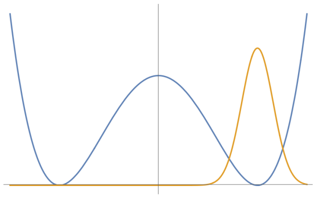


Figure 14. A first guess at the ground state wavefunction

The trouble is, of course, that this guess runs afoul of the theorems above. In particular, it's not unique. There is an equally good candidate localised around the left-hand minimum. If we assume that the potential is symmetric, so $V(-x) = V(x)$, then the other candidate ground state is

$$\psi_{\text{left}}(x) = \exp\left(-\frac{1}{2a^2}(x + x_{\text{min}})^2\right)$$

This looks the same as ψ_{right}, but now peaked around the left-hand minimum.

What to do? Our analysis of the harmonic oscillator suggests that both of these should (at least for suitably chosen parameters) be good approximations to the ground state but they can't both be the ground state.

The right way to proceed is to take linear superpositions of these states. Indeed, we saw earlier that for an even potential $V(x) = V(-x)$, all energy eigenstates are either odd or even functions. This tells us that the true energy eigenstates should be closer to

$$\psi_{\pm}(x) = \psi_{\text{right}}(x) \pm \psi_{\text{left}}(x)$$

Furthermore, we know that the ground state has no nodes. This means that $\psi_+(x)$ must be the approximation to the ground state while $\psi_-(x)$, which has a single node, should be the first excited state. Note the energy of $\psi_-(x)$ is (again for suitably chosen parameters) expected to be much closer to $\psi_+(x)$ than to the excited states of the harmonic oscillator around either vacuum. The two states are shown in Figure 15.

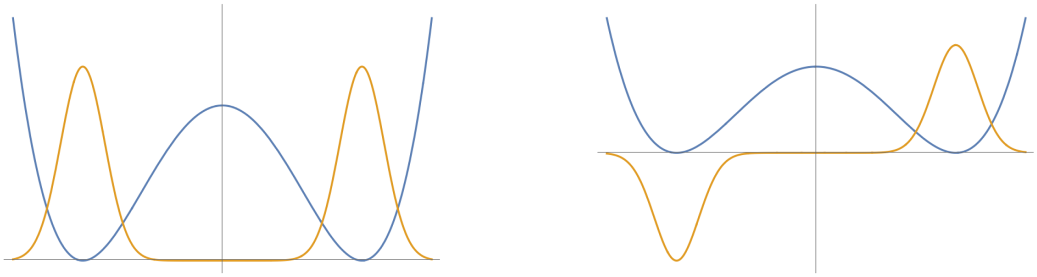


Figure 15. An approximation to the ground state, on the left, and to the first excited state, on the right.

There is some striking physics that emerges from these simple considerations. Suppose that we put the particle in one of the wells, say the right. Classically the particle would stay trapped in that well provided that it's kinetic energy wasn't sufficient to get up and over the barrier in the middle. But that's not what happens in the quantum world. Instead, the particle will lower its energy by sitting in a superposition of states like $\psi_+(x)$. Even if the particle does not have sufficient energy to get up and over the barrier it will, in time, leak through the barrier and have equal probability to be in either well. This phenomenon is known as *quantum tunnelling*. We'll see another manifestation of it in the next section.

2.4 Scattering

The basic principle behind scattering is simple: you take a particle, throw it at an object, and watch as it bounces off. Ideally, you can then use the information about how it bounces off to tell you something about the object in question.

In this section, we're going to set up the basics of scattering in quantum mechanics. We will only solve some very simple situations and our goal is to continue to build intuition for how quantum particles behave.

Our set-up is the same as in Section 2.3. We have some potential $V(x)$ that is localised in space and asymptotes suitably quickly to

$$V(x) \;\rightarrow 0 \;\;\text{as}\; |x| \;\rightarrow\; \infty \tag{2.41}$$

In the last section, we understood that such potentials typically have some finite number of negative energy bound states, trapped in the potential. Here we instead ask: what happens if we stand far from the potential and throw in a quantum particle. Will it

Figure 16. An intuitive idea of scattering, where an ingoing wavepacket (in red on the left) scatters off a potential (in blue) resulting into two outgoing wavepackets (in red on the right) is too hard!

bounce back, or will it pass through the potential? Or, this being a quantum particle, will it do both?

Our first task is to set up the problem mathematically. One approach would be to construct a wavepacket, localised in space far from the potential, and send it moving towards the region where $V(x) \neq 0$. This has the advantage that the wavepacket gels nicely with our classical expectation of a particle. It has the disadvantage that it is mathematically challenging. As we've seen, the wavepacket solution (2.15) is fairly complicated even for a free particle and becomes much more so in the presence of a potential.

Instead we're going to take a different path. This involves resurrecting the wavefunctions of the form

$$\psi_k = Ae^{ikx}$$

for some constant $A \in \mathbf{C}$. Recall that these have definite momentum $p = \hbar k$, but are not valid states of the system because they are not normalisable. This last statement remains true in the presence of a potential satisfying (2.41).

However, it is possible to endow wavefunctions of this kind with a different interpretation. Rather than thinking of them as quantum probabilities for a single particle, we will instead consider them as describing a continuous beam of particles, with the "probability density"

$$P(x,t) = |\psi(x,t)|^2 = |A|^2$$

now interpreted as the average density of particles. To reinforce this perspective, we can compute the probability current (1.6) to find

$$J(x,t) = -\frac{i\hbar}{2m}\left(\psi_k^\star \frac{d\psi_k}{dx} - \psi_k \frac{d\psi_k^\star}{dx}\right) = -\frac{i\hbar}{2m} \times |A|^2 \times 2ik = |A|^2 \times \frac{p}{m} \tag{2.42}$$

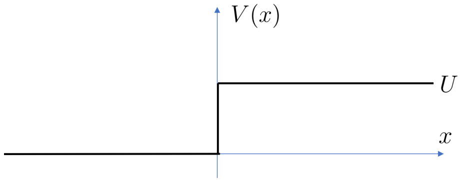
where this last expression has the interpretation of the average density of particles multiplied by their velocity or, alternatively, as the average flux of particles.

There is a lot to say about scattering in quantum mechanics and the later lecture notes on Topics in Quantum Mechanics have a full chapter devoted to scattering theory. One of the highlights is understanding how we can reconstruct the spectrum of bound states of the potential by standing at infinity, throwing in particles, and looking at what bounces back. Here we will restrict ourselves to just two simple examples to build more intuition about the wavefunction and what it can do.

2.4.1 A Step Potential

Our first potential is a step function

$$V(x) = \begin{cases} 0 & x < 0 \\ U & x > 0 \end{cases}$$



We will throw a particle – or more precisely a beam of particles – in from the left and see what happens. Our expectation would be that the beam will bounce back if the energy of the particles is less than U, while if the energy is $E \gg U$ it should presumably fly over the small step without noticing. For energies that are just slightly greater than U, something more interesting might happen.

Let's now see how to set up the problem. We want to find a solution to the Schrödinger equation which includes a component at $x \to -\infty$ corresponding to an ingoing beam of particles,

$$\psi(x) \sim Ae^{ikx} \quad \text{as } x \to -\infty$$

with A the density of the beam. We should also remember to take $k > 0$ since this tells us that the initial beam is travelling to the right and will hit the potential. Clearly the energy of the particles in the beam is

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

However, the solution that we're looking for will include a part of the wavefunction that bounces off the step and returns to $x \to -\infty$, but with opposite momentum. In other words, we really want to look for solutions with the property

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{as } x \to -\infty \tag{2.43}$$

Note that the ingoing wave e^{ikx} and the outgoing wave e^{-ikx} must have the same energy so this wavefunction is a solution of the Schrödinger equation. However, the densities of the beams can differ and, in general, we would expect $B < A$ telling us that not everything bounces back.

Although we set up the solution (2.43) as the boundary condition at $x \to -\infty$, the fact that the potential vanishes means that this solution holds for all $x < 0$. It only changes when it encounters the step.

Next we look in the region $x > 0$ where the potential energy is $V(x) = U$. Because the potential is constant, the general solution here is straightforward and given by

$$\psi(x) = Ce^{ik'x} + De^{-ik'x} \qquad x > 0 \tag{2.44}$$

where, to solve the Schrödinger equation , the wavenumber k' is given by

$$E - U = \frac{\hbar^2 k'^2}{2m} \quad \Rightarrow \quad k' = \sqrt{\frac{2m(E-U)}{\hbar^2}} \tag{2.45}$$

Note that if the energy of the incoming beam is bigger than the step, $E > U$, then k' is real. If, however, the energy isn't big enough to get over the step, $E < U$, then k' is imaginary. As we go on, we'll understand how to think of an imaginary momentum.

At this stage, we need to think again about the physics. Suppose first that $E > U$ and so k' is real. Then the first term $Ce^{ik'x}$ in (2.44) has the interpretation of an outgoing wave moving to the right, while the second term $De^{-ik'x}$ has the interpretation of a left-moving incoming wave, sent in from $x \to +\infty$. But we didn't send anything in from that end! Only from the $x \to -\infty$ end. That means that we should look for solutions with $D = 0$.

We reach the same conclusion if the beam had energy $E < U$, in which case $k' = i\eta$ for some $\eta > 0$. In this situation, the $De^{-ik'x} = De^{+\eta x}$ is non-normalisable at $x \to \infty$ and so should be discarded.

In either case, the upshot is that we're looking for solutions of the form

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} & x > 0 \end{cases} \tag{2.46}$$

Now we patch. We learned how to do this in the previous section: both $\psi(x)$ and $\psi'(x)$ should be continuous at $x = 0$. This gives two conditions.

$$\begin{aligned} \psi(x) \text{ cts at } x = 0 \Rightarrow &\quad A + B = C \\ \psi'(x) \text{ cts at } x = 0 \Rightarrow &\quad ik(A - B) = ik'C \end{aligned}$$

Recall that A determines the density of the original, incident beam while B and C determine the densities of the reflected and transmitted beams respectively. We can solve the equations above to get expressions for the latter in terms of the former

$$B = \frac{k-k'}{k+k'}A \quad \text{and} \quad C = \frac{2k}{k+k'}A \tag{2.47}$$

We can view these in terms of the particle flux defined in (2.42). For the original, incident beam we have

$$J_{\rm inc} = |A|^2\,\frac{\hbar k}{m}$$

We've learned the flux in the reflected beam is

$$J_{\rm ref} = |B|^2\,\frac{\hbar k}{m} = |A|^2\,\frac{\hbar k}{m}\left(\frac{k-k'}{k+k'}\right)^2$$

where, by convention, this reflected flux is taken to be positive. Meanwhile, the transmitted flux is

$$J_{\rm trans} = |C|^2\,\frac{\hbar k'}{m} = |C|^2\,\frac{\hbar k'}{m} = |A|^2\,\frac{\hbar k'}{m}\frac{4k^2}{(k+k')^2}$$

Let's now think about how to interpret these results. We start with the case $E > U$ so that k' is real. This means that the particles aren't forbidden from crossing the step on energetic grounds. But what do they do?

The answer to this is best seen by looking at the ratios of fluxes. We define

$$R = \frac{J_{\rm ref}}{J_{\rm inc}} = \left(\frac{k-k'}{k+k'}\right)^2 \tag{2.48}$$

and

$$T = \frac{J_{\rm trans}}{J_{\rm inc}} = \frac{4kk'}{(k+k')^2} \tag{2.49}$$

These are known as the *reflection and transmission coefficients*. They tell us what fraction of the incident beam is reflected and what fraction makes it over to the other side. Or, since we're dealing with quantum mechanics, they tell us the probability that a particle is reflected or transmitted.

As a quick sanity check, note that

$$R + T = 1$$

This is the statement that we don't lose any of the beam. Nothing gets trapped at the step.

The result $R+T=1$ continues to hold for any potential. In particular, if you scatter a quantum particle off the kind of finite well potential that we discussed earlier, then we get $R+T=1$, telling us that everything either bounces back or passes through. This means, in particular, that quantum golf is a rubbish game. The ball can't drop into the hole and stay there because bound states necessarily have $E<0$ while our beam has $E>0$. Anything that goes in must come out.

Although the expressions (2.48) and (2.49) are fairly straightforward when written in terms of k and k', we should really think of them just as a function of the incoming momentum k, with k' determined in terms of k by (2.45). You can quickly convince yourself that the formulae look much more complicated when written solely in terms of k. But we can see that the physics sits well with our basic intuition. In particular, when $E\to U$, the outgoing momentum $k'\to 0$ and so we see that

$$E\to U \quad\Rightarrow\quad T\to 0 \ \text{ and } \ R\to 1$$

This makes sense: if the particle barely has enough energy to make it up and over the barrier then it is simply reflected back.

Conversely, in the limit $E\to\infty$ we have $k'\approx k$, since the step U is more or less negligible. In this limit

$$E\to \infty \quad\Rightarrow\quad T\to 1 \ \text{ and } \ R\to 0$$

again, in agreement with our expectations. If you want to know the reflection and transmission at any intermediate value, then I don't have anything for you other than the exact answer (2.48) and (2.49).

We still have one question left: what happens when the energy $E<U$, so the particle can't make it over the barrier. The key piece of physics can be seen in the wavefunction (2.46) which, for $x>0$ is

$$\psi(x)=Ce^{-\eta x} \tag{2.50}$$

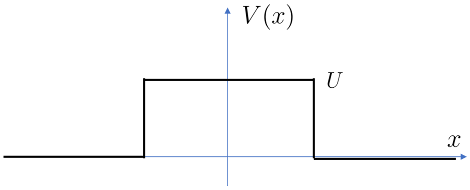
Our expression for C given in (2.47) still holds, but with $k'=i\eta$ where $\eta>0$. This, then, is the meaning of imaginary momentum: it tells us that the wavefunction decays exponentially inside the barrier. In contrast to classical mechanics, there is some non-negligible probability to find the particle a distance $x\approx 1/\eta$ inside the barrier but beyond this point, the probability drops off quickly.

The calculation that we did previously only changes when we compute the fluxes. A wavefunction that drops off exponentially like (2.50) has vanishing current $J = 0$. It's not transporting anything anywhere. The upshot is that $T = 0$ when the energy is below the barrier height. You can check that, correspondingly, $R = 1$: everything bounces back.

2.4.2 Tunnelling

Our next example is a finite potential barrier, like a bump in the road

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



where $U > 0$. This is mirror of the finite well (2.32) whose bound states we studied earlier.

By now we know what to do: we write down solutions to the free Schrödinger equation in each region and patch at the join. We're going to be interested in situations where the energy $E < U$, which means that a classical particle would just bounces back. The question is: does a quantum particle with such low energy make it through the barrier?

Following our earlier discussion, we look for solutions of the form

$$\psi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & x < -a \\ Be^{-\eta x} + Ce^{+\eta x} & |x| < a \\ De^{ikx} & x > a \end{cases}$$

Note that we've set the density of the incoming beam to unity, as seen in the e^{ikx} term in the first line. This is in anticipation that this will drop out of the things we want to calculate, like R and T, and so it's not worth keeping the extra baggage in the equations. The two exponents in the wavefunction are given by

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \eta = \sqrt{\frac{2m(U-E)}{\hbar^2}} \tag{2.51}$$

Both are positive. The matching conditions at $x = -a$ are

$$\begin{aligned} \psi(x) \text{ cts at } x = -a \Rightarrow \quad & e^{-ika} + Ae^{+ika} = Be^{+\eta a} + Ce^{-\eta a} \\ \psi'(x) \text{ cts at } x = -a \Rightarrow \quad & ik(e^{-ika} - Ae^{+ika}) = -\eta(Be^{+\eta a} - Ce^{-\eta a}) \end{aligned}$$

Meanwhile, the matching conditions at $x = a$ are

$$\begin{aligned}\psi(x) \text{ cts at } x = +a \Rightarrow &\quad De^{ika} = Be^{-\eta a} + Ce^{+\eta a} \\ \psi'(x) \text{ cts at } x = +a \Rightarrow &\quad ikDe^{ika} = -\eta(Be^{-\eta a} - Ce^{+\eta a})\end{aligned}$$

We have four equations. Our goal is to solve for D in terms of k and η, since this will tell us the transmitted flux. It's straightforward, if a little tedious. Here's some handholding to help you along your way. First use the second pair of equations to write

$$2\eta Be^{-\eta a} = (\eta - ik)De^{ika} \quad \text{and} \quad 2\eta Ce^{\eta a} = (\eta + ik)De^{ika} \tag{2.52}$$

Next, use the first pair of equations to write

$$2ke^{-ika} = B(k + i\eta)e^{\eta a} + C(k - i\eta)e^{-\eta a}$$

We now substitute the expressions (2.52) into B and C in the equation above. A little bit of algebra then gives

$$D = \frac{2k\eta e^{-2ika}}{2k\eta \cosh 2\eta a - i(k^2 - \eta^2)\sinh 2\eta a} \tag{2.53}$$

We want to compute the transmission probability which, in this case, is just

$$T = |D|^2$$

Using (2.53), we get

$$\begin{aligned}T &= \frac{4k^2\eta^2}{4k^2\eta^2\cosh^2(2\eta a) + (k^2 - \eta^2)^2\sinh^2(2\eta a)} \\ &= \frac{4k^2\eta^2}{4k^2\eta^2 + (k^2 + \eta^2)^2\sinh^2(2\eta a)}\end{aligned} \tag{2.54}$$

We see that there is a non-vanishing probability that the particle makes it through the barrier and over to the other side, even though a classical particle wouldn't be able to do so. This is another manifestation of quantum tunnelling.

To get some feel for the equation (2.54), let's look at the extreme case of a very low energy particle. Low energy means $U - E \gg$ something, where "something" has to have the dimensions of energy. Some dimensional analysis shows that the requirement is

$$U - E \gg \frac{\hbar^2}{2ma^2} \quad \Rightarrow \quad \eta a \gg 1$$

So the low energy limit is the same as the limit of a wide barrier. In this regime, the sinh function in the denominator dominates. Written as a function of the incoming energy E, transmission probability then becomes

$$T(E) \approx f(E)\, \exp\left(-\frac{4a}{\hbar}\sqrt{(2m(U-E)}\right)$$

where the exponent is multiplied by $f(E) = 16k^2\eta^2/(k^2+\eta^2)^2$, with both k and η viewed as functions of the energy using (2.51). The key feature, however, is the exponential suppression of the probability. This is characteristic of tunnelling phenomena.

A very similar effect is at play in radioactive decay. In, admittedly rather simplified models, an alpha particle can be thought of as trapped inside the nucleus by a finite, but large potential energy barrier. A classical particle would be consigned to rattle around in the nucleus forever; a quantum particle can, with some exponentially suppressed probability, tunnel through the barrier and out the other side. The small probability manifests itself in the long lifetime of many unstable nuclei.

3 The Formalism of Quantum Mechanics

In the previous section we made good headway in building some intuition for simple quantum systems by solving the Schrödinger equation and trying to interpret the results. But, at times, it felt like we were making up the rules as we went along. Our goal in this section is bring some order to the table and describe the mathematical structure that underlies quantum mechanics.

There are four facets of quantum mechanics. These are

- States
- Observables
- Time Evolution
- Measurement

We've already said all there is to say about time evolution, at least for these lectures: the evolution of the wavefunction is governed by the time-dependent Schrödinger equation. Here we will elaborate on the other three.

3.1 States

Recall the basic tenet: a quantum state is described by a normalisable wavefunction $\psi(\mathbf{x}, t)$, where normalisable means that it obeys

$$\int d^3x \; |\psi|^2 < \infty \tag{3.1}$$

Until now, it largely appears that quantum mechanics is, like many other areas of physics, all about solving differential equations. That's not entirely wrong, but it misses the key fact: at heart, quantum mechanics is really a theory of linear algebra. This will become apparent as we unveil the bigger picture.

We've already got a sniff of this linear algebra aspect in the principle of superposition. If $\psi(\mathbf{x}, t)$ and $\phi(\mathbf{x}, t)$ are both viable states of a system, then so too is any linear combination $\alpha\psi(\mathbf{x}, t) + \beta\phi(\mathbf{x}, t)$ where $\alpha, \beta \in \mathbf{C}$. Mathematically, this is the statement that the states form a *vector space* over the complex numbers.

3.1.1 The Inner Product

There is one important structure on our vector space: an *inner product*. This is a map that takes two vectors and spits out a number.

We're very used to inner products for finite dimensional vector spaces. Given two vectors in $\mathbf{R}^N$ – call them $\vec{u}$ and $\vec{v}$ – the inner product is simply $\vec{u}\cdot\vec{v}$. We introduce new notation and write the inner product on $\mathbf{R}^N$ as

$$\langle \vec{u}\,|\,\vec{v}\rangle = \vec{u}\cdot\vec{v}$$

The vertical line in the symbol on the left-hand side is a quantum mechanical affectation. In other areas of mathematics, the inner product is usually denoted as $\langle \vec{u},\vec{v}\rangle$, or sometimes $(\vec{u},\vec{v})$. The notation with the vertical line is part of a wider set of conventions used in quantum mechanics known as *Dirac notation*. For our present purposes, the vertical line will be the only sign that we're early adopters of this notation.

A slight amendment to the inner product is needed if we're dealing with a complex vector space like $\mathbf{C}^N$. In this case, the inner product is

$$\langle \vec{u}\,|\,\vec{v}\rangle = \vec{u}^\star\cdot\vec{v} \tag{3.2}$$

where we take the complex conjugation of the first vector before we take the dot product. This has the advantage that the inner product of any vector with itself is necessarily non-negative

$$\langle \vec{u}\,|\,\vec{u}\rangle = \vec{u}^\star\cdot\vec{u}\ \geq 0$$

This means that we get to use the inner product to define the length of a vector $||\vec{u}|| = \sqrt{\langle \vec{u}\,|\,\vec{u}\rangle}$. Inner products with this property are said to be *positive definite*.

This now brings us to the infinite dimensional vector space of functions that we work with in quantum mechanics. The inner product between two complex functions $\psi(\mathbf{x})$ and $\phi(\mathbf{x})$, each functions over $\mathbf{R}^3$, is defined by

$$\langle \psi\,|\,\phi\rangle = \int d^3x\ \psi^\star(\mathbf{x})\phi(\mathbf{x}) \tag{3.3}$$

Note, again, the star in the first argument which ensures that the inner product of a function with itself is positive definite. In fact, our normalisability requirement (3.1) can be restated in terms of the inner product

$$\langle \psi\,|\,\psi\rangle < \infty$$

From the definition, we see that the inner product is linear in the second argument

$$\langle \psi \,|\, \alpha\phi_1 + \phi_2 \rangle = \alpha \langle \psi \,|\, \phi_1 \rangle + \langle \psi \,|\, \phi_2 \rangle$$

for any $\alpha \in \mathbf{C}$. However, it is *anti-linear* in the first argument, which simply means that the complex conjugation on ψ gives us

$$\langle \alpha\psi_1 + \psi_2 \,|\, \phi \rangle = \alpha^\star \langle \psi_1 \,|\, \phi \rangle + \langle \psi_2 \,|\, \phi \rangle$$

Alternatively, this anti-linear statement follows by noticing that complex conjugation exchanges the two entries in the inner product

$$\langle \psi \,|\, \phi \rangle^\star = \langle \phi \,|\, \psi \rangle$$

We'll make use of some of these simple mathematical identities as we proceed.

In more fancy mathematical language, a vector space, whether finite or infinite dimensional, with a positive-definite inner product is called a *Hilbert space* $\mathcal{H}$. (In fact this statement is only almost true: there is an extra requirement in the case of an infinite dimensional vector space that the space is "complete" which, roughly speaking, means that as your vector evolves it can't suddenly exit the space.)

Hilbert space is the stage for quantum mechanics. The first thing you should do when describing any quantum system is specify its Hilbert space. Indeed, you can already see this in the examples from the last section: if we're dealing with a particle on a line or particle on a circle then states are specified by normalisable functions on the line or circle respectively.

Again some fancy mathematical language. If a particle is moving on some space M then the relevant Hilbert space is called $\mathcal{H} = L^2(M)$, which is the space of square-normalisable functions on M. Here the L is for "Lebesgue", while the word "square" and the superscript 2 both reflect the fact that you should integrate $|\psi|^2$ to determine whether it's normalisable. The Hilbert spaces in the last section were $\mathcal{H} = L^2(\mathbf{R})$ and $\mathcal{H} = L^2(\mathbf{S}^1)$.

As our theories get more advanced and abstract, we need different Hilbert spaces. Sometimes these are simpler: for example, there is a lot of interesting physics lurking in the finite dimensional Hilbert space $\mathcal{H} = \mathbf{C}^2$ where a state is just a two-dimensional complex vector. But sometimes the Hilbert spaces are vastly more complicated, like the space in quantum field theory where M itself is an infinite dimensional space of functions and $L^2(M)$ is something ghastly and poorly understood. In these lectures we'll meet nothing more complicated than $\mathcal{H} = L^2(\mathbf{R}^3)$, the space of normalisable functions on $\mathbf{R}^3$.

3.2 Operators and Observables

The quantum state is described by a wavefunction. But how does this wavefunction encode the information contained in the state?

It's useful to first return to the classical world. There we know that the state of a particle is described by its position $\mathbf{x}$ and velocity $\dot{\mathbf{x}}$. Equivalently, but more usefully for what's to come, we can say that it's encoded in the position $\mathbf{x}$ and momentum $\mathbf{p} = m\dot{\mathbf{x}}$ of the particle.

Given the state, the questions that we can ask are all possible functions of $\mathbf{x}$ and $\mathbf{p}$. We call these *observables*. Among the more trivial observables are position and momentum themselves. But we can also use our information of the state to calculate other observables such as angular momentum

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}$$

or energy

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$$

In general, any function $f(\mathbf{x}, \mathbf{p})$ can be considered a classical observable. Clearly all of them are simple to evaluate once you know the state $\mathbf{x}$ and $\mathbf{p}$.

What about in the quantum world? The state is now the wavefunction $\psi(\mathbf{x})$ which, abstractly, we think of as a vector in a Hilbert space. What is the observable associated to, say, momentum or angular momentum?

In quantum mechanics, all observables are represented by *operators* on the Hilbert space. In the present case, this is an object $\hat{O}$ that acts on the wavefunction $\psi(\mathbf{x})$ and gives you back a new function. Throughout these lectures we will dress any such operator with a hat. (As we mentioned previously, this convention tends to get dropped in later quantum courses.)

To be more precise, observables in quantum mechanics are related to a particular kind of *linear operator*. Here "linear" means that operators obey

$$\hat{O}\left[\alpha\psi_1(\mathbf{x}) + \psi_2(\mathbf{x})\right] = \alpha\hat{O}[\psi_1(\mathbf{x})] + \hat{O}[\psi_2(\mathbf{x})]$$

for any $\alpha \in \mathbf{C}$.

Returning to our analogy with finite dimensional vector spaces: if you're dealing with N-dimensional vectors, then the corresponding linear operators are just $N \times N$ matrices. Now, however, we're dealing with infinite dimensional vector spaces – or, more precisely, Hilbert spaces – where the vectors themselves are functions. What replaces the matrices? The answer, as we will now see, is differential operators.

We'll start by giving some physical examples. As this section proceeds, we'll see what it actually means to say that an observable is represented by an operator.

- For a particle moving in 3d there are three position operators, one for each direction. Combining these into a vector, they are simply $\hat{\mathbf{x}} = \mathbf{x}$. These operators act on a wavefunction by multiplication

  $$\hat{x}\psi(\mathbf{x}) = x\psi(\mathbf{x}) \ , \quad \hat{y}\psi(\mathbf{x}) = y\psi(\mathbf{x}) \ , \quad \hat{z}\psi(\mathbf{x}) = z\psi(\mathbf{x})$$

  You can also take any function of $\mathbf{x}$ and turn it into an operator. This acts in the obvious way, with $V(\hat{\mathbf{x}})\psi(\mathbf{x}) = V(\mathbf{x})\psi(\mathbf{x})$.

- The momentum operator for a particle moving in 3d is

  $$\hat{\mathbf{p}} = -i\hbar\nabla$$

  or, written out long hand,

  $$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \ , \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \ , \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

  Again, these operators should all be thought of in terms their action on the wavefunctions so, for example,

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

- Other operators now follow from our specification of position and momentum. The *angular momentum operator* is shorthand for a collection of three such operators,

  $$\hat{\mathbf{L}} = -i\hbar\,\hat{\mathbf{x}} \times \nabla$$

  We'll devote Section 4.1 to a detailed study of the properties of this operator. Finally the energy operator is

  $$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{\mathbf{x}})$$

  The energy operator is the only one that gets a special name, with $\hat{H}$ for Hamiltonian rather than $\hat{E}$ for energy. This is because of the special role it plays in time evolution of the state through the Schrödinger equation.

3.2.1 Eigenfunctions and Eigenvalues

Given an $N \times N$ matrix A, it is often useful to determine its eigenvalues. Recall that these are a collection of (up to) N numbers λ which solve the equation

$$A\vec{u} = \lambda\vec{u} \;\; \text{for some vector } \vec{u}$$

The corresponding vector $\vec{u}$ is then called the eigenvector.

We can play the same game with operators. Given an operator $\hat{O}$, its *eigenvalues* λ solve the equation

$$\hat{O}\psi(\mathbf{x}) = \lambda\psi(\mathbf{x}) \;\; \text{for some function } \psi(\mathbf{x})$$

The corresponding function $\psi(\mathbf{x})$ is called the *eigenfunction* or *eigenstate.* The collection of all eigenvalues is called the *spectrum* of the operator $\hat{O}$.

This has an important interpretation in physics. If you measure the value of a physical observable $\hat{O}$ then the answer that you get will be one of the eigenvalues of $\hat{O}$. This is the key idea that relates operators to observables. I don't put many things in boxes in my lecture notes, but this statement is so special that I'm going to make an exception:

$$\boxed{\text{The outcome of any measurement of } \hat{O} \text{ lies in the spectrum of } \hat{O}.}$$

We've already met this idea in the previous section. The time independent Schrödinger equation is simply the eigenvalue equation for the Hamiltonian

$$\hat{H}\psi = E\psi$$

The spectrum of the Hamiltonian determines the possible energy levels of the quantum system. In most cases this spectrum is discrete, like the harmonic oscillator. In other simple, but mildly pathological cases, the spectrum is continuous, like a particle on a line.

All physical observables have an associated eigenvalue equation. For the momentum operator this is

$$\hat{\mathbf{p}}\psi = \mathbf{p}\psi \quad \Rightarrow \quad -i\hbar\nabla\psi = \mathbf{p}\psi$$

Eigenvalue equations in quantum mechanics often look like the first equation above where you have to squint to notice the hat on the left-hand side which elevates the statement above a tautology. (As you can imagine, this has the potential to get confusing when the hat is dropped in subsequent lectures!)

The momentum eigenvalue equation can easily be solved. The (unnormalised) momentum eigenstates are

$$\psi = e^{i\mathbf{k}\cdot\mathbf{x}} \quad \Rightarrow \quad \hat{\mathbf{p}}\psi = \hbar\mathbf{k}\psi$$

These are called *plane wave states* on account of the fact that the wave is in the $\mathbf{k}$ direction and the function is uniform in the plane perpendicular to $\mathbf{k}$. The associated momentum eigenvalue is $\mathbf{p} = \hbar\mathbf{k}$. As we mentioned previously, this is the grown-up version of de Broglie's relationship between momentum and wavelength.

As we saw in Section 2, there's something a little bit fiddly about momentum eigenstates. Everything is nice if we put the particle on a finite volume space, say a torus $\mathbf{T}^3$. In fancy language, we take the Hilbert space to be $L^2(\mathbf{T}^3)$. This means that each spatial direction is periodic. We'll take the sizes of the three dimensions to be L_i, with $i = 1, 2, 3$, meaning that we identify

$$x_i \equiv x_i + L_i \quad i = 1, 2, 3$$

The requirement that the wavefunctions are single valued functions then tells us that

$$e^{ik_iL_i} = 1 \qquad \text{no sum over } i$$

which is satisfied provided that the wavenumbers only take certain discrete values

$$k_i = \frac{2\pi n}{L_i} \quad \Rightarrow \quad p_i = \frac{2\pi\hbar n}{L_i} \quad \text{with } n \in \mathbf{Z}$$

So when the particle lives on a torus, the spectrum of the momentum operator is discrete. Moreover, in this case there's no difficulty in normalising the momentum eigenstates $e^{i\mathbf{k}\cdot\mathbf{x}}$.

In contrast if the particles lives in an infinite space, so the Hilbert space is $L^2(\mathbf{R}^3)$, then the spectrum of the momentum operator is continuous. But the corresponding eigenstates $e^{i\mathbf{k}\cdot\mathbf{x}}$ do not strictly speaking live in the Hilbert space $L^2(\mathbf{R}^3)$ because they're not L^2! This is the same issue that we saw for a one-dimensional particle. It's a slightly annoying technical feature of quantum mechanics.

Finally, what about the position operator? To avoid any unnecessary confusion, I'll briefly revert to a one-dimensional system. A position eigenstate must then obey

$$\hat{x}\psi(x) = x\psi(x) = X\psi(x) \tag{3.4}$$

where $X \in \mathbf{R}$ is the eigenvalue. This is a strange looking equation. Clearly we must have $\psi(x) = 0$ whenever $x \neq X$, but the equation does leave open the possibility that $\psi(X) \neq 0$. There's no function with this property, but there is a generalised function that does the job. This is the Dirac delta function $\delta(x - X)$, roughly defined as

$$\delta(x - X) = \begin{cases} \infty & x = X \\ 0 & \text{otherwise} \end{cases}$$

but with the additional property that it integrates to something nice:

$$\int_{-\infty}^{+\infty} dx\ \delta(x - X) = 1$$

To check that $\psi(x) = \delta(x - X)$ does indeed solve (3.4), we can integrate it against an arbitrary function $f(x)$. We want to check that the following holds

$$\int_{-\infty}^{+\infty} dx\ x\delta(x - X)f(x) \stackrel{?}{=} \int_{-\infty}^{+\infty} dx\ X\delta(x - X)f(x)$$

for all $f(x)$. But this is true: both sides evaluate to $Xf(X)$.

We see that the spectrum of the position operator is continuous, with the eigenvalue any $X \in \mathbf{R}$. But, as with the momentum operator, the eigenfunctions are not normalisable.

$$\int_{-\infty}^{+\infty} dx\ |\psi|^2 = \int_{-\infty}^{+\infty} dx\ |\delta(x - X)|^2 = \delta(0) = \infty$$

This time it doesn't help if you put your system on a periodic space: the position eigenstates remain non-normalisable. The only get out is to consider space itself to be a discrete lattice. This is an interesting direction and will be discussed in the lectures on Solid State Physics. However, just like the plane wave momentum eigenstates, the position eigenstates are too useful to throw away completely.

There is a straightforward generalisation of the story above to position eigenstates in 3d. Now we have

$$\mathbf{x}\psi(\mathbf{x}) = \mathbf{X}\psi(\mathbf{x}) \quad \Rightarrow \quad \psi(\mathbf{x}) = \delta^3(\mathbf{x} - \mathbf{X}) = \delta(x - X)\delta(y - Y)\delta(z - Z)$$

Again, these states are non-normalisable.

3.2.2 Hermitian Operators

Not any old linear operator qualifies as a physical observable in quantum mechanics. We should restrict attention to those operators that are *Hermitian*.

To explain this, we first introduce the concept of an adjoint operator. Given an operator $\hat{O}$, its adjoint $\hat{O}^\dagger$ is defined by the requirement that the following inner-product relation holds

$$\langle \psi \,|\, \hat{O}\phi \rangle = \langle \hat{O}^\dagger \psi \,|\, \phi \rangle$$

for all states ψ and ϕ. Written in terms of integrals of wavefunctions, this means

$$\int d^3x \; \psi^\star \hat{O}\phi = \int d^3x \; (\hat{O}^\dagger \psi)^\star \phi$$

An operator is said to be *Hermitian* or *self-adjoint* if

$$\hat{O} = \hat{O}^\dagger$$

(In fact there's a tiny bit of a lie in that previous statement. The terms "Hermitian" and "self-adjoint" are only synonymous for finite dimensional Hilbert spaces. When we're dealing with infinite dimensional Hilbert spaces of functions there is a subtle distinction between them that we will largely sweep under the rug in these lectures. We'll touch upon it briefly in Section 4.2.3.)

All physical observables correspond to Hermitian operators. Let's check that this is the case for the operators that we just met. First the position operator. We have

$$\langle \psi \,|\, \hat{\mathbf{x}}\phi \rangle = \int d^3x \; \psi^\star \, \mathbf{x}\phi = \int d^3x \; (\mathbf{x}\psi)^\star \phi = \langle \hat{\mathbf{x}}\psi \,|\, \phi \rangle$$

So we learn that $\hat{\mathbf{x}} = \hat{\mathbf{x}}^\dagger$ as promised. Here the calculation was trivial: it is just a matter of running through definitions. The calculation for the momentum operator is marginally less trivial. We have

$$\begin{aligned} \langle \psi \,|\, \hat{\mathbf{p}}\phi \rangle &= \int d^3x \; \psi^\star \, (-i\hbar \nabla \phi) \\ &= \int d^3x \; i\hbar (\nabla \psi^\star) \phi \\ &= \int d^3x \; (-i\hbar \nabla \psi)^\star \phi = \langle \hat{\mathbf{p}}\psi \,|\, \phi \rangle \end{aligned}$$

In the second line we integrated by parts, picking up one minus sign, and in the third line we took the factor of i inside the brackets with the complex conjugation giving us a second minus sign. The two minus signs cancel out to give $\hat{\mathbf{p}} = \hat{\mathbf{p}}^\dagger$. This is one way to see why the momentum operator necessarily comes with a factor of i.

Note that, when we integrated by parts, we threw away the total derivative. This is justified on the grounds that the states ψ and ϕ are normalisable and so asymptote to zero at infinity.

The Hermiticity of the Hamiltonian follows immediately because it's a real function of $\hat{x}$ and $\hat{p}$. Alternatively, you check explicitly that the Hamiltonian is Hermitian by doing the kind of integration-by-parts calculation that we saw above.

Properties of Hermitian Matrices

Hermitian operators have a number of properties that make them the right candidates for physical observables. To explain these, we're first going to regress to the simpler world of $N \times N$ complex matrices acting on N-dimensional complex vectors.

A complex matrix A is said to be Hermitian is it obeys $A^\dagger := (A^\star)^T = A$. This means that the components of the matrix obey $A_{ij} = A^\star_{ji}$. To see that this coincides with our previous definition, recall that the inner product for two complex vectors is (3.2)

$$\langle \vec{u} \,|\, \vec{v} \rangle = \vec{u}^\star \cdot \vec{v}$$

For a Hermitian matrix A we have

$$\langle \vec{u} \,|\, A\vec{v} \rangle = \vec{u}^\star \cdot A\vec{v} = u_i^\star A_{ij} v_j = u_i^\star A^\star_{ji} v_j = (A\vec{u})^\star \cdot \vec{v} = \langle A\vec{u} \,|\, \vec{v} \rangle$$

in agreement with our earlier, more general definition.

The eigenvalues and eigenvectors of a Hermitian matrix A are determined by the equation

$$A\vec{u}_n = \lambda_n \vec{u}_n$$

where $n = 1, \ldots, N$ labels the eigenvalues and eigenvectors. These have a number special properties. The first two are:

- The eigenvalues λ_n are real.
- If two eigenvalues are distinct $\lambda_n \neq \lambda_m$ then their corresponding eigenvectors are orthogonal: $\vec{u}_n^\star \cdot \vec{u}_m = 0$.

Both are simple to prove. We take the inner product of A between two different eigenvectors.

$$\begin{aligned} \langle \vec{u}_n \,|\, A\vec{u}_m \rangle = \langle A\vec{u}_n \,|\, \vec{u}_m \rangle \quad &\Rightarrow \quad \lambda_n^\star \vec{u}_n^\star \cdot \vec{u}_m = \lambda_m \vec{u}_n^\star \cdot \vec{u}_m \\ &\Rightarrow \quad (\lambda_n^\star - \lambda_m)\, \vec{u}_n^\star \cdot \vec{u}_m = 0 \end{aligned}$$

Set $n = m$ to find $\lambda_n = \lambda_n^\star$ so that the eigenvalue is real. Alternatively, pick distinct eigenvalues $\lambda_n \neq \lambda_m$ to show that the eigenvectors are orthogonal, $\vec{u}_n^\star \cdot \vec{u}_m = 0$ if $m \neq n$.

If the matrix has two or more eigenvalues that coincide, then it's still possible to pick the eigenvectors to be orthogonal. We won't prove this statement, but it follows straightforwardly by just picking an orthogonal basis for the space spanned by the eigenvectors.

There is one final property of Hermitian matrices that we won't prove: they always have N eigenvectors. This is important. Because the eigenvectors can be taken to be orthogonal, they necessarily span the space $\mathbf{C}^N$, meaning that any vector can be expanded in terms of eigenvectors

$$\vec{v} = \sum_{n=1}^{N} a_n \vec{u}_n$$

for some complex coefficients a_n.

With these results in mind, let's now return to Hermitian operators that act on infinite dimensional Hilbert spaces.

Properties of Hermitian Operators

The eigenvalue for a Hermitian operator is

$$\hat{O}\phi_n = \lambda_n \phi_n$$

where λ_n is the eigenvalue and we've shifted notation slightly from our earlier discussion and will refer to eigenfunctions as ϕ_n. Now the label runs over $n = 1, \ldots, \infty$ reflecting the fact that we've got an infinite dimensional Hilbert space.

For a Hermitian operator $\hat{O}$, the eigenvalues and eigenfunctions have the following two properties:

- The eigenvalues λ_n are real.
- If two eigenvalues are distinct $\lambda_n \neq \lambda_m$ then their corresponding eigenfunctions are orthogonal: $\langle \phi_n \,|\, \phi_m \rangle = 0$.

Recall our important boxed statement from earlier: the outcome of any measurement of $\hat{O}$ is given by one of the eigenvalues of $\hat{O}$. The first of the properties above ensures that, happily, the result of any measurement is guaranteed to be a real number. That's a good thing. If you go into a lab you'll see dials and needles and rulers and other complicated things. All of them measure real numbers, never complex.

The proof of the two properties above is identical to the proof for finite matrices. If $\hat{O}$ is Hermitian, we have

$$\begin{aligned}\langle\phi_n\,|\,\hat{O}\phi_m\rangle = \langle\hat{O}\phi_n\,|\,\phi_m\rangle \quad &\Rightarrow \quad \lambda_n^\star\langle\phi_n\,|\,\phi_m\rangle = \lambda_m\langle\phi_n\,|\,\phi_m\rangle \\ &\Rightarrow \quad (\lambda_n^\star - \lambda_m)\,\langle\phi_n\,|\,\phi_m\rangle = 0\end{aligned}$$

Agan, set $n = m$ to find $\lambda_n = \lambda_n^\star$ so that the eigenvalue is real. Alternatively, pick distinct eigenvalues $\lambda_n \neq \lambda_m$ to show that the eigenfunctions are orthogonal, which now means

$$\langle\phi_n\,|\,\phi_m\rangle = \int d^3x\ \phi_n^\star\phi_m = 0 \quad \text{if } m \neq n$$

An operator with distinct eigenvalues is said to have a *non-degenerate* spectrum. If, on the other hand, two or more eigenvalues coincide then we say it has a *degenerate* spectrum. In this case, as with matrices, it's still possible to pick orthogonal eigenfunctions. Again, we won't prove this. However, it means that in all cases, if we normalise the eigenstates then we can always take them to obey

$$\langle\phi_n\,|\,\phi_m\rangle = \int d^3x\ \phi_n^\star\phi_m = \delta_{mn} \tag{3.5}$$

Eigenfunctions that obey this are said to be *orthonormal*.

Finally, one last important statement that we make without proof: the eigenfunctions of any Hermitian operator are *complete*. This means that we can expand any wavefunction $\psi(\mathbf{x})$ in terms of eigenstates of a given operator $\hat{O}$

$$\psi(\mathbf{x}) = \sum_{n=1}^{\infty} a_n\phi_n(\mathbf{x}) \tag{3.6}$$

for some complex coefficients a_n. If you know both ψ and the normalised eigenfunctions ϕ_n, then it's simple to get an expression for these coefficients: we use the orhonormality relation (3.5), together with linearity of the inner product, to get

$$\langle\phi_n\,|\,\psi\rangle = \sum_m a_m\langle\phi_n\,|\,\phi_m\rangle = \sum_m a_n\delta_{mn} = a_n$$

Or, in terms of integrals,

$$a_n = \int d^3x\ \phi_n^\star(\mathbf{x})\,\psi(\mathbf{x})$$

Relatedly, the norm of a wavefunction $\psi(\mathbf{x})$ is

$$||\psi(\mathbf{x})||^2 := \int d^3x\ |\psi(\mathbf{x})|^2 = \sum_m\sum_n\int d^3x\ a_n^\star\phi_n^\star\,a_m\phi_m = \sum_n |a_n|^2$$

where we have again used the orthonormality condition (3.5). We see that a wavefunction is normalised only in $\sum_n |a_n|^2 = 1$.

3.2.3 Momentum Eigenstates and the Fourier Transform

The idea that any function can be expressed as a sum of eigenstates of a Hermitian operator is not totally unfamiliar. When the operator in question is the momentum operator $\hat{p}$, this coincides with the Fourier transform of a function.

To keep things simple, we'll work in one dimension. We'll start by considering a particle on a circle of radius R, in which case the momentum eigenstates solve

$$\hat{p}\phi_n(x) = -i\hbar\frac{d\phi_n}{dx} = p_n\phi_n(x)$$

As we saw above, the eigenstates and eigenvalues are

$$\phi_n = \sqrt{\frac{1}{2\pi R}}\,e^{inx/R} \quad \text{and} \quad p_n = \frac{\hbar n}{R}\ ,\ n \in \mathbf{Z}$$

Notice that we've now normalised the wavefunction. You can check that the eigenstates are orthonormal, obeying

$$\langle \phi_n \,|\, \phi_m \rangle = \frac{1}{2\pi R}\int_0^{2\pi R} dx\ e^{i(m-n)x/R} = \delta_{mn}$$

Any periodic complex function on the circle, such that $\psi(x) = \psi(x + 2\pi R)$, can be expanded in terms of these eigenstates, meaning that

$$\psi(x) = \sqrt{\frac{1}{2\pi R}}\sum_{n\in\mathbf{Z}} a_n e^{inx/R}$$

where, in contrast to our previous expression (3.6), we now label the eigenstates by the integers n rather than just the positive integers. (These are equivalent...welcome to Hilbert's hotel.) We have

$$a_n = \int_0^{2\pi R} dx\ \phi_n^\star\psi = \sqrt{\frac{1}{2\pi R}}\int_0^{2\pi R} dx\ e^{-inx/R}\psi(x)$$

In this context, a_n are known as *Fourier coefficients.*

We can also think about what happens to the particle on the line. Now the eigenstates are labelled by a continuous variable $k \in \mathbf{R}$ rather than a discrete variable,

$$\phi_k(x) = \sqrt{\frac{1}{2\pi}}e^{ikx}$$

As we've seen several times, these states are non-normalisable. Nonetheless, there is a version of the orthogonality relation (3.5), which is now

$$\langle \phi_k \,|\, \phi_{k'} \rangle = \frac{1}{2\pi} \int dx \; e^{i(k-k')x} = \delta(k-k') \tag{3.7}$$

where $\delta(k)$ is the Dirac delta function. Similarly, we can expand a function $\psi(x)$ in these eigenstates, with the sum over states in (3.6) now replaced by an integral

$$\psi(x) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{+\infty} dk \; \tilde{\psi}(k)\, e^{ikx} \tag{3.8}$$

The Fourier coefficients a_n are now promoted to full function $\tilde{\psi}(k)$. We can use the orthogonality condition (3.7) to invert the expression above and write $\tilde{\psi}(k)$ in terms of the original function $\psi(x)$,

$$\tilde{\psi}(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{+\infty} dx \; \psi(x)\, e^{-ikx} \tag{3.9}$$

The relations (3.8) and (3.9) are, as advertised, the Fourier transform of a function.

3.3 Measurement

Now we turn to the final facet of quantum mechanics: measurement. Suppose that we have a quantum system in a given state $\psi(\mathbf{x})$. We want to measure an observable that is associated to an operator $\hat{O}$ whose eigenvalue equation is

$$\hat{O}\phi_n = \lambda_n \phi_n$$

We stated before that the possible result of any measurement is taken from the spectrum of eigenvalues $\{\lambda_n\}$. But how does this result depend on the state ψ?

Here is the answer. We first decomposes the state ψ in terms of orthonormal eigenstates of $\hat{O}$,

$$\psi(\mathbf{x}) = \sum_n a_n \phi_n(\mathbf{x})$$

We will take both ϕ_n and the wavefunction ψ to be normalised, which means that $\sum_n |a_n|^2 = 1$. Assuming that the spectrum is non-degenerate, the probability that the result of the measurement gives the answer λ_n is given by the *Born rule*,

$$\text{Prob}(\lambda_n) = |a_n|^2 \tag{3.10}$$

A normalised wavefunction ensures that the sum of probabilities is $\sum_n \text{Prob}(\lambda_n) = 1$.

We make a measurement and get the result λ_n for some particular n. Now there's no doubt about the value of the observable: we've just measured it and know that it's λ_n. To reflect this, there is a "collapse of the wavefunction" which jumps to

$$\psi(\mathbf{x}) \longrightarrow \phi_n(\mathbf{x}) \tag{3.11}$$

This ensures that if we make a second measurement of $\hat{O}$ immediately after the first then we get the same answer: λ_n.

The discontinuous jump of the wavefunction (3.11) is very different in character from the smooth evolution under the guidance of the time dependent Schrödinger equation. In particular, the collapse of the wavefunction is not even a linear operation: if you add two wavefunctions together, you first have to normalise the sum to compute the probability and that's a simple, but non-linear calculation.

Given that measurement of quantum states is performed by stuff that's made out of atoms and therefore should itself be governed by the Schrödinger equation, it seems like there should be a more unified description of how states evolve. We'll make a few further comments about this in Section 3.5.

There's a simple generalisation of the story above when the spectrum is degenerate. In that case, the probability that we get a given result λ is

$$\text{Prob}(\lambda) = \sum_{n\,|\,\lambda_n=\lambda} |a_n|^2 \tag{3.12}$$

After the measurement, the wavefunction collapses to $\psi \longrightarrow C\sum_{n|\lambda_n=\lambda} a_n\phi_n$ where C is the appropriate normalisation factor.

First One Thing, Then The Other

Let's look at one obvious implication of the measurement procedure described above. Suppose that we measure a (non-degenerate) observable $\hat{O}$ and get a definite result, say λ_6. Immediately after the measurement the system sits in the state

$$\psi(\mathbf{x}) = \phi_6(\mathbf{x})$$

We already noted that if we again measure $\hat{O}$ then there's no doubt about the outcome: we get the result λ_6 again for sure. The general statement is that the system has a definite value for some observable only if it sits in an eigenstate of that observable.

Now we measure a different observable, $\hat{M}$. In general, this will have a different set of eigenstates,

$$\hat{M}\chi_n(\mathbf{x}) = \mu_n \chi_n(\mathbf{x})$$

and a different set of outcomes $\{\mu_n\}$. There's no reason that the eigenstates of $\hat{M}$ should have anything to do with the eigenstates of $\hat{O}$: they will typically be entirely different functions. We now have to play the game all over again: we take our state, which we know is ϕ_6, and expand

$$\phi_6(\mathbf{x}) = \sum_m b_m \chi_m(\mathbf{x})$$

There is no certainty about what we get when we measure $\hat{M}$: the result μ_m appears with probability $\text{Prob}(\mu_m) = |b_m|^2$ and the wavefunction will immediately collapse to the corresponding eigenstate $\chi_m(\mathbf{x})$. Suppose that we do the experiment and find the result μ_{17}. Now the wavefunction collapses again, to

$$\phi_6(\mathbf{x}) \ \longrightarrow \chi_{17}(\mathbf{x})$$

Now comes the rub. We are capricious and decide to go back and measure the original observable $\hat{O}$. It wasn't so long ago that we measured it and found the result λ_6. But now, having measured $\hat{M}$, there's no guarantee that we'll get λ_6 again! Instead, we need to go through the same process and expand our wavefunction

$$\chi_{17}(\mathbf{x}) = \sum_n c_n \phi_n(\mathbf{x})$$

The probability that we get the result λ_6 again is $|c_6|^2$. But now it's just one among many options. There's no reason to have $|c_6| = 1$.

There are different words that we can drape around this. First, it's clear that the measurement of a quantum system is never innocent. You can't just take a small peek and walk away pretending that you've not done anything. Instead, any measurement of a quantum system necessarily disturbs the state.

Moreover, if the state originally had a specific value for one observable $\hat{O}$ and you measure a different observable $\hat{M}$ then you destroy the original property of the state. It's tempting to say that there's no way to *know* the values of both $\hat{O}$ and $\hat{M}$ at the same time. But that's not what the mathematics is telling us. Instead, the quantum particle can't *have* specific values of $\hat{O}$ and $\hat{M}$ at the same time. Indeed, most of the time it doesn't have a specific value for either since its wavefunction is a superposition of eigenstates. But, providing the eigenstates of the two operators don't coincide, if the quantum state takes a definite value for one observable, then it cannot for the other. We'll quantify this idea in Section 3.4 where we introduce the Heisenberg uncertainty relatations.

The lectures on Topics in Quantum Mechanics have a section on the Foundations of Quantum Mechanics where ideas of measurement are discussed in more detail.

3.3.1 Expectation Values

Take a normalised state $\psi(\mathbf{x})$ and measure the observable $\hat{O}$, with eigenstates and eigenvalues given by

$$\hat{O}\phi_n = \lambda_n \phi_n$$

As we've seen, if we expand the original state in orthonormal eigenfunctions

$$\psi(\mathbf{x}) = \sum_n a_n \phi_n(\mathbf{x})$$

then the probability that we measure λ_n is $|a_n|^2$ (assuming a non-degenerate spectrum). This means that if we have many systems, all in the same state ψ, and perform the same measurement on each then the results will differ but the average will be

$$\langle \hat{O} \rangle_\psi = \sum_n |a_n|^2 \lambda_n$$

Note the little subscript ψ on the angular brackets, reminding us that the average value depends on the state of the system. We call this average the *expectation value*. It has a nice expression in terms of the inner product.

Claim: For a normalised wavefunction $\psi(\mathbf{x})$, the expectation value can be written as

$$\langle \hat{O} \rangle_\psi = \langle \psi \,|\, \hat{O}\psi \rangle = \int d^3x \; \psi(\mathbf{x})^\star \, \hat{O}\psi(\mathbf{x}) \tag{3.13}$$

If $\psi(\mathbf{x})$ is un-normalised, this should be replaced by

$$\langle \hat{O} \rangle_\psi = \frac{\langle \psi \,|\, \hat{O}\psi \rangle}{\langle \psi \,|\, \psi \rangle}$$

which follows from (3.13) by first normalising ψ.

Proof: We don't need to do anything clever: just follow our previous definition. It's simplest to start with a normalised wavefunction and work backwards:

$$\begin{aligned}\int d^3x\ \psi(\mathbf{x})^\star\,\hat{O}\psi(\mathbf{x}) &= \sum_n\sum_m \int d^3x\ a_n^\star a_m\,\phi_n^\star(\mathbf{x})\,\hat{O}\phi_m(\mathbf{x}) \\ &= \sum_n\sum_m \int d^3x\ a_n^\star a_m\,\phi_n^\star(\mathbf{x})\,\lambda_m\phi_m(\mathbf{x}) \\ &= \sum_n\sum_m a_n^\star a_m\lambda_m\delta_{nm} = \sum_n |a_n|^2\lambda_n\end{aligned}$$

where, in the last step, we used the orthonormality of the eigenstates (3.5). □

We can look at some simple examples to check that this coincides with our earlier results. The expectation values of the position operator is

$$\langle\hat{\mathbf{x}}\rangle_\psi = \int d^3x\ \mathbf{x}\,|\psi(\mathbf{x})|^2 \tag{3.14}$$

This is telling us that $|\psi(\mathbf{x})|^2$ must have the interpretation of the probability distribution over position. This, of course, was how we first motivated the wavefunction in Section 1.1.

The expectation value of the momentum operator is

$$\langle\hat{\mathbf{p}}\rangle_\psi = -i\hbar\int d^3x\ \psi(\mathbf{x})^\star\nabla\psi(\mathbf{x})$$

We already met the 1d version of this in Section 2.1.4 when looking at Gaussian wavepackets. It's fruitful to think about the wavefunction written in terms of momentum eigenstates. Recall that this is just the Fourier transform (3.8)

$$\psi(\mathbf{x}) = \left(\frac{1}{2\pi}\right)^{3/2}\int d^3k\ \tilde{\psi}(\mathbf{k})\,e^{i\mathbf{k}\cdot\mathbf{x}}$$

Substituting this into our expression (3.14) we find

$$\begin{aligned}\langle\hat{\mathbf{p}}\rangle_\psi &= \frac{1}{(2\pi)^3}\int d^3k\int d^3k'\ \hbar\mathbf{k}'\,\tilde{\psi}(\mathbf{k})^\star\tilde{\psi}(\mathbf{k}')\int d^3x\ e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} \\ &= \int d^3k\int d^3k'\ \hbar\mathbf{k}'\,\tilde{\psi}(\mathbf{k})^\star\tilde{\psi}(\mathbf{k}')\,\delta^3(\mathbf{k}-\mathbf{k}') \\ &= \int d^3k\ \hbar\mathbf{k}\,|\tilde{\psi}(\mathbf{k})|^2\end{aligned}$$

where, to go from the first to second line, we've used the Fourier representation of the Dirac delta function, essentially just three copies of the 1d result (3.7). The upshot is that we learn something rather nice: while the mod-squared of the original wavefunction $|\psi(\mathbf{x})|^2$ has the interpretation as a probability distribution over position, the mod-squared of its Fourier transform $|\tilde{\psi}(\mathbf{k})|^2$ has the interpretation as a probability distribution over momentum.

3.4 Commutation Relations

There is an algebraic way of formalising whether two observables can be simultaneously measured or whether, as is usually the case, a measurement of one messes up a previous measurement of the other. The underlying structure is known as *commutation relations*.

Given two operators $\hat{O}$ and $\hat{M}$, their *commutator* is defined to be

$$[\hat{O}, \hat{M}] = \hat{O}\hat{M} - \hat{M}\hat{O} \tag{3.15}$$

The key idea is familiar from matrices. If you multiply two matrices A and B then the order matters. Typically AB is not the same as BA. The commutator $[A, B]$ captures the difference between these. Clearly $[A, B] = -[B, A]$ and the same also holds for operators: $[\hat{O}, \hat{M}] = -[\hat{M}, \hat{O}]$.

Some care should be taken with formulae like (3.15). The operators have a job to do: they act on functions. It's important to remember this when manipulating these kind of equations. A good rule of thumb is to think of operator equations like (3.15) as meaning

$$[\hat{O}, \hat{M}]\psi = \hat{O}\hat{M}\psi - \hat{M}\hat{O}\psi \quad \text{for all } \psi(\mathbf{x}) \tag{3.16}$$

When we do calculations, at least initially, it's useful to use this phrasing to avoid any slip ups.

For all the examples in these lectures, the fundamental operators are position $\hat{\mathbf{x}}$ and the momentum operator $\hat{\mathbf{p}}$. It will prove useful to compute their commutators.

Claim: The commutation relations of $\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$ and $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$ are

$$[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0 \quad \text{and} \quad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{3.17}$$

These are known as the *canonical commutation relations* on account of the important role that they play in quantum mechanics. Note that the right-hand side of the final relation is just a constant, but this too should be viewed as an operator: it's the trivial operator that just multiplies any function by a constant.

The last commutation relation is perhaps surprising. In 1d, it reads simply $[\hat{x}, \hat{p}] = i\hbar$. This kind of relation is not possible for finite matrices A and B: the analogous result would be $[A, B] = i\hbar \mathbb{1}$ with $\mathbb{1}$ the unit matrix. But if we take the trace of the left-hand side we find

$$\text{Tr}[A, B] = \text{Tr}(AB - BA) = 0$$

because $\text{Tr}(AB) = \text{Tr}(BA)$. Yet clearly $\text{Tr}\,\mathbb{1} \neq 0$. However, infinite matrices, a.k.a. operators, can do things that finite matrices cannot, the canonical commutation relations (3.17) among them.

Proof: The canonical commutation relations follow straightforwardly from the definitions

$$\hat{x}_i = x_i \quad \text{and} \quad \hat{p}_i = -i\hbar \frac{\partial}{\partial x_i} \tag{3.18}$$

Recalling that we should view all operators as acting on functions, as in (3.16), the commutation of position operators is

$$[\hat{x}_i, \hat{x}_j]\psi(\mathbf{x}) = (x_i x_j - x_j x_i)\psi(\mathbf{x}) = 0 \quad \text{for all } \psi(\mathbf{x})$$

while the commutation of momentum operators is

$$[\hat{p}_i, \hat{p}_j]\psi(\mathbf{x}) = \left(\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} - \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i}\right)\psi(\mathbf{x}) = 0 \quad \text{for all } \psi(\mathbf{x})$$

which follows because the order in which we take partial derivatives doesn't matter. That leaves us just with the more interesting commutation relation. It is

$$[\hat{x}_i, \hat{p}_j]\psi(\mathbf{x}) = -i\hbar\left(x_i \frac{\partial}{\partial x_j} - \frac{\partial}{\partial x_j} x_i\right)\psi(\mathbf{x})$$

We can see the issue: the first derivative hits only the function ψ. Meanwhile the second derivative acts on $x_i\psi$, giving us an extra term from the chain rule. Moreover, the $\partial\psi/\partial x_j$ terms cancel, leaving us only with this extra term

$$[\hat{x}_i, \hat{p}_j]\psi(\mathbf{x}) = i\hbar \frac{\partial x_i}{\partial x_j}\psi(\mathbf{x}) = i\hbar\delta_{ij}\psi(\mathbf{x}) \quad \text{for all } \psi(\mathbf{x})$$

This is the claimed result. □

Note that the proof ultimately boils down to the operator equation

$$x_i \frac{\partial}{\partial x_j} - \frac{\partial}{\partial x_j} x_i = -\delta_{ij}$$

When you first meet these kinds of equations, it's not immediately obvious why they're true. As we saw above, the right way to proceed is to check that it holds on when evaluated on any arbitrary function $\psi(\mathbf{x})$.

The logic that we've presented above is to first introduce the position and momentum operators and subsequently derive the canonical commutation relations. This, it turns out, is inverted. In more advanced presentations of quantum mechanics, the canonical commutation relations (3.17) are the starting point. There is then a theorem – due to Stone and von Neumann – that, roughly speaking, says that one can derive the form of the operators (3.18) from the canonical commutation relations.

One reason why the canonical commutation relations hold such a prominent position is because very similar equations can be found in classical mechanics. In that context, the relation involves neither commutators nor $\hbar$, but something called a *Poisson bracket*. This is a concept that arises in the more sophisticated, Hamiltonian approach to classical mechanics. You can read about this in the lectures on Classical Dynamics. For now, let me just say that while the physics of quantum mechanics is a huge departure from our classical world, the underlying mathematical structure turns out to be surprisingly close.

Occasionally on our quantum travels, we will run into two operators that commute, meaning

$$[\hat{O}, \hat{M}] = 0$$

This is interesting because ...

Claim: $[\hat{O}, \hat{M}] = 0$ if and only if $\hat{O}$ and $\hat{M}$ share the same eigenfunctions.

Proof: First suppose that both $\hat{O}$ and $\hat{M}$ share the same eigenfunctions, so that

$$\hat{O}\phi_n(\mathbf{x}) = \lambda_n \phi_n(\mathbf{x}) \quad \text{and} \quad \hat{M}\phi_n(\mathbf{x}) = \mu_n \phi_n(\mathbf{x})$$

Then any function $\psi(\mathbf{x})$ can be expanded in terms of these eigenstates $\psi = \sum_n a_n \phi_n$, giving

$$[\hat{O}, \hat{M}]\psi = \sum_n a_n [\hat{O}, \hat{M}]\phi_n = \sum_n a_n (\lambda_n \mu_n - \mu_n \lambda_n)\phi_n = 0 \quad \text{for all } \psi(\mathbf{x})$$

Conversely, suppose that $[\hat{O},\hat{M}]=0$. We will restrict ourselves to the case where $\hat{O}$ has a non-degenerate spectrum. (The claim holds more generally but we have to work a little harder.) If ϕ is an eigenstate of $\hat{O}$, then we have

$$\begin{aligned}\hat{O}\phi=\lambda\phi \quad &\Rightarrow \quad \hat{M}\hat{O}\phi=\lambda\hat{M}\phi \\ &\Rightarrow \quad \hat{O}\hat{M}\phi=\lambda\hat{M}\phi\end{aligned}$$

where the second line follows because $[\hat{O},\hat{M}]=0$. But this tells us that $\hat{M}\phi$ is also an eigenstate of $\hat{O}$ with eigenvalue λ. By assumption, there is only one eigenstate with eigenvalue λ, which means that we must have

$$M\phi=\mu\phi$$

for some μ. But this is the statement that ϕ is also an eigenstate of $\hat{M}$. The two operators need not have the same eigenvalues, but they do have the same eigenstates. $\square$

The physical interpretation of the claim follows from our discussion in Section 3.3. It *is* possible for a quantum system to have simultaneous values for commuting observables. If you measure $\hat{O}$ and then measure $\hat{M}$, the state will not be perturbed as long as $[\hat{O},\hat{M}]=0$. (Actually this last statement does require that the spectrum of $\hat{O}$ is non-degenerate.) If you then measure $\hat{O}$ again, you'll get the same answer as the first time. We'll meet examples of commuting operators in Section 4.1 when we look at the angular momentum operators in more detail.

3.4.1 The Heisenberg Uncertainty Principle

A probability distribution is characterised by its moments. The simplest of these is the average, or mean, which is the expectation value (3.13). The next simplest is the variance, which gives some indication of the spread of the distribution.

In quantum mechanics the variance is called *uncertainty*. In a state ψ, the uncertainty of an observable $\hat{O}$ is denoted $\Delta_\psi O$ and is defined as

$$\begin{aligned}(\Delta_\psi O)^2 &= \langle(\hat{O}-\langle\hat{O}\rangle_\psi)^2\rangle_\psi \\ &= \langle\hat{O}^2-2\langle\hat{O}\rangle_\psi\hat{O}+\langle\hat{O}\rangle_\psi^2\rangle_\psi \\ &= \langle\hat{O}^2\rangle_\psi-\langle\hat{O}\rangle_\psi^2\end{aligned}$$

In statistics, the uncertainty $\Delta_\psi O$ is also known as the *standard deviation* of the distribution. Using our expression (3.13) for the expectation value, and assuming a normalised wavefunction, we can write the uncertainty as

$$(\Delta_\psi O)^2 = \langle \psi \,|\, \hat{O}^2 \psi \rangle - \langle \psi \,|\, \hat{O}\psi \rangle^2$$

$$= \int d^3x \; \psi^\star \hat{O}^2 \psi - \left(\int d^3x \; \psi^\star \hat{O}\psi \right)^2 \tag{3.19}$$

To motivate the name "uncertainty", suppose that the state of the system is an eigenstate of $\hat{O}$,

$$\psi(\mathbf{x}) = \phi(\mathbf{x}) \quad \text{with} \quad \hat{O}\phi(\mathbf{x}) = \lambda \phi(\mathbf{x})$$

Then the uncertainty of $\hat{O}$ in this state is

$$(\Delta_\phi O)^2 = \langle \phi \,|\, \hat{O}^2 \phi \rangle - \langle \phi \,|\, \hat{O}\phi \rangle^2 = \lambda^2 - \lambda^2 = 0$$

This makes sense: in an eigenstate ϕ we know exactly what the value of $\hat{O}$ is, so there is no uncertainty. Of course, in the same state the uncertainty for other observables will necessarily be non-zero. Indeed, unless $[\hat{O}, \hat{M}] = 0$, the uncertainties $\Delta_\psi O$ and $\Delta_\psi M$ cannot both vanish.

In fact, the story is more interesting. It turns out for certain pairs of observables, as you reduce the uncertainty in one, the uncertainty in the other necessarily grows. One such pair is our favourite position and momentum. It's simplest if we work in one dimension. (The generalisation to higher dimensions is trivial.) The canonical commutation relations (3.17) tell us that

$$[\hat{x}, \hat{p}] = i\hbar \tag{3.20}$$

This is all we need to derive the following result:

Claim: In any state ψ, we necessarily have

$$\Delta_\psi x \, \Delta_\psi p \geq \frac{\hbar}{2} \tag{3.21}$$

This is the mathematical expression of the *Heisenberg uncertainty relation.* Because it follows purely from (3.20), any operators that obey the same commutation relation will have the same uncertainty relation.

Proof: To make life simple, we will assume that we have a state for which $\langle \hat{x} \rangle_\psi = \langle \hat{p} \rangle_\psi = 0$. (If this isn't the case, you can rescue the proof below by defining new operators $\hat{X} = \hat{x} - \langle \hat{x} \rangle_\psi$ and $\hat{P} = \hat{p} - \langle \hat{p} \rangle_\psi$ which do obey $\langle \hat{X} \rangle_\psi = \langle \hat{P} \rangle_\psi = 0$.)

Next, consider the one-parameter family of states defined by

$$\Psi_s(\mathbf{x}) = (\hat{p} - is\hat{x})\,\psi(\mathbf{x}) \qquad s \in \mathbf{R}$$

The norm of this state is, like all others, positive definite, meaning

$$\langle \Psi_s \,|\, \Psi_s \rangle = \int dx\; |\Psi_s|^2 \;\geq 0$$

Translated back to the original state ψ, this tells us that

$$0 \leq \langle (\hat{p} - is\hat{x})\psi \,|\, (\hat{p} - is\hat{x})\psi \rangle = \langle \psi \,|\, (\hat{p} + is\hat{x})(\hat{p} - is\hat{x})\psi \rangle$$

where the equality uses the fact that both $\hat{x}$ and $\hat{p}$ are Hermitian. Expanding out, we have

$$0 \leq \langle \psi \,|\, (\hat{p}^2 + is[\hat{x}, \hat{p}] + s^2 \hat{x}^2)\psi \rangle = \langle \psi \,|\, (\hat{p}^2 - s\hbar + s^2\hat{x}^2)\psi \rangle$$

where, this time, the equality uses the commutation relation $[\hat{x}, \hat{p}] = i\hbar$. The $\hat{p}^2$ and $\hat{x}^2$ terms in this expression are just the uncertainties (3.19), a fact that follows because we've chosen $\langle \hat{x} \rangle_\psi = \langle \hat{p} \rangle_\psi = 0$. So we have

$$(\Delta_\psi p)^2 - s\hbar + s^2 (\Delta_\psi x)^2 \geq 0 \quad \text{for all } s \in \mathbf{R}$$

Now we're in familiar territory. This is a quadratic in s and the inequality tells us that it has either one root or no roots. This can only be true if the discriminant "$b^2 - 4ac$" is non-positive, i.e.

$$4(\Delta_\psi x)^2 (\Delta_\psi p)^2 \geq \hbar^2$$

This is the Heisenberg uncertainty relation (3.21). □

You can have some fun trying to come up with experiments that might evade the Heisenberg uncertainty relation, and then see how Nature finds a way to avoid this conclusion and ensure that (3.21) is always satisfied.

For example, the obvious way to figure out where a particle is sitting is to look at it. But if you want to resolve something on a distance scale Δx, then you have to use light of wavelength $\lambda \lesssim \Delta x$. Ultimately, light is made up of particles called photons. We haven't said anything so far about photons in these lectures. (We'll make a few comments in Section 4.4.) However, all we need to know is that, like all other quantum particles, photons have a momentum given by the de Broglie formula (2.7)

$$p = \frac{2\pi\hbar}{\lambda}$$

Clearly there's a pay-off: if you want to be sure that the particle is sitting in a smaller and smaller region Δx then you have to hit it with higher and higher momentum photons, and these will impart some recoil on the particle of order $\Delta p \sim 2\pi\hbar/\Delta x$. The intrusive nature of measurement means that we can't know both the position and momentum to better than $\Delta p \Delta x \sim 2\pi\hbar$. The Heisenberg uncertainty relation (3.21) provides the more accurate bound.

For more examples along the same lines, you could do worse than look up the intellectual jousting of the original Einstein-Bohr debates. Einstein's thinking is pellucid in its clarity; Bohr appears muddled, bordering on obscurantist. Yet Bohr had the overwhelming advantage of being right.

The Gaussian Wavepacket Revisited

We already met a baby version of the Heisenberg uncertainty relation when we studied the Gaussian wavepacket in Section 2.1. We can return to this example now that we have a better idea of what we're doing.

We'll forget about time dependence (as we have for much of this section) and look at the normalised Gaussian wavefunction in one dimension

$$\psi(x) = \left(\frac{a}{\pi}\right)^{1/4} e^{-ax^2/2}$$

It's not hard to check that $\langle \hat{x} \rangle_\psi = \langle \hat{p} \rangle_\psi = 0$. What about the uncertainty?

The uncertainty in position is given by

$$(\Delta_\psi x)^2 = \langle \hat{x}^2 \rangle_\psi = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\ x^2 e^{-ax^2} \tag{3.22}$$

This integral is straightforward. We start from the Gaussian integral

$$\int_{-\infty}^{+\infty} dx\ e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

Then we differentiate both sides with respect to a. This gives

$$\frac{\partial}{\partial a} \int_{-\infty}^{+\infty} dx\ e^{-ax^2} = -\int_{-\infty}^{+\infty} dx\ x^2 e^{-ax^2} = \frac{\partial}{\partial a}\sqrt{\frac{\pi}{a}} = -\frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$

So we have the result

$$\int_{-\infty}^{+\infty} dx\ x^2 e^{-ax^2/2} = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$

Substituting this into (3.22), we get the uncertainty in position to be

$$(\Delta_\psi x)^2 = \frac{1}{2a}$$

This is to be expected: it is the usual variance of a Gaussian distribution.

For the uncertainty in momentum, we have

$$\begin{aligned}
(\Delta_\psi p)^2 = \langle \hat{p}^2 \rangle_\psi &= \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} dx\; e^{-ax^2/2} \left[-\hbar^2 \frac{d^2}{dx^2} e^{-ax^2/2} \right] \\
&= \sqrt{\frac{a}{\pi}} \hbar^2 \int_{-\infty}^{+\infty} dx\; (a - a^2 x^2) e^{-ax^2} \\
&= \sqrt{\frac{a}{\pi}} \hbar^2 \left[\sqrt{\frac{\pi}{a}} a - \frac{a^2}{2} \sqrt{\frac{\pi}{a^3}} \right] = \frac{1}{2} \hbar^2 a
\end{aligned}$$

Multiplying these results together gives

$$\Delta_\psi x \, \Delta_\psi p = \frac{\hbar}{2}$$

We see that the Gaussian wavepacket is rather special: it saturates the bound from the Heisenberg uncertainty relation. The class of Gaussian wavefunctions, parameterised by a, does the best job possible of balancing the twin requirements of localising in both position and momentum.

3.5 Interpretations of Quantum Mechanics

There is, I think it's fair to say, a level of disquiet about certain aspects of quantum mechanics.

In large part, this nervousness rests on the two ways in which the wavefunction can evolve. For much of the time, this evolution is governed by the time dependent Schrödinger equation. There is nothing random about this process: it is as deterministic and reversible as anything in classical mechanics. But then you decide to take a peek. Or, in more standard language, to make a measurement. At this point the wavefunction changes discontinuously, collapsing to one of the eigenstates in a probabilistic fashion.

Related to this are two distinct ways of thinking about the wavefunction. On the one hand, the wavefunction clearly captures certain innate properties of the system. This is exhibited in the interference pattern of the double slit experiment or, as we will see in the next section, the spectral lines of the hydrogen atom. On the other hand, the wavefunction also encodes some aspect of our knowledge of the system as manifest in the probabilistic nature of measurement. The dichotomy posed by philosophers is whether the wavefunction is *ontic*, meaning describing some external aspect of the world, or *epistemic*, meaning relating only to our knowledge. The clear answer from quantum mechanics is that the wavefunction is both.

In this section we will briefly look at some of the ways in which people have grappled with these questions. I should warn you that we haven't yet covered enough background to describe these in any detail. This means that, in some places, I will do little more than drop some relevant names which should, if nothing else, give you a starting point to explore the rabbit warren of articles on the subject.

Finally, before we proceed, I want to point out that a much better name for the title of this section would be "Interpretations of Classical Mechanics". At the fundamental level, the world is quantum and probabilistic. Yet, from this emerges the classical world with its deterministic laws of physics. If there's a question to answer at all, it's how the latter arises from the former. If, instead, you're looking for an explanation of quantum behaviour in terms of your prejudiced, classical worldview then you've got it backwards. That's like turning to botany in the hope that it will help you understand the properties of quarks.

3.5.1 Hidden Variables

One very reasonable approach to understanding quantum mechanics is to wonder if perhaps it is not the final answer after all. Maybe it's just a stepping stone to something deeper and more fundamental.

One suggestion along these lines postulates that when we specify the wavefunction of a system, we are not giving complete information about the system. Instead, there may exist some more fundamental degrees of freedom, known as *hidden variables*, that underlie the wavefunction. Maybe we could ultimately access these hidden variables or maybe they would be, for some reason, forever hidden from us. Either way, the idea is that the probabilities in quantum mechanics arise in our current experiments because we don't know the true value of these hidden variables. In this way, the randomness in quantum mechanics is once again due to our ignorance and is no different from, say, the seeming randomness in the weather. Such a hidden variables theory would allow us to return to the comfortable, rosy classical world that we knew as children, where everything is predestined.

Hidden variables theories have an advantage over other interpretations. This is because, in some circumstances, they may deviate from the predictions of quantum mechanics, allowing an experiment to distinguish between the two. After all, the power of science derives from our ability to be wrong. Hidden variables theories hold a special place among interpretations of quantum mechanics because they are falsifiable. In fact, not only are they falsifiable, they are falsified!

It may seem odd to spend time discussing an interpretation that is known to be wrong. But because there are observable differences between hidden variables and common-or-garden quantum mechanics, this alternative viewpoint has taught us much more about the nature of the quantum world than any other interpretation and that's a story worth telling.

The story starts with Einstein who, together with Podolsky and Rosen, was concerned about the instantaneous collapse of the wavefunction. The word "instantaneous" does not sit well with the tenets of special relativity, where the ordering of spacelike separated events can be different for different observers. In Minkowski space, simultaneity is tantamount to acausality.

In 1935, the trio of EPR conceived of a thought experiment in which the knowledge of a measurement performed in one part of space would instantaneously give rise to knowledge of an experiment performed in a far flung region of the universe. This, they argued, was untenable and so quantum mechanics must be incomplete: to be compatible with locality and causality it should be replaced by a new theory at shorter distance scales. These are the hidden variables.

Thirty years later, the physicist John Bell presented a glorious judo move of an argument in which he used the strength of the EPR result against them. He derived an inequality, now known as the *Bell inequality*, which is necessarily satisfied by any local, causal hidden variable theory but is violated by quantum mechanics. In other words, he found a way to experimentally distinguish between hidden variables and quantum mechanics. Needless to say, when the experiments were done they came down firmly on the side of quantum mechanics.

The Bell inequality greatly sharpened our understanding of quantum mechanics and helped us see what it can and can't do. We now understand that there is no acausal behaviour in the collapse of the wavefunction. There is no way that one can use the collapse of the wavefunction to transmit information faster than the speed of light. Instead, the acausality only arises if, like EPR, you insist on some underlying classical mechanism to explain the observed quantum behaviour.

Strictly speaking, hidden variables theories are not quite dead. The Bell arguments only rule out *local* hidden variables theories, meaning those whose dynamics is compatible with special relativity and, consequentially, causality. But these properties were one of the main motivations for introducing hidden variables in the first place! Moreover, there is overwhelming evidence that dynamics in our universe is local and so little reason to think that, at the fundamental level things are non-local but that somehow this is hidden from our view.

Indeed, the lesson to take from EPR and Bell is that quantum mechanics is subtle and clever and achieves things through local dynamics that we may have naively thought impossible. Furthermore, this way of thinking has been astonishingly fruitful: one can draw a clear line from the arguments of Bell to applications such as quantum computing that harness some of the more surprising aspects of the quantum world. You can read more about the EPR argument and the Bell inequalities and their applications in the lectures on Topics in Quantum Mechanics.

3.5.2 Copenhagen and Many Worlds

When people talk about an interpretation of quantum mechanics, they don't usually have in mind a new theory that will ultimately replace quantum mechanics, nor something that can be tested with experiment. Instead, they are searching for some comforting words that they can drape around the equations to help them sleep better at night.

Here I describe two attempts at constructing these words. Neither are comforting. In fact, both are jarring. They do, however, demonstrate the unsettling novelty that necessarily accompanies quantum mechanics.

The *Copenhagen interpretation* was the approach favoured by many (but not all) of the founding fathers of quantum mechanics, and advocated most strongly, but not always clearly, by Niels Bohr. The idea is to take the collapse of the wavefunction seriously. The universe in which we live should be divided into two: the quantum world, described by wavefunctions and the Schrödinger equation, and the familiar classical world described by Newtonian laws of physics. The measurement process provides a bridge between the two, where the nebulous nature of the quantum transmutes into concrete statements of the classical. The price you pay for this is probability.

There is much that is deeply unsatisfying about the Copenhagen interpretation. Both you and me and (for some us) our experimental apparatus are made of atoms which should also obey the laws of quantum mechanics and it seems very odd to deny this.

Moreover, it's far from clear where the dividing line should be drawn between classical and quantum. In fact, it seems preferable to keep the dividing line deliberately fuzzy and ill defined since it helps render certain unpalatable questions illegitimate. While unsatisfying, it does seem that the Copenhagen interpretation is a consistent logical viewpoint, although it may take a lifetime of study to be able to nimbly deflect the awkward questions with the skill of Niels Bohr.

The second approach is known as the *many worlds interpretation*. It was first suggested in the 1950s by Hugh Everett III and gained traction in the subsequent decades. The idea is to take the time dependent Schrödinger equation seriously. A particle that passes through two slits is described by a wavefunction that is non-vanishing in the vicinity of both slits. We say that the particle is in a superposition of states, sitting in two places at the same time. If there's a detection apparatus placed on one slit then the wavefunction doesn't collapse: instead it continues to obey the Schrödinger equation. The detection apparatus now also sits in a superposition of "particle detected" and "particle not detected". When we subsequently look at the apparatus, we too split into a superposition. And so on. The "many worlds" are the different branches of the wavefunction. All of this follows from simply putting our faith in the veracity of the Schrödinger equation.

There is much that is deeply unsatisfying about the many worlds interpretation. The collapse of the wavefunction is largely ignored and the all-important Born rule for constructing probabilities must be added by hand. Relatedly, there is nothing that explains why I only feel myself in one branch of the wavefunction, rather than in a superposition of all possible outcomes. (Admittedly, I don't know what I would feel if I were, in fact, in a superposition of states.)

There is one important facet of quantum mechanics that brings balm to both interpretations above, a process known as *quantum decoherence*. This is one of those topics that is beyond the scope of these lectures, but roughly speaking the idea of decoherence is that as an increasingly large number of particles become entangled in the superposition, so it becomes increasingly difficult to exhibit any quantum interference effects. This, at least, explains why peculiar quantum properties cannot be observed for macroscopic objects. It also helps in understanding how the blurry Copenhagen dividing line can arise, or how the splitting of the many worlds might practically occur. Decoherence is, like the Bell inequalities, an important part of our understanding of quantum dynamics. But it falls short of resolving all the difficulties of either interpretation.

The two interpretations above are painted only with the very broadest brush. There is an almost infinitely bifurcating tree of different viewpoints, with fights frequently breaking out in otherwise dull conferences between the Everettian People's Front and the People's Front of Everett. (Splitters.) Of course, the fiercest arguments are between Copenhagenists and Many Worlders, but they now tend to go to different conferences.

There is, however, an alternative approach, a third way. This is the approach advertised in the heading of this section: you should accept both Copenhagen and many worlds, together with anything that lies in between. At any given moment, choose the one that gives you the warmest feeling when applied to the problem at hand. If you experience a nagging sense of shame or inconsistency in adopting all viewpoints, simply shrug it off. The church of your choice matters not one iota for the simple reason that there is no experimental way to distinguish between them. Should that situation ever change, then so too should your perspective.

Before proceeding, I should mention one pseudo-experimental hope that is often raised in conjunction with the interpretation of quantum mechanics. This is the suggestion that a better understanding of the meaning of quantum mechanics is needed before we can solve some thorny problem, usually mooted as something like quantum gravity or human consciousness. For example, you might want to think about quantum cosmology, where we apply quantum mechanics to the entire universe and it is difficult to envisage the role of an external observer who can collapse the wavefunction. Although a popular opinion, it seems to me that the underlying logic is weak, roughly following the lines "we don't understand Topic X and I'm nervous about quantum mechanics so probably they're related". The same logic could equally well be applied to, say, high temperature superconductivity or the question of why the Higgs boson has its particular mass, but it's never suggested that these can be solved only after invoking the right interpretation of quantum mechanics because it would sound silly. I suspect that the idea that a novel interpretation of quantum mechanics is needed before we can make progress on other important problems is similarly ill-judged.

3.5.3 Shut Up and Calculate

The phrase "shut up and calculate" was coined by the solid state physicist David Mermin as a somewhat cynical, but largely approving take on what is, by any measure, the most popular interpretation of quantum mechanics among practising physicists.

Mermin's point is a simple one. Quantum mechanics is, by some margin, the most successful scientific framework of all time. The formalism provides unambiguous answers to any experiment we care to perform and the fact that these answers are necessarily of a statistical nature is more than offset by the fact that these answers are right.

Embracing quantum mechanics has led, in the century since its discovery, to an unprecedented understanding of the world and resulted in an enormous body of work that, collectively, represents one of the great triumphs of human intellect. Sitting within this body are the subjects of atomic and molecular physics, condensed matter physics, statistical physics, quantum information, mathematical physics, particle physics, and early universe cosmology. Anyone who pauses at the starting point, having deep thoughts about what it all means and muttering the words “ontic” and “epistemic”, is in danger of missing the stunning quantum vistas that await just around the corner. The true meaning of quantum mechanics can be found in the answers it gives about the world we inhabit.

4 A Quantum Particle in Three Dimensions

We will now continue our explorations of the Schrödinger equation, this time focussing on a quantum particle moving in three dimensions, described by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x})$$

where

$$\nabla^2 = \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}$$

Throughout this section, we will focus on central potentials, with

$$V(\mathbf{x}) = V(r) \quad \text{with } r = |\mathbf{x}|$$

These are both the simplest potentials to study and, happily, the kinds of potentials that are most useful for physics.

It's worth recalling how we approached such potentials when we first met them in Classical Mechanics. In that context, everything became easier once we made use of the angular momentum vector

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}$$

This is a conserved quantity in a central potential. To see this we just need to note that $\dot{\mathbf{x}}$ is parallel to $\mathbf{p}$ and $\dot{\mathbf{p}}$ is parallel to $\mathbf{x}$. This latter fact follows from the classical equation of motion $\dot{\mathbf{p}} = -\nabla V$ with the observation that ∇V is parallel to $\mathbf{x}$ for a central potential. We then have

$$\frac{d\mathbf{L}}{dt} = \dot{\mathbf{x}} \times \mathbf{p} + \mathbf{x} \times \dot{\mathbf{p}} = 0$$

When solving central body problems in classical mechanics, we use the conservation of angular momentum twice. First we use the fact that the direction of $\mathbf{L}$ is fixed to reduce the problem from 3d to 2d since the particle only moves in the plane $\mathbf{L} \cdot \mathbf{x} = 0$. Later we use the fact that the magnitude $|\mathbf{L}|$ is fixed to reduce the problem to motion in the radial direction. Then we solve what is essentially a 1d problem.

In this section we will see that a similar strategy works for quantum mechanics. The Schrödinger equation

$$\hat{H}\psi = E\psi$$

is a partial differential equation. By the time we get to grips with angular momentum, it will be an ordinary differential equation of the same kind that we solved when considering a particle moving in one dimension.

4.1 Angular Momentum

The angular momentum operator is

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = -i\hbar \hat{\mathbf{x}} \times \nabla$$

In components, with $\mathbf{x} = (x_1, x_2, x_3)$, this means

$$\begin{aligned}
\hat{L}_1 &= -i\hbar \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \\
\hat{L}_2 &= -i\hbar \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \\
\hat{L}_3 &= -i\hbar \left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1} \right)
\end{aligned}$$

Alternatively, these can be summarised in index notation as

$$\hat{L}_i = -i\hbar \, \epsilon_{ijk} \, x_j \frac{\partial}{\partial x_k}$$

It's not hard to check that the angular momentum operators are Hermitian. Indeed, this really follows immediately from the fact that both $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ are Hermitian.

4.1.1 Angular Momentum Commutation Relations

The three angular momentum operators do not mutually commute. They obey the relations

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k \tag{4.1}$$

From a physics perspective, this means that a quantum particle cannot have a well defined angular momentum in all three directions simultaneously! If, for example, you know the angular momentum L_x then there will necessarily be some uncertainty in the angular momentum in the other two directions.

Although it goes beyond the scope of this course, I should point out that the commutation relations (4.1) are very famous in mathematics and appear in many places that have nothing to do with quantum mechanics. These equations define what mathematicians call a *Lie algebra*, in this case the algebra $su(2)$. It is very closely related to the group $SU(2)$ which, in turn, is almost (but not quite!) the same thing as the group of rotations $SO(3)$. In some sense, the commutation relations (4.1) distill the essence of rotation. The "almost but not quite" of the previous sentence opens up a number of weird and wonderful loopholes that the quantum world exploits. (Like, for example, the fact that there are particles called fermions that don't come back to themselves when rotated by 360°.) We discussed some of these issues briefly when exploring special relativity in the lectures on Dynamics and Relativity and we'll meet them many more times in later courses.

Let's prove the commutation relations (4.1). It will suffice to prove just one case, say

$$[\hat{L}_1, \hat{L}_2] = i\hbar \hat{L}_3 \tag{4.2}$$

To check this, we recall that operator equations of this kind should be viewed in terms of their action on functions and then just plug in the appropriate definitions,

$$\begin{aligned}[\hat{L}_1, \hat{L}_2]\psi = -\hbar^2 &\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)\psi \\ &+\hbar^2 \left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\psi\end{aligned}$$

A little algebra will convince you that nearly all terms cancel. The only ones that survive are

$$[\hat{L}_1, \hat{L}_2]\psi = \hbar^2\left(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1}\right)\psi = i\hbar\hat{L}_3\psi$$

Because this holds for all $\psi(\mathbf{x})$, it is equivalent to the claimed result (4.2). The other commutation relations (4.1) follow in the same vein.

Total Angular Momentum

We can also look at the magnitude of the angular momentum. It's more useful to look at the $\mathbf{L}^2$ rather than $|\mathbf{L}|$. This is associated to the *total angular momentum* operator

$$\hat{\mathbf{L}}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2$$

This is again a Hermitian operator. It commutes with all $\hat{L}_i$,

$$[\hat{\mathbf{L}}^2, \hat{L}_i] = 0 \tag{4.3}$$

This is important. As we saw above, quantum mechanics doesn't allow us to assign simultaneous values to the angular momentum in all directions. However, a quantum state can have a specific total angular momentum – meaning that it is an eigenstate of $\hat{\mathbf{L}}^2$ – and also a specific value of angular momentum in one chosen direction – meaning that it is also an eigenstate of, say, $\hat{L}_3$.

To prove (4.3) we will first need a simple lemma. For any operators $\hat{O}$ and $\hat{M}$,

$$[\hat{O}^2, \hat{M}] = \hat{O}[\hat{O}, \hat{M}] + [\hat{O}, \hat{M}]\hat{O} \tag{4.4}$$

To prove this, we start from the right-hand side and expand out

$$\begin{aligned}\hat{O}[\hat{O}, \hat{M}] + [\hat{O}, \hat{M}]\hat{O} &= \hat{O}^2\hat{M} - \hat{O}\hat{M}\hat{O} + \hat{O}\hat{M}\hat{O} - \hat{M}\hat{O}^2 \\ &= \hat{O}^2\hat{M} - \hat{M}\hat{O}^2 = [\hat{O}^2, \hat{M}]\end{aligned}$$

We now just use this result repeatedly to prove (4.3). We want to show that, for example,

$$[\hat{L}_1^2, \hat{L}_1] + [\hat{L}_2^2, \hat{L}_1] + [\hat{L}_3^2, \hat{L}_1] = 0$$

The first of these is trivial: all operators commute with themselves so $[\hat{L}_1^2, \hat{L}_1] = 0$. Using (4.4), the next two can be written as

$$\begin{aligned}[\hat{L}_2^2, L_1] &= \hat{L}_2[\hat{L}_2, L_1] + [\hat{L}_2, \hat{L}_1]\hat{L}_2 \\ &= -i\hbar(\hat{L}_2\hat{L}_3 + \hat{L}_3\hat{L}_2) \end{aligned} \tag{4.5}$$

where, to get to the second line, we've used the commutation relations (4.1). We also have

$$\begin{aligned}[\hat{L}_3^2, L_1] &= \hat{L}_3[\hat{L}_3, L_1] + [\hat{L}_3, \hat{L}_1]\hat{L}_3 \\ &= i\hbar(\hat{L}_3\hat{L}_2 + \hat{L}_2\hat{L}_3) \end{aligned} \tag{4.6}$$

Adding (4.5) and (4.6) gives us the result (4.3) that we wanted.

Angular Momentum in a Central Potential

In classical mechanics, angular momentum is only useful when we have a central potential

$$V(\mathbf{x}) = V(r)$$

Only in this case is angular momentum conserved.

The corresponding statement in quantum mechanics is that, for a central potential, we have

$$[\hat{H}, \hat{L}_i] = [\hat{H}, \hat{\mathbf{L}}^2] = 0 \tag{4.7}$$

Again, this is important. It means that eigenstates of the Hamiltonian can also be chosen to be eigenstates of the total angular momentum and of angular momentum in *one* chosen direction. A quantum particle can have simultaneous values for all three of these quantities. As we move forward, this is the result that we will allow us to solve the 3d Schrödinger equation.

Before we can do that, we first have to prove (4.7). It follows from some straightforward algebra that is very similar in spirit to what we've done so far. You can first show that

$$[\hat{L}_i, \hat{x}_j] = i\hbar\,\epsilon_{ijk}\hat{x}_k \quad \text{and} \quad [\hat{L}_i, \hat{p}_j] = i\hbar\,\epsilon_{ijk}\hat{p}_k$$

From this, it's a small step to show that

$$\begin{aligned} [\hat{L}_i, \hat{\mathbf{x}}^2] &= [\hat{L}_i, \hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2] = 0 \\ \text{and} \quad [\hat{L}_i, \hat{\mathbf{p}}^2] &= [\hat{L}_i, \hat{p}_1^2 + \hat{p}_2^2 + \hat{p}_3^2] = 0 \end{aligned}$$

But this is all we need. The Hamiltonian for a central potential is a function only of $\hat{\mathbf{p}}^2$ and $\hat{\mathbf{x}}^2$,

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r)$$

where $r^2 = \mathbf{x}^2$. So we're guaranteed to get $[\hat{H}, \hat{L}_i] = 0$. Since the Hamiltonian commutes with each angular momentum operator, it also commutes with the total angular momentum operator $\hat{\mathbf{L}}^2$.

The upshot of this analysis is that a particle moving in a central potential can sit in simultaneous eigenstates of three operators, which we usually take to be:

$$\hat{H}\ ,\quad \hat{\mathbf{L}}^2\ ,\quad \text{and} \quad \hat{L}_3$$

The associated eigenvalues are energy, total angular momentum, and the angular momentum in the $z = x_3$ direction. In what follows, all energy eigenstates are labelled by these three numbers.

Note also, that this is the maximum set of mutually commuting operators. For a generic central potential $V(r)$, there are no further operators lurking out there that also commute with these three.

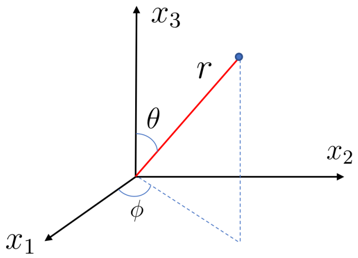
4.1.2 The Eigenfunctions are Spherical Harmonics

Our next task is to figure out the eigenfunctions and eigenvalues of the angular momentum operators $\hat{\mathbf{L}}$. As you might expect, things become significantly simpler if we work in spherical polar coordinates. These are defined to be

$$\begin{aligned} x_1 &= r\sin\theta\cos\phi \\ x_2 &= r\sin\theta\sin\phi \\ x_3 &= r\cos\theta \end{aligned} \tag{4.8}$$

The relevant ranges of the angle are $0 \le \theta \le \pi$ and $0 \le \phi < 2\pi$ as shown in the figure.

It's straightforward to write the angular momentum operators in spherical polar coordinates. We just need to use the chain rule to get, for example,



$$\begin{aligned}\frac{\partial}{\partial x_1} &= \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x_1}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x_1}\frac{\partial}{\partial \phi} \\ &= \sin\theta\cos\phi\frac{\partial}{\partial r} + \cos\theta\cos\phi\frac{1}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{\sin\theta}\frac{1}{r}\frac{\partial}{\partial\phi}\end{aligned}$$

with similar results for $\partial/\partial x_2$ and $\partial/\partial x_3$.

Combining these, we can write the angular momentum operators as

$$\begin{aligned}\hat{L}_1 &= i\hbar\left(\cot\theta\cos\phi\frac{\partial}{\partial\phi} + \sin\phi\frac{\partial}{\partial\theta}\right) \\ \hat{L}_2 &= i\hbar\left(\cot\theta\sin\phi\frac{\partial}{\partial\phi} - \cos\phi\frac{\partial}{\partial\theta}\right) \\ \hat{L}_3 &= -i\hbar\frac{\partial}{\partial\phi}\end{aligned} \tag{4.9}$$

Note that the angular momentum operators care nothing for how the wavefunctions depend on the radial coordinate r. The angular momentum of a state is, perhaps unsurprisingly, encoded in how the wavefunction varies in the angular directions θ and ϕ. Furthermore, $\hat{L}_3$ takes a particularly straightforward form, simply because x_3 is singled out as a special direction in spherical polar coordinates.

We also need an expression for the total angular momentum operator. This can be written most simply as

$$\hat{\mathbf{L}}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2 = -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right] \tag{4.10}$$

Again, we should be careful in interpreting what this means. In particular, the first $\partial/\partial\theta$ acts both on the $\sin\theta$ in round brackets, and also on whatever function the operator $\hat{\mathbf{L}}^2$ hits.

Our goal is to find simultaneous eigenfunctions for $\hat{L}_3$ and $\hat{\mathbf{L}}^2$. We'll ignore all r dependence for now, and reconsider it in the following sections when we solve the Schrödinger equation. The $\hat{L}_3$ eigenfunction is straightforward: we can take

$$\psi(\theta,\phi) = Y(\theta)e^{im\phi} \tag{4.11}$$

for any function $Y(\theta)$. The wavefunction is single valued in ϕ, meaning $\psi(\theta,\phi) = \psi(\theta,\phi+2\pi)$, only if m is an integer. Using (4.9), we see that the corresponding eigenvalues are

$$\hat{L}_3 e^{im\phi} = m\hbar\, e^{im\phi} \qquad m \in \mathbf{Z}$$

We learn that the angular momentum in the $z = x_3$ direction is quantised in units of $\hbar$. So too, of course, is the angular momentum in any other direction. But, as we've stressed above, if we sit in an eigenstate of $\hat{L}_3$, then we can't also sit in an eigenstate of $\mathbf{n}\cdot\hat{\mathbf{L}}$ for any direction $\mathbf{n}$ other than the z-direction, with $\mathbf{n} = (0,0,1)$.

Next we turn to the $\hat{\mathbf{L}}^2$ eigenvalue equation. We keep the ansatz (4.11) and look for solutions

$$\hat{\mathbf{L}}^2\, Y(\theta)e^{im\phi} = \lambda Y(\theta)e^{im\phi}$$

Using our expression (4.10), this becomes

$$\begin{aligned} & -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right] Y(\theta)e^{im\phi} = \lambda Y(\theta)e^{im\phi} \\ \Longrightarrow\quad & -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - m^2\right] Y(\theta) = \lambda Y(\theta) \end{aligned} \tag{4.12}$$

Solutions to this equation are a well-studied class of mathematical functions called *associated Legendre Polynomials.* Their construction comes in two steps. First, we introduce an associated set of functions known as (ordinary) *Legendre Polynomials*, $P_l(x)$. These obey the differential equation

$$\frac{d}{dx}\left[(1-x^2)\frac{dP_l}{dx}\right] + l(l+1)P_l(x) = 0 \qquad l = 0,1,2,\ldots$$

The $P_l(x)$, with $l = 0,1,2,\ldots$ are polynomials of degree l. The eigenfunction solutions (4.12) are then associated Legendre polynomials $P_{l,m}(\cos\theta)$, defined by

$$Y(\theta) = P_{l,m}(\cos\theta) = (\sin\theta)^{|m|}\,\frac{d^{|m|}}{d(\cos\theta)^{|m|}}P_l(\cos\theta)$$

The corresponding eigenvalue is

$$\lambda = l(l+1)\hbar^2$$

Because $P_l(\cos\theta)$ is a polynomial of degree l, you only get to differentiate it l times before it vanishes. This means that the $\hat{L}_3$ angular momentum is constrained to take values that lie in the range

$$-l \le m \le l$$

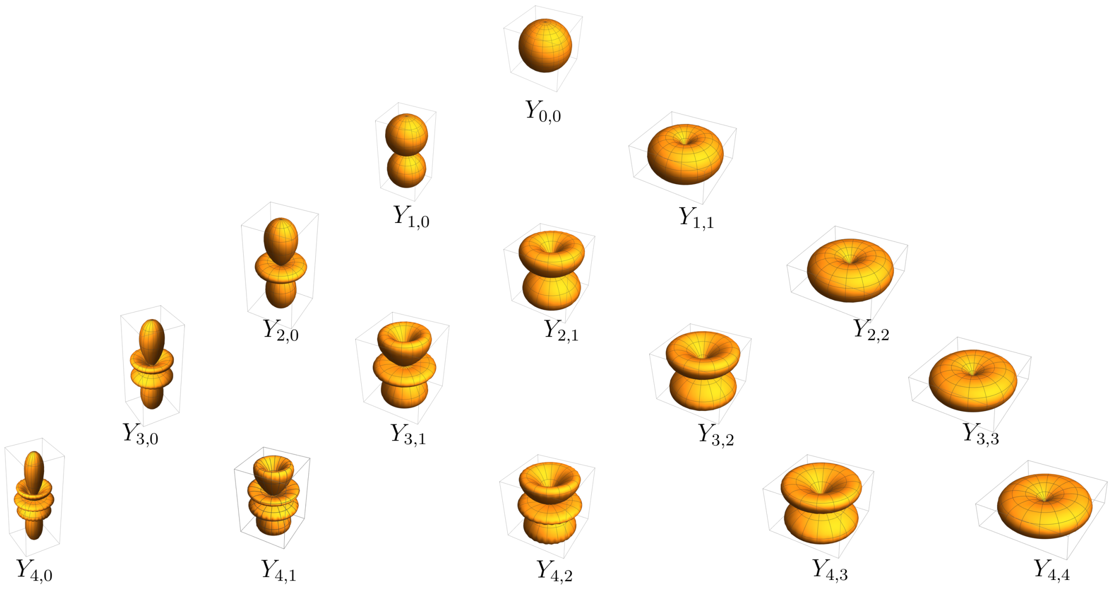


Figure 17. The $l = 0, 1, 2, 3$ and 4 spherical harmonics.

The upshot of this analysis is that the simultaneous eigenstates of $\hat{\mathbf{L}}^2$ and $\hat{L}_3$ are given by functions that are labelled by two integers, l and m with $|m| \leq l$,

$$\psi(\theta, \phi) = Y_{l,m}(\theta, \phi)$$

These functions are called *spherical harmonics* and are given by

$$Y_{l,m}(\theta, \phi) = P_{l,m}(\cos\theta)e^{im\phi}$$

The corresponding eigenvalues are

$$\begin{aligned} \hat{\mathbf{L}}^2 Y_{l,m}(\theta, \phi) &= l(l+1)\hbar^2\, Y_{l,m}(\theta, \phi) \\ \hat{L}_3 Y_{l,m}(\theta, \phi) &= m\hbar\, Y_{l,m}(\theta, \phi) \end{aligned}$$

The integer l is called the *total angular momentum quantum number* (even though, strictly speaking, the total angular momentum is really $\sqrt{l(l+1)}\hbar$.) The integer m is called the *azimuthal angular momentum.*

The requirement that $|m| \leq l$ is simply telling us that the angular momentum in a any given direction (in this case z) can't be more than the total angular momentum. When $m = +l$ (or $m = -l$) you should think of the object as having angular momentum as maximally aligned (or anti-aligned) with the z-axis. When $|m| < l$, you should think

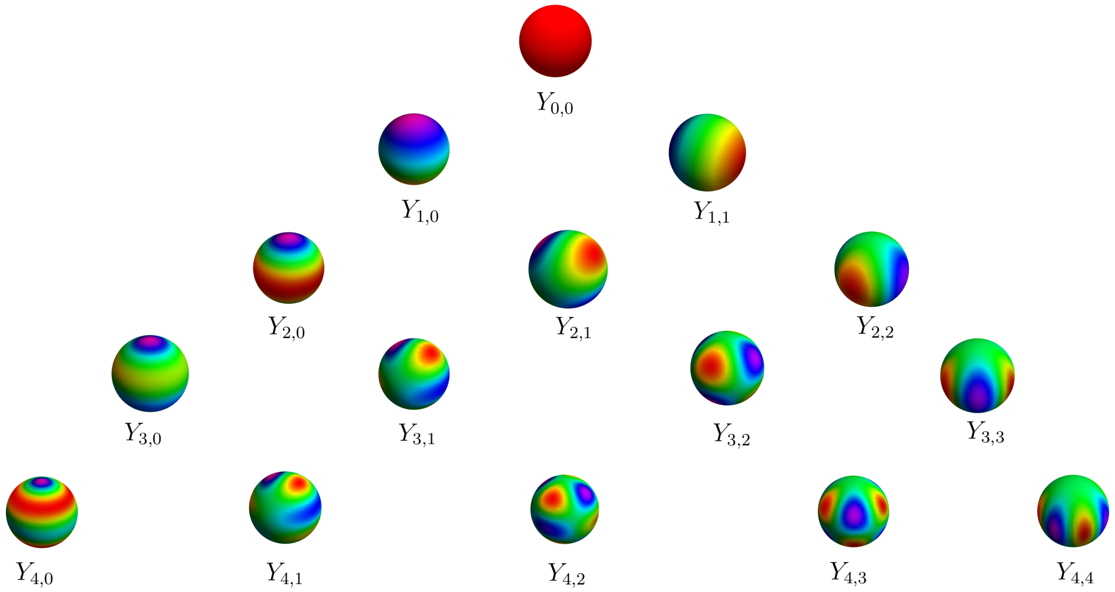


Figure 18. An alternative way of depicting the $l = 0, 1, 2, 3$ and 4 spherical harmonics.

of the angular momentum as aligned in some intermediate direction. Of course, all of these thoughts should be quantum thoughts: even when $m = l$, if you measure that angular momentum in a perpendicular direction like $\hat{L}_1$ then you're not guaranteed to get zero. Instead there will be a probability distribution of answers centred around zero.

To build some intuition, here are some of the first spherical harmonics. The $l = 0$ case is just a constant

$$Y_{0,0} = 1$$

This is the case when a particle has no angular momentum and, correspondingly, its wavefunction has no angular dependence. In the context of atomic physics, it is referred to as an *s-wave*. The next collection of spherical harmonics all have total angular momentum $l = 1$,

$$Y_{1,-1} = \sin\theta\, e^{-i\phi} \quad , \quad Y_{1,0} = \cos\theta \quad , \quad Y_{1,1} = \sin\theta\, e^{i\phi}$$

In the context of atomic physics, these are called *p-wave* states. The next, $l = 2$ collection are *d-waves*,

$$Y_{2,\pm 2} = \sin^2\theta\, e^{\pm 2i\phi} \quad , \quad Y_{2,\pm 1} = \sin\theta\, \cos\theta\, e^{\pm i\phi} \quad , \quad Y_{2,0} = 3\cos^2\theta - 1$$

There are various ways to visualise spherical harmonics. For example, in Figure 17,we plot the absolute value $|Y_{l,m}(\theta, \phi)|$ as the distance from the origin in the (θ, ϕ) direction. Taking the absolute value removes the $e^{im\phi}$ dependence, so these plots are symmetric around the z-axis. Alternatively, in Figure 18, we plot $\text{Re}(Y_{l,m}(\theta, \phi))$ on the sphere, with the value denoted by colour.

4.2 Solving the 3d Schrödinger Equation

We now return to the Schrödinger equation which, for a particle moving in a 3d central potential, is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

As we've seen, the symmetry of the problem strongly suggests that we work in spherical polar coordinates (4.8), in terms of which the Laplacian becomes

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2}$$

Crucially, the angular parts of the Laplacian are identical to the total angular momentum operator $\hat{\mathbf{L}}^2$ that we met in (4.10). This means that we can equally well write the Laplacian as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2}$$

Now we can see the utility of working with angular momentum eigenstates. We look for solutions to the Schrödinger equation of the form

$$\psi(r, \theta, \phi) = R(r)Y_{l,m}(\theta, \phi)$$

where $R(r)$ the radial wavefunction. All of the angular dependence now sits in an eigenstate of $\hat{\mathbf{L}}^2$. Substituting this into the Schrödinger equation, what looks like a complicated partial differential equation turns into a more straightforward ordinary differential equation

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + V_{\text{eff}}(r)R = ER \tag{4.13}$$

where the potential $V(r)$ is replaced with the effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$$

We've met this effective potential before. It's exactly the same as the effective potential that emerges when solving classical mechanics problems in a central potential. The additional term is called the *angular momentum barrier.* The only difference from our previous classical result is that the angular momentum is now quantised in units of $\hbar^2$.

Note that the azimuthal angular momentum quantum number m doesn't appear in the Hamiltonian. (Sadly for us, there is an "m" sitting in both the kinetic term and in the effective potential, but this is the mass! Not the angular momentum quantum number. Sorry! The canonical name for both is m. It's rare that it leads to confusion precisely because the azimuthal quantum number doesn't appear in the Hamiltonian.)

Because the energy doesn't depend on the $\hat{L}_3$ eigenvalue m, it means that the energy spectrum for any particle moving in a central potential will always be degenerate, with multiple eigenstates all having the same energy. In contrast, the energy will usually depend on the total angular momentum l. This means that we expect each energy eigenvalue to have

$$\text{Degeneracy} = 2l + 1 \tag{4.14}$$

which comes from the different $Y_{l,m}$ states with $m = -l, -l + 1, \ldots, l - 1, l$.

The effective Schrödinger equation (4.13) takes a very similar form to those that we solved in Section 2. The only slight difference is the more complicated kinetic term, together with some associated issues about the need for a finite wavefunction at $r = 0$. However, these issues notwithstanding, we're now largely on familiar territory. In the rest of this section we'll briefly look at some appetisers before, in Section 4.3, we turn to our main course: the hydrogen atom.

4.2.1 The 3d Harmonic Oscillator

The harmonic oscillator provides a particularly simple example of the 3d Schrödinger equation because we can solve it in either Cartesian or polar coordinates. In Cartesian coordinates, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$$

We see that the Hamiltonian just decomposes into three copies of the 1d harmonic oscillator: one for each direction. This means that we can just read off the energy spectrum from our earlier result (2.29). The spectrum of the 3d harmonic oscillator is given by

$$E = \hbar\omega\left(\frac{3}{2} + N\right) \tag{4.15}$$

where

$$N = n_1 + n_2 + n_3 \quad , \quad n_i = 0, 1, 2, \ldots$$

All of the subtleties lie in the degeneracy of the spectrum. The ground state has energy $E = \frac{3}{2}\hbar\omega$ and is unique. But there are three excited states with energy $E = \frac{5}{2}\hbar\omega$ associated to exciting the harmonic oscillator in the x, y or z direction. There are then 6 states with energy $E = \frac{7}{2}\hbar\omega$, because we could excite one oscillator twice or two oscillators once each. In general, the degeneracy of the N^{th} level is $\frac{1}{2}(N+1)(N+2)$.

How does this look in polar coordinates? It's best to work with the form of the Schrödinger equation (4.13) which is now

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{1}{2}m\omega^2r^2 + \frac{l(l+1)\hbar^2}{2mr^2}\right)R = ER$$

We're now awash with various constants and life will be easier if we can get rid of a few. We make the same scaling (2.22) that we used for the 1d oscillator,

$$y = \sqrt{\frac{m\omega}{\hbar}}r \quad \text{and} \quad \tilde{E} = \frac{2E}{\hbar\omega}$$

The Schrödinger equation then becomes

$$\frac{1}{y^2}\frac{d}{dy}\left(y^2\frac{dR}{dy}\right) - \left(y^2 + \frac{l(l+1)}{y^2}\right)R = -\tilde{E}\psi \tag{4.16}$$

We're going to solve it using the same kind of polynomial expansion that we used for the 1d harmonic oscillator. First, look at the large distance $y \to \infty$ behaviour. Here the dominant terms are

$$\frac{d^2R}{dy^2} - y^2R \approx 0 \quad \Longrightarrow \quad R \approx e^{-y^2/2} \quad \text{as } y \to \infty$$

Next, look at the behaviour near the origin $y \ll 1$. Here the dominant terms in the equation are

$$\frac{d^2R}{dy^2} + \frac{2}{y}\frac{dR}{dy} - \frac{l(l+1)}{y^2}R \approx 0 \quad \text{for } y \ll 1$$

If we make the power-law ansatz $R \sim y^\alpha$, we find

$$\alpha(\alpha-1) + 2\alpha - l(l+1) = 0 \quad \Longrightarrow \quad R \sim y^l \quad \text{as } y \to 0 \tag{4.17}$$

Here we've discarded the second solution $\alpha = -(l+1)$ on the grounds that the resulting wavefunction diverges at the origin. Putting this together, our ansatz for the general solution is

$$R(y) = y^l h(y) e^{-y^2/2}$$

where we take

$$h(y) = \sum_{k=0}^{\infty} a_k y^k$$

At this stage we've got a little bit of algebra to do, plugging our ansatz into the Schrödinger equation (4.16). Once the dust settles, you'll find the result

$$\sum_{k=0}^{\infty} a_k \Big(k(2l+k+1) y^{l+k-2} + (\tilde{E} - (2l+2k+3)) y^{l+k} \Big) = 0 \tag{4.18}$$

We start our recurrence relation by setting

$$a_0 = 1$$

This is just the statement that the small y behaviour is indeed $R \sim y^l$ rather than some higher power. Now note that the first term in our equation will have term proportional to $a_1 y^{l-1}$. But there's nothing to cancel this in the second term. This means that we must set

$$a_1 = 0$$

As we'll see, our recurrence relation will then set $a_k = 0$ for all odd k. To find this recurrence relation, we shift the summation variable $k \to k+2$ in the first term in (4.18) so that all terms have the same power of y^{l+k},

$$\left[\sum_{k=0}^{\infty} a_{k+2}(k+2)(2l+k+3) + \sum_{k=0}^{\infty} a_k \Big(\tilde{E} - (2l+2k+3) \Big) \right] y^{l+k} = 0$$

For this to hold for all y, we must have the following recurrence relation

$$a_{k+2} = \frac{\tilde{E} - (2l+2k+3)}{(k+2)(2l+k+3)}\, a_k$$

At this stage, the argument is the same as we used for the 1d harmonic oscillator. If the recurrence relation fails to terminate then $a_{k+2} \to 2a_k/k$ for large k, but that's bad: it messes up the $e^{-y^2/2}$ behaviour at large y and turns it into a non-normalisable $e^{+y^2/2}$ behaviour. This means that we must find solutions where the recurrence relation terminates. This immediately allows us to read off the energy. If we are to have $a_{2q+2} = 0$ (recall that all a_k for odd k already vanish) then the energy of the state must be

$$E = \hbar\omega \left(\frac{3}{2} + l + 2q \right) \qquad l, q = 0, 1, 2, \ldots \tag{4.19}$$

Let's compare this to our Cartesian result (4.15). Clearly they agree, but the extra work we did in polar coordinates brings more information: it tells us how the energy depends on the total angular momentum l. In particular, the lowest energy state with angular momentum l has $E = \hbar\omega(\frac{3}{2} + l)$.

We also have a better understanding of the degeneracy of states. When N is even, the states with energy $E = \hbar\omega(\frac{3}{2} + N)$ comprise of all even angular momentum states $l = 0, 2, 4, \ldots, N$. Since there are $2l + 1$ states (4.14) associated to each angular momentum l, the total number of states at level N must be

$$\text{Total Degeneracy} = \sum_{k=0}^{N/2} 4k + 1 = N\left(\frac{N}{2} + 1\right) + \frac{N}{2} + 1 = \frac{1}{2}(N+1)(N+2)$$

which agrees with the count from the Cartesian calculation. Similarly, when N is odd the states at energy $E = \hbar\omega(\frac{3}{2} + N)$ comprise of all odd angular momentum states $l = 1, 3, 5, \ldots, N$: again, the total count is $\frac{1}{2}(N+1)(N+2)$.

4.2.2 Bound States in 3d

It is simple to adapt our earlier discussions to understand bound states in 3d. Here we'll be brief as there is only one small punchline that we want to reach.

Consider the spherical finite potential well,

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & \text{otherwise} \end{cases}$$

Clearly this is the 3d version of the 1d finite well that we considered in Section 2.3. The associated 3d radial Schrödinger equation (4.13) is

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right]R = ER$$

Our strategy is to massage the Schrödinger equation into the same form we saw in 1d and then simply invoke some of our earlier results. The only thing we need to fix is the unusual looking derivative terms. But this is easily achieved: we redefine the radial wavefunction as

$$\chi(r) = rR(r) \tag{4.20}$$

Then, written in terms of the new function $\chi(r)$, the Schrödinger equation takes the 1d form

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + \left[V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right]\chi = E\chi \tag{4.21}$$

However, we haven't quite washed away all traces of our 3d origin. Some remnant survives in the boundary conditions that we must impose on χ. First, the wavefunction must be normalisable. Since the $Y_{l,m}$'s don't cause us any trouble, we're left with the requirement

$$\int d^3x\ |\psi|^2 \sim \int_0^\infty dr\ r^2|R|^2 = \int_0^\infty dr\ |\chi|^2 < \infty$$

where the r^2 factor in the middle equation comes from the integration measure for polar coordinates. We see that the normalisability condition restricts the asymptotic $\rightarrow \infty$ behaviour of $\chi(r)$ as it would for a 1d wavefunction. The only novelty is what happens at the origin $r = 0$. If we require that the wavefunction $R(r)$ doesn't diverge at the origin, then clearly the function $\chi(r) = rR(r)$ must obey

$$\chi(0) = 0 \tag{4.22}$$

The derivative $\chi'(r = 0)$ must then be finite.

Here we'll look just for s-wave bound states, with $l = 0$. In this case, the Schrödinger equation (4.21) is identical to those we solved for the 1d problem, but with the novelty that the coordinate $r \in [0, \infty)$ rather than the $x \in (-\infty, +\infty)$, together with the additional requirement (4.22).

There is a simple fix to both these issues. We solve the Schrödinger equation (4.21) pretending that $r \in (-\infty, +\infty)$, defining $V(-r) = V(+r)$. But we then look for *odd* solutions with

$$\chi(-r) = -\chi(+r)$$

This condition ensures that we have $\chi(0) = 0$ as required. Moreover, we're not missing any solutions. As we saw in Section 2, with an even potential all solutions are either even or odd, but the even solutions have $\chi(0) \neq 0$ and so are illegitimate for our present purposes.

This is all we need. We solved for the parity odd solutions in Section 2.3.1. In contrast to the parity even solutions, their existence is not guaranteed. They only arise when the potential is suitably deep or suitably wide, meaning (2.38)

$$\frac{8mV_0}{\hbar^2\pi^2} > \frac{1}{a^2}$$

This is our minor punchline. In 1d, there are potentials (like the finite well) where a bound state is always guaranteed. This is no longer the case in 3d where very shallow potentials do not house bound states.

Perhaps surprisingly, the case of $d = 2$ turns out to be that same as $d = 1$ with bound states guaranteed for certain classes of potentials, no matter how shallow. It is only in $d \geq 3$ that you need a deep, wide potential to trap a quantum particle.

4.2.3 Why Can't the Wavefunction Diverge at the Origin?

Above we confidently asserted that the wavefunction $R(r)$ should be finite at the origin. This gives a suitable boundary condition that allows us to determine which bound states exist. In the next section, we'll use the same boundary condition to determine the bound states of the hydrogen atom. It also underlies the rest of the periodic table and all of chemistry. All of which is to say, the requirement that $R(r)$ is finite at the origin is rather important. So why is it the right thing to impose?

The obvious answer is that we need the wavefunction to be normalisable, i.e. $\psi \in L^2(\mathbf{R}^3)$,

$$\int_0^\infty dr\ r^2|R|^2 < \infty \tag{4.23}$$

From the analysis (4.17), we see that the discarded, divergent solution scales as

$$R(r) \sim r^{-(l+1)} \quad \text{as} \quad r \to 0$$

with l the angular momentum. For $l \geq 1$, this is indeed non-normalisable and it's clear that we must throw it away. But for the $l = 0$ s-wave, the wavefunction goes as $R(r) \sim 1/r$ near the origin and there's no problem with normalisability, with the r^2 in the measure of (4.23) coming to our rescue. Nonetheless, this wavefunction should also be discarded. Why?

The answer is rather subtle and requires us to look more closely at the relevant Hilbert space and, more importantly, at the operators that act on it. Recall that back in Section 3.2, we argued that observables in quantum mechanics should be Hermitian, or self-adjoint. As we now show, it turns out that the Hamiltonian in our 3d examples is *not* self-adjoint on the whole Hilbert space $L^2(\mathbf{R}^3)$, but only on a subspace of function that obey a certain boundary condition at the origin. And this means that when searching for physical states, we should restrict to this smaller Hilbert space.

To see this, it's sufficient to just look at the radial part of the Hamiltonian, which acts on a radial wavefunction $R(r)$ as

$$\hat{H}_{\text{rad}} R = -\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)$$

To show that $\hat{H}_{\text{rad}}$ is a self-adjoint operator, we simply need to do an integration by parts. Given two radial wave wavefunctions $R(r)$ and $S(r)$ (both of which we take to be real), we have

$$\begin{aligned}
\langle S|\hat{H}_{\text{rad}}R\rangle &= \int_0^\infty dr\ r^2 S\,\hat{H}_{\text{rad}}R \\
&= -\frac{\hbar^2}{2m}\int_0^\infty dr\ S\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) \\
&= -\frac{\hbar^2}{2m}\left[r^2 S\frac{dR}{dr}\right]_0^\infty + \frac{\hbar^2}{2m}\int_0^\infty dr\ r^2\frac{dS}{dr}\frac{dR}{dr} \\
&= -\frac{\hbar^2}{2m}\left[r^2 S\frac{dR}{dr} - r^2\frac{dS}{dr}R\right]_0^\infty - \frac{\hbar^2}{2m}\int_0^\infty dr\ \frac{d}{dr}\left(r^2\frac{dS}{dr}\right)R
\end{aligned}$$

We see that we only have a self-adjoint Hamiltonian, with $\langle S|\hat{H}_{\text{rad}}R\rangle = \langle \hat{H}_{\text{rad}}S|R\rangle$ if the boundary terms, that we picked up when doing an integration by parts, vanish. This means that we must have

$$\lim_{r\to 0} r^2\left[S\frac{dR}{dr} - \frac{dS}{dr}R\right] = 0 \quad \text{for all } S(r) \text{ and } R(r) \tag{4.24}$$

This is clearly satisfied if R and S are finite at the origin. But it is *not* satisfied if, for example, S is finite at the origin while $R(r) \sim 1/r$. This means that to have a self-adjoint Hamiltonian, and all the goodness that brings, we can't admit all functions in $L^2(\mathbf{R}^3)$ as physical states. We must throw some out so the physical Hilbert space is a subspace of $L^2(\mathbf{R}^3)$. And we throw out those that diverge as $R \sim 1/r$ at the origin.

4.3 The Hydrogen Atom

The hydrogen atom is the simplest of all atoms. It consists of a single electron orbiting a proton, held in place by the Coulomb force

$$F = -\frac{\partial V}{\partial r} = -\frac{e^2}{4\pi\epsilon_0 r^2}$$

Here the electron has charge $-e$ and the proton charge $+e$. The constant ϵ_0 is a way to characterise the strength of the electrostatic force. For now, we'll give values for neither e nor ϵ_0 but we'll return to this after we've computed the energy spectrum. The associated Coulomb potential is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Our task in this section is to solve the 3d Schrödinger equation with this potential.

Following our discussion earlier in this section, we know that solutions will be characterised by three integers, n, l and m, such that:

- n labels the energy state. We will take it run from $n = 1, 2, 3, \ldots$. In the context of the hydrogen atom it is sometimes called the *principal quantum number.*.
- l labels the total angular momentum. It appears in the eigenvalue of $\hat{\mathbf{L}}^2$ as $l(l+1)\hbar^2$.
- m labels the azimuthal angular momentum, also known as the angular momentum in the z direction. It appears as the eigenvalue $m\hbar$ of $\hat{L}_3$.

We look for wavefunctions of the form

$$\psi(r, \theta, \phi) = R(r)\, Y_{l,m}(\theta, \phi)$$

The Schrödinger equation (4.13) for the hydrogen atom is then given by,

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + \left(-\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e r^2}\right) R = ER$$

where m_e is the electron mass (and the subscript helps avoid confusion with the azimuthal angular momentum). Before we get going, let's introduce some new variables so that we don't have to lug around all those constants on our journey. We write

$$\beta = \frac{e^2 m_e}{2\pi\epsilon_0\hbar^2} \quad \text{and} \quad \frac{1}{a^2} = -\frac{2m_e E}{\hbar^2} \tag{4.25}$$

In this second of these redefinitions, we've anticipated the fact that we're looking for negative energy bound states of the Coulomb potential, so that $a^2 > 0$. You can check that a has dimension of length. This cleans up the Schrödinger equation a little, which now reads

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{l(l+1)}{r^2}R + \frac{\beta}{r}R = \frac{R}{a^2} \tag{4.26}$$

All we have to do now is solve it.

4.3.1 The Energy Spectrum

First, let's look at the asymptotic behaviour of solutions as $r \to \infty$. Here the Schrödinger equation (4.26) is dominated by

$$\frac{d^2R}{dr^2} \approx \frac{R}{a^2} \quad \Longrightarrow \quad R(r) \approx e^{-r/a} \quad \text{as } r \to \infty$$

We see that a, which recall is related to the inverse energy of the system, sets the characteristic size of the wavefunction. Meanwhile, near the origin $r = 0$ the dominant terms are

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{l(l+1)}{r^2}R \approx 0 \quad \text{for } r \ll 1$$

This is the same equation that we got when studying the 3d harmonic oscillator in Section 4.2. If we make the power-law ansatz $R \sim r^\alpha$, we find

$$\alpha(\alpha - 1) + 2\alpha - l(l+1) = 0 \quad \Longrightarrow \quad R \sim r^l \text{ as } r \to 0$$

where we've again discarded the second solution $\alpha = -(l+1)$ because it results in a wavefunction that diverges at the origin.

All of this motivates us to look for solutions of the form

$$R(r) = r^l f(r) e^{-r/a} \tag{4.27}$$

where $f(r)$ is a polynomial

$$f(r) = \sum_{k=0} c_k r^k \tag{4.28}$$

where we must have $c_0 \neq 0$ so that we get the right behaviour at small r.

Now we've got to roll up our sleeves and substitute this into the Schrödinger equation to get a recurrence relation for the coefficients c_k. It's best to go slowly. First you can check that if you plug the ansatz (4.27) into (4.26), then the function $f(r)$ must satisfy

$$\frac{d^2f}{dr^2} + 2\left(\frac{l+1}{r} - \frac{1}{a}\right)\frac{df}{dr} - \frac{1}{ar}\left(2(l+1) - \beta a\right) f = 0$$

Next, substitute the power-law ansatz (4.28) into this differential equation to find

$$\sum_{k=0}^{\infty} c_k \left[(k(k-1) + 2k(l+1)) r^{k-2} - \frac{1}{a}(2k + 2(l+1) - \beta a) r^{k-1} \right] = 0$$

Finally, shift the dummy summation variable $k \to k - 1$ in the second term to get a uniform power of r^{k-2}. This then gives us our desired recurrence relation

$$c_k = \frac{1}{ak}\frac{2(k+l) - \beta a}{k + 2l + 1}\, c_{k-1} \tag{4.29}$$

The argument that we now make follows that of the harmonic oscillator. Suppose that this recurrence relation fails to terminate. Then, as $k \to \infty$, we have

$$c_k \to \frac{2}{ak} c_{k-1}$$

But, as we explained in Section 2.2, this is the kind of expansion that we get from exponentially divergent functions of the form $f(r) = e^{2r/a}$. On a mathematical level, there's nothing wrong with these solutions: they just change the asymptotic form of (4.27) from $e^{-r/a}$ to $e^{+r/a}$. But we've no use of such solutions for physics because they're badly non-normalisable.

This means that, once again, we need to restrict attention to series that terminate. Which, in turn, means that there should be a positive integer q for which $c_q = 0$, while $c_k \neq 0$ for all $k < q$. Clearly this holds only if a takes special values,

$$a = \frac{2}{\beta}(q + l) \quad \text{with } q = 1, 2, \ldots$$

Alternatively, since both q and l are integers, we usually define the integer

$$n = q + l$$

which obviously obeys $n > l$. We then have

$$a = \frac{2}{\beta} n$$

All that's left is to chase through the definition of the various variables in this expression. These can be found in (4.25). The length scale a is related to the energy scale E which is given by

$$E = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \qquad n = 1, 2, \ldots \tag{4.30}$$

This is our final result for the energy spectrum of the hydrogen atom. The integer n coincides with what we previously called the *principal quantum number*.

There's a whole lot to unpick in this expression. First, we can substitute this expression for E into the rescaling that we performed in (4.25) to get an expression for the length scale a that appeared in the equations. We have

$$a = n r_B \quad \text{with} \quad r_B = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} = \frac{\hbar}{m_e c \alpha} \approx 5.3 \times 10^{-11}\ m \tag{4.31}$$

We've factored out the state-dependent integer n to get a length scale r_B, written purely in terms of fundamental constants. This is the *Bohr radius*. As we will soon see, it sets the characteristic size of the hydrogen atom.

Next, there's the ugly morass of constants sitting on the right-hand side. Clearly they set the energy scale of the bound states. There's actually a better way to organise them to see what's going on. To this end, we introduce the *fine structure constant*,

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$$

At first glance, you may think that this doesn't help matters because, rather than simplifying things, we've introduced a new physical constant c, the speed of light. However, the advantage of the fine structure constant is that it's a dimensionless quantity. As you can see, it includes the expression $e^2/4\pi\epsilon_0$ familiar from the Coulomb force and it should be viewed as the convention-independent way to characterise the strength of electromagnetism. Moreover, it takes a value that's easy to remember:

$$\alpha \approx \frac{1}{137} \approx 0.0073$$

Written in terms of the fine structure constant, the energy eigenvalues are

$$E = -\frac{\alpha^2 m_e c^2}{2}\frac{1}{n^2}$$

This makes it clear what's really setting the energy scale of the hydrogen atom: it is the rest mass energy of the electron! This is given by

$$m_e c^2 \approx 0.51 \times 10^6 \text{ eV}$$

A million electronvolts is an energy scale of relativistic particle physics. It is much larger than the typical energy scales of atomic physics but we can see why: there are two powers of the fine structure constant that interpolate between the two. The energy scale of the hydrogen atom is set by

$$\text{Ry} = \frac{\alpha^2 m_e c^2}{2} \approx 13.7 \text{ eV}$$

This is called the *Rydberg*. As you can see, the (negative) ground state energy of the hydrogen atom is exactly one Rydberg; the higher excited states have energy $E = -\text{Ry}/n^2$. Note that the hydrogen atom has an infinite number of negative energy bound states.

Next there's a surprise. The energy spectrum of hydrogen does not depend on the angular momentum l. At least, that's almost true: it depends only in the sense that the states for a given energy $E = -\text{Ry}/n^2$ only include angular momentum $l < n$. We saw a similar phenomenon for the 3d harmonic oscillator in Section 4.2 and this might lead you to think that this is common. It's not. In fact, the only two systems where the energy spectrum doesn't explicitly depend on angular momentum are the harmonic oscillator and the hydrogen atom!

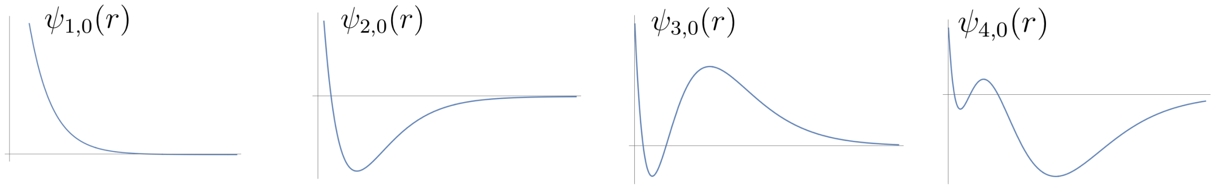


Figure 19. The (un-normalised) s-wave states for $n = 1, 2, 3$ and 4. The functions are plotted on the same range along the x-axis, although the y-axis range varies. Although it's not obvious from these plots, all wavefunctions approach a finite value at $x = 0$.

The angular momentum does affect the degeneracy of the spectrum. Recall that there are $2l + 1$ states (4.14) associated to each total angular momentum l. These are the states labelled by $m = -l, \ldots, +l$. For a fixed energy level n, we can have any total angular momentum $l = 0, \ldots n - 1$. This means that the degeneracy of the state at level n is

$$\text{Total Degeneracy} = \sum_{l=0}^{n-1} (2l + 1) = n^2$$

The $n = 1$ ground state is unique: it sits in $l = 0$ s-wave. There are four $n = 2$ excited states corresponding to the s-wave and three $l = 1$ states of the p-wave. There are nine $n = 3$ excited states, corresponding to the s-wave, the three $l = 1$ p-wave states and five $l = 2$ d-wave states. And so on.

The energy spectrum (4.30) is not quite the end of the story for the hydrogen atom. There are corrections due to special relativity. These corrections split the n^2 degeneracy so that the states with different l, but the same n, have different energies. These splitting are of order α^4, much smaller than the original energies that are of order α^2, and are referred to as the *fine structure* of the hydrogen atom. (In fact, this is where the name "fine structure constant" comes from.) You can read about these corrections in the lectures on Topics in Quantum Mechanics where we also start to explore multi-electron atoms and how to build up the periodic table of elements.

4.3.2 The Wavefunctions

The recurrence relation (4.29) allows us to easily construct the corresponding wavefunctions. A state with energy $E = -\text{Ry}/n^2$ has a wavefunction

$$\psi_{n,l,m}(r, \theta, \phi) = r^l f_{n,l}(r) e^{-\beta r/2n}\, Y_{l,m}(\theta, \phi)$$

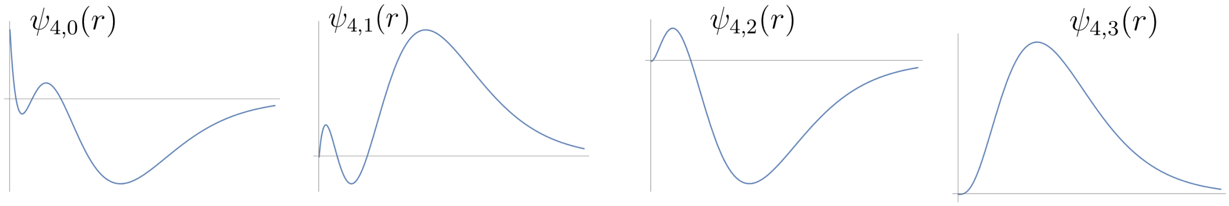


Figure 20. The (un-normalised) wavefunctions for fixed $n = 4$ with angular momentum varying from $l = 0$ (s-wave) to $l = 1$ (p-wave) to $l = 2$ (d-wave) to $l = 3$ (f-wave).

where $\beta = e^2 m_e / 2\pi\epsilon_0\hbar^2$ and $f_{n,l}(r)$ is a polynomial of degree $n - l - 1$, defined by

$$f_{n,l}(r) = \sum_{k=0}^{n-l-1} c_k r^k$$

with

$$c_k = \frac{2}{ak}\frac{k+l-n}{k+2l+1}\, c_{k-1}$$

These are known as *generalised Laguerre polynomials*. They are more conventionally written as $f_{n,l}(r) := L^{2l+1}_{n-l-1}(2r/nr_B)$.

The $n = 1$ ground state wavefunction necessarily has vanishing angular momentum. It is simply

$$\psi(r) = \sqrt{\frac{1}{\pi r_B^3}}\, e^{-r/r_B}$$

where the coefficient in front is chosen to normalise the wavefunction. We now see clearly that the Bohr radius r_B, defined in (4.31), does indeed set the size of the ground state of the hydrogen atom.

To get some sense for the higher wavefunctions, we've plotted the s-wave states for $n = 1$ to $n = 4$ in Figure 19. Note that each successive higher energy state contains an additional $\psi = 0$ node. In Figure 20 we've fixed the energy level to $n = 4$ and plotted successive higher angular momentum modes. This time we lose a node each time that l increases.

Figure 21. The Balmer $m \longrightarrow 2$ series of the hydrogen spectrum, starting with the $m = 3$ line in red and then showing successive lines towards the ultra-violet.

For any wavefunction in the n^{th} energy level, the peak can be approximated by writing $\psi(r) \approx r^{n-1}e^{-r/r_Bn}$, corresponding to a probability distribution $P(r) \approx r^{2(n-1)}e^{-2r/r_Bn}$. This has a maximum when $P'(r) = 0$, or

$$\frac{2(n-1)}{r} \approx \frac{2}{r_B n} \quad \Longrightarrow \quad r \approx n(n-1)r_B$$

We see that the spatial extent of the higher energy states grows roughly as n^2.

4.4 A Pre-Quantum Quantum History

The formalism of quantum mechanics that we have seen in these lectures was laid down in a flurry of creativity in the years 1925 and 1926. The primary builders of this new theory were Werner Heisenberg, Erwin Schrödinger, Max Born, Pascual Jordan, and Paul Dirac, several of them under the watchful grandfatherly eye of Niels Bohr.

The emergence of quantum mechanics was preceded by a quarter of a century of confusion, a time in which it was known that some old classical ideas must be jettisoned to explain various experiments, but it was far from clear what should replace them.

With hindsight, the first clear hint of the need for quantum mechanics came from the spectral lines of hydrogen. Take a tube filled with hydrogen gas and pass a current through it. The gas will glow but emit light only at very particular frequencies. In 1885, a Swiss school teacher called Johann Balmer noted that the wavelengths of the most prominent visible lines, shown in Figure 21, could be fitted to the formula

$$\lambda = \frac{4}{R_H}\frac{m^2}{m^2-4}$$

for $m = 3$ (the red line), 4,5,6 and 7. Later Rydberg generalised this to the formula

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

which coincides with the Balmer formula when $n = 2$. Here R_H is known as the *Rydberg constant*. The more prominent $n = 1$ lines appear only in the UV and were not known to Balmer.

We now know that whenever integers appear in the laws of physics, they signify some underlying quantum effect. Indeed, the Rydberg formula follows straightforwardly from the spectrum of the hydrogen atom which, as we've seen, takes the form

$$E_n = -\frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \qquad n = 1, 2, \ldots \tag{4.32}$$

If an electron sits in an excited state E_m and drops to a lower state E_n, $n < m$, it will emit a photon with energy

$$\hbar\omega = E_m - E_n = \frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

The wavelength λ is related to the frequency ω by $\omega = 2\pi c/\lambda$, so this immediately reproduces the Rydberg formula with

$$R_H = \frac{e^4 m_e}{64\pi^3\epsilon_0^2 c\hbar^3}$$

Of course, going backwards from the answer (4.32) is easy. But, in the early 1900's, it was far from clear what to make of the Rydberg formula.

4.4.1 The Bohr Model

An important halfway house was provided by Bohr in 1913. This was only two years after Rutherford had shown that the atom consists of a tiny nucleus, with the electrons in remote orbits. Bohr took a collection of simple classical results and meshed them together with some quantum handwaving in a forced and somewhat unnatural manner to arrive at a remarkably accurate picture of the hydrogen atom. Here is his argument.

We start with the Coulomb force between an electron and proton

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

We assume that the electron orbits the proton on a classical trajectory that we take to be a circle. The Coulomb force must give the requisite centripetal force,

$$F = -\frac{m_e v^2}{r}$$

From this, we can determine the radius of the orbit r in terms of the angular momentum $L = mvr$,

$$r = \frac{4\pi\epsilon_0 L^2}{e^2 m_e}$$

Similarly, the total energy can also be expressed in terms of the angular momentum

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^4 m_e}{32\pi^2\epsilon_0 L^2}$$

Now comes the quantum handwaving. Bohr postulated that angular momentum cannot take any value, but only integer amounts

$$L = n\hbar \quad n = 1, 2, 3, \ldots$$

This implies that the energy is quantised to take values

$$E = -\frac{e^4 m_e}{2\pi^2\epsilon_0\hbar^2}\frac{1}{n^2} \tag{4.33}$$

Remarkably, this is exactly the same as our exact result (4.32) from solving the Schrödinger equation. Furthermore, the minimum orbit of the electron is r_B, given by

$$r_B = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

This is the Bohr radius; it also made an appearance as the size of our wavefunctions (4.31).

What's going on here? There is clearly much that is wrong with the Bohr model. It assumes a classical trajectory which is far from the picture we now have of electrons as smeared clouds probability. It makes the wrong assumption for the quantisation of angular momentum, guessing that $L^2 = n^2\hbar^2$ rather than, as we now know, $L^2 = l(l+1)\hbar^2$. It also gets the connection between angular momentum and energy $l = n$ wrong; the correct answer should be $l < n$. And yet, the end result (4.33) is miraculously exactly right! How can this be?

A pretty good answer to this question is simply: dumb luck. The hydrogen atom is unique among quantum systems in that these simple minded half-classical, half-quantum approaches give the right answers to certain important questions, most notably the energy spectrum. It's not, however, a lesson that we can take and use elsewhere. In all other cases, to get the exact quantum result you have to do the hard work of solving the Schrödinger equation. The one exception to this is for the highly excited states, where Bohr's kind of simple minded arguments do often provide a useful caricature of the physics. (For example, when the angular momentum is large there is not much difference between $L^2 = n^2\hbar^2$ and $L^2 = l(l+1)\hbar^2$.)

In fact, this same dumb luck arose earlier in the history of physics, although it was not realised at the time. Rutherford figured out the structure of the atom by interpreting the scattering of alpha particles off the nucleus. In particular, he derived a formula for the probability that an alpha particle would be deflected by some angle. (We derived Rutherford's formula in the lectures on Dynamics and Relativity.) Of course, he derived this formula using classical mechanics even though we now know that classical mechanics is not a valid description for this scattering: one should use quantum mechanics. Here too, something miraculous occurs. The scattering formulae coming from quantum mechanics are typically very different from those derived using classical mechanics. There is just one exception: for the hydrogen atom, the two results coincide! The full quantum result will be calculated in the lectures on Topics in Quantum Mechanics.

We do, in fact, have a little better understanding of why the hydrogen atom is so special. It turns out that many of these seemingly miraculous properties can be traced to the existence of an extra operator that commutes with $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$. This is called the Runge-Lenz vector. We won't discuss it further in these lectures.

4.4.2 What About the Photon?

Much of the early history of quantum mechanics revolves around an object that we have barely mentioned in these lectures: the photon.

The first equation of quantum mechanics was proposed, somewhat unwittingly and, in later life begrudgingly, by Max Planck in his study of so-called *blackbody radiation*. This is the silly name given to the colour of light emitted by a hot object. The classical theory of Maxwell seemed to give nonsensical answers. Planck was able to derive a formula that agreed well with experiment but, buried with his derivation, was the suggestion that light comes in packets with energy given by

$$E = \hbar\omega = \frac{2\pi\hbar c}{\lambda} \tag{4.34}$$

where ω is the (angular) frequency of light and λ is its wavelength. We already invoked this formula in our discussion of the spectral lines of hydrogen: it is used to relate the wavelength of emitted light to the difference in energy levels. You can read about the derivation of Planck's blackbody radiation formula in the lectures on Statistical Physics.

Soon after Planck's work, the formula (4.34) was put to good use by Einstein in his explanation of the *photoelectric effect*. If you shine a light on a metal, electrons are emitted. The surprise is that the electrons are emitted only if the frequency, rather than the intensity, of the light is sufficient. If the frequency is below a critical value, $E_{\text{crit}}/\hbar$, then no electrons will be emitted no matter how strong the light. We now know that this occurs because the light is made of photons, each of energy $\hbar\omega$. Any individual photon can dislodge an electron only if $\hbar\omega > E_{\text{crit}}$. If the frequency is too low, none of the photons can do the job.

We have met equations very similar to (4.34) in these lectures. For example, a stationary state has time dependence $e^{i\omega t}$ and energy $E = \hbar\omega$. Furthermore, a non-relativistic particle with momentum p has an associated de Broglie wavelength

$$\lambda = \frac{2\pi\hbar}{p}$$

These all gel nicely with the formula (4.34) if we further invoke the relativistic energy-momentum relation $E = pc$ for a photon.

However, although we can get by with these simple minded formulae for a photon, it's somewhat tricky to go any further. For example, we can't easily write down an analog of the Schrödinger equation for the photon. The reason can, at heart, be traced to the factor of c in (4.34). Anywhere the speed of light appears tells us that we are really dealing with special relativity. There is a formulation of quantum mechanics that is fully compatible with special relativity: it goes by the name of quantum field theory. For example, this framework allows us to start with the Maxwell equations of electromagnetism and derive the Planck formula (4.34), rather than postulate it as a further axiom. We will see how to do this when we come to study Quantum Field Theory.

4.5 A First Look at Renormalisation

There is a scene in the movie Back to the Future where Marty McFly introduces the unsuspecting audience at the Enchantment Under the Sea dance to a little bit of rock and roll. Things start off pretty well. Then he gets carried away. As the song finishes, Marty opens his eyes to see a stunned, silenced audience staring back at him and sheepishly admits "I guess you guys aren't ready for that yet…but your kids are going to love it."

This section is our Enchantment Under the Sea moment. We will discuss the topic of renormalisation. You should be aware that this is a ridiculously inappropriately advanced topic to include in introductory lectures on quantum mechanics. Chances are you guys aren't ready for it yet. But your future selves are going to love it.

What is Renormalisation?

The topic of renormalisation usually only arises when we discuss quantum field theory. It is, moreover, a topic that is woefully described in various popular science accounts, all of which seem to be rooted in a 1950s view of the world.

The topic starts with the observation that quantum field theory is hard. In these lectures we've found various exact solutions to the Schrödinger equation. That's a luxury that we no longer have when it comes to the more interesting classes of quantum field theories. Instead, if we want to solve them we must develop approximation techniques and the simplest of these goes by the name of *perturbation theory*. This means that we start by finding an approximate solution to the problem and then systematically improve matters by adding increasingly small corrections, not unlike a Taylor series approximation to a function.

In the early days of quantum field theory, the first stab at the solution gave pretty impressive results. But the successive improvements were a disaster. They all gave the answer infinity. Needless to say, it's difficult to view infinity as a small correction to the original answer.

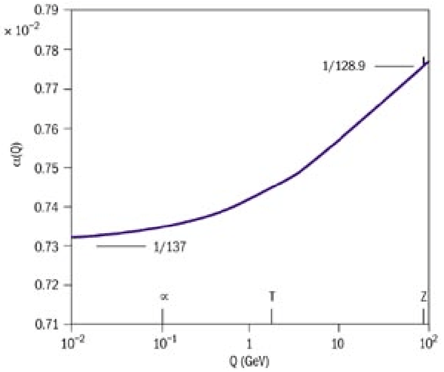
A solution of sorts was found in the 1950s by Tomonaga, Schwinger and Feynman, and synthesised by Dyson. Their solution can be paraphrased by the following equation

$$\infty - \infty = \text{finite}$$

In other words, they found a way to subtract an infinity from the original infinity to leave behind an unambiguous, finite answer. Physically, the results were nothing short of spectacular. The calculations gave agreement between theory and experiment to many significant figures. However, the technique left a lot to be desired. Why should we be forced to resort to such mathematical nonsense as subtracting one infinity from another?

A physical understanding of renormalisation came only in the 1970s, primarily through the work of Kenneth Wilson. First he showed that, despite appearances, renormalisation has nothing to do with physical infinities. Indeed, viewed the right way, there are no infinities in quantum field theory. They arose in the earlier calculations because theorists implicitly assumed that their theories should hold to arbitrarily small distance scales. A little humility, and an acceptance that we don't yet know what's happening on the very smallest distances, then serves to eliminate the infinity. Although it's not immediately obvious, this perspective on renormalisation has a striking consequence:

it turns out that the constants of nature depend on the distance scale at which they're measured.



For example, we've already met the fine structure constant α that characterises the strength of the electromagnetic force. It is roughly

$$\alpha \approx \frac{1}{137}$$

Strictly speaking, however, we should say that α asymptotes to this value at distance scales larger than 10^{-12} metres. Of course, most experiments that we do involving electromagnetism take place on scales much larger than this which is why we always quote the $1/137$ value. But when it comes to to the realm of particle physics, we routinely probe distances smaller than 10^{-12} m. And when we do, we see that α starts to increase. The experimental data is shown in the figure, with α plotted on the vertical axis and the log of the inverse distance plotted on the horizontal axis ($Q \sim 1/r$). You can read more about a cartoon version of renormalisation in the lectures on Particle Physics. You can learn about the details of Wilson's approach to renormalisation in the lectures on Statistical Field Theory.

By the time you get to quantum field theory, it's difficult to ignore renormalisation. In the world of non-relativistic quantum mechanics, however, you need to seek it out. Happily there is a simple quantum mechanical example that exhibits many of the features of renormalisation, but in a setting where we can happily understand what's going on using nothing more than the Schrödinger equation.

4.5.1 A Delta Function Potential in the Plane

We consider a particle moving on the plane with a delta function potential at the origin

$$V(\mathbf{x}) = -g\delta^2(\mathbf{x})$$

The delta function is taken with a negative sign and $g > 0$ so that it is attractive. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{x}) - g\delta^2(\mathbf{x})\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

We solved the corresponding problem in 1d in Section 2.3.2 without a hitch. There we found that there was precisely one bound state localised around the delta function.

We'll now see that things are significantly more subtle in 2d. We'll first argue that there can be no bound states in a 2d delta function. We'll then look a little more closely and see that, when viewed the right way, the 2d delta function does admit a bound state after all.

First, note that the 2d problem has a surprising property. If we define

$$\tilde{g} = \frac{mg}{\hbar^2} \quad \text{and} \quad \tilde{E} = \frac{mE}{\hbar^2}$$

then the Schrödinger equation becomes

$$-\frac{1}{2}\nabla^2\psi(\mathbf{x}) - \tilde{g}\delta^2(\mathbf{x})\psi(\mathbf{x}) = \tilde{E}\psi(\mathbf{x}) \tag{4.35}$$

To proceed, let's do some dimensional analysis. Suppose that we generalise the above problem to a particle moving in d spatial dimensions. The kinetic term ∇^2 always has dimensions of $(\text{length})^{-2}$ while the delta function has dimensions of $(\text{length})^{-d}$ because you integrate it over $\int d^dx$ to get the number one. This picks out $d = 2$ spatial dimensions as special because only there do ∇^2 and $\delta^2(\mathbf{x})$ both have dimensions of $(\text{length})^{-2}$.

This has consequence. First, it would seem to preclude the possibility of bound states. Such a bound state would have some negative energy

$$E = -\mathcal{E}$$

But what could $\mathcal{E}$ be? The only parameter is $\tilde{g}$ but this is dimensionless, while $\mathcal{E}$ has dimension of $(\text{length})^{-2}$. There's simply no scale in the problem that could set a value for $\mathcal{E}$.

Another way of saying this is to note that the Schrödinger equation has a novel symmetry. Suppose that we find a solution, whether a bound state with negative energy $\tilde{E} < 0$ or a state that can be interpreted as in terms of scattering with $\tilde{E} > 0$. We then rescale the spatial coordinates

$$\mathbf{x} \rightarrow \lambda\mathbf{x}$$

The Schrödinger equation becomes

$$-\frac{1}{2\lambda^2}\nabla^2\psi(\lambda\mathbf{x}) - \frac{\tilde{g}}{\lambda^2}\delta^2(\mathbf{x})\psi(\lambda\mathbf{x}) = \tilde{E}\psi(\lambda\mathbf{x})$$

If $\psi(\mathbf{x})$ solves the Schrödinger equation with energy $\tilde{E}$ then $\psi(\lambda\mathbf{x})$ solves the Schrödinger equation with energy $\lambda^2\tilde{E}$. In other words, there is a continuum of states. This is to be expected for scattering states with positive energy: asymptotically these states look like $e^{i\mathbf{k}\cdot\mathbf{x}}$. But it's not what we expect for bound states with negative energy. In particular, it would mean that there are bound states of arbitrarily negative energy.

This all sounds like a very good reason to discount the possibility of bound states in this problem. That would certainly avoid all the issues mentioned above. In fact, as we now see, the truth is significantly more interesting.

We will solve the Schrödinger equation with a flurry of Fourier transforms. We write the wavefunction as

$$\psi(\mathbf{x}) = \frac{1}{2\pi}\int d^2k'\ \tilde{\psi}(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{x}} \tag{4.36}$$

We then substitute this Fourier transform only in the ∇^2 and $\tilde{E}$ terms of (4.35) to get

$$\frac{1}{2\pi}\int d^2k' \left(\frac{k'^2}{2} - \tilde{E}\right)\tilde{\psi}(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{x}} = \tilde{g}\delta^2(\mathbf{x})\psi(0)$$

where, on the right-hand side we've replaced $\psi(\mathbf{x}) = \psi(0)$ on account of the fact that this is the only value the delta function sees. Now, we use the Fourier transform once again, but this time for the delta function itself, which can be written as

$$\delta^2(\mathbf{x}) = \frac{1}{(2\pi)^2}\int d^2k'\ e^{i\mathbf{k}'\cdot\mathbf{x}}$$

This gives us

$$\frac{1}{2\pi}\int d^2k' \left(\frac{k'^2}{2} - \tilde{E}\right)\tilde{\psi}(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{x}} = \frac{\tilde{g}}{(2\pi)^2}\int d^2k'\ e^{i\mathbf{k}'\cdot\mathbf{x}}\psi(0)$$

Finally, we multiply both sides by $e^{-i\mathbf{k}\cdot\mathbf{x}}$ and integrate over $\mathbf{x}$,

$$\frac{1}{2\pi}\int d^2x \int d^2k'\ \left(\frac{k'^2}{2} - \tilde{E}\right)\tilde{\psi}(\mathbf{k}')e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}} = \frac{\tilde{g}}{(2\pi)^2}\int d^2x \int d^2k'\ e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}}\psi(0)$$

This is a clever thing to do as everything now simplifies. The integral over x gives us a delta function

$$\int d^2x\ e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}} = (2\pi)^2\delta^2(\mathbf{k}'-\mathbf{k})$$

which then, in turn, kills the integral over k' on the left-hand side. We're left with the simple equation

$$2\pi\left(\frac{k^{,2}}{2} - \tilde{E}\right)\tilde{\psi}(\mathbf{k}) = \tilde{g}\psi(0)$$

This looks like we've done our job. The bound state solutions with energy $\tilde{E} = -\mathcal{E}$ have Fourier coefficients

$$\tilde{\psi}(\mathbf{k}) = \frac{\tilde{g}}{2\pi}\frac{\psi(0)}{k^2/2+\mathcal{E}} \tag{4.37}$$

The value $\psi(0)$ is an arbitrary constant which, for a bound state, should be non-zero as this is the only thing the delta function knows about. We can now do a consistency check. The value of $\psi(0)$ is also given by our original Fourier transform (4.36),

$$\psi(0) = \frac{1}{2\pi}\int d^2k\ \tilde{\psi}(\mathbf{k})$$

We can compare this with the integral of (4.37): we get

$$\psi(0) = \frac{\tilde{g}}{(2\pi)^2}\int d^2k\ \frac{\psi(0)}{k^2/2+\mathcal{E}} \tag{4.38}$$

We don't care about the value of $\psi(0)$ in this equation: just that it's non-vanishing. Instead, (4.38) should be viewed as an integral equation to determine the bound state energy $\mathcal{E}$. If you evaluate the equivalent integral for the 1d delta function, you'll reproduce our earlier answer (2.40) which is satisfying. But for the 2d delta function there's a problem because the integral does not converge. It is given by

$$\int d^2k\ \frac{1}{k^2/2+\mathcal{E}} = 2\pi\int_0^\infty dk\ \frac{k}{k^2/2+\mathcal{E}} = \infty \tag{4.39}$$

This is entirely analogous to the infinities that were encountered in the early days of quantum field theory. Of course, in the present context we could simply shrug and say "see, I told you there should be no bound states". But our quantum field theoretic forefathers didn't have this option and we can learn from their perseverance.

4.5.2 Renormalisation in Quantum Mechanics

To make sense of the ∞ in the integral (4.39), let's first render it finite. We do this by changing the integral

$$2\pi\int_0^\infty dk\ \frac{k}{k^2/2+\mathcal{E}} \ \longrightarrow\ 2\pi\int_0^\Lambda dk\ \frac{k}{k^2/2+\mathcal{E}} = 2\pi\log\left(1+\frac{\Lambda^2}{2\mathcal{E}}\right)$$

Here Λ is called the *UV-cut off*. It "cuts off" the integral at high k, where the Fourier modes oscillate on very small distance scales. (The name "UV-cut off" is a quaint nod to the idea that UV light also has a high frequency. Admittedly, if the analogy was in anyway accurate it would be called "gamma-ray cut-off", but the term UV has stuck.)

What physical motivation do we have for changing the integral in this way? Well, one answer might be that we're not entirely sure that our original quantum mechanical model was correct. After all, we included an infinitely thin delta function potential which doesn't sound particularly realistic. In most situations, delta function potentials are introduced as a simple toy model to capture the key physics and their infinitely spikey nature should not be taken too seriously. But, if this is the reason that we're studying the delta-function then it doesn't bode particularly well for trusting our theory when it comes to very short distance scales.

The introduction of the UV cut-off Λ should be thought of as an injection of humility into the proceeding. The UV cut-off is simply an expression of our ignorance of what's going on at short distance scales. The rub is that no physical property can depend on our ignorance. That means that, somehow, Λ must drop out of any final answer that we submit.

Let's see how we do. Our consistency condition (4.38) becomes

$$1 = \frac{\tilde{g}}{(2\pi)^2}\int d^2k\ \frac{1}{k^2/2+\mathcal{E}} = \frac{\tilde{g}}{2\pi}\log\left(1+\frac{\Lambda^2}{2\mathcal{E}}\right)$$

Rearranging, we find the bound state energy

$$\mathcal{E} = \frac{\Lambda^2}{2}\frac{1}{e^{2\pi/\tilde{g}}-1} \tag{4.40}$$

At first glance, it doesn't look like this is much of an improvement. First, the bound state energy explicitly depends on the UV cut-off. Moreover, as we send $\Lambda \to \infty$ to recover the original theory, we see that the bound state energy disappears off to infinity. Once again, all signs suggest that our delta function doesn't have a bound state.

Now we introduce the key idea: the dimensionless coupling $\tilde{g}$ should also depend on the distance scale of the theory. In particular, if we change the UV cut-off then we should also change $\tilde{g}$ at the same time. In fact, we see that we get to realise our dream of having the physical bound state energy independent of Λ if we take

$$\tilde{g}(\Lambda) = \frac{2\pi}{\log(1+\Lambda^2/2\mathcal{E})} \tag{4.41}$$

This is called the *running* of the coupling.

What's going on here? It's tempting to think that we can define a quantum theory by specifying a Hilbert space and a Hamiltonian, with various parameters set to specific values. That's what we've done throughout these lectures, and it's what we continue to do in nearly all problems in non-relativistic quantum mechanics. However, it turns out that it's not the right way to think in quantum field theory and, perhaps surprisingly, it's not the right approach with our 2d delta function either. Instead, the correct definition of the theory describing a particle moving in the presence of a two-dimensional delta function includes *both* a UV cut-off Λ and a dimensionless coupling $\tilde{g}$. From these two, we then get the bound state energy scale (4.40). Within this more generalised class of theories, the 2d delta function has a single bound state, just like its 1d counterpart.

However, Λ and $\tilde{g}$ come together in a pair. They're not independent. You can change the UV cut-off *without* changing the underlying theory by making a compensating change to the coupling constant. The formula (4.41) tells you how to do this.

The fact that the coupling $\tilde{g}$ varies with the cut-off also has physical implications. We could, for example, study scattering off the delta-function potential. With a cut-off Λ in place, you will find that the probability for scattering at energy E (captured in so-called *phase shifts*) will depend on $\tilde{g}(\sqrt{2E})$. In other words, it appears as if the effective strength of the delta function varies in energy in the same way as the running of the coupling (4.41). This is entirely analogous to the energy dependent fine structure constant that we mentioned previously. We will discuss scattering in higher dimensions in the lectures on Topics in Quantum Mechanics, although we will steer clear of any discussion of renormalisation in that context.

Our previous arguments suggesting that a bound state cannot exist are all nullified by the presence of the UV cut-off. In particular, Λ provides the dimensions necessary to set the energy scale of $\mathcal{E}$ and breaks the scaling symmetry $\mathbf{x} \to \lambda \mathbf{x}$ that we naively thought was a property of the Hamiltonian.

In fact, all of these previous arguments really took place in a theory in which we implicitly took $\Lambda \to \infty$ while keeping $\tilde{g}$ fixed. This lead us to believe that there is no finite energy bound state. The formula (4.41) tells us what's really going on: as we remove the cut-off, we can keep the finite energy bound state but only by sending $\tilde{g} \to 0$ as $\Lambda \to \infty$. We see that there is a delicate balancing act between these two parameters. An arbitrarily weak delta function can still lead to a finite energy bound state if we admit arbitrarily small wavelength modes in our theory.

Theories which have the property that some dimensionless parameter, like $\tilde{g}$, vanishes as we go to higher and higher energies are said to be *asymptotically free*. In particle physics, the strong nuclear force, which is described by Yang-Mills theory, has this property.

It's also worth looking at what happens in the limit of small $\tilde{g}$. Here the formula for the bound state energy (4.40) is

$$\mathcal{E} \approx \frac{\Lambda^2}{2} e^{-2\pi/\tilde{g}} \tag{4.42}$$

This ensures that the energy scale of the bound state is way below the cut-off: $\mathcal{E} \ll \Lambda^2$. This is good! As we stressed above, the cut-off is a parameterisation of our ignorance. We should only trust physics on distance scales much bigger than $1/\Lambda$ or, equivalently, on energy scales much less than Λ^2.

In fact, a better characterisation of (4.42) would be $\mathcal{E} \lll \Lambda^2$. For small $\tilde{g}$, the function $e^{-2\pi/\tilde{g}}$ is really tiny. To get some sense of this, we could try to Taylor expand $e^{-2\pi/\tilde{g}}$. The first term is zero. The next term is also zero. In fact, the Taylor expansion of $e^{-2\pi/\tilde{g}}$ vanishes identically because, for small $\tilde{g}$ the function is smaller than $\tilde{g}^n$ for any n.

There are quite a few places in physics where two different energy scales are related by a small number of the form $e^{-1/g}$ for some g. Whenever this arises, it is always interesting. Prominent examples include how electrons pair up in superconductors, how quarks bind together into protons and neutrons, and how D-branes emerges in string theory. There is a whole lot of physics goodness in these ideas that we will come to in future courses.