Quantum Mechanics

Lachlan Dufort-Kennett

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Preface

Chapter 1

Principles of Quantum Mechanics

1.1 Quantum States

Quantum states are described by **vectors** in a complex vector space, specifically a **Hilbert space**, which is a complete inner product space. The exact properties of the Hilbert space are determined by the nature of the physical problem we are studying. Physically distinct states of the system are represented by orthogonal directions in Hilbert space. We will discuss what this means more rigorously in later chapters. A Hilbert space may be finite-dimensional, where the system can only be in finitely-many states, or infinite-dimensional, which is certainly the case for any particle that can move.

Transformations on the state of the system, such as time-evolution or change of basis, are described using **linear operators**, which are a generalisation of matrices from finite-dimensional linear algebra.

1.1.1 Dirac Notation

States in the Hilbert space are written as $|\psi\rangle$, where ψ is some label we have made up for the state. This notation is called a **ket**. Recall that the inner product can be defined as the action of a corresponding **linear functional** or **covector** from the **dual space** on the vector. For ket vectors there is a corresponding reversed notation $\langle\psi|$, called a **bra**, which represents the corresponding linear functional. Then the inner product between two states $|\psi\rangle$ and $|\phi\rangle$ can be written as

$$\langle\phi|\psi\rangle = -\langle\psi|\phi\rangle. \tag{1.1}$$

This expression is known as a "bra-ket" (= bracket). This notation is due to Paul Dirac, and is known as **Dirac notation** or **Bra-ket notation**.

In a system where the Hilbert space is finite-dimensional with n dimensions, it is isomorphic to $\mathbb{C}^n$. Then the kets can be associated with column vectors and the bras with row vectors, just like how we would write linear functionals from the dual space in finite-dimensional linear algebra, and the inner product is defined by matrix multiplication. In this case, linear operators really are just $n \times n$ matrices.

All our familiar ideas from linear algebra carry over to Hilbert space, in particular if we have

an operator $\hat{O}$ and it acts on the state $|\psi\rangle$ to get

$$\hat{O}|\psi\rangle = O|\psi\rangle, \tag{1.2}$$

then this is an **eigenvalue equation**. We say that $|\psi\rangle$ is an **eigenket** of $\hat{O}$ with eigenvalue O.

There exists bases for the Hilbert space for which we can write the state $|\psi\rangle$ as a linear combination. In particular there is a special basis which is formed from the solutions to the Schrodinger equation (see the next section) called the **energy eigenbasis**, which is usually labelled $|n\rangle$ where n is an integer label that can take some range of values specified by the problem. The expansion of an arbitrary state $|\psi\rangle$ in the energy eigenbasis looks like

$$|\psi\rangle = \sum_n c_n |n\rangle = \sum_n \langle n|\psi\rangle |\psi\rangle, \tag{1.3}$$

, where c_n is the inner product of the state $|\psi\rangle$ with the eigenstate $|n\rangle$. We will study energy eigenbases again and again throughout the following chapters, as they are pretty much the most important objects of study in quantum mechanics.

1.1.2 The Wavefunction

For a system with spatial degrees of freedom, we also have a continuous basis that we can express our state in, the position basis $|x\rangle$. Since the position basis is continuous, an arbitrary quantum state ψ is represented in the position basis by an integral:

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x,t)|x\rangle \, \mathrm{d}x. \tag{1.4}$$

The quantity $\psi(x,t)$ is called the **wavefunction**, and is basically the continuous list of coefficients in the linear combination of position eigenkets.

We can isolate the value of the wavefunction at a position x by calculating the inner product of the state $|\psi\rangle$ with the relevant position eigenket $\hat{x}$ (taking care to use a different dummy variable for the integration):

$$\langle x|\psi\rangle = \int_{-\infty}^{\infty} \langle x|\psi(x',t)|x'\rangle \, \mathrm{d}x' \tag{1.5}$$

$$= \int_{-\infty}^{\infty} \psi(x',t)\langle x|x'\rangle \, \mathrm{d}x' \tag{1.6}$$

$$= \int_{-\infty}^{\infty} \psi(x',t)\delta(x-x') \, \mathrm{d}x' \tag{1.7}$$

$$= \psi(x,t). \tag{1.8}$$

For systems with only spatial degrees of freedom, which we will study exclusively in the first few chapters, we can actually get by using only the wavefunction to describe the full state of the system and ignoring the more abstract kets and bras. However, when we come to describe systems with internal degrees of freedom such as spin, we will need Dirac notation to describe the system state. To keep on top of things, we will keep track of ways that important concepts such as superpositions and expectation values can be described using both notations throughout.

1.2   The Schrodinger Equation

1.2.1   The Time-Dependent Schrodinger Equation

The **wavefunction** $\psi(x,t)$ of a non-relativistic particle of mass m obeys the **time-dependent Schrodinger equation** (TDSE), which is a second-order partial differential equation given by

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}, \tag{1.9}$$

where $\hbar$ is the reduced Planck constant, defined as $\hbar = \frac{h}{2\pi}$.

The TDSE takes the form

$$\text{(kinetic energy operator)} \times \psi(x,t) + \text{(potential energy operator)} \times \psi(x,t) =$$
$$\text{(total energy operator)} \times \psi(x,t). \tag{1.10}$$

Recall that in classical mechanics, kinetic energy is defined as

$$K = \frac{1}{2}mv^2 = \frac{p^2}{2m}. \tag{1.11}$$

In quantum mechanics, physical quantities are represented by **operators**, which are linear transformations that act on the wavefunction. Operators obey the same relations as their corresponding quantities in classical mechanics. Hence, the kinetic energy operator in quantum mechanics is defined as

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{1.12}$$

Operators act successively to the right, so the product of two derivative operators becomes a second derivative which is then applied to the wavefunction that the operator is acting on.

The total energy operator, or **Hamiltonian operator** is defined as the sum of the kinetic energy and potential energy operators.

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{1.13}$$

The potential energy operator $\hat{V}$ becomes just the function $V(x)$ because the position operator $\hat{x} = x$. Note that the potential energy function $V(x)$ is often referred to in quantum mechanics as simply "potential", but this should not be confused with other similarly named functions such as electric potential (voltage, equal to potential energy per unit charge) and gravitational potential (potential energy per unit mass), which are physically different quantities!

The TDSE can be written more compactly using the Hamiltonian as

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}. \tag{1.14}$$

The TDSE is a *linear* differential equation. This means the the solutions obey the principle of superposition, i.e. if ψ_1 and ψ_2 are solutions, then $A\psi_1 + B\psi_2$ is also a solution. This is where the superposition states in quantum mechanics come from.

It is also first-order in time, which implies that specifying the wavefunction at some time t_0 uniquely specifies the wavefunction for all future times. Thus the wavefunction evolves deterministically according to the Schrodinger equation if the particle is left alone without measurement.

1.2.2 The Time-Independent Schrodinger Equation

We can make one step towards solving the Schrodinger equation in general by separating the time evolution out of the equation. We will assume that the wavefunction $\psi(x,t)$ is the product of a spatial part, that depends only on x, and a temporal part that depends only on t and describes the time evolution.

$$\psi(x,t) = u(x)T(t). \tag{1.15}$$

This technique is known as **separation of variables**.

If we substitute this into the TDSE (equation 1.9), we get

$$-\frac{\hbar^2}{2m}T(t)\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} + V(x)u(x)T(t) = i\hbar u(x)\frac{\mathrm{d}T(t)}{\mathrm{d}t}. \tag{1.16}$$

If we divide by $u(x)T(t)$, we can get all terms depending on x on one side and all terms depending on t on the other:

$$-\frac{\hbar^2}{2m}\frac{1}{u(x)}\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} + V(x) = \hbar\frac{1}{T(t)}\frac{\mathrm{d}T(t)}{\mathrm{d}t}. \tag{1.17}$$

Now since both sides only depend on a single variable, they must both be constant. This constant must have units of energy, since it must have the same units as $V(x)$, and it must be equal to the total energy of the particle since that is what is on the left hand side.

If we set the left-hand side equal to the total energy and multiply both sides by $u(x)$, we get

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} + V(x)u(x) = Eu(x). \tag{1.18}$$

This equation is of the form

$$(\text{operator}) \times u(x) = (\text{constant}) \times u(x), \tag{1.19}$$

which is an **eigenvalue equation**. This means that $u(x)$ represents an *eigenfunction* of the Hamiltonian operator, with eigenvalue E. This equation is known as the **time-independent Schrodinger equation** (TISE). Note that the full time dependent separable wavefunction $\psi(x,t)$ is also an eigenfunction of the Hamiltonian, since the spatial derivative does not act on the temporal part. These eigenfunctions, which are usually labelled with some subscript to denote the energy, are known as **energy eigenstates**.

The TISE can be written more compactly using the Hamiltonian as

$$\hat{H}\psi = E\psi. \tag{1.20}$$

Note that only the energy eigenstates solve the TISE, but any superposition of energy eigenstates can solve the TDSE.

1.2.3 Solving the Temporal Part of the Schrodinger Equation

Looking at the right hand side of equation 1.17, we see that there is nothing unknown, and therefore we are able to solve it in general. Setting the right hand side equal to E and rearranging a bit, we get

$$\frac{\mathrm{d}T(t)}{\mathrm{d}t} = -\frac{iE}{\hbar}T(t). \tag{1.21}$$

This equation has the solution

$$T(t) = e^{-\frac{iE}{\hbar}t},$$ (1.22)

which holds for *any* potential energy $V(x)$. This is therefore the temporal part of the energy eigenstates for any problem. It means we do not actually need to solve the full TDSE for every problem we want to study in quantum mechanics. We need only solve the TISE, which is different for every problem because of the presence of the potential, to find the spatial part of the energy eigenstates, and then the full eigenfunctions are given by

$$\psi(x,t) = u(x)e^{-\frac{iE}{\hbar}t},$$ (1.23)

where the spatial part $u(x)$ is the eigenfunction of $\hat{H}$ with eigenvalue E.

In particular, the linearity of the TDSE implies that the time-evolution of a superposition of energy eigenstates is equal to the superposition of the time-evolution of those eigenstates. We will use this principle repeatedly to find the most general solutions to the TDSE.

1.3 Conditions for Valid Wavefunctions

From what we have derived so far, there are some constraints we have on what type of wavefunctions can represent physical states. In classical mechanics, the trajectory $x(t)$ which is the solution of Newton's second law is the object which we impose constraints on smoothness on. For quantum mechanics, the role of the trajectory is replaced by the wavefunction, the square magnitude of which represents probability density. This means that while it also has the smoothness requirements determined by the Schrodinger equation, the wavefunction needs some additional constraints which we will see below.

1.3.1 Smoothness

As stated above, the form of Newton's second law requires the trajectory to be not only continuous, but twice-differentiable.

The wavefunction must be continuous, because a discontinuity in ψ at x_0 would like to ambiguous probabilities near x_0. It must also have a continuous slope, except at points where the potential energy is infinite. To see why, we can rearrange the TISE to

$$\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}(V(x) - E)u(x),$$ (1.24)

and then integrate over a small interval $[x_0, x_0 + \varepsilon]$ to get

$$\left.\frac{\mathrm{d}u(x)}{\mathrm{d}x}\right|_{x_0} - \left.\frac{\mathrm{d}u(x)}{\mathrm{d}x}\right|_{x_0+\varepsilon} = \frac{2m}{\hbar^2}\int_{x_0}^{x_0^\varepsilon}(V(x) - E)u(x)\,\mathrm{d}x.$$ (1.25)

If the left-hand side is not equal to zero in the limit $\varepsilon \to 0$, then the slope $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ is nonzero at x_0. When can the right-hand side be nonzero? The term $Eu(x)$ is finite so the integral goes to zero in the limit $\varepsilon \to 0$, and the same will be true for the term $V(x)u(x)$ even if $V(x)$ is discontinuous at x_0. Only if $V(x)$ is infinite at x_0 will the integral be nonzero in the limit $\varepsilon \to 0$.

1.3.2 Normalisation

As alluded to above, the fact that the square magnitude of $\psi(x,t)$ represents a probability density necessitates an extra constraint on the wavefunction. Namely, the integral of the probability density over all space must be equal to one. This represents the fact that the particle must be located *somewhere*.

$$\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)\,\mathrm{d}x = \int_{-\infty}^{\infty} |\psi(x,t)|^2\,\mathrm{d}x = 1. \tag{1.26}$$

This constraint is called the **normalisation condition**. If wavefunctions do not have this property, then the probabilities calculated from them will not make sense.

This gives us a requirement that the physically realisable wavefunction must be **square integrable**, which implies that the integral of the square magnitude over all space is finite:

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2\,\mathrm{d}x = N < \infty. \tag{1.27}$$

If a given wavefunction $\psi(x,t)$ is square integrable, then $\frac{1}{\sqrt{N}}\psi(x,t)$ where N is given by the equation above will be a correctly normalised wavefunction.

Square integrability imposes that $\psi(x,t)$ decays to zero sufficiently rapidly as $x \to \pm\infty$. This makes physical sense, because it would not make sense for a particle to have a nonzero probability to be located infinitely far away. Wavefunctions which are not square integrable are called **unnormalisable**.

In Dirac notation, the normalisation condition is written as

$$\langle \psi | \psi \rangle = 1. \tag{1.28}$$

1.4 Expectation Values

Generally speaking, if we make a measurement of a quantum mechanical system, the state of the system will be changed. This means that there is no additional precision to be gained from repeated measurements, unlike with classical systems. Once a measurement is made, the system's wavefunction collapses into one of the eigenstates of the operator. The eigenvalues represent all possible measurement outcomes of that operator.

In order to make repeated measurements in the same way we would with a classical system, what we need to do is prepare a large number of systems in identical initial states, then measure them all. This gives us an ensemble average for the quantity, which is called the **expectation value**. Expectation values are denoted with angle brackets around the quantity, sometimes with a subscript ψ to denote for which state we are taking the average value, e.g. $\langle \hat{x} \rangle_\psi$ represents the average position in the state ψ.

Note that the name "expectation value" can be slightly misleading, for it does not denote what we "expect" to measure when we do a measurement. It simply means the average of many measurements of systems in identical states.

1.4.1 Operators with Discrete Eigenvalues

Suppose an operator $\hat{O}$ has a discrete set of measurement outcomes (eigenvalues) labelled O_n. Then the expectation value is simply the sum of each outcome weighted by the probability:

$$\langle \hat{O} \rangle = \sum_i O_i P(O_i). \tag{1.29}$$

1.4.2 Operators with Continuous Eigenvalues

In the case that the set of measurement outcomes is continuous, the sum should change into an integral. But what should the integral look like?

We know that the wavefunction represents probability density in space, so the average value of position, which is simply the expectation value of the $\hat{x}$ operator, is

$$\langle \hat{x}(t) \rangle = \int_{-\infty}^{\infty} \hat{x} \psi(x,t)^* \psi(x,t) \, \mathrm{d}x = \int_{-\infty}^{\infty} x |\psi(x,t)|^2 \, \mathrm{d}x. \tag{1.30}$$

Notice that the time-dependence of $\langle \hat{x} \rangle$ comes purely from the wavefunction.

This is the quantum analogue of the trajectory in classical mechanics.

Can we extend this to other operators? For position, since $\hat{x} = x$, it does not matter where we put $\hat{x}$ in the integral in equation 1.30, but for other operators, like momentum, it does matter. To see why, note that momentum contains a derivative $\frac{\partial}{\partial x}$, then note that

$$\psi^* \frac{\partial \psi}{\partial x} \neq \frac{\partial \psi^*}{\partial x} \psi, \tag{1.31}$$

in general.

Note that in classical mechanics, the trajectory follows Newton's second law

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{p(t)}{m}. \tag{1.32}$$

We would like that the same thing would happen in classical mechanics, i.e. that

$$\frac{\mathrm{d}\langle x(t) \rangle}{\mathrm{d}t} = \frac{\langle p(t) \rangle}{m}, \tag{1.33}$$

but we do not know a priori if this is the case.

Let's calculate the time derivative of $\langle x(t) \rangle$ to see what happens.

$$\frac{\mathrm{d}\langle x(t) \rangle}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \left(\int_{-\infty}^{\infty} x |\psi(x,t)|^2 \, \mathrm{d}x \right) \tag{1.34}$$

$$= \int_{-\infty}^{\infty} x \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) \mathrm{d}x. \tag{1.35}$$

Now, we can change the temporal derivatives to spatial derivatives by rearranging the TDSE (equation 1.9) and its complex conjugate for $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$:

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi} \frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar} \psi, \quad \frac{\partial \psi^*}{\partial t} = \frac{\hbar}{2mi} \frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar} \psi^*. \tag{1.36}$$

Substituting these in, we get

$$\frac{\mathrm{d}\langle x(t)\rangle}{\mathrm{d}t} = \frac{\hbar}{2mi} \int_{-\infty}^{\infty} x \left(\frac{\partial^2 \psi^*}{\partial x^2}\psi - \frac{V}{i\hbar}|\psi| - \psi^* \frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}|\psi| \right) \mathrm{d}x \tag{1.37}$$

$$= \frac{\hbar}{2mi} \int_{-\infty}^{\infty} \left(\frac{\partial^2 \psi^*}{\partial x^2}x\psi - \psi^* x \frac{\partial^2 \psi}{\partial x^2} \right) \mathrm{d}x. \tag{1.38}$$

Looking at the first term and integrating by parts, we get

$$\int_{-\infty}^{\infty} \frac{\partial^2 \psi^*}{\partial x^2} x\psi \, \mathrm{d}x = \frac{\partial \psi^*}{\partial x}x\psi \bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi}{\partial x} \frac{\partial}{\partial}(x\psi) \, \mathrm{d}x \tag{1.39}$$

$$= - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \left(\psi + x \frac{\partial \psi}{\partial x} \right) \mathrm{d}x. \tag{1.40}$$

The "surface" terms go to zero because the wavefunction is square integrable, and therefore must go to zero at $\pm\infty$. Integrating by parts again and using the same trick, we get

$$\int_{-\infty}^{\infty} \frac{\partial^2 \psi^*}{\partial x^2} x\psi \, \mathrm{d}x = - \psi^* \left(\psi + x \frac{\partial \psi}{\partial x} \right) \bigg|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \psi^* \left(2\frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \right) \mathrm{d}x \tag{1.41}$$

$$= \int_{-\infty}^{\infty} \psi^* \left(2\frac{\partial \psi}{\partial x} + x \frac{\partial^2 \psi}{\partial x^2} \right) \mathrm{d}x. \tag{1.42}$$

Substituting this into the time derivative for the expectation value for position, we get

$$\frac{\mathrm{d}\langle x(t)\rangle}{\mathrm{d}t} = \frac{\hbar}{2mi} \int_{-\infty}^{\infty} \left(2\psi^* \frac{\partial \psi}{\partial x} + \psi^* x \frac{\partial^2 \psi}{\partial x^2} - \psi^* x \frac{\partial^2 \psi}{\partial x^2} \right) \mathrm{d}x \tag{1.43}$$

$$= \frac{1}{m} \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi \, \mathrm{d}x \tag{1.44}$$

$$= \frac{1}{m} \int_{-\infty}^{\infty} \psi^* \hat{p}\psi \, \mathrm{d}x, \tag{1.45}$$

where we have substituted the definition of the momentum operator. So if we interpret this integral as the expectation value of momentum, equation 1.33 holds.

We thus have the following generalisation.

Definition 1.1. For an operator $\hat{O}$ with continuous measurement outcomes, the expectation value of $\hat{O}$ for a state ψ is defined as

$$\langle \hat{O} \rangle_{\psi} = \int_{-\infty}^{\infty} \psi(x,t)^* \hat{O}\psi(x,t) \, \mathrm{d}x. \tag{1.46}$$

In Dirac notation, this is denoted

$$\langle \hat{O} \rangle_{\psi} = \langle \psi | \hat{O} | \psi \rangle. \tag{1.47}$$

1.5 Quantum Uncertainty

The most famous appearance of uncertainty in quantum mechanics is the Heisenberg uncertainty principle between position and momentum.

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \tag{1.48}$$

This means that, in contrast to classical mechanics, there are no possible states a particle can be in where it has both definite momentum and position. This has dramatic consequences, such as the loss of a well-defined trajectory for quantum particles.

It also implies that particles confined to finite spaces must have nonzero kinetic energy.

Mathematically, the quantum uncertainty of any observable is defined as the standard deviation of the probability distribution *prior to measurement*. If we have a particle in an eigenstate of a given observable and we measure that observable, we know which eigenvalue we will get back and so there is no uncertainty. For any superposition state, there is nonzero uncertainty. This represents the fact that the outcome of a measurement is truly random, quantum uncertainty does *not* represent our lack of knowledge of a definite state.

The uncertainty in position is

$$\Delta x = \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2}. \tag{1.49}$$

One way to remember which way round the two terms in the square root are is by noting that uncertainty must be real. The first term, which is an average of squares i.e. things that are ≥ 0, must therefore be greater than the second term, which is an average of things that can be positive or negative.

Does this formula generalise to all operators? Suppose $\hat{O}$ is an operator with a discrete set of measurement outcomes O_i with probabilities $P(O_i)$. Then the standard deviation is defined as

$$\Delta O = \sqrt{\sum_i (O_i - \langle \hat{O} \rangle)^2 P(O_i)} \tag{1.50}$$

$$= \sqrt{\sum_i O_i^2 P(O_i) - 2\langle \hat{O} \rangle \sum_i O_i P(O_i) + \langle \hat{O} \rangle^2 \sum_i P(O_i)} \tag{1.51}$$

$$= \sqrt{\langle \hat{O}^2 \rangle - 2\langle \hat{O} \rangle^2 + \langle \hat{O} \rangle^2} \tag{1.52}$$

$$= \sqrt{\langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2}, \tag{1.53}$$

so the relation holds.

Definition 1.2. For an observable operator $\hat{O}$, the uncertainty is given by

$$\Delta O = \sqrt{\langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2}. \tag{1.54}$$

Example 1.1. Suppose we are going to measure the momentum of a particle, which has probability 0.5 to have momentum $+p_0$, and probability 0.5 to have momentum $-p_0$.

What is the uncertainty in the measurement?
Using equation 1.54, we have

$$\Delta p = \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2}. \tag{1.55}$$

We need to calculate both terms inside the square root.
Since the two possible measurement outcomes are equidistant from zero with equal probability, we expect the average value of measurement to be zero. We can verify this by calculating:

$$\langle \hat{p} \rangle = p_0 \times 0.5 - p_0 \times 0.5 = 0. \tag{1.56}$$

On the other hand, the average value of squared momentum is

$$\langle \hat{p}^2 \rangle = p_0^2 \times 0.5 + (-p_0)^2 \times 0.5 = p_0^2. \tag{1.57}$$

Then the uncertainty is

$$\Delta p = \sqrt{p_0^2 - 0} = p_0. \tag{1.58}$$

1.6 Probability Current

Consider a wire carrying some electric current I. Mathematically, current is defined as the amount of charge passing a point per unit time. By analogy, we can also define a "probability current", which denotes the amount of probability passing through a point per unit time.

1.6.1 Probability Conservation

The total probability of finding a particle for $x \in (-\infty, \infty)$ is one, and this does *not* change with time. This means that the total probability is **conserved**.

However, we can actually make a stronger claim than this. For the probability of finding a particle in a small interval $(x_0, x_0 + \mathrm{d}x)$ to change, some probability must "flow" in or out of this interval. This is known as **local conservation**. We say that there is nonzero **probability current** j in or out of the segment. The net change in probability current in the small interval is defined as

$$j(x_0 + \mathrm{d}x, t) - j(x_0, t) = \mathrm{d}j(x_0, t), \tag{1.59}$$

and the probability of finding the particle in the interval is

$$|\psi(x_0, t)|^2 \, \mathrm{d}x, \tag{1.60}$$

so for probability to be conserved locally we must have

$$\mathrm{d}j(x_0, t) = -\frac{\partial}{\partial t} |\psi(x_0, t)|^2. \tag{1.61}$$

The minus sign is there because the left-hand side being *positive* implies that probability is *leaving* the region.

In the limit where the interval becomes infinitesimally small, we get

$$\frac{\partial |\psi(x, t)^2|}{\partial t} = -\frac{\partial j(x, t)}{\partial x}. \tag{1.62}$$

This is known as the **continuity equation**, and it appears in all sorts of context in physics whenever we have local conservation (e.g. charge conservation in electromagnetism, mass conservation in fluid dynamics, etc.). The greater the magnitude of the slope of the probability current, the faster probability is flowing through a given point. Probability current j has units s^{-1}, or "probability per unit time".

1.6.2 Calculating Probability Current

To calculate the probability current j for a given state ψ, we can start from the continuity equation 1.62 and use the Schrodinger equation to write the temporal derivative in terms of a spatial derivative just like we did in section 1.4.2.

Starting with the left-hand side of equation 1.62 and using the product rule, we have

$$\frac{\partial |\psi|^2}{\partial t} = \frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} \tag{1.63}$$

$$= \left(\frac{\hbar}{2mi}\frac{\partial^2 \psi^*}{\partial x^2} - \frac{V}{i\hbar}\psi^*\right)\psi + \psi^*\left(-\frac{\hbar}{2mi}\frac{\partial^2 \psi}{\partial x^2} + \frac{V}{i\hbar}\psi\right) \tag{1.64}$$

$$= \frac{\hbar}{2mi}\left(\frac{\partial^2 \psi^*}{\partial x^2}\psi - \psi^*\frac{\partial^2 \psi}{\partial x^2}\right), \tag{1.65}$$

where in the second line we have used relations 1.36.

It would be nice if we could write this expression as a derivative of something, because then we could just straightforwardly integrate the continuity equation to obtain j. Luckily, by adding zero we can see that this expression has the form

$$\frac{\partial^2 \psi^*}{\partial x^2}\psi - \psi^*\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi^*}{\partial x^2}\psi + \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} - \psi^*\frac{\partial^2 \psi}{\partial x^2} - \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial x} \tag{1.66}$$

$$= \frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x}\psi - \psi^*\frac{\partial \psi}{\partial x}\right), \tag{1.67}$$

and hence we have

$$\frac{\partial |\psi|^2}{\partial t} = \frac{\hbar}{2mi}\frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x}\psi - \psi^*\frac{\partial \psi}{\partial x}\right). \tag{1.68}$$

So by equation 1.62, j takes the form

$$j(x,t) = \frac{h}{2mi}\left(\psi^*\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right). \tag{1.69}$$

Chapter 2

Quantum Mechanics in One Dimension

2.1 The Free Particle

Now that we have done plenty of exposition, we will finally study at what the motion of a quantum particle actually looks like. We will first analyse the simplest case, which is that of a free particle.

2.1.1 Solving the Schrodinger Equation

A free particle is under the influence of no forces, so the potential $V(x)$ is zero. The TISE (equation 1.18) then becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} = Eu(x) \tag{2.1}$$

$$\implies \frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}u(x). \tag{2.2}$$

For a free particle, the total energy E is just the kinetic energy $\frac{p^2}{2m}$, so inputting this gives

$$\frac{\mathrm{d}^2u(x)}{\mathrm{d}x^2} = -\frac{p^2}{\hbar^2}u(x) = -k^2u(x), \tag{2.3}$$

where we have defined $k^2 = \frac{p^2}{\hbar^2}$.

This happens to be an equation we know very well, the equation for simple harmonic motion! This implies that the spatial part of the energy eigenfunctions take the form

$$u(x) = Ae^{ikx}. \tag{2.4}$$

These solutions are known as **plane wave** solutions. Plane waves of the form e^{-ikx} are also solutions, but we will ignore them for now and bring them back later.

As we learned in section 1.2.3, the temporal part of the solution is given by equation 1.23. We multiply this with the spatial part to get the full energy eigenfunctions for the free particle:

$$\psi(x,t) = Ae^{\frac{i}{\hbar}(px - Et)} = Ae^{i(kx - \omega t)}, \tag{2.5}$$

where we have introduced the frequency ω of the temporal oscillation given by

$$E = \hbar\omega. \tag{2.6}$$

This is the well-known Einstein relation. k represents the wavenumber of the oscillation in space, and is related to the particle's momentum by

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

This is known as the de Broglie relation.

Having already derived two seminal results of early quantum mechanics, you might think we are not doing too bad, however there are a couple of problems with these energy eigenfunctions.

The first issue is that these plane waves clearly do not represent the most general solution to the Schrodinger equation. In principle, we should be able to choose any valid initial wavefunction $\psi(x,0)$, which need not even be separable, and then the Schrodinger equation determines its evolution. However, for a plane wave, we can only specify A which is its amplitude (and initial phase if A is complex) at $t = 0$.

The second issue is more serious, and it is that the plane wave solutions are *unnormalisable*. To see this, we can calculate the integral of probability density over all space:

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, \mathrm{d}x = \int_{-\infty}^{\infty} |Ae^{i(kx - \omega t)}|^2 \, \mathrm{d}x = |A|^2 \int_{-\infty}^{\infty} \mathrm{d}x = \infty. \tag{2.8}$$

This happens because plane waves do not decay as $x \to \pm\infty$. Physically, this happens because plane waves have *definite* momentum and therefore, by the uncertainty principle, their position is *completely undefined*. This reflects the fact that if we calculate the probability density for a plane wave, it is *constant* everywhere in space!

$$|\psi(x,t)|^2 = |Ae^{i(kx - \omega t)}|^2 = |A|^2. \tag{2.9}$$

The fact that plane waves have definite momentum is elucidated by the fact that they are eigenstates of the momentum operator. This means that if we measure the momentum of a plane wave, we get back a definite result.

$$\hat{p}\psi(x,t) = -i\hbar A \frac{\partial}{\partial x} e^{\frac{i}{\hbar}(px - Et)} = -i\hbar A \frac{ip}{\hbar} e^{\frac{i}{\hbar}(px - Et)} = p\psi(x,t). \tag{2.10}$$

To be clear, the fact that momentum eigenstates are unnormalisable means that they are **unphysical**, a free particle can *never* be found in a stationary state.

Luckily both of these problems, the lack and generality and the unnormalisability, can be solved using the linearity of the Schrodinger equation, i.e. using the superposition principle.

2.1.2 Wave Packets

For a wavefunction to be normalisable, it must be localised to some extent in space. Using the principle of superposition, we can add together momentum eigenstates to get a normalisable wavefunction. This will have the consequence of the particle no longer having definite momentum, but that means that position will no longer be undefined.

Let us consider a superposition of two momentum eigenstates with wavenumbers k_1 and k_2. Note that wavenumber k is basically synonymous with momentum in quantum mechanics, as the two are related by the de Broglie relation 2.7.

$$\psi(x,t) = Ae^{i(k_1 x - \omega_1 t)} + Be^{i(k_2 x - \omega_2 t)}. \tag{2.11}$$

The temporal frequencies ω_1 and ω_2 are given by the Einstein relation 2.6, so $\omega_1 = \frac{E_1}{\hbar} = \frac{p_1^2}{2m\hbar}$ and similarly for ω_2. In the same way that wavenumber is synonymous with momentum, temporal frequency is synonymous with energy. This solution is no longer separable, i.e. it is not of the form $\psi(x,t) = u(t)e^{i\omega t}$. Now, the probability density is not uniform over all space and this wavefunction is no longer a momentum eigenstate, however this wavefunction is still not normalisable as it is periodic.

In fact, we can add together infinitely many plane waves, and this would still be the case.

$$\psi(x,t) = \sum_n A_n e^{i(k_n x - \omega_n t)}. \tag{2.12}$$

Notice that this is a **Fourier series**, which are always periodic over the domain $(-\infty, \infty)$.

To fully eliminate the periodicity, we need to make the range of wavenumbers continuous, and so the sum becomes an integral.

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k)e^{i(kx - \omega t)} \, \mathrm{d}k. \tag{2.13}$$

The intuition for why this is the case is that as the spacing between wavenumbers decreases, the spacing between maxima in the Fourier sum increases. So in the limit that the wavenumber spacing goes to zero and becomes continuous, the spacing between maxima goes to infinity. Notice that the amplitudes and initial phases of the plane waves A_n have become a function of the wavenumber $A(k)$. This definition of $\psi(x,t)$ in terms of an integral of plane waves is known as a **wave packet**. The factor $1/\sqrt{2\pi}$ in front of the integral is placed there because it happens to be the correct normalisation (so the integral of $|\psi(x,t)|^2$ over all space is one), which will be explained in a moment.

If we absorb the time evolution into $A(k)$ so it becomes $A(k,t) = A(k)e^{-i\omega t}$, then this wavefunction becomes

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k,t)e^{ikx} \, \mathrm{d}k, \tag{2.14}$$

which shows that the wavefunction $\psi(x,t)$ is the **Fourier transform** of $A(k,t)$. Likewise, we can say that the amplitude $A(k,t)$ is the Fourier transform of the wavefunction $\psi(x,t)$:

$$A(k,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x,t)e^{-ikx} \, \mathrm{d}x. \tag{2.15}$$

There is a result from mathematics called **Parseval's theorem**, which says that if $\psi(x,t)$ is normalised, then its Fourier transform $A(k,t)$ is normalised, and vice versa. This means that if we enforce

$$\int_{-\infty}^{\infty} |A(k,t)|^2 \, \mathrm{d}k = 1, \tag{2.16}$$

then $\psi(x,t)$ will be a correctly normalised wavefunction.

Note that we can also define this Fourier integral in terms of momentum using the de Broglie relation 2.7:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p,t) e^{\frac{i}{\hbar}px} \, \mathrm{d}p \tag{2.17}$$

$$\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x,t) e^{-\frac{i}{\hbar}px} \, \mathrm{d}x, \tag{2.18}$$

where the normalisation factor has changed to $1/\sqrt{2\pi\hbar}$.

We can interpret $|A(k,t)|^2$ as the **wavenumber probability density** and $|\phi(p,t)|^2$ as the **momentum probability density**, i.e. $|\phi(p,t)|^2 \, \mathrm{d}p$ represents the probability that a measurement of a particle's momentum will be in the range $(p, p + \mathrm{d}p)$ at time t.

In summary, we have found that by choosing an appropriate range of momenta and amplitudes for their corresponding plane waves (namely a $\phi(p,t)$ or $A(k,t)$ which is normalisable), we can construct a normalised wave packet $\psi(x,t)$. This all followed from the principle of superposition. Furthermore, note that the Fourier transform relations above hold for *any* system in quantum mechanics, not just the free particle. However, there is an important caveat that $E = p^2/2m$ does not hold in general, only for the free particle.

2.2   Gaussian Wave Packets

We will now look at a concrete example of a valid state for a free particle constructed as a wave packet and study its properties to get a general idea of how wavefunctions behave in quantum mechanics. As discussed in section 2.1.2 above, this begins with choosing a set of wavenumbers and their amplitudes $A(k)$. We will start with constructing the wave packet at $t = 0$, then we will discuss how it evolves with time.

2.2.1   Choosing an Amplitude $A(k)$

It would be nice to choose $A(k)$ to be a Gaussian shape, because then the Fourier transform $\psi(x,0)$ will also be a Gaussian, and Gaussians are nice to work with.

Recall that a Gaussian function has the general form

$$\frac{a}{\sqrt{\pi}} e^{-\frac{(x-c)^2}{b^2}}, \tag{2.19}$$

which is a bell curve centered at c, with height $\frac{a}{\sqrt{\pi}}$, width b, and area ab. This means if we want our wavenumber probability density to be a Gaussian centered at some wavenumber k_0 with width Δk, we should choose $a = \frac{1}{\Delta k}$ so that it will be normalised.

$$A(k)^2 = \frac{1}{\Delta k \sqrt{\pi}} e^{-\frac{(k-k_0)^2}{\Delta k^2}}. \tag{2.20}$$

The width Δk is the distance from the centre at e^{-1} of the maximum height. It is a rough measure of the range of wavenumbers of the plane waves that make up the wave packet. Note that $\Delta p = \hbar \Delta k$, so the width Δk is directly related to the uncertainty in momentum.

2.2.2 Calculating the Wavefunction $\psi(x, 0)$

Using the Fourier transform given by equation 2.14, the wavefunction at $t = 0$ is given by

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} \, \mathrm{d}x \tag{2.21}$$

$$= \frac{1}{\sqrt{\Delta k \sqrt{\pi}} \sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{2\Delta k^2}} e^{ikx} \, \mathrm{d}k, \tag{2.22}$$

where in the second line we inserted the square root of equation 2.20 for $A(k)$. To integrate this we use the standard result for Gaussian integrals:

$$\int_{-\infty}^{\infty} e^{-\alpha q^2} e^{-\beta q} \, \mathrm{d}q = \sqrt{\frac{\pi}{\alpha}} e^{\frac{\beta^2}{4\alpha}}. \tag{2.23}$$

With $q = k - k_0$ (so $\mathrm{d}q = \mathrm{d}k$), we get

$$\psi(x, 0) = \frac{1}{\sqrt{\Delta k \sqrt{\pi}} \sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{q^2}{2\Delta k^2}} e^{i(q+k_0)x} \, \mathrm{d}q \tag{2.24}$$

$$= \frac{1}{\sqrt{\Delta k \sqrt{\pi}} \sqrt{2\pi}} e^{ik_0 x} \int_{-\infty}^{\infty} e^{-\frac{q^2}{2\Delta k^2}} e^{iqx} \, \mathrm{d}q. \tag{2.25}$$

We can now use the standard integral with $\alpha = \frac{1}{2\Delta k^2}$ and $\beta = -ix$ to get

$$\psi(x, 0) = \frac{\sqrt{2\pi \Delta k^2}}{\sqrt{\Delta k \sqrt{\pi}} \sqrt{2\pi}} e^{ik_0 x} e^{-\frac{\Delta k^2 x^2}{2}} \tag{2.26}$$

$$= \sqrt{\frac{\Delta k}{\sqrt{\pi}}} e^{ik_0 x} e^{-\frac{x^2 \Delta k^2}{2}}. \tag{2.27}$$

What is the probability density at $t = 0$? We can calculate this directly by taking the magnitude square:

$$|\psi(x, 0)|^2 = \frac{\Delta k}{\sqrt{\pi}} e^{-x^2 \Delta k^2} = \frac{\Delta k}{\sqrt{\pi}} e^{-\frac{x^2}{\Delta x_0^2}}, \tag{2.28}$$

where we have defined $\Delta x_0 = \frac{1}{\Delta k}$ as the width at $t = 0$. So the probability density is also a Gaussian, this time centered at $x = 0$, with width $\Delta x_0 = \frac{1}{\Delta k}$.

Notice that $\Delta x_0 \Delta k = 1$, which can be expressed in term of momentum via the de Broglie relation:

$$\Delta x_0 \Delta p = \hbar. \tag{2.29}$$

This is a manifestation of the uncertainty principle. The factor of 1 arises from our definition of width of a Gaussian. Notice that the width of the position probability density is inversely proportional to the width of the wavenumber probability density. This reflects the fact that due to the uncertainty principle, if the uncertainty in momentum Δk is small then the uncertainty in position Δx_0 must be wide and vice versa.

2.2.3 Time-evolution of the Gaussian Wave Packet

As we found in section 2.1.2, the time evolution of our wave packet is given by

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx-\omega t)} \, \mathrm{d}k. \tag{2.30}$$

To evaluate this, we need to keep in mind that ω is a function of k through the Einstein and de Broglie relations. Specifically, for a free particle only we have $E = \frac{p^2}{2m}$, which gives

$$E = \frac{p^2}{2m} \tag{2.31}$$

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \tag{2.32}$$

$$\implies \omega(k) = \frac{\hbar k^2}{2m}. \tag{2.33}$$

This is our **dispersion relation** for matter waves. Note that the ω is not proportional to k, so matter waves are **dispersive**. This means that different wavelength will travel at different speeds. The phase velocity is given by

$$v_{\mathrm{ph}}(k) = \frac{\omega}{k} = \frac{\hbar k}{2m}, \tag{2.34}$$

so shorter wavelengths (larger k) travel faster. This makes physical sense as large k corresponds to large momentum. Meanwhile the group velocity for a wave packet centered at k_0 is

$$v_{\mathrm{gr}}(k) = \left. \frac{\mathrm{d}\omega}{\mathrm{d}k} \right|_{k_0} = \frac{\hbar k_0}{2m} = 2v_{\mathrm{ph}}(k_0). \tag{2.35}$$

This is the speed that the envelope of the wave packet will travel at. Combining these ideas together, we expect that the wave packet will be smudged out over time, as some wavelengths in it travel faster and some slower.

Let's see if we can show this explicitly. Substituting the square root of equation 2.20 for $A(k)$ and equation 2.33 for $\omega(k)$ into the integral, we get

$$\psi(x,t) = \frac{1}{\sqrt{\Delta k \sqrt{\pi}}\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{2\Delta k^2}} e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} \, \mathrm{d}k. \tag{2.36}$$

We would like to use the standard integral 2.23 for Gaussians again. Making the same substitution as in section 2.2.2 above ($q = k - k_0$) gives

$$\psi(x,t) = \frac{1}{\sqrt{\Delta k \sqrt{\pi}}\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{q^2}{2\Delta k^2}} e^{i(q+k_0)x} e^{-\frac{i\hbar(q+k_0)^2}{2m}t} \, \mathrm{d}q \tag{2.37}$$

$$= \frac{1}{\sqrt{\Delta k \sqrt{\pi}}\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{q^2}{2\Delta k^2}} e^{iqx} e^{ik_0 x} e^{-\frac{i\hbar q^2}{2m}t} e^{-\frac{i\hbar q k_0}{m}t} e^{-\frac{i\hbar k_0^2}{2m}t} \, \mathrm{d}q. \tag{2.38}$$

We can simplify the notation a bit by defining $\omega_0 = \frac{\hbar k_0^2}{2m}$, the frequency of the state with wavenumber k_0, and using the group velocity $v_{\mathrm{gr}}(k_0) = \frac{\hbar k_0}{m}$. The fifth and sixth exponentials can be

rewritten in terms of these quantities, and then the third and fifth exponentials can be taken out of the integral to get

$$\psi(x,t) = \frac{1}{\sqrt{\Delta k \sqrt{\pi}}\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} e^{-\left(\frac{1}{2\Delta k^2} + \frac{i\hbar}{2m}t\right)q^2} e^{-i(v_{\mathrm{gr}}(k_0)t - x)q} \, dq. \tag{2.39}$$

Now we can use the standard integral with

$$\alpha = \frac{1}{2\Delta k^2} + \frac{i\hbar}{2m}t \tag{2.40}$$

$$\beta = i(v_{\mathrm{gr}}(k_0)t - x), \tag{2.41}$$

to get

$$\psi(x,t) = \frac{1}{\sqrt{\Delta k \sqrt{\pi}}\sqrt{2\pi}} \sqrt{\frac{\pi}{\frac{1}{2\Delta k^2} + \frac{i\hbar}{2m}t}} e^{i(k_0 x - \omega_0 t)} e^{-\frac{(x - v_{\mathrm{gr}}(k_0)t)^2}{4\left(\frac{1}{2\Delta k^2} + \frac{i\hbar}{2m}t\right)}} \tag{2.42}$$

$$= \sqrt{\frac{\Delta k}{\sqrt{\pi}\left(1 + \frac{i\hbar\Delta k^2 t}{m}\right)}} e^{i(k_0 x - \omega_0 t)} e^{-\frac{\Delta k^2 (x - v_{\mathrm{gr}}(k_0)t)^2}{2\left(1 + \frac{i\hbar\Delta k^2 t}{m}\right)}}. \tag{2.43}$$

Calculating the probability density, we get

$$|\psi(x,t)|^2 = \frac{\Delta k}{\sqrt{\pi}\sqrt{1 + \frac{\hbar^2 \Delta k^4 t^2}{m^2}}} e^{-\frac{\Delta k^2 (x - v_{\mathrm{gr}}(k_0)t)^2}{1 + \frac{\hbar^2 \Delta k^4 t^2}{m^2}}}. \tag{2.44}$$

This is quite a complicated expression, but there are a few key things we can pick out that tell us in simple terms how the wave packet behaves. The structure of the probability density is basically

$$|\psi(x,t)|^2 = C(t) e^{-\frac{(x - x_0(t))^2}{\Delta x(t)^2}}, \tag{2.45}$$

so we see that the height, width, and centre of the wave packet all change with time while retaining a Gaussian form.

Comparing the two expressions, the centre of the wave packet x_0 evolves as

$$x_0(t) = v_{\mathrm{gr}}(k_0)t, \tag{2.46}$$

so the position of the peak of the wavepacket moves to the right with a constant speed, the speed of the central wavenumber (or equivalently, the speed of the envelope). This makes sense, there are no forces acting on the particle so its speed stays constant with time.

The width of the wave packet is

$$\Delta x(t) = \frac{1}{\Delta k}\sqrt{1 + \frac{\hbar^2 \Delta k^4 t^2}{m^2}} = \Delta x_0 \sqrt{1 + \frac{\hbar^2 \Delta k^4 t^2}{m^2}}, \tag{2.47}$$

where we have reintroduced $\Delta x_0 = \frac{1}{\Delta k}$, the width of the wave packet at $t = 0$ from before. Thus the width Δx increases over time just like we predicted.

The height has the form

$$C(t) = \frac{1}{\sqrt{\pi}\Delta x(t)}, \tag{2.48}$$

so since the width increases with time, the height decreases. This makes sense, as to preserve the normalisation of the wave packet the amplitude must decrease as it spreads out.

Notice that in the limit $t \to 0$, we get back our previous results for the initial wave packet $\psi(x, 0)$. If Δk is larger at $t = 0$, i.e. if the uncertainty in momentum Δp is larger, the the wavepacket spreads out more slowly.

Does the uncertainty in momentum Δp increase over just like Δx? From equation 2.17, we have

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p, t) e^{\frac{i}{\hbar}px} \, \mathrm{d}p \tag{2.49}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p, 0) e^{\frac{i}{\hbar}(px - Et)} \, \mathrm{d}p. \tag{2.50}$$

For the free particle, we have $E = \frac{p^2}{2m}$ and so

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p, 0) e^{-\frac{i}{\hbar}\frac{p^2}{2m}t} e^{\frac{i}{\hbar}px} \, \mathrm{d}p. \tag{2.51}$$

Hence we have that

$$|\phi(p, t)|^2 = |\phi(p, 0) e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}|^2 = |\phi(p, 0)|^2, \tag{2.52}$$

so the momentum probability density remains the same over time and Δp does not change. This is not a general fact, it only holds for the free particle. We will find that when there are forces present, Δp does indeed increase over time. In that sense, this is sort of a quantum analogue of Newton's first law.

2.3 The Infinite Square Well

We will now study the motion of a free particle that is confined to a finite region of space. This is known as the **infinite square well** because the situation is described by an infinitely deep potential well, or sometimes it is called the **particle in a box** problem.

2.3.1 Setting up the Schrodinger Equation

Our square well will go from $x = 0$ to $x = L$, then as stated above, the potential energy for this system takes the piecewise form

$$V(x) = \begin{cases} \infty & \text{for } x \leq 0 \\ 0 & \text{for } 0 < x < L \\ \infty & \text{for } x \geq L. \end{cases} \tag{2.53}$$

Inside the well, the TISE will therefore look just like it does for the free particle (since there are no forces acting inside the well), which is given by equation 2.1:

$$\frac{\mathrm{d}^2 u(x)}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2} u(x). \tag{2.54}$$

This equation may look the same as for the free particle, but the solutions take a slightly different form because the **boundary conditions** are different: equation 2.54 is only valid inside the well.

Outside the well, the potential is infinite, so the wavefunction cannot exist and must be zero.

2.3.2 Energy Eigenfunctions

Equation 2.54 has the general solution

$$u(x) = A\sin(kx) + B\cos(kx), \tag{2.55}$$

where the wavenumber is

$$k = \frac{\sqrt{2mE}}{\hbar}. \tag{2.56}$$

We could write this using complex exponentials like we did for the free particle, but using trigonometric functions simplifies things here as we will see shortly.

We now need to take into account the boundary conditions. Recall from section 1.3.1, that the wavefunction needs to be continuous over all space. For this to be the case, we must have that the wavefunction vanishes at the boundaries of the well.

$$u(0) = u(L) = 0. \tag{2.57}$$

The first condition implies that B must be zero, and the second implies

$$A\sin(kL) = 0 \tag{2.58}$$

$$\implies k_n = \frac{n\pi}{L}, \tag{2.59}$$

where n is a positive integer (negative integers give the same solutions multiplied by -1 since sine is an odd function, so we just ignore them, and $n = 0$ makes the wavefunction zero everywhere, which is not interesting so we ignore that too). So the wavenumber can only take on a discrete set of values given by positive integer multiples of $\frac{\pi}{L}$, which we have labelled k_n with a subscript.

A is the normalisation constant, which we can calculate by looking at the probability density:

$$\int_{-\infty}^{\infty} |A\sin(k_n x)| \, dx = |A|^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx \overset{!}{=} 1. \tag{2.60}$$

The integral is $\frac{L}{2}$, which implies that $A = \sqrt{\frac{2}{L}}$.

Thus, in contrast to the particle which is free over all space, the particle confined to a finite region has a **discrete** set of eigenfunctions, the spatial parts of which are given by

$$u_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, \ldots \tag{2.61}$$

The energy eigenvalues are given by equation 2.56:

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}n^2. \tag{2.62}$$

So the total energy is only allowed to be from a discrete set of values as well.

The full time-dependent energy eigenstates are

$$\psi_n(x, t) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)e^{-\frac{\pi^2\hbar}{2mL^2}n^2 t}, \quad n = 1, 2, 3, \ldots \tag{2.63}$$

In Dirac notation, these are written as $|n\rangle$. Although it can be ambiguous whether the wavefunction for a state $|n\rangle$ (i.e. $\langle x|n\rangle$) is the full time-dependent eigenfunction ψ_n or just the spatial part u_n, it is usually either determined by context or it does not matter.

As n increases, the spacing between the energy levels gets larger. Also note that the more narrow the well (smaller L), the higher the energy levels. Note that the lowest possible energy, what we call the **ground state**, is found when $n = 1$, so the particle can never have zero energy. These are manifestations of the uncertainty principle, specifically that localising a particle necessitates if having a higher momentum uncertainty as we saw in section 1.5. A particle which has any localisation at all can never have zero energy, since that would imply it has zero momentum for certain.

2.3.3 Probability Density

As we can see from equation 2.63, the wavefunction of the particle oscillates faster in both space and time the large n is. This carries over to the spatial probability density, which is

$$|\psi_n(x,t)|^2 = \frac{2}{L} \sin^2\left(\frac{n\pi}{L}x\right). \tag{2.64}$$

How does this compare to the probability density of a classical free particle in an infinite well? This would be like a particle sliding back and force on a frictionless surface between two walls, with elastic collisions at both ends. Since the particle's speed is constant, it is equally likely to be found anywhere within the well, so we have

$$P_{\text{Cl}} = \frac{1}{L}. \tag{2.65}$$

The correspondence principle suggests that the quantum probability density would reduce to the classical probability density in the classical limit of large energy (large n). This does not appear to be the case here, but we need to look at the actual probability rather than just the values of probability density. It is the case that as $n \to \infty$, $|\psi_n|^2 \Delta x$ tends to $P_{\text{Cl}}\Delta x$ for any interval Δx.

Why then does the quantum probability density oscillate with ever shorter wavelength for increasing n? The answer comes from looking at the expectation value of the particle's kinetic energy. We saw that the kinetic energy operator was given by equation 1.12, so the expectation value for a general wavefunction $\psi(x,t)$ is

$$\langle \hat{T} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{T} \psi \, \mathrm{d}x \tag{2.66}$$

$$= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \psi}{\partial x^2} \, \mathrm{d}x. \tag{2.67}$$

Integrating by parts and using the same argument as in section 1.4.2 to justify that the surface terms vanish, we get

$$\langle \hat{T} \rangle = -\frac{\hbar^2}{2m} \left[\psi^* \frac{\partial \psi}{\partial x} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} \, \mathrm{d}x \right] \tag{2.68}$$

$$= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{\partial \psi}{\partial x} \right|^2 \mathrm{d}x. \tag{2.69}$$

So the average kinetic energy is related to the "wiggliness" of the wavefunction. In particular, for the infinite square well we find that the expectation of kinetic energy for the energy eigenstates $\langle \hat{T} \rangle_{\psi_n} = E_n$, so as n increases the wavefunction oscillates with shorter wavelengths.

2.4 Properties of Energy Eigenstates

We will now discuss some properties of the energy eigenstates. These apply for the eigenstates of the infinite square well (equation 2.63), but also to the solutions of the TISE for any other problem.

2.4.1 Orthonormality

Orthonormality consists of two properties of a set of functions: being mutually orthogonal, and being all normalised. Orthogonality of wavefunctions in quantum mechanics is measured using an **inner product**, which is defined by the integral:

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m \, \mathrm{d}x. \tag{2.70}$$

If this integral is zero, the two wavefunctions are orthogonal. If it is non zero, then they are not orthogonal. Sometimes the inner product is referred to as the **overlap** of the two wavefunctions. A set of wavefunctions being mutually orthogonal means that each wavefunction in the set is orthogonal to every other one.

Taking the two conditions together, a set of wavefunctions ψ_n are said to be mutally orthonormal if

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m \, \mathrm{d}x = \delta_{n,m} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m. \end{cases} \tag{2.71}$$

This statement implies that the wavefunctions are mutually orthogonal except in the case where we are taking the inner product of a wavefunction with itself, in which case we have the integral of the magnitude squared which would be one to have the wavefunction normalised. We have introduced the **Kronecker delta** $\delta_{n,m}$ which is shorthand for the piecewise definition on the right so simplify the notation. In Dirac notation, this is written as

$$\langle n | m \rangle = \delta_{n,m}. \tag{2.72}$$

Why is it always the case that the wavefunctions are orthonormal? We will prove later on that it is because the Hamiltonian is a Hermitian operator.

2.4.2 Eigenfunctions form a Basis

For any problem in quantum mechanics, the energy eigenfunctions form what is known as a **basis**. This means that we can expand any valid wavefunction ψ which fulfills the boundary conditions as a linear superposition of energy eigenstates:

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x,t) = \sum_{n=1}^{\infty} c_n u_n(x) e^{-\frac{iE_n}{\hbar}t}, \tag{2.73}$$

where $\psi_n(x,t)$ are the energy eigenfunctions, $u_n(x)$ are the spatial part, E_n are the energy eigenvalues, and c_n are the coefficients in the superposition. Note that we have taken $n = 1$ to ∞ to be the indices for the sum since those are the indices for the eigenfunctions of the infinite square well, but when applying this to other problems we could have different labels.

This is exactly what we saw in section 2.2 when we constructed a normalisable wave packet as an integral over energy/momentum eigenstates. In that case (for the free particle), a finite or

even discretely infinite superposition was still not normalisable, but in general it will be because the energy eigenstates are normalisable. Note that the probability density of a superposition does depend on time in almost all cases, because the time-dependent phases in the energy eigenstates rotate at different frequencies. This causes them to have a phase difference which causes the time-dependence.

For the wavefunction ψ to be correctly normalised, we must then have

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \tag{2.74}$$

There is a physical interpretation for the coefficients of the superposition c_n. If we look at the expectation value of the Hamiltonian for the above superposition, we get

$$\langle \hat{H} \rangle_{\psi} = \int_{-\infty}^{\infty} \psi^* \hat{H} \psi \, \mathrm{d}x \tag{2.75}$$

$$= \int_{-\infty}^{\infty} \sum_{m=1}^{\infty} c_m^* \psi_m^* \sum_{n=1}^{\infty} c_n \hat{H} \psi_n \, \mathrm{d}x \tag{2.76}$$

$$= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} E_n c_m^* c_n \int_{-\infty}^{\infty} \psi_m^* \psi_n \, \mathrm{d}x \tag{2.77}$$

$$= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} E_n c_m^* c_n \delta_{n,m} \tag{2.78}$$

$$= \sum_{n=1}^{\infty} E_n |c_n|^2. \tag{2.79}$$

If we compare this to equation 1.29, we see that $|c_n|^2$ is the probability of finding the value E_n if the particle's energy is measured.

This is immediately apparent if we write the superposition using Dirac notation, it takes the form of equation 1.3:

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n |n\rangle = \sum_{n=1}^{\infty} \langle n|\psi\rangle |n\rangle, \tag{2.80}$$

where $\langle n|\psi\rangle$, the inner product or overlap between $|\psi\rangle$ and the eigenstate $|n\rangle$, is the probability that we find the particle in state $|n\rangle$ upon measuring the energy.

2.4.3 Expanding in the Energy Eigenbasis

What about if we have a wavefunction that is not clearly written as a superposition of energy eigenstates. How can we find its time evolution? For example, consider an initial state for the infinite square well

$$\psi(x,0) = N \sin^3 \left(\frac{\pi x}{L} \right) \quad \text{for } 0 < x < L, \tag{2.81}$$

where $\psi(x,0) = 0$ outside the well. This is a valid wavefunction for the system (it is a valid wavefunction which can be normalised for a suitable choice of N and it goes to zero at the boundaries of the well), but it is not written in the form 2.73.

Since it is not of the form of one of the energy eigenfunctions, given by equation 2.61, it must be a superposition state. The challenge is finding the right coefficients c_n to write it in the

form 2.73. This is basically a generalised Fourier series problem, with the energy eigenfunctions taking the place of sine and cosine. Notice that the energy eigenfunctions share the same essential properties for solving this problem that sine and cosine have, namely that they for a complete and orthonormal basis for the set of functions we are interested in.

Let us suppose that $\psi(x, 0)$ from above takes the form

$$\psi(x, 0) = \sum_{m=1}^{\infty} c_m u_m(x), \tag{2.82}$$

and then, inspired by the connection to Fourier series, let us multiply by $u_n(x)**$ and integrate over all space.

$$\int_{-\infty}^{\infty} u_n(x)^* \psi(x, 0) \, \mathrm{d}x = \int_{-\infty}^{\infty} u_n(x)^* \sum_{m=1}^{\infty} c_m u_m(x) \, \mathrm{d}x \tag{2.83}$$

$$= \sum_{m=1}^{\infty} c_m \int_{-\infty}^{\infty} u_n(x)^* u_m(x) \, \mathrm{d}x \tag{2.84}$$

$$= \sum_{m=1}^{\infty} c_m \delta_{n,m} \tag{2.85}$$

$$= c_n. \tag{2.86}$$

So we have found that for any initial wavefunction $\psi(x, 0)$, we can expand in energy eigenfunctions with coefficients given by the inner product of the spatial part of the energy eigenfunction with the wavefunction:

$$c_n = \int_{-\infty}^{\infty} u_n^* \psi(x, 0) \, \mathrm{d}x. \tag{2.87}$$

Of course, we know this already from equation 2.80, but it is nice to prove it another way. Once we have the coefficients c_n, the time evolution is straightforwardly given by 2.73.

This derivation makes sense because it shows that, in the same way that Fourier series work, if a given wavefunction looks "similar" to one of the eigenstates, the inner product between them, and therefore the corresponding coefficient, will be larger than the others. This means that the time evolution of the superposition will be mostly similar to that of the most similar eigenstate.

2.4.4   Time Evolution of Superpositions

Let us consider, as a simple example, the following superposition of two energy eigenstates:

$$\psi(x, t) = \frac{1}{\sqrt{2}}(u_1(x)e^{-\frac{iE_1}{\hbar}t} + u_2(x)e^{-\frac{iE_2}{\hbar}t}). \tag{2.88}$$

The time evolution of the probability density is given by

$$|\psi(x, t)|^2 = \frac{1}{2}|u_1(x)|^2 + \frac{1}{2}|u_2(x)|^2 + u_1^*(x)u_2(x) \cos\left(\frac{(E_2 - E_1)t}{\hbar}\right). \tag{2.89}$$

If no measurement of the particle is made then its wavefunction evolves deterministically like this, governed by the Schrodinger equation. If the particle's energy is measured, its state will instantly and non-deterministically collapse into one of the energy eigenstates. For example when

measuring the energy of the two-energy state above, we can tell from the coefficients that we have 50% probability to measure E_1 and 50% probability to measure E_2. Suppose we measure E_2, then the particle's wavefunction becomes

$$\psi(x,t) = u_2(x)e^{-\frac{iE_2}{\hbar}t}, \tag{2.90}$$

i.e. the particle is now in an energy eigenstate and the probability density is constant over time. All subsequent measurements of the energy will therefore return E_2.

If we measured an observable $\hat{O}$ whos eigenfunctions are not also eigenfunctions of the Hamiltonian, then the collapsed state after measurement will evolve as a superposition state. For example, if we had a particle in an infinite square well and we measured the particle's momentum, then its wavefunction would collapse into a momentum eigenstate. As we have seen, these are not energy eigenstates, so they must be superpositions of energy eigenstates. Such observables with different sets of eigenfunctions are called **incompatible**, and we will study them more in section 2.6.

Note that when an observable operator $\hat{O}$ acts on a state ψ which is not an eigenstate of $\hat{O}$, the result $\hat{O}\psi$ is *not* what we measure. $\hat{O}\psi$ is a superposition of eigenstates of $\hat{O}$ multiplied by eigenvalues and probability amplitudes of measuring each value. The wavefunction after measurement collapses into one of the eigenstates of $\hat{O}$.

2.5 Hermitian Operators

The goal of this section is to think a little bit more about what kinds of operators we can have in quantum mechanics. We have seen that operators represent observable properties of a quantum system, with their eigenvalues representing possible measurement outcomes, but is this the case for all operators? Do all operators represent observable quantities? If not, how can we tell if an operator does represent an observable?

It turns out that only a special subset of operators are observables. These operators are the so-called **Hermitian operators**, which is a mathematical property. We will go over what this means and why Hermitian operators are observable below, but first we need to introduce another property of operators, the adjoint.

2.5.1 The Adjoint

For every operator $\hat{O}$ we can define a generalisation of the complex conjugate of a scalar called the **adjoint**, or **Hermitian conjugate**, denoted with $\hat{O}^\dagger$. But how do we define the complex conjugate of an operator? In a finite dimensional Hilbert space where operators are matrices, the generalisation of the complex conjugate is the conjugate transpose. But how do we define the conjugate transpose of an operator in an infinite dimensional Hilbert space?

Instead of trying to wrap our heads around what different types of operators in infinite dimensions can look like and trying to define a generalisation of conjugate transpose for them, let's look at how the conjugate transpose acts on vectors. In finite dimensions, we have that for a complex vector $\boldsymbol{u}$ and a matrix A:

$$(A\boldsymbol{u})^\dagger = \boldsymbol{u}^\dagger A^\dagger, \tag{2.91}$$

where the † denotes conjugate transpose. This means for the inner product of $A\boldsymbol{u}$ with another complex vector $\boldsymbol{v}$ we have

$$A\boldsymbol{u} \cdot \boldsymbol{v} = (A\boldsymbol{u})^\dagger \boldsymbol{v} = \boldsymbol{u}^\dagger A^\dagger \boldsymbol{v} = \boldsymbol{u} \cdot (A^\dagger \boldsymbol{v}). \tag{2.92}$$

In Dirac notation this would be written as

$$\langle \hat{A}u | v \rangle = \langle u | \hat{A} | v \rangle. \tag{2.93}$$

We can now simply *define* the adjoint of an operator in an infinite dimensional Hilbert space to satisfy this relation.

Definition 2.1. For an operator $\hat{O}$, the **adjoint**, or **Hermitian conjugate**, of $\hat{O}$, denoted $\hat{O}^\dagger$, is the operator which for any states $|\psi\rangle$ and $|\phi\rangle$ satisfies:

$$\langle \hat{O}\psi | \phi \rangle = \langle \psi | \hat{O}^\dagger | \phi \rangle, \tag{2.94}$$

or in the position basis:

$$\int_{-\infty}^{\infty} (\hat{O}\psi)^* \phi \, \mathrm{d}x = \int_{-\infty}^{\infty} \psi^* \hat{O}^\dagger \phi \, \mathrm{d}x. \tag{2.95}$$

Some operators are equal to their own adjoint.

$$\hat{O}^\dagger = \hat{O}. \tag{2.96}$$

These operators are called **self-adjoint**, or more commonly among physicists, **Hermitian**.

Definition 2.2. A **Hermitian operator** is an operator $\hat{O}$ that is equal to its own adjoint $\hat{O}^\dagger$. Hermitian operators can therefore be defined by the following identity:

$$\langle \hat{O}\psi | \phi \rangle = \langle \psi | \hat{O} | \phi \rangle, \tag{2.97}$$

or in the position basis:

$$\int_{-\infty}^{\infty} (\hat{O}\psi)^* \phi \, \mathrm{d}x = \int_{-\infty}^{\infty} \psi^* \hat{O}\phi \, \mathrm{d}x. \tag{2.98}$$

Hermitian operators can be viewed as the "real numbers" of operators.

Before moving on to defining what an observable is, we will calculate the adjoint of a product of two operators. By definition of the adjoint (2.94), we have

$$\langle \hat{A}\hat{B}\psi | \phi \rangle = \langle \psi | (\hat{A}\hat{B})^\dagger | \phi \rangle. \tag{2.99}$$

However, by defining $|\chi\rangle = \hat{B}|\psi\rangle$, we can apply the definition of the adjoint differently to get

$$\langle \hat{A}\chi | \phi \rangle = \langle \chi | \hat{A}^\dagger | \phi \rangle = \langle \hat{B}\psi | \hat{A}^\dagger | \phi \rangle. \tag{2.100}$$

Then, defining $|v\rangle = \hat{A}^\dagger |\phi\rangle$ and applying the definition of the adjoint one more time, we have

$$\langle \hat{B}\psi | v \rangle = \langle \psi | \hat{B}^\dagger | v \rangle = \langle \psi | \hat{B}^\dagger \hat{A}^\dagger | \phi \rangle. \tag{2.101}$$

Comparing this to equation 2.99, we have shown that

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger. \tag{2.102}$$

So the adjoint of the product of two operators is equal to the product of the adjoints in the opposite order. Note that these equations could equivalently be written with the position basis integral notation, but we will use Dirac notation from now on because it is less cumbersome.

2.5.2 What are Observables?

Let us think about what properties we require of operators for them to represent physical observables. We would like that all the eigenvalues are real, since they represent measurement outcomes. Additionally, we also require that eigenvectors corresponding to distinct eigenvalues are orthogonal, otherwise our probabilistic interpretation of state vectors in Hilbert space wouldn't work. Finally, we would like that the eigenvectors of an observable form a basis for Hilbert space, so that any valid state of the system can be expressed as a superposition of eigenstates.

Looking at the first property, we will first show that all eigenvalues of an operator being real is equivalent to the expectation value of the operator for any valid state being real. Let $\hat{O}$ be an operator with eigenstates $|i\rangle$ and eigenvalues O_i, so

$$\hat{O}|i\rangle = O_i|i\rangle \quad \forall i. \tag{2.103}$$

Suppose the expectation value for *any* state $|\psi\rangle$, $\langle \hat{O} \rangle_\psi$ is real. Then the expectation value of $\hat{O}$ for each eigenstate is

$$\langle \hat{O} \rangle_i = \langle i|\hat{O}|i\rangle = O_i\langle i|i\rangle = O_i, \tag{2.104}$$

which implies that O_i must be real. Conversely, if we assume that all of the O_i's are real, then the expectation value of $\hat{O}$ for an arbitrary state $|\psi\rangle$ is

$$\langle \hat{O} \rangle_\psi = \langle \psi|\hat{O}|\psi\rangle = \sum_{i,j} c_i^* c_j \langle i|\hat{O}|j\rangle = \sum_{i,j} c_i^* c_j O_j \langle i|j\rangle = \sum_{i,j} c_i^* c_j O_j \delta_{i,j} = \sum_i |c_i|^2 O_i, \tag{2.105}$$

which is a sum of real numbers and is therefore itself real.

Now, note that the complex conjugate of an expectation value is given by

$$\langle \hat{O} \rangle_\psi^* = (\langle \psi|\hat{O}|\psi\rangle)^* = \langle \hat{O}\psi|\psi\rangle. \tag{2.106}$$

Finally, for the expectation value an operator $\hat{O}$ to be real, we must have

$$\langle \hat{O} \rangle_\psi^* = \langle \hat{O} \rangle_\psi \tag{2.107}$$

$$\implies \langle \hat{O}\psi|\psi\rangle = \langle \psi|\hat{O}|\psi\rangle, \tag{2.108}$$

and this is exactly the definition of a Hermitian operator! So this implies that if $\hat{O}$ is Hermitian, all of its eigenvalues are real and thus it seems to be a valid candidate for an observable. The converse is also true: if all of the eigenvalues of an operator are real, then that operator is Hermitian. This equivalency leads us to believe that *all* observables are Hermitian operators (and vice versa!).

What about the other properties? It turns out that Hermitian operators fulfill them too.

Consider a Hermitian operator $\hat{O}$ and let $|i\rangle$ and $|j\rangle$ be eigenstates of $\hat{O}$ with eigenvalues O_i and O_j respectively. Then because $\hat{O}$ is Hermitian, we have that

$$\langle i|\hat{O}|j\rangle - \langle j|\hat{O}|i\rangle^* = 0, \tag{2.109}$$

but by expanding these inner products we find

$$\langle i|\hat{O}|j\rangle - \langle j|\hat{O}|i\rangle^* = O_j\langle i|j\rangle - O_i\langle j|i\rangle^* \tag{2.110}$$
$$= (O_j - O_i)\langle i|j\rangle. \tag{2.111}$$

Thus if $O_i \neq O_j$ then $\langle i|j\rangle = 0$ so the eigenstates must be orthogonal. What if $O_i = O_j$? Then a linear combination of $|i\rangle$ and $\hat{j}$ is also an eigenvector! Luckily, it is always possible to find two linear combinations that are orthogonal. We will come back to study this case in more detail in chapter 4.

Since the Hamiltonian is Hermitian (it represents total energy which is observable), this implies that the energy eigenfunctions (with distinct eigenvalues) are mutually orthogonal. We already saw this was the case for the infinite square well, but this implies that it is true for any system.

Finally, it can be shown that eigenvectors of Hermitian operators form a basis for the Hilbert space. This means that for a set of eigenvectors $|i\rangle$ of a Hermitian operator $\hat{O}$, any state $|\psi\rangle$ can be written

$$|\psi\rangle = \sum_i c_i|i\rangle = \sum_i |i\rangle\langle i|\psi\rangle. \tag{2.112}$$

Where we have introduced the orthonormality condition of the eigenvectors to show that the coefficients $c_i = \langle i|\psi\rangle$ (as we saw when we were expanding an arbitrary state in terms of the energy eigenfunctions for the infinite square well in section 2.4.3).

We can pull an interesting fact from this equation. If we put brackets around all the terms including i,

$$|\psi\rangle = \left(\sum_i |i\rangle\langle i|\right)|\psi\rangle, \tag{2.113}$$

then since this equation holds for any state $|\psi\rangle$, the term in the brackets must be equal to the identity operator!

$$\sum_i |i\rangle\langle i| = I. \tag{2.114}$$

This is called a **resolution of the identity**. This is a fact that comes in useful sometimes for evaluating complicated expressions and we will use it later on. In particular, it lets us write down the diagonal representation of $\hat{O}$, which is given by

$$\hat{O} = \sum_i O_i|i\rangle\langle i|. \tag{2.115}$$

Example 2.1. Consider the operator $\hat{D} = \frac{\partial}{\partial x}$. Does this operator represent an observable?
The easiest way to check this is to calculate the adjoint $\hat{D}^\dagger$ using the position basis

definition 2.95. We will start from the left hand side and integrate by parts:

$$\int_{-\infty}^{\infty} (\hat{D}\psi)^* \psi \, \mathrm{d}x = \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \psi \, \mathrm{d}x \tag{2.116}$$

$$= \psi^* \psi |_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} \, \mathrm{d}x \tag{2.117}$$

$$= \int_{-\infty}^{\infty} \psi^*(-\hat{D})\psi \, \mathrm{d}x. \tag{2.118}$$

By the definition of the adjoint, this is equal to the right hand side of equation 2.95, therefore we have

$$\hat{D}^\dagger = -\hat{D} = -\frac{\partial}{\partial x}, \tag{2.119}$$

so $\hat{D}$ is not Hermitian and therefore cannot be an observable.

2.6   Commutators

We have seen that we some operators it matters which order we apply them in. For example, if we apply $\hat{x}$ then $\hat{p}$, we may get a different result to if we apply $\hat{p}$ then $\hat{x}$. We can measure the degree to which two operators fail to commute using a simple expression called the commutator, denoted with square brackets.

Definition 2.3. The **commutator** of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{2.120}$$

If $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ commute, that is changing their order of application does not change the result.

Example 2.2. What is the commutator of position $\hat{x} = x$ and momentum $\hat{p} = -i\hbar\frac{\partial}{\partial x}$? To calculate this commutator, we need to act it on an arbitrary state $|\psi\rangle$ as if it was an operator, since $\hat{p}$ contains a derivative.

$$[\hat{x}, \hat{p}]|\psi\rangle = \hat{x}\hat{p}|\psi\rangle - \hat{p}\hat{x}|\psi\rangle \tag{2.121}$$

$$= x\left(-i\hbar\frac{\partial}{\partial x}\right)|\psi\rangle - \left(-i\hbar\frac{\partial}{\partial x}\right)(x|\psi\rangle) \tag{2.122}$$

$$= -i\hbar x \frac{\partial|\psi\rangle}{\partial x} + i\hbar\frac{\partial}{\partial x}(x|\psi\rangle) \tag{2.123}$$

$$= -i\hbar x \frac{\partial|\psi\rangle}{\partial x} + i\hbar x \frac{\partial}{\partial|\psi\rangle} + i\hbar|\psi\rangle \tag{2.124}$$

$$= i\hbar|\psi\rangle. \tag{2.125}$$

This implies that

$$[\hat{x}, \hat{p}] = i\hbar, \tag{2.126}$$

so $\hat{x}$ and $\hat{p}$ do not commute.

Going back to products of two operators briefly, when is the product of two Hermitian operators itself Hermitian? In section 2.5.1, we showed that

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger. \tag{2.127}$$

Where $\hat{A}$ and $\hat{B}$ are Hermitian, we have

$$(\hat{A}\hat{B})^\dagger = \hat{B}\hat{A} \tag{2.128}$$

$$= \hat{B}\hat{A} - \hat{A}\hat{B} + \hat{A}\hat{B} \tag{2.129}$$

$$= \hat{A}\hat{B} - [\hat{A}, \hat{B}]. \tag{2.130}$$

So the product of two Hermitian operators is Hermitian *only* if they commute, i.e. $[\hat{A}, \hat{B}] = 0$.

Note that for two general operators that do not commute, we can switch their order in an expression by introducing the commutator:

$$\hat{A}\hat{B} = \hat{A}\hat{B} - \hat{B}\hat{A} + \hat{B}\hat{A} \tag{2.131}$$

$$= \hat{B}\hat{A} + [\hat{A}, \hat{B}]. \tag{2.132}$$

Also, we have for any commutator that

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = -(\hat{B}\hat{A} - \hat{A}\hat{B}) = -[\hat{B}, \hat{A}], \tag{2.133}$$

so all commutators are antisymmetric.

You might think that two operators commuting is handy for manipulating expressions with products of operators but not much use beyond that, but actually the value of a the commutator has important implications for measurements. In particular, we can show that two observables commuting is equivalent to them *sharing* a common basis of eigenfunctions. This means that the two observables can be "measured simultaneously", which means that we can know exactly which state the particle is in with respect to both observables at the same time.

Let $\hat{A}$ and $\hat{B}$ be Hermitian operators which commute.

$$[\hat{A}, \hat{B}] = 0. \tag{2.134}$$

Suppose the kets $|i\rangle$ are the basis of $\hat{A}$ with eigenvalues A_i.

$$\hat{A}|i\rangle = A_i|i\rangle \quad \forall i. \tag{2.135}$$

Then because the commutator is zero, the order of application does not matter and we have

$$\hat{A}(\hat{B}|i\rangle) = \hat{B}(\hat{A}|i\rangle) = \hat{B}(A_i|i\rangle) = A_i(\hat{B}|i\rangle). \tag{2.136}$$

Note that the parentheses are not strictly necessary, they are just there for clarity. The first and last parts taken together are an eigenvalue equation. If each eigenstate $|i\rangle$ has a distinct eigenvalue, then this implies that $\hat{B}|i\rangle$ is a scalar multiple of $|i\rangle$. This further implies that $|i\rangle$ is an eigenstate of $\hat{B}$, and so we have shown that $\hat{A}$ and $\hat{B}$ share an eigenbasis.

Conversely, suppose that we don't know what $[\hat{A}, \hat{B}]$ is but we do know that $\hat{A}$ and $\hat{B}$ share an eigenbasis. So $\hat{A}|i\rangle = A_i|i\rangle$ and $\hat{B}|i\rangle = B_i|i\rangle$ for all values of i. Then we have that

$$[\hat{A}, \hat{B}]|i\rangle = \hat{A}(\hat{B}|i\rangle) - \hat{B}(\hat{A}|i\rangle) \tag{2.137}$$

$$= B_i\hat{A}|i\rangle - A_i\hat{B}|i\rangle \tag{2.138}$$

$$= B_iA_i|i\rangle - A_iB_i|i\rangle \tag{2.139}$$

$$= 0, \tag{2.140}$$

for all i, hence $[\hat{A}, \hat{B}]$ must be zero $\hat{A}$ commutes with $\hat{B}$.

Being able to measure two observables simultaneously makes a bit more sense now. Suppose we measure $\hat{A}$ first, then if the particle is not in an eigenstate of $\hat{A}$ already then it will collapse into one. Then, when we measure $\hat{B}$, the particle is already in an eigenstate of $\hat{B}$ and so we will get that eigenvalue and the particle will still be in the state we measured for $\hat{A}$. This would not be the case if $\hat{A}$ and $\hat{B}$ did not commute. Then upon measuring $\hat{B}$, the particle would be in a superposition state with respect to $\hat{A}$ and we would no longer know its state with respect to $\hat{A}$ for certain.

As we stated in section 2.4.4, observables which do not share a set of eigenfunctions, i.e. do not commute, are called **incompatible observables**. The most famous set of incompatible observables is certainly position and momentum. As we saw in example 2.2, position and momentum do not commute, meaning there do not exist simultaneous eigenfunctions of $\hat{x}$ and $\hat{p}$. There are therefore no quantum states with definite values of both position and momentum.

2.6.1 Uncertainty from Incompatibility

The fact that observables which do not commmute do not share eigenfunctions is directly responsible for the uncertainty principle. It can be shown that for two observables $\hat{A}$ and $\hat{B}$, the product of their uncertainties obeys the relation:

$$\Delta A \Delta B \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|. \tag{2.141}$$

This is known as the **general uncertainty relation**. The right hand side means we find the commutator of $\hat{A}$ and $\hat{B}$, then calculate the expectation value of the result, then take the modulus of that.

Example 2.3. Prove the famous Heisenberg uncertainty relation 1.48:

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \tag{2.142}$$

Putting $\hat{x}$ and $\hat{p}$ into equation 2.141 and using 2.126 gives

$$\Delta x \Delta p \geq \frac{1}{2}|\langle[\hat{x}, \hat{p}]\rangle| \tag{2.143}$$

$$\geq \frac{1}{2}|\langle i\hbar \rangle| \tag{2.144}$$

$$=\geq \frac{1}{2}|i\hbar| \tag{2.145}$$

$$=\geq \frac{\hbar}{2}. \tag{2.146}$$

2.7 Conservation Laws

In classical mechanics, and especially in advanced problem solving techniques, conserved quantities are of upmost importance because of their ability to simplify problems. A conserved quantity is defined classically as one with a time derivative of zero. Unfortunately, in quantum mechanics

we cannot really define conserved quantities in the same way, since a particle's state is fundamentally uncertain until measurement. What we can look at is the time derivative of expectation values.

Let $\hat{O}$ be a Hermitian operator, and assume that it does not explicitly depend on time, i.e. $\frac{\partial \hat{O}}{\partial t} = 0$. Then the expectation value, which may depend on time through the time dependence of the state $|\psi\rangle$, is

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{O} \rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle \psi | \hat{O} | \psi \rangle \tag{2.147}$$

$$= \frac{\partial}{\partial t}(\langle \psi |)\hat{O}|\psi\rangle + \langle \psi | \hat{O} \frac{\partial}{\partial t}|\psi\rangle, \tag{2.148}$$

where in the second line the first partial derivative only acts on the bra. Now we will use the same trick we have used several times already to get rid of the time derivatives by substituting in the Schrodinger equation and its complex conjugate. This time we will substitute in the TDSE. In Dirac notation, the substitution looks like:

$$\frac{\partial |\psi\rangle}{\partial t} = -\frac{i}{\hbar}\hat{H}|\psi\rangle, \quad \frac{\partial \langle \psi |}{\partial t} = \frac{i}{\hbar}\langle \psi | \hat{H}. \tag{2.149}$$

So we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{O} \rangle = \frac{i}{\hbar}\langle \psi | \hat{H}\hat{O} | \psi \rangle - \frac{i}{\hbar}\langle \psi | \hat{O}\hat{H} | \psi \rangle \tag{2.150}$$

$$= \frac{i}{\hbar}\langle \psi | [\hat{H}, \hat{O}] | \psi \rangle \tag{2.151}$$

$$= \frac{i}{\hbar}\langle [\hat{H}, \hat{O}] \rangle. \tag{2.152}$$

If the commutator $[\hat{H}, \hat{O}] = 0$, then the expectation value is zero. This tells us that if $\hat{O}$ does not explicitly depend on time and commutes with the Hamiltonian, its expectation value will be constant over time. This is the quantum analogue of a conserved quantity.

The result above can be applied to position and momentum to show that they actually obey Newton's laws of motion *on average*. Specifically, we have

$$m\frac{\mathrm{d}\langle \hat{x} \rangle}{\mathrm{d}t} = \langle \hat{p} \rangle \tag{2.153}$$

$$\frac{\mathrm{d}\langle \hat{p} \rangle}{\mathrm{d}t} = -\left\langle \frac{\mathrm{d}V(x)}{\mathrm{d}x} \right\rangle. \tag{2.154}$$

These two results are known as the **Ehrenfest theorem**.

Chapter 3

The Quantum Harmonic Oscillator

3.1 Introduction to the Quantum Harmonic Oscillator

The square well has introduced to the key concepts of quantum mechanical systems. However, it is not the most realistic model in the world, although it has some uses. In this chapter, we will study the quantum analogue of the simple harmonic oscillator from classical mechanics, which is a very useful quantum mechanical model.

3.1.1 The Importance of the Harmonic Oscillator

It is not an understatement to say that the simple harmonic oscillator is quite possibly the most important model in classical mechanics. Why is this?

The prototypical example of a system exhibiting simple harmonic motion is a mass on a spring, for which the force acting on the mass is given by Hooke's law $F = -kx$. This leads to sinusoidal motion with frequency $\omega = \sqrt{\frac{k}{m}}$.

The reason why Hooke's law works so well in so many scenarios is that it is always a good approximation around a stable equilibrium point. To see why this is, we take the Taylor expansion of a potential energy function (it does not matter what shape it is) about a minimum located at x_0,

$$V(x) = V(x_0) + \frac{\mathrm{d}V(x_0)}{\mathrm{d}x}(x - x_0) + \frac{1}{2}\frac{\mathrm{d}^2V(x_0)}{\mathrm{d}x^2}(x - x_0)^2 + \ldots. \tag{3.1}$$

The term with the first derivative vanishes since x_0 is a minimum, so for x close to x_0, the potential is approximately given by

$$V(x) \approx V(x_0) + \frac{1}{2}\frac{\mathrm{d}^2V(x_0)}{\mathrm{d}x^2}(x - x_0)^2. \tag{3.2}$$

This gives rise to a force with the same form as Hooke's law:

$$F = -\frac{\mathrm{d}V(x)}{\mathrm{d}x} = -\frac{\mathrm{d}^2V(x_0)}{\mathrm{d}x^2}(x - x_0). \tag{3.3}$$

If we apply this to situations in quantum mechanics, we could approximate the behaviour of, for example, vibrations in diatomic molecules that consist of two bound atoms such as hydrogen chloride. These interatomic forces can be modelled classically using the Lennard-Jones potential, but at the equilibrium point we can approximate the potential as parabolic. This means that the quantum harmonic oscillator will be a good approximation of the ground state and the first few excited states of this system!

3.1.2 Setting up the Quantum Harmonic Oscillator

For the classical harmonic oscillator, the potential energy is

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2. \tag{3.4}$$

For the quantum harmonic oscillator, we will write the potential energy with the natural frequency ω because it is more helpful than referring to an abstract "spring constant" k.

In quantum mechanics, our position variable x gets promoted to an operator $\hat{x}$, so the potential energy operator for the quantum harmonic oscillator would be

$$\hat{V}(x) = \frac{1}{2}m\omega^2 \hat{x}^2. \tag{3.5}$$

The Hamiltonian operator for the system is then

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2, \tag{3.6}$$

which, when written in the position basis, becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2. \tag{3.7}$$

The time-dependent Schrodinger equation is therefore

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \psi(x,t) = i\hbar\frac{\partial \psi(x,t)}{\partial t}. \tag{3.8}$$

Just like in the last chapter, we can separate the time-dependence out to get the time-dependent Schrodinger equation for the QHO:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u(x)}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 u(x) = Eu(x), \tag{3.9}$$

where the full wavefunction is then given by $\psi(x,t) = u(x)e^{-\frac{iEt}{\hbar}}$.

3.2 Solving the Quantum Harmonic Oscillator

We will now go through all the stages of solving equation 3.9 to find the energy eigenstates.

3.2.1 Changing to Dimensionless Quantities

The first step is change our variable from x to some dimensionless variable y. This will simplify the notation somewhat, which makes it easier to see what is going on.

We have three physical constants, $\hbar$, m, and ω in equation 3.9. These have units of $\mathrm{kg\,m^2\,s^{-1}}$, kg, and $\mathrm{s^{-1}}$ respectively. If we combine these in the form $\frac{\hbar}{m\omega}$, this has units of $\mathrm{m^2}$. Therefore, if we define

$$x_0 = \sqrt{\frac{\hbar}{m\omega}}, \tag{3.10}$$

this is a natural length scale for the problem, so we can define our new dimensionless length parameter y as

$$y = \frac{x}{x_0} = \sqrt{\frac{m\omega}{\hbar}}x. \tag{3.11}$$

Note that x_0 has nothing to do with equilibrium position. For a given oscillator, this is a constant. Substituting $x = yx_0$ into equation 3.9 and expanding the definition of x_0, we get

$$-\frac{\hbar^2}{2m}\frac{1}{x_0^2}\frac{\mathrm{d}^2u}{\mathrm{d}y^2} + \frac{1}{2}m\omega^2 x_0^2 y^2 u = Eu \tag{3.12}$$

$$-\frac{\hbar^2}{2m}\frac{m\omega}{\hbar}\frac{\mathrm{d}^2u}{\mathrm{d}y^2} + \frac{1}{2}m\omega^2 \frac{\hbar}{m\omega} y^2 u = Eu \tag{3.13}$$

$$-\frac{\hbar\omega}{2}\left(\frac{\mathrm{d}^2u}{\mathrm{d}y^2} - y^2 u\right) = Eu \tag{3.14}$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}y^2} - y^2 u = -\varepsilon u, \tag{3.15}$$

where we have defined

$$\varepsilon = \frac{2E}{\hbar\omega}, \tag{3.16}$$

as the dimensionless energy parameter.

3.2.2 Simplifying Using Asymptotic Analysis

As $y \to \pm\infty$, we can neglect εu compared to $y^2 u$ as the former will be negligible. Equation 3.15 then becomes

$$\frac{\mathrm{d}^2u}{\mathrm{d}y^2} = y^2 u. \tag{3.17}$$

If we guess a solution of the form $Ae^{-\frac{y^2}{2}}$, then we get

$$\frac{\mathrm{d}}{\mathrm{d}y}Ae^{-\frac{y^2}{2}} = -Aye^{-\frac{y^2}{2}} \tag{3.18}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}Ae^{-\frac{y^2}{2}} = -Ae^{-\frac{y^2}{2}} + Ay^2e^{-\frac{y^2}{2}} \approx Ay^2e^{-\frac{y^2}{2}}, \tag{3.19}$$

where in the last part we have neglected terms that are small when $y \to \pm\infty$. Therefore, this function is a solution to the TISE for large y. Note that $Be^{+\frac{y^2}{2}}$ is also a valid solution, but is does not have a finite limit as $y \to \pm\infty$ and is therefore not normalisable, so we will throw it out.

So the behaviour of the full solution to the TISE must be Gaussian for large y, but what about the rest of the function? We now suppose that it takes the form

$$u(y) = h(y)e^{-\frac{y^2}{2}}, \tag{3.20}$$

and substitute this into equation 3.15 to see what we get.

Taking derivatives, we find

$$\frac{\mathrm{d}u}{\mathrm{d}y} = \frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} - yhe^{-\frac{y^2}{2}} \tag{3.21}$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}y^2} = \frac{\mathrm{d}^2h}{\mathrm{d}y^2}e^{-\frac{y^2}{2}} - y\frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} - he^{-\frac{y^2}{2}} - y\frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} + y^2he^{-\frac{y^2}{2}} \tag{3.22}$$

$$= \frac{\mathrm{d}^2h}{\mathrm{d}y^2}e^{-\frac{y^2}{2}} - 2y\frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} - he^{-\frac{y^2}{2}} + y^2he^{-\frac{y^2}{2}}. \tag{3.23}$$

Substituting these in, we get

$$\frac{\mathrm{d}^2h}{\mathrm{d}y^2}e^{-\frac{y^2}{2}} - 2y\frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} - he^{-\frac{y^2}{2}} + y^2he^{-\frac{y^2}{2}} + (\varepsilon - y^2)he^{-\frac{y^2}{2}} = 0 \tag{3.24}$$

$$\frac{\mathrm{d}^2h}{\mathrm{d}y^2}e^{-\frac{y^2}{2}} - 2y\frac{\mathrm{d}h}{\mathrm{d}y}e^{-\frac{y^2}{2}} + (\varepsilon - 1)he^{-\frac{y^2}{2}} = 0 \tag{3.25}$$

$$\frac{\mathrm{d}^2h}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}h}{\mathrm{d}y} + (\varepsilon - 1)h = 0. \tag{3.26}$$

If we solve this differential equation for $h(y)$, we get the full solution for equation 3.15. Luckily, this equation is a well-known equation in mathematics called "Hermite's Equation" (with $2\lambda = \varepsilon - 1$)! We will now go through the solution via a series method.

3.2.3 Solving for $h(y)$ via a Series Expansion

Assuming that $h(y)$ can be written as an infinite polynomial (a power series), we can substitute the following into equation 3.26:

$$h(y) = \sum_{n=0}^{\infty} a_n y^n. \tag{3.27}$$

What we find is a recurrence relation for the coefficients:

$$\frac{a_{j+2}}{a_j} = \frac{2j + 1 - \varepsilon}{(j+2)(j+1)}. \tag{3.28}$$

The limiting behaviour for the ratio of the subsequent coefficients is

$$\lim_{j \to \infty} \frac{a_{j+2}}{a_j} = \frac{2}{j}, \tag{3.29}$$

which diverges more quickly than the Gaussian converges. This means that for the solutions to be valid wavefunctions, meaning for them to be normalisable, the power series must terminate. For each solution with a series terminating at $j = 1$, $j = 2$, $j = 3$, etc., we obtain one valid eigenstate.

For some j to be the highest non-vanishing coefficient, we must have the numerator of the recurrence relation be zero, i.e.

$$2j + 1 - \varepsilon = 0. \tag{3.30}$$

If we substitute back in $\varepsilon = \frac{2E}{\hbar\omega}$, this gives us the energy eigenvalues of the quantum harmonic oscillator:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \tag{3.31}$$

where we have replaced j with n. Note that in contrast to the infinite square well, the label for the energy eigenvalues starts at 0 instead of 1. This is just a matter of preference for how the equations look and doesn't mean anything physically.

The ground state energy is $E_0 = \frac{1}{2}\hbar\omega$, the first excited state is $E_1 = \frac{3}{2}\hbar\omega$, and so on. The energy levels are equally spaced, increasing in single units of $\hbar\omega$.

So what are the polynomials $h_n(y)$? To determine the coefficients, we need a_0 to calculate all the even coefficients and a_1 to calculate all the odd coefficients. Both the even and odd coefficients must terminate for the whole series to terminate, but the value of E only allows us to terminate one or the other. Therefore, valid eigenstates will either have $a_0 = 0$ and only odd powers of x or $a_1 = 0$ and only even power of x in $h(y)$.

For the ground state, only $a_0 \neq 0$, so $h(y) = a_0$ and the ground state eigenfunction is

$$u_0(y) = a_0 e^{-\frac{y^2}{2}}. \tag{3.32}$$

For the first excited state, only $a_1 \neq 0$, so $h(y) = a_1 y$ and the eigenfunction is therefore

$$u_1(y) = a_1 y e^{-\frac{y^2}{2}}. \tag{3.33}$$

For the second excited state, a_0 and a_2 are nonzero so $h(y) = a_0 + a_2 x^2$. The dimensionless energy has the value

$$\varepsilon = \frac{2E}{\hbar\omega} = \frac{2 \times \frac{5}{2}\hbar\omega}{\hbar\omega} = 5, \tag{3.34}$$

so the recurrence relation gives

$$\frac{a_2}{a_0} = \frac{2(0) + 1 - 5}{(0+2)(0+1)} = -\frac{4}{2} = -2. \tag{3.35}$$

Hence the eigenfunction takes the form

$$u_2(y) = a_0(1 - 2y^2)e^{-\frac{y^2}{2}}. \tag{3.36}$$

The process carries on like this. The polynomials generated are called **Hermite polynomials**, and denoted $h_n(y)$. Note that it is conventional to introduce a minus sign to the normalisation constant a_0 or a_1 so that the leading-order terms in the polynomial have a positive sign. The first few Hermite polynomials are

$$h_0(y) = 1 \tag{3.37}$$
$$h_1(y) = 2y \tag{3.38}$$
$$h_2(y) = 4y^2 - 2 \tag{3.39}$$
$$h_3(y) = 8y^3 - 12y \tag{3.40}$$
$$h_4(y) = 16y^4 - 48y^2 + 12 \tag{3.41}$$
$$h_5(y) = 32y^5 - 160y^3 + 120y. \tag{3.42}$$

These coefficients are slightly different to the ones calculated above, but it doesn't matter since we have to normalise the whole wavefunction anyway.

3.3 Energy Eigenstates of the QHO

There is one final step to writing out the eigenstates, which is to return to physical units and remove the dimensionless length y. Once we do this, the energy eigenstates (including time dependence) have the form:

$$\psi_n(x,t) = N_n h_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{m\omega}{2\hbar}x^2}e^{-i\omega t\left(n+\frac{1}{2}\right)}. \tag{3.43}$$

The normalisation constant N_n turns out to be

$$N_n = \frac{1}{\sqrt{2^n n!}}\sqrt[4]{\frac{m\omega}{\pi\hbar}}. \tag{3.44}$$

The spatial part of the first few eigenstates is

$$u_0(x) = N_0 e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.45}$$

$$u_1(x) = N_1 x e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.46}$$

$$u_2(x) = N_2\left(\frac{2m\omega}{\hbar}x^2 - 1\right)e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.47}$$

$$u_3(x) = N_3\left(8\sqrt{\left(\frac{m\omega}{\hbar}\right)^3}y^3 - 12\sqrt{\frac{m\omega}{\hbar}}y\right)e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.48}$$

$$\tag{3.49}$$

3.3.1 Comparison of the Quantum to Classical Harmonic Oscillator

Here are the probability density of the first few eigenstates, with the classical probability density of a simple harmonic oscillator with energy $E = \hbar\omega\left(n+\frac{1}{2}\right)$ overlayed. We can see that as n increases, the spatial probability density of the oscillator is more spread out, just like how the amplitude of them classical turning points increase for higher energy. The quantum probability density is actually nonzero beyond the classical turning point, so we have some tunnelling, but it decays exponentially in this region. Also note that the wavelength of ψ_n is shortest at the center of the well, which is where a classical particle would be travelling the fastest.

3.3.2 Parity

Recall that we saw in section 3.2.3 that the Hermite polynomials are either even or odd. This property is passed on to the eigenstates as well. We can investigate this symmetry by defining an operator which will detect whether a given wavefunction is odd or even.

> **Definition 3.1.** The **parity** operator switches x to $-x$, and can be defined by its action on a wavefunction as
> $$\hat{P}\psi(x,t) = \psi(-x,t). \tag{3.50}$$

What are the possible eigenvalues of parity? If we apply parity twice, we get

$$\hat{P}^2\psi(x) = \hat{P}\hat{P}\psi(x) = \hat{P}\psi(-x) = \psi(x), \tag{3.51}$$

so *all* wavefunctions are eigenfunctions of $\hat{P}^2$ with eigenvalue $+1$. Using this fact, we can show that the eigenvalues of $\hat{P}$ are ± 1. Suppose that $\psi(x)$ is an eigenfunction of $\hat{P}$ with eigenvalue P, then

$$\hat{P}^2\psi(x) = \hat{P}P\psi(x) = P^2\psi(x), \tag{3.52}$$

implies that $P^2 = 1$, hence $P = \pm 1$. If a wavefunction is an eigenfunction of parity with $\hat{P}\psi(x) = \psi(x)$, then this means that $\psi(x)$ is an even function (symmetric about $x = 0$) since this implies $\psi(-x) = \psi(x)$. Likewise, if we have $\hat{P}\psi(x) = -\psi(x)$, then $\psi(x)$ must be odd (antisymmetric about $x = 0$) since this implies $\psi(x) = -\psi(-x)$. Not all wavefunctions are even or odd, therefore not all wavefunctions are eigenfunctions of parity.

Is parity Hermitian? We can test this by calculating the adjoint, note that the integral has to be from $-\infty$ to ∞ for the harmonic oscillator.

$$\langle \hat{P}^\dagger \rangle = \int_{-\infty}^{\infty} (\hat{P}\psi(x))^*\psi(x)\,\mathrm{d}x \tag{3.53}$$

$$= \int_{-\infty}^{\infty} \psi^*(-x)\psi(x)\,\mathrm{d}x, \tag{3.54}$$

now we make a substitution $y = -x$ to get

$$\langle \hat{P}^\dagger \rangle = -\int_{\infty}^{-\infty} \psi^*(y)\psi(-y)\,\mathrm{d}y \tag{3.55}$$

$$= \int_{-\infty}^{\infty} \psi^*(y)\hat{P}\psi(y)\,\mathrm{d}y \tag{3.56}$$

$$= \langle \hat{P} \rangle, \tag{3.57}$$

hence $\hat{P}$ is Hermitian and therefore it is observable.

3.3.3 Superposition States

We can write superposition states just like we can for the infinite square well, using an expansion of energy eigenfunctions.

$$\psi(x,t) = \sum_{n=0}^{\infty} c_n u_n(x) e^{-\frac{iE_n t}{\hbar}}. \tag{3.58}$$

The only difference between this formula and the one for the infinite square well is that the index n starts from 0 instead of 1.

3.4 Solving the QHO with Ladder Operators

In this section we are going to introduce a technique to solve for the energy eigenvalues and eigenfunctions without solving the complicated differential equation 3.9. This method will be to factorise the Hamiltonian using two new operators, which we will call ladder operators for reasons that will become clear, and then see what their effect on an unknown eigenfunction is.

3.4.1 Factorising the Hamiltonian

Notice that the QHO Hamiltonian (equation 3.6) is a sum of squares of operators. We would like to write it in a more symmetric form and then factorise.

We can do this by removing the units. Define the dimensionless position operator by

$$\hat{X} = \frac{\hat{x}}{x_0}, \tag{3.59}$$

where $x_0 = \sqrt{\frac{\hbar}{m\omega}}$ is the natural length scale created using the constants in the Hamiltonian. We can define a dimensionless momentum operator by creating a nautral momentum scale, which is created by dividing $\hbar$ by x_0:

$$p_0 = \frac{\hbar}{x_0} = \sqrt{\hbar m\omega}. \tag{3.60}$$

Then we can define

$$\hat{P} = \frac{\hat{x}}{p_0}, \tag{3.61}$$

as the dimensionless momentum operator.

Substituting these into equation 3.6, we get

$$\hat{H} = \frac{p_0^2 \hat{P}^2}{2m} + \frac{1}{2}m\omega^2 x_0^2 \hat{X}^2 \tag{3.62}$$

$$= \frac{\hbar m\omega}{2m}\hat{P}^2 + \frac{m\omega^2\hbar}{m\omega}\hat{X}^2 \tag{3.63}$$

$$= \frac{\hbar\omega}{2}(\hat{P}^2 + \hat{X}^2). \tag{3.64}$$

Recall that an expression $u^2 + v^2$ can be factored using complex numbers as $(u+iv)(u-iv)$. When using the same idea with operators, we need to keep in mind that two operators may not necessarily commute. The two parentheses expand to

$$(\hat{U} - i\hat{V})(\hat{U} + i\hat{V}) = \hat{U}^2 + \hat{V}^2 + i\hat{U}\hat{V} - i\hat{V}\hat{U} \tag{3.65}$$

$$= \hat{U}^2 + \hat{V}^2 + i[\hat{U}, \hat{V}], \tag{3.66}$$

therefore for the QHO Hamiltonian, we get

$$\hat{H} = \frac{\hbar\omega}{2}((\hat{X} - i\hat{P})(\hat{X} + i\hat{P}) - i[\hat{X}, \hat{P}]), \tag{3.67}$$

where we have to subtract of i times the commutator of $\hat{X}$ and $\hat{P}$ to account for the cross terms. The commutator between dimensionless position and momentum is given by

$$[\hat{X}, \hat{P}] = \left[\frac{\hat{x}}{x_0}, \frac{\hat{p}}{p_0}\right] \tag{3.68}$$

$$= \frac{1}{x_0 p_0}[\hat{x}, \hat{p}] \tag{3.69}$$

$$= \sqrt{\frac{m\omega}{\hbar}}\frac{1}{\sqrt{\hbar m\omega}}i\hbar \tag{3.70}$$

$$= i, \tag{3.71}$$

So the Hamiltonian simplifies to

$$\hat{H} = \frac{\hbar\omega}{2}((\hat{X} - i\hat{P})(\hat{X} + i\hat{P}) + 1). \tag{3.72}$$

Now we will define new operators to be the combination in parentheses:

$$\hat{A} = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}) \tag{3.73}$$

$$\hat{A}^\dagger = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}). \tag{3.74}$$

These operators are called the **ladder operators** for reasons that will become very clear in the next section. If we substitute these into the Hamiltonian, we get

$$\hat{H} = \hbar\omega\left(\hat{A}^\dagger\hat{A} + \frac{1}{2}\right). \tag{3.75}$$

This equation looks suspiciously like equation 3.31 for the energy eigenvalues but with operators! This implies that the product $\hat{A}^\dagger\hat{A}$ is a "number operator", it has the energy eigenstates as its eigenfunctions with their corresponding quantum number n as its eigenvalues.

But what do the operators $\hat{A}$ and $\hat{A}^\dagger$ actually do? Note that $\hat{A}^\dagger$ is the adjoint of $\hat{A}$, as we can tell by the notation and because it is defined as the "complex conjugate" of $\hat{A}$. Because $\hat{A} \neq \hat{A}^\dagger$, neither of them are Hermitian and therefore they do not represent observables. We will look at the action of these operators on an energy eigenstate in the next section.

3.5 Ladder Operators

To work out the action of the ladder operators on an energy eigenstate u_n, we will first calculate some commutators involving them and then do some algebra to find the result.

3.5.1 Properties of Ladder Operators

We have already seen that since $\hat{A}$ and $\hat{A}^\dagger$ are different operators, they cannot be Hermitian.

The first commutator we will need is the commutator of $\hat{A}$ with its adjoint $\hat{A}^\dagger$, which is

$$[\hat{A}, \hat{A}^\dagger] = \frac{1}{2}[\hat{X} + i\hat{P}, \hat{X} - i\hat{P}] \tag{3.76}$$

$$= \frac{1}{2}([\hat{X}, \hat{X}] + i[\hat{P}, \hat{X}] - i[\hat{X}, \hat{P}] - i^2[\hat{P}, \hat{P}]) \tag{3.77}$$

$$= \frac{1}{2}(0 - i^2 - i^2 + 0) \tag{3.78}$$

$$= 1, \tag{3.79}$$

So $\hat{A}$ and $\hat{A}^\dagger$ do not commute.

The next commutator to calculate is that of the ladder operators with the Hamiltonian.

Looking at $\hat{A}$ first, this is

$$[\hat{H}, \hat{A}] = \hbar\omega \left[\left(\hat{A}^\dagger \hat{A} + \frac{1}{2} \right), \hat{A} \right] \tag{3.80}$$

$$= \hbar\omega \left([\hat{A}^\dagger \hat{A}, \hat{A}] + \left[\frac{1}{2}, \hat{A} \right] \right) \tag{3.81}$$

$$= \hbar\omega(\hat{A}^\dagger[\hat{A}, \hat{A}] + [\hat{A}^\dagger, \hat{A}]\hat{A}) \tag{3.82}$$

$$= -\hbar\omega\hat{A}. \tag{3.83}$$

By a similar calculation, it can be shown that $[\hat{H}, \hat{A}^\dagger] = +\hbar\omega\hat{A}^\dagger$.

3.5.2 The Lowering Operator

Suppose we have the an energy eigenstate u_i, so $\hat{H}u_i = E_i u_i$. We will now calculate what $\hat{A}$ when it acts on u_i by acting the Hamiltonian on $\hat{A}u_i$. When doing this calculation, we will deliberately "add zero" (add and subtract the same term) in order to introduce the commutators we have calculated above.

$$\hat{H}(\hat{A}u_i) = (\hat{H}\hat{A} - \hat{A}\hat{H} + \hat{A}\hat{H})u_i \tag{3.84}$$

$$= [\hat{H}, \hat{A}]u_i + \hat{A}(\hat{H}u_i) \tag{3.85}$$

$$= -\hbar\omega\hat{A}u_i + E_i\hat{A}u_i \tag{3.86}$$

$$= (E_i - \hbar\omega)\hat{A}u_i. \tag{3.87}$$

This does not really look like we have made much progress, but notice that the last line is an eigenvalue equation, which implies that $\hat{A}u_i$ is an energy eigenfunction with energy $E_i - \hbar\omega$. Of course, since we know what the energy eigenvalues are, we can see that $\hat{A}u_i$ must be proportional to u_{i-1} because $E_i - \hbar\omega = E_{i-1}$!

Let us apply $\hat{A}$ twice to u_i and see what happens. Using the same trick, we get

$$\hat{H}(\hat{A}^2 u_i) = \hat{H}\hat{A}(\hat{A}u_i) \tag{3.88}$$

$$= (\hat{H}\hat{A} - \hat{A}\hat{H} + \hat{A}\hat{H})(\hat{A}u_i) \tag{3.89}$$

$$= [\hat{H}, \hat{A}](\hat{A}u_i) + \hat{A}\hat{H}(\hat{A}u_i) \tag{3.90}$$

$$= -\hbar\omega\hat{A}^2 u_i + (E_i - \hbar\omega)\hat{A}^2 u_i \tag{3.91}$$

$$= (E_i - 2\hbar\omega)\hat{A}^2 u_i, \tag{3.92}$$

so we see, in the same way, that $\hat{A}^2 u_i$ is proportional to u_{i-2} since $E_i - 2\hbar\omega = E_{i-2}$.

One can show that in general,

$$\hat{H}(\hat{A}^n u_i) = (E_i - n\hbar\omega)\hat{A}^n u_i. \tag{3.93}$$

So the action of $\hat{A}$ is to *lower* an eigenstate u_i by one energy unit of $\hbar\omega$. For this reason, $\hat{A}$ is called the **lowering operator**.

3.5.3 The Raising Operator

If $\hat{A}$ lowers an energy eigenstate by one unit of $\hbar\omega$, one would expect that its adjoint $\hat{A}^\dagger$ raises it up by one. Indeed, we find that this is the case, so $\hat{A}^\dagger$ is called the **raising operator**.

We can show that this is the case by doing a similar calculation to above.

$$\hat{H}(\hat{A}^\dagger u_i) = (\hat{H}\hat{A}^\dagger - \hat{A}^\dagger\hat{H} + \hat{A}^\dagger\hat{H})u_i \tag{3.94}$$

$$= [\hat{H}, \hat{A}^\dagger]u_i + \hat{A}^\dagger(\hat{H}u_i) \tag{3.95}$$

$$= \hbar\omega\hat{A}^\dagger u_i + E_i\hat{A}^\dagger u_i \tag{3.96}$$

$$= (E_i + \hbar\omega)\hat{A}^\dagger u_i, \tag{3.97}$$

as predicted.

Again, one can show in general that

$$\hat{H}(\hat{A}^{\dagger\,n} u_i) = (E_i + n\hbar\omega)\hat{A}^{\dagger\,n} u_i. \tag{3.98}$$

One easy way to remember which operator raises and which one lowers is by imagining the Hermitian dagger † as a little "+" symbol, which denotes raising.

3.5.4 The Ladder of Energy Levels

The raising and lowering operators imply that we have a "ladder" of energy levels, equally spaced apart by $\hbar\omega$. However, there is one problem. It appears that there is nothing stopping us from applying the lowering operator $\hat{A}$ indefinitely, implying that there are infinitely many rungs in both directions! We know that this is impossible, since the potential energy $V(x)$ has a minimum value of $V = 0$, which means there are *no bound states* with $E_i < 0$.

We can also show directly that the energy must be greater than or equal to zero. Recall that the expectation value of the Hamiltonian for an energy eigenstate u_n is E_n:

$$\langle u_n|\hat{H}|u_n\rangle = \int_{-\infty}^{\infty} u_n^*\hat{H}u_n \,\mathrm{d}x = E_n \int_{-\infty}^{\infty} u_n^* u_n \,\mathrm{d}x = E_n. \tag{3.99}$$

Then if we insert equation 3.75, we get

$$E_n = \hbar\omega \int_{-\infty}^{\infty} u_n^* \left(\hat{A}^\dagger\hat{A} + \frac{1}{2}\right) u_n \,\mathrm{d}x \tag{3.100}$$

$$= \hbar\omega \left[\int_{-\infty}^{\infty} u_n^*\hat{A}^\dagger\hat{A}u_n \,\mathrm{d}x + \frac{1}{2}\int_{-\infty}^{\infty} u_n^* u_n \,\mathrm{d}x\right] \tag{3.101}$$

$$= \hbar\omega \left[\int_{-\infty}^{\infty} (\hat{A}u_n)^*\hat{A}u_n \,\mathrm{d}x + \frac{1}{2}\right] \tag{3.102}$$

$$= \hbar\omega \left[\int_{-\infty}^{\infty} |\hat{A}u_n|^2 \,\mathrm{d}x + \frac{1}{2}\right] \tag{3.103}$$

$$\geq 0. \tag{3.104}$$

Note that in the third-last line, we used the fact that $u_n^*\hat{A}^\dagger$ is the complex conjugate of $\hat{A}u_n$, and to go from the second-last line to the last we recall that probability density must be non-negative everywhere.

All this is to say that we need to impose that there exists a ground state with a minimum energy. To do this, we define the lowering operator to completely annihilate the ground state wavefunction

$$\hat{A}u_0 = 0. \tag{3.105}$$

This is known as the **ladder termination condition**. It implies that any repeated application of the lowering operator will eventually end up returning zero (since $\hat{A}^n u_0 = 0$ for any n). This actually gives us the value of the ground state energy. If we apply $\hat{H}$ to u_0, we get

$$\hat{H}u_0 = \hbar\omega\left(\hat{A}^\dagger\hat{A} + \frac{1}{2}\right)u_0 \tag{3.106}$$

$$= \hbar\omega\hat{A}^\dagger(\hat{A}u_0) + \frac{1}{2}\hbar\omega u_0 \tag{3.107}$$

$$= \frac{1}{2}\hbar\omega u_0, \tag{3.108}$$

since the first term becomes zero. So the ground state energy is $\frac{1}{2}\hbar\omega$, which is what we found before by solving the Schrodinger equation.

This, along with equation 3.97, gives us the full spectrum of energy levels

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \tag{3.109}$$

as found previously.

3.5.5 Finding the Eigenfunctions Using Ladder Operators

The only thing we haven't recovered yet from our knowledge of the QHO using this method is the form of the energy eigenstates in the position basis. According to equation 3.97, $\hat{A}^\dagger u_n$ is proportional to u_{n+1}. We can calculate the constant of proportionality by setting $\hat{A}^\dagger u_n = C u_{n+1}$ and using the fact that the energy eigenstates are normalised.

$$1 = \int_{-\infty}^{\infty} u_{n+1}^* u_{n+1}\, \mathrm{d}x \tag{3.110}$$

$$= \frac{1}{C^2}\int_{-\infty}^{\infty} (\hat{A}^\dagger u_n)^* \hat{A}^\dagger u_n\, \mathrm{d}x \tag{3.111}$$

$$= \frac{1}{C^2}\int_{-\infty}^{\infty} u_n^* \hat{A}\hat{A}^\dagger u_n\, \mathrm{d}x. \tag{3.112}$$

We will now use a nifty trick that comes in handy when manipulating expressions with ladder operators. With the commutator $[\hat{A}, \hat{A}^\dagger] = 1$, we can rewrite

$$\hat{A}\hat{A}^\dagger = \hat{A}\hat{A}^\dagger - \hat{A}^\dagger\hat{A} + \hat{A}^\dagger\hat{A} = [\hat{A}, \hat{A}^\dagger] + \hat{A}^\dagger\hat{A} = 1 + \hat{A}^\dagger\hat{A}. \tag{3.113}$$

Using this and substituting the Hamiltonian, we get

$$1 = \frac{1}{C^2} \int_{-\infty}^{\infty} u_n^* (1 + \hat{A}^\dagger \hat{A}) u_n \, \mathrm{d}x \tag{3.114}$$

$$= \frac{1}{C^2} \int_{-\infty}^{\infty} u_n^* \left(1 + \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \right) u_n \, \mathrm{d}x \tag{3.115}$$

$$= \frac{1}{C^2} \int_{-\infty}^{\infty} u_n^* \left(\frac{\hat{H}}{\hbar\omega} u_n + \frac{1}{2} u_n \right) \mathrm{d}x \tag{3.116}$$

$$= \frac{1}{C^2} \int_{-\infty}^{\infty} u_n^* \left(\left(n + \frac{1}{2} \right) u_n + \frac{1}{2} u_n \right) \mathrm{d}x \tag{3.117}$$

$$= \frac{n+1}{C^2} \int_{-\infty}^{\infty} u_n^* u_n \, \mathrm{d}x \tag{3.118}$$

$$= \frac{n+1}{C^2}, \tag{3.119}$$

which implies $C = \sqrt{n+1}$. Thus, we have

$$\hat{A}^\dagger u_n = \sqrt{n+1} u_{n+1}. \tag{3.120}$$

By a similar calculation, one can show that

$$\hat{A} u_n = \sqrt{n} u_{n-1}. \tag{3.121}$$

Using the ladder termination condition and expanding $\hat{A}$ in the position basis, we can find the form of the ground state wavefunction in the position basis.

$$\hat{A} u_0 = 0 \tag{3.122}$$

$$\frac{1}{\sqrt{2}} (\hat{X} + i\hat{P}) u_0 = 0 \tag{3.123}$$

$$\left(\frac{\hat{x}}{x_0} + i \frac{\hat{p}}{p_0} \right) u_0 = 0 \tag{3.124}$$

$$\sqrt{\frac{m\omega}{\hbar}} u_0 + \frac{i}{\sqrt{\hbar m\omega}} \left(-i\hbar \frac{\mathrm{d}u_0}{\mathrm{d}x} \right) = 0 \tag{3.125}$$

This gives us a first-order differential equation which we can solve by integrating:

$$\frac{\mathrm{d}u_0}{\mathrm{d}x} = -\frac{m\omega}{\hbar} x u_0 \tag{3.126}$$

$$\int \frac{\mathrm{d}u_0}{u_0} = -\frac{m\omega}{\hbar} \int x \, \mathrm{d}x \tag{3.127}$$

$$\ln u_0 = -\frac{m\omega}{2\hbar} x^2 + c \tag{3.128}$$

$$u_0 = N_0 e^{-\frac{m\omega}{2\hbar} x^2}, \tag{3.129}$$

which is exactly the wavefunction we found by solving the Schrodinger equation. Note that if we were solving this problem from scratch using ladder operators, this would be the *only* differential

equation we have to solve, and also the only time that we have to refer back to the definition of the ladder operators in terms of $\hat{X}$ and $\hat{P}$!

The rest of the eigenstates can be found using equation 3.120 and by expanding the definition of $\hat{A}^\dagger$. For example, for the first excited state we have $\hat{A}^\dagger u_0 = \sqrt{0+1}u_1 = u_1$, so we get

$$u_1 = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P})u_0 \tag{3.130}$$

$$= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}x - \sqrt{\frac{\hbar}{m\omega}}\frac{\mathrm{d}}{\mathrm{d}x}\right)N_0 e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.131}$$

$$= N_0\sqrt{\frac{2m\omega}{\hbar}}xe^{-\frac{m\omega}{2\hbar}x^2}, \tag{3.132}$$

which is the same as equation 3.46. Note that when using this method for generating the eigenfunctions, they are already normalised!

Chapter 4

Quantum Mechanics in Multiple Dimensions

4.1 The 3D Quantum Harmonic Oscillator

Solving the quantum harmonic oscillator in one dimension proved to be quite a slog, but we will see that in more than one dimension it is much easier! This is because we can use the method of separation of variables to break down the problem into copies of the one-dimensional problem, for which we already know the solution.

4.1.1 Schrodinger Equation for the 3D QHO

The first thing we need to do is write out the potential energy so that we can write down the Schrodinger equation. The particle is going to be under the influence of a central force $\boldsymbol{F} = -\sqrt{\omega/m}\boldsymbol{r}$, which gives a potential energy

$$\hat{V} = \frac{1}{2}m\omega^2\hat{r}^2 = \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2 + \hat{z}^2). \tag{4.1}$$

Note that here we are assuming that force grows in magnitude with the same rate in every direction, and therefore the natural frequency ω is the same in all directions. We call an oscillator like this **isotropic**.

For kinetic energy, we can write

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\hat{\boldsymbol{p}} \cdot \hat{\boldsymbol{p}}}{2m}, \tag{4.2}$$

where $\hat{\boldsymbol{p}}$ is the 3D momentum operator, which components $\hat{\boldsymbol{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$ given by

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{4.3}$$

$$\hat{p}_y = -i\hbar\frac{\partial}{\partial y} \tag{4.4}$$

$$\hat{p}_z = -i\hbar\frac{\partial}{\partial z}. \tag{4.5}$$

Therefore, kinetic energy in 3D can be written as

$$\hat{T} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) \tag{4.6}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{4.7}$$

$$= -\frac{\hbar^2}{2m}\nabla^2. \tag{4.8}$$

where ∇^2 is the Laplacian operator.

Putting these together, the time-independent Schrodinger equation in the position basis is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2 r^2\right)u(\boldsymbol{r}) = Eu(\boldsymbol{r}) \tag{4.9}$$

$$\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)\right)u(x,y,z) = Eu(x,y,z). \tag{4.10}$$

The TISE is now a partial differential equation, rather than an ordinary one, as the spatial part of the wavefunction now depends on three variables: x, y, and z. As in the 1D case, the full energy eigenfunctions are obtained by multiplying the spatial part with the temporal part, so we get

$$\psi(x,y,z,t) = u(x,y,z)e^{-\frac{iEt}{\hbar}}, \tag{4.11}$$

for whatever the energy eigenvalues E happen to be.

4.1.2 Solving the TISE by Separation of Variables

Note that the potential energy has the form $V(x,y,z) = V_x(x) + V_y(y) + V_z(z)$. For a classical oscillator with a potential like this, the motion along each dimension is unaffected by the motion along the others. Therefore, we assume that the eigenfunctions are separable, so they take the form

$$u(x,y,z) = u_x(x)u_y(y)u_z(z). \tag{4.12}$$

Inserting this form into equation 4.10 gives

$$-\frac{\hbar^2}{2m}\left(u_y u_z \frac{\mathrm{d}^2 u_x}{\mathrm{d}x^2} + u_x u_z \frac{\mathrm{d}^2 u_y}{\mathrm{d}y^2} + u_x u_y \frac{\mathrm{d}^2 u_z}{\mathrm{d}z^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)u_x u_y u_z = Eu_x u_y u_z, \tag{4.13}$$

then dividing by $u_x u_y u_z$ so that each term only depends on a single variable, we get

$$\left(-\frac{\hbar^2}{2m}\frac{1}{u_x}\frac{\mathrm{d}^2 u_x}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{u_y}\frac{\mathrm{d}^2 u_y}{\mathrm{d}y^2} + \frac{1}{2}m\omega^2 y^2\right)$$
$$+ \left(-\frac{\hbar^2}{2m}\frac{1}{u_z}\frac{\mathrm{d}^2 u_z}{\mathrm{d}z^2} + \frac{1}{2}m\omega^2 z^2\right) = E \tag{4.14}$$

Now, the whole left-hand side must equal the total energy E, which is a constant. However, x, y, and z can all be varied completely independently. This means that each term in large parentheses must itself be equal to a constant. These constants represent the energy along each axis, so we will denote them E_x, E_y, and E_z. By equation 4.14, we have

$$E = E_x + E_y + E_z. \tag{4.15}$$

We then have three separate ordinary differential equations:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u_x}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 u_x = E_x u_x \tag{4.16}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u_y}{\mathrm{d}y^2} + \frac{1}{2}m\omega^2 y^2 u_y = E_y u_y \tag{4.17}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u_z}{\mathrm{d}z^2} + \frac{1}{2}m\omega^2 z^2 u_z = E_z u_z. \tag{4.18}$$

These are three copies of the 1D quantum harmonic oscillator! We therefore know what the forms of u_x, u_y, and u_z will be as we have solved for them already. The energy eigenstates of the 3D isotropic quantum harmonic oscillator will then be products of the the one-dimensional eigenstates.

The solution for each coordinate axis will have its own quantum number to describe which energy level the particle is on along that direction. We call these three labels n_x, n_y, n_z. Then the energy eigenvalues along each axis are

$$E_x = \hbar\omega\left(n_x + \frac{1}{2}\right) \tag{4.19}$$

$$E_y = \hbar\omega\left(n_y + \frac{1}{2}\right) \tag{4.20}$$

$$E_z = \hbar\omega\left(n_z + \frac{1}{2}\right), \tag{4.21}$$

just like in the one-dimensional case.

This means that the total energy has three quantum numbers which label the eigenvalues, which are given by

$$E_{n_x n_y n_z} = E_x + E_y + E_z = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right). \tag{4.22}$$

Each quantum number starts from zero, and they can all take on any value independent of each other. Clearly we will have some combinations of values which have the same energy, for example $n_x = n_y = n_z = 1$, or $n_x = 2$, $n_y = 1$, and $n_z = 0$, or $n_x = 3$ and $n_y = n_z = 0$! We will discuss what this means in the next section.

4.2   Degeneracy

4.2.1   Energy Eigenstates of the 3D Isotropic QHO

As derived in the last section, the energy eigenvalues of the 3D isotropic quantum harmonic oscillator are

$$E_{n_x n_y n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right), \tag{4.23}$$

and the spatial parts of the eigenfunctions are

$$u_{n_x n_y n_z}(x, y, z) = u_{n_x}(x)u_{n_y}(y)u_{n_z}(z) \tag{4.24}$$

$$= N_{n_x} N_{n_y} N_{n_z} h_{n_x}\left(\frac{x}{x_0}\right) h_{n_y}\left(\frac{y}{x_0}\right) h_{n_z}\left(\frac{z}{x_0}\right) e^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)}, \tag{4.25}$$

where we recall the natural length scale $x_0 = \sqrt{\frac{\hbar}{m\omega}}$. The full time-dependent eigenfunctions will then simply be

$$\psi_{n_x n_y n_z}(x, y, z, t) = u_{n_x n_y n_z}(x, y, z)e^{-\frac{iE_{n_x n_y n_z}t}{\hbar}} \tag{4.26}$$

$$= u_{n_x}(x)e^{-\frac{iE_{n_x}}{\hbar}}u_{n_y}(y)e^{-\frac{iE_{n_y}}{\hbar}}u_{n_z}(z)e^{-\frac{iE_{n_z}}{\hbar}}, \tag{4.27}$$

where in the last line we have shown explicitly that the full wavefunction really is the product of the three individual wavefunctions for each direction using $E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z}$.

The ground state energy for the 3D QHO is found when $n_x = n_y = n_z = 0$, which gives

$$E_{000} = \hbar\omega\left(0 + 0 + 0 + \frac{3}{2}\right) = \frac{3}{2}\hbar\omega. \tag{4.28}$$

This is three times as much energy as for a 1D oscillator. Since the quantum numbers n_x, n_y, and n_z can vary independently, the spacing between energy levels is still $\hbar\omega$ just like in the one-dimensional case.

The ground state wavefunction looks like

$$\psi_{000}(x, y, z, t) = N_{000}e^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)}e^{-\frac{3}{2}i\omega t}. \tag{4.29}$$

In dirac notation, we denote the eigenstates by $|n_x n_y n_z\rangle$, so the ground state would be denoted $|000\rangle$.

The first excited state is the state with the second lowest energy, which would be $E = \frac{5}{2}\hbar\omega$ for the 3D isotropic oscillator. However, from equation 4.22, we can see that there are several states that have this energy! They are:

$$E_{100} = E_{010} = E_{001} = \frac{5}{2}\hbar\omega. \tag{4.30}$$

This was not possible in for the one-dimensional oscillator, but becomes possible now because of the extra degrees of freedom and because of the symmetry of the situation.

The three eigenstates that have this eigenvalue have three *distinct* wavefunctions, given by

$$\psi_{100}(x, y, z, t) = N_{100}xe^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)}e^{-\frac{5}{2}i\omega t} \tag{4.31}$$

$$\psi_{010}(x, y, z, t) = N_{010}ye^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)}e^{-\frac{5}{2}i\omega t} \tag{4.32}$$

$$\psi_{001}(x, y, z, t) = N_{001}ze^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)}e^{-\frac{5}{2}i\omega t} \tag{4.33}$$

These wavefunctions, which correspond to the states $|100\rangle$, $|010\rangle$, and $|001\rangle$, are still orthonormal and so they represent physically distinct states, yet they have the same energy. These are known as **degenerate states**.

> **Definition 4.1. Degenerate states** are states that share the same eigenvalue of a Hermitian operator.
> The number of states with the same eigenvalue is called the **degeneracy** of the eigenvalue. For example, the first excited state of the 3D isotropic quantum harmonic oscillator can correspond to three different eigenstates, so we say that the first excited state has a

degeneracy of 3.

Chapter 5

The Hydrogen Atom

5.1 The Hydrogen Hamiltonian

We will now look at the major early success story of quantum mechanics, solving for the motion of an electron in a hydrogen atom. Our assumptions are that the nucleus (the proton) is a particle with mass m_p and charge $+e$, and the electron is a particle with mass m_e and charge $-e$. Reality, or rather our latest understanding of the hydrogen atom, is more complex and there are things that we are neglecting here such as coupling between spin and angular momentum, special relativity, and the quantum vacuum.

5.1.1 Setting up the Problem

The electron is bound to the proton by the Coulomb force, which is

$$\boldsymbol{F} = -\frac{e^2}{4\pi\varepsilon_0 r^2}\hat{\boldsymbol{r}}, \tag{5.1}$$

where ε_0 is the permittivity of free space and r is the distance between the two particles.

To find the potential energy, we integrate from ∞ to r (we are taking the potential energy to be zero at infinity) to calculate the work done to bring the electron from infinity to r, so we get

$$V(r) = -\int_\infty^r F(r')\,\mathrm{d}r' = \int_\infty^r \frac{e^2}{4\pi\varepsilon_0 r'^2}\,\mathrm{d}r' = -\frac{e^2}{4\pi\varepsilon_0 r}. \tag{5.2}$$

The Coulomb force does positive work to bring the electron closer to the proton, so the potential energy is negative for any finite separation. This means that the energy eigenvalues will also be negative.

Taking the reduced mass of the electron as

$$\mu = \frac{m_p m_e}{m_p + m_e}, \tag{5.3}$$

the kinetic energy operator is

$$\hat{T} = \frac{\hat{p}^2}{2\mu} = -\frac{\hbar^2}{2\mu}\nabla^2. \tag{5.4}$$

Combining these, the time-independent Schrodinger equation for the hydrogen atom electron can be written as

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = E\psi. \tag{5.5}$$

This potential has spherical symmetry, so we will solve the Schrodinger equation in spherical coordinates. Expanding the Laplacian, the full equation is

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi \tag{5.6}$$

5.1.2 Separating and Solving

Equation 5.6 is separable, so we look for solutions of the form

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \tag{5.7}$$

This gives us the derivatives of the wavefunction:

$$\frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\mathrm{d}R}{\mathrm{d}r}, \quad \frac{\partial\psi}{\partial\theta} = R\Phi\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}, \quad \frac{\partial\psi}{\partial\phi} = R\Theta\frac{\mathrm{d}\Phi}{\mathrm{d}\phi}. \tag{5.8}$$

Now, if we substitute these into equation 5.6 and rearrange so that we have all terms containing r on one side and all terms containing θ and ϕ on the other, we get

$$\frac{1}{\Theta\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right). \tag{5.9}$$

Using the method of separation of variables, both sides must be equal to the same constant, which we will set to be $-\lambda^2$. Thus we have the **radial equation** (rearranging slightly and cancelling off the minus sign from all terms):

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R(r) = \lambda^2 R(r), \tag{5.10}$$

and the **angular equation**:

$$\frac{1}{\Theta(\theta)\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right) + \frac{1}{\Phi(\phi)\sin^2\theta}\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2} = -\lambda^2. \tag{5.11}$$

Notice that equation 5.11 is completely independent of the potential energy, and it is also separable. Moving all terms with θ onto one side and all terms with ϕ onto the other, we get

$$-\lambda^2\sin^2\theta - \frac{\sin\theta}{\Theta(\theta)}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right) = \frac{1}{\Phi(\phi)}\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2}. \tag{5.12}$$

Now setting both sides equal to a separation constant $-m^2$, we get the **polar equation**:

$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right) = (m^2 - \lambda^2\sin^2\theta)\Theta(\theta), \tag{5.13}$$

and the **azimuthal equation**:

$$\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2} = -m^2\Phi(\phi). \tag{5.14}$$

5.2 Solving the Hydrogen Atom

To find the eigenfunctions of the hydrogen Hamiltonian, we will have to solve all three equations 5.10, 5.13, and 5.14, find the possible values of the separation constants, and calculate the normalisation coefficients. Let's do the simplest one, the azimuthal equation, first.

5.2.1 The Azimuthal Equation

Equation 5.14 is the simple harmonic motion equation, and its solutions are

$$\Phi(\phi) = Ce^{\pm im\phi}. \tag{5.15}$$

For this wavefunction to be normalised, we must have

$$\int_0^{2\pi} |\Phi(\phi)|^2 \, \mathrm{d}\phi = \int_0^{2\pi} |C|^2 = 1, \tag{5.16}$$

which implies

$$C = \frac{1}{\sqrt{2\pi}}. \tag{5.17}$$

What are the possible values of m? Note that $\Phi(\phi)$ must be single-valued, and ϕ is a periodic variable, which enforces the following constraint for any value of ϕ:

$$\Phi(\phi) = \Phi(\phi + 2\pi) \tag{5.18}$$

$$\frac{1}{\sqrt{2\pi}}e^{im\phi} = \frac{1}{\sqrt{2\pi}}e^{im(\phi+2\pi)} = \frac{1}{\sqrt{2\pi}}e^{im\phi}e^{2\pi im}. \tag{5.19}$$

This implies that $e^{2\pi im}$ must be 1, and therefore m must be an integer. The condition that $\Phi(\phi)$ must be periodic is our boundary condition that we are using to constrain m.

m is called the **magnetic quantum number**. We will come back to why it is called this later.

Finally, note that since $|e^{im\phi}|^2 = 1$ for all values of ϕ, the final probability density $|\psi|^2$ will be *independent* of ϕ.

5.2.2 The Polar Equation

To solve equation 5.13, we will first make the substitution $u = \cos\theta$ along with

$$\frac{\mathrm{d}u}{\mathrm{d}\theta} = -\sin\theta \tag{5.20}$$

$$\frac{\mathrm{d}}{\mathrm{d}\theta} = \frac{\mathrm{d}u}{\mathrm{d}\theta}\frac{\mathrm{d}}{\mathrm{d}u} = -\sin\theta\frac{\mathrm{d}}{\mathrm{d}u} = -\sqrt{1-u^2}\frac{\mathrm{d}}{\mathrm{d}u}, \tag{5.21}$$

where in the last equality we have used the identity $\sin\theta = \sqrt{1-\cos^2\theta}$ over the range $0 \leq \theta \leq \pi$. With these substitutions,

$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta} = \sqrt{1-u^2}\left(-\sqrt{1-u^2}\frac{\mathrm{d}}{\mathrm{d}u}\right) = (u^2-1)\frac{\mathrm{d}}{\mathrm{d}u}, \tag{5.22}$$

so equation 5.13 becomes

$$(u^2 - 1)\frac{\mathrm{d}}{\mathrm{d}u}\left((u^2 - 1)\frac{\mathrm{d}\Theta}{\mathrm{d}u}\right) = (m^2 - \lambda^2(1 - u^2))\Theta \tag{5.23}$$

$$\frac{\mathrm{d}}{\mathrm{d}u}\left((1 - u^2)\frac{\mathrm{d}\Theta}{\mathrm{d}u}\right) = \left(\frac{m^2}{1 - u^2} - \lambda^2\right)\Theta, \tag{5.24}$$

where in the last line we have divided by $-(u^2 - 1)$.

This is a well-known differential equation called the **general Legendre equation**. Its solutions are the **associated Legendre polynomials** $P_\ell^m(u)$, where ℓ is a non-negative integer related to the separation constant λ^2 by

$$\lambda^2 = \ell(\ell + 1). \tag{5.25}$$

This can be derived by a power series solution.

The form of the associated Legendre polynomials can be given in terms of the (regular) **Legendre polynomials** $P_\ell(u)$, which are solutions of the (regular) **Legendre equation**, which is the general Legendre equation with $m = 0$. The Legendre polynomials can be defined by **Rodrigues' formula**:

$$P_\ell(u) = \frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}u^\ell}[(u^2 - 1)^\ell]. \tag{5.26}$$

From this, the associated Legendre polynomials are given by

$$P_\ell^m(u) = (-1)^m(1 - u^2)^{\frac{m}{2}}\frac{\mathrm{d}^m P_\ell(u)}{\mathrm{d}u^m} \tag{5.27}$$

$$= \frac{(-1)^m}{2^\ell \ell!}(1 - u^2)^{\frac{m}{2}}\frac{\mathrm{d}^{\ell+m}}{\mathrm{d}u^{\ell+m}}[(u^2 - 1)^\ell]. \tag{5.28}$$

This formula implies that we have the constraint

$$0 \leq |m| \leq \ell, \tag{5.29}$$

which is also something that falls out from the series solution.

ℓ is called the **orbital angular momentum quantum number**, and again we will discuss its name later.

5.2.3 Spherical Harmonics

Taking the solutions to the azimuthal and polar equations together, the solutions to the whole angular part of the TISE for the hydrogen atom (equation 5.11) are

$$Y_\ell^m(\theta, \phi) = Ne^{im\phi}P_\ell^m(\cos\theta), \tag{5.30}$$

where N is a normalisation constant such that

$$\int_0^{2\pi}\int_0^\pi |Y_\ell^m(\theta, \phi)|^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = 1. \tag{5.31}$$

N turns out to be given by

$$N = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}}. \tag{5.32}$$

The allowed values of the orbital angular momentum and magnetic quantum numbers are

$$\ell = 0, 1, 2, 3, \ldots \tag{5.33}$$

$$m = -\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell. \tag{5.34}$$

Since the angular equation 5.11 did not depend on the potential at all, the angular part of the TISE would be the same for *any* problem where the potential energy only depended on radial distance. For this reason, the functions $Y_\ell^m(\theta, \phi)$ are quite important and they appear in any problem with spherical symmetry. They are known as the **spherical harmonics** and are to the surface of a sphere what sine and cosine are to a circle, i.e. they form a **complete and orthonormal basis** for functions defined on the surface of the unit sphere.

The first few (normalised) spherical harmonics are given by

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \tag{5.35}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta, \quad Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} \tag{5.36}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \quad Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{i\phi}, \quad Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\phi}, \tag{5.37}$$

the spherical harmonics with negative m are given by

$$Y_\ell^{-m}(\theta, \phi) = (-1)^m (Y_\ell^m(\theta, \phi))^*. \tag{5.38}$$

The magnitude squared of the spherical harmonics gives the probability distribution of finding the electron in a certain direction from the proton. If we plot the magnitude squared, looking at the distance of the surface from the origin in a given direction gives us an idea of the likelihood of finding an electron in that direction (the larger the magnitude squared, the higher the probability). As we mentioned before, since the azimuthal part of the spherical harmonics is always just a complex exponential, we have that $|Y_\ell^m|^2$ does not depend on ϕ, which means that all the spherical harmonics are rotationally symmetric about the z-axis. Furthermore, we have that

$$|Y_\ell^m|^2 = |Y_\ell^{-m}|^2, \tag{5.39}$$

we will come back to the implications of this later.

The state with $\ell = m = 0$ is the only one that is spherically symmetric, the electron is equally likely to be found in any direction. For $\ell > 0$ we see that when $m = 0$ the electron is most likely to be found on the z-axis, whereas for $|m| = \ell$ it is most likely to be found in the x-y plane.

5.2.4 The Radial Equation

Finally we turn to solving the radial equation 5.10. Substituting the separation constant that we found earlier $\lambda^2 = \ell(\ell + 1)$, we have

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R(r) = \ell(\ell + 1)R(r), \tag{5.40}$$

The solutions can then be derived explicitly using a series solution to be

$$R_{n\ell}(r) = \sum_{p=0}^{n-\ell-1} c_p \left(\frac{r}{a_0}\right)^{p+\ell} e^{-\frac{r}{na_0}},\tag{5.41}$$

where the c_p's are coefficients, n is a *positive* integer, and a_0 is the **Bohr radius**, given by

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}.\tag{5.42}$$

Technically this is the *reduced* Bohr radius as the official definition has the electron mass instead of the reduced mass, but the difference is incredibly small since the electron is so much less massive than the proton.

The series solution imposes another constraint that

$$\ell \leq n - 1.\tag{5.43}$$

We find that the energy eigenvalues only depend on n, and are given by

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{R_H}{n^2},\tag{5.44}$$

where we have defined the **Rydberg constant** $R_H = \frac{\hbar^2}{2\mu a_0^2}$. Because E_n depends only on the quantum number n, it is called the **principal quantum number**.

These radial parts of the wavefunction should be normalised using the condition

$$\int_0^\infty |R_{n\ell}|^2 r^2 \,\mathrm{d}r = 1,\tag{5.45}$$

and the first few eigenfunctions are:

$$R_{10}(r) = N_{10} e^{-\frac{r}{a_0}}\tag{5.46}$$

$$R_{20}(r) = N_{20}\left(1 - \frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}, \quad R_{21}(r) = N_{21}\frac{r}{a_0}e^{-\frac{r}{2a_0}},\tag{5.47}$$

where $N_{n\ell}$ are the normalisation constants.

Multiplying the radial part with the spherical harmonics found earlier, we finally get the whole spatial part of the energy eigenstates as

$$u_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi).\tag{5.48}$$

The spherical harmonics have no units, so since the magnitude squared of the whole spatial part should have units of m^{-3} (or "probability per unit volume") the magnitude squared of the radial part $|R_{n\ell}|^2$ also has units of m^{-3}. This means that the radial part $R_{n\ell}$ itself has units of $\mathrm{m}^{-\frac{3}{2}}$.

5.2.5 Radial Probability Density

The radial part of the wavefunction gives information about the likelihood of finding the electron a certain distance from the proton. Let's calculate the probability of finding the electron in a

spherical shell between r_1 and r_2.

$$P(r_1 < r < r_2) = \int_0^{2\pi} \int_0^{\pi} \int_{r_1}^{r_2} |u(r, \theta, \phi)|^2 r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \tag{5.49}$$

$$= \int_0^{2\pi} \int_0^{\pi} |Y_\ell^m(\theta, \phi)|^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \int_{r_1}^{r_2} |R_{n\ell}(r)|^2 r^2 \, \mathrm{d}r \tag{5.50}$$

$$= \int_{r_1}^{r_2} |R_{n\ell}(r)|^2 r^2 \, \mathrm{d}r, \tag{5.51}$$

where in the last line we have used the fact that the spherical harmonics are normalised. The integrand $|R_{n\ell}|^2 r^2$ has units of m^{-1} or "probability per radial metre", and so we must interpret this quantity as the **radial probability density**, not the radial part of the wavefunction. This means that the most likely radial distance to find the electron from the proton is given by the maximum of $|R_{n\ell}|^2 r^2$, *not* $|R_{n\ell}|^2$.

Example 5.1. What is the most likely distance to find the electron in the ground state R_{10}?

The radial part of the wavefunction is given by $R_{10}(r) = N_{10} e^{-\frac{r}{a_0}}$, so the most likely distance is given by the maximum of

$$|R_{10}(r)|^2 r^2 = |N_{10}|^2 e^{-\frac{2r}{a_0}} r^2. \tag{5.52}$$

We can find this by differentiating and setting the derivative to zero:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(|N_{10}|^2 e^{-\frac{2r}{a_0}} r^2\right) = 2|N_{10}|^2 r e^{-\frac{2r}{a_0}} - \frac{2|N_{10}|^2}{a_0} r^2 e^{-\frac{2r}{a_0}} = 0 \tag{5.53}$$

$$\implies 2r\left(1 - \frac{r}{a_0}\right) = 0. \tag{5.54}$$

One solution to this equation is $r = 0$ which is a minimum, and the other solution is $r = a_0$, which must be the maximum.

This justifies the common statement that the "size" of a hydrogen atom is a_0.

In general, the radial probability density has $n - \ell$ maxima. For a fixed n, the radius of the first maximum increases with increasing ℓ. The maximum values also *increase* with increasing radius, which makes sense because there is more volume, so we are more likely to find the electron there.

5.3   Energy Eigenstates of Hydrogen

5.3.1   Summary of the Eigenstates of Hydrogen

Putting the radial and angular parts of the eigenfunctions together, the whole spatial part of the electron eigenstate is

$$u_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi) \tag{5.55}$$

$$= N_{n\ell} \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}} \sum_{p=0}^{n-\ell-1} c_p \left(\frac{r}{a_0}\right)^{p+\ell} e^{-\frac{r}{na_0}} e^{im\phi} P_\ell^m(\cos\theta), \tag{5.56}$$

where P_ℓ^m are the associated Legendre polynomials and the principal, orbital angular momentum, and magnetic quantum numbers take the following values:

$$n = 1, 2, 3, \ldots \tag{5.57}$$

$$\ell = 0, 1, 2, \ldots, n-1 \tag{5.58}$$

$$m = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell-1, \ell. \tag{5.59}$$

These eigenstates have energy eigenvalues given by

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{R_H}{n^2}, \tag{5.60}$$

where the (reduced) Bohr radius is given by

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}. \tag{5.61}$$

The **ground state energy** E_1 is given by

$$E_1 = -R_H = -13.6\,\text{eV}. \tag{5.62}$$

This is the **ionisation energy** of hydrogen, i.e. the energy required to completely remove the electron from the influence of the proton.

Since the energy only depends on the principal quantum number, and for $n > 1$ we can have multiple values of ℓ and m, we have a set of **degenerate** states for all energy levels above the ground state. For example, for the first excited state $n = 2$, we can have $\ell = 0, 1$ and $m = -1, 0, 1$, which leads to four degenerate states

$$u_{200},\ u_{210},\ u_{211},\ \text{and}\ u_{21-1}, \tag{5.63}$$

all with energy $E_2 = -\frac{R_H}{4}$.

For a given ℓ, there are $2\ell+1$ possible values of m. Thus in can be shown that for a given n, the total degeneracy is

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2. \tag{5.64}$$

The greater the principal quantum number n for a given ℓ, the greater the expectation value of radial distance $\langle r \rangle$ i.e. the more spread out the probability distribution is. For a given n, ℓ determines the number of polar nodes, which are the nodes as you go from $\theta = 0$ to $\theta = \pi$.

In Dirac notation, the eigenstates are labelled

$$|n\ell m\rangle, \tag{5.65}$$

and they have the orthonormality condition

$$\langle n\ell m|n'\ell'm'\rangle = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}. \tag{5.66}$$

5.3.2 Spectroscopic Notation

For historical reasons, scientists working in atomic and nuclear physics adopt a notation for the eigenstates of hydrogen based on different series of spectral lines that were observed before electron orbitals were fully understood. Early spectroscopists denoted the first four values of ℓ by the letters s, p, d, and f, standing for "sharp", "principal", "diffuse", and "fundamental" respectively. These names do not mean anything in the quantum mechanical description, but the notation remains widespread.

In this notation the ground state is called the 1s orbital, the first excited states are called the 2s and the 2p orbitals, the second excited states would be the 3s, 3p, and 3d orbitals, and so on. After $\ell = 4$, the letters continue in alphabetical order from g for $\ell = 5$ onwards, missing out the letter "j".

Note that a p orbital stands for three eigenstates with $m = -1, 0, 1$, a d orbital stands for five eigenstates with $m = -2, -1, 0, 1, 2$, etc.

5.3.3 Hydrogen-like Atoms and Ions

We have solved for the motion of a single electron in a hydrogen atom, but what about electrons in other atoms?

We can apply the same model that we have developed so far to ions with a single electron such as He^+ (a helium nucleus with a single electron), Li^{2+} (a lithium nucleus with a single electron), Be^{3+} (a beryllium nucleus with a single electron), etc. In this case, the charge of the nucleus is now Ze, where Z is the atomic number, or the number of protons in the nucleus, equal to 2 for helium, 3 for lithium, 4 for beryllium, etc. The potential energy then increases in magnitude by a factor of Z, and the energy levels shift down by a factor of Z^2.

$$E_n = -\frac{Z^2 R_H}{n^2}. \tag{5.67}$$

The electrons are more strongly bound. Note that for our description of hydrogen, the reduced mass would also change slightly.

What about atoms with more than one electron? The dynamics get complicated, since we have to consider interactions between the electrons. For this reason, studying multi-electron atoms in general is out of the scope of these notes. What we *can* begin to look at are the **alkali metals** (lithium, sodium, potassium, rubidium, etc.). These atoms are neutral, so they have Z protons in the nucleus and Z electrons in orbitals, but $Z - 1$ of these electrons are tightly bound in closed shells. This means that the most weakly bound outermost electron (the **valence electron**) is in its own shell. It is not really possible to say anything about the form of the eigenstates of the valence electron using the framework we have created so far, but by considering two extreme scenarios we can make claims about its energy levels.

If the valence electron is at very large radii, much greater than the inner electrons, then the nuclear charge would be "screened" such that the valence electron would only notice an effective charge of $+e$ coming from the centre. This would mean that the energy levels would be roughly the same as for hydrogen. In the other extreme case, where the valence electron is at very small radii, inside the inner electron shells, then it would see the full unscreened nuclear charge $+Ze$. Therefore the actual potential energy curve must lie somewhere between these two extremes.

Spectroscopy experiments also show that for alkali metals the degeneracy between the different values of ℓ is broken. For a given n, the smaller values of ℓ have slightly lower energy.

Why is this? If we assume that the shape of the radial probability density will be roughly the same for the valence electron as for the hydrogen atom electron, then recall that for a given n the radius of the first maxima increases for increasing ℓ. This means that for smaller ℓ (for a given n), the electron is more likely to be found closer in to the nucleus and therefore further into the unscreened regime where the Coulomb force is stronger. This results in these states being slightly more tightly bound and therefore being slightly lower in energy.

Quantitatively, we can write the energy levels for the valence electron in an alkali metal as

$$E_{n\ell} = -\frac{R_H}{(n - \Delta(n,\ell))^2},$$
(5.68)

where $\Delta(n,\ell)$ is the **quantum defect**, an empirically determined quantity which denotes how far the energy levels are shifted down compared to hydrogen. Notice that we label the energy levels $E_{n\ell}$ now instead of just E_n because the states with different ℓ are now no longer degenerate.

For example, the 3s orbital in sodium has $\Delta(3,0) = 1.37$, the 3p orbital has $\Delta(3,1) = 0.88$, and the 3d orbital has $\Delta(3,2) = 0.01$, meaning this state has almost the same energy as E_3 for hydrogen.

5.4 Angular Momentum

5.4.1 Quantum Mechanical Definition of Angular Momentum

Classically, angular momentum is defined as

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}.$$
(5.69)

It is a useful quantity to study in classical mechanics because it is conserved for any particle under the influence of a central force such that the Coulomb force. We should therefore expect that angular momentum is conserved for the electron in hydrogen as well, so let's investigate.

Quantum mechanically, we define angular momentum in the same way it is defined classically, except using (vector) *operators* instead of just vectors.

> **Definition 5.1.** The **angular momentum operator** is defined in terms of the position and momentum operators as
> $$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}.$$
> (5.70)
>
> Writing out the cross product, we see that the components of the angular momentum operator are
> $$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$
> (5.71)
> $$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$
> (5.72)
> $$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$
> (5.73)

Recall that $\hat{r}_i\hat{p}_j$ commute as long as $i \neq j$, so the ordering does not matter when writing out the components. However, given that we cannot know all components of $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ simultaneously due to the uncertainty principle, it seems like we will not be able to know all components of angular momentum simultaneously either.

5.4.2 Commutation Relations

Let us test this out by finding some commutators. Note that as a general tip for calculating commutators, it is almost always useful to use standard commutator identities to simplify as much as possible before expanding the commutators themselves. For example, when finding the commutator of $\hat{L}_x$ and $\hat{L}_y$, we use the fact that

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}], \tag{5.74}$$

to write

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \tag{5.75}$$
$$= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x]. \tag{5.76}$$

The last two terms contain only things that all commute with each other, so they must be zero. Similarly, in the first two terms involving y and x commute with everything else in their commutators, so we can pull them out as constants:

$$[\hat{L}_x, \hat{L}_y] = \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{p}_y[\hat{z}, \hat{p}_z]\hat{x}. \tag{5.77}$$

Now we can insert the value of the commutator that we know, $[\hat{z}, \hat{p}_z] = i\hbar$, to get

$$[\hat{L}_x, \hat{L}_y] = -i\hbar\hat{y}\hat{p}_x + i\hbar\hat{p}_y\hat{x} \tag{5.78}$$
$$= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \tag{5.79}$$
$$= i\hbar\hat{L}_z. \tag{5.80}$$

Hence the x and y components of angular momentum do not commute and we cannot know them both simultaneously. Calculating the commutators between the other components, we find the same outcome. The values are

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \tag{5.81}$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y. \tag{5.82}$$

Notice that these commutators follow a cyclic pattern under the exchange of labels x, y, and z. This is just a consequence of the definition of $\hat{\boldsymbol{L}}$ as a cross product.

What properties can be know about the electron's angular momentum simultaneously? What about one of the components and the total magnitude? To try this, we calculate the commutator of one of the components with the operator $\hat{L}^2$, which is defined as

$$\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \tag{5.83}$$

So the commutator between $\hat{L}_x$ and $\hat{L}^2$ is

$$[\hat{L}_x, \hat{L}^2] = [\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] \tag{5.84}$$
$$= [\hat{L}_x, \hat{L}_x\hat{L}_x] + [\hat{L}_x, \hat{L}_y\hat{L}_y] + [\hat{L}_x, \hat{L}_z\hat{L}_z]. \tag{5.85}$$

The first term will be zero, and using the identity

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}, \tag{5.86}$$

the second and third terms can be written as

$$[\hat{L}_x, \hat{L}^2] = \hat{L}_y[\hat{L}_x, \hat{L}_y] + [\hat{L}_x, \hat{L}_y]\hat{L}_y + \hat{L}_z[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_z \tag{5.87}$$

$$= \hat{L}_y(i\hbar\hat{L}_z) + i\hbar\hat{L}_z\hat{L}_y + \hat{L}_z(-i\hbar\hat{L}_y) + (-i\hbar\hat{L}_y)\hat{L}_z \tag{5.88}$$

$$= i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y - \hat{L}_z\hat{L}_y - \hat{L}_y\hat{L}_z) \tag{5.89}$$

$$= 0. \tag{5.90}$$

Hence we can know the total magnitude of angular momentum and one of its components simultaneously, as one can show similarly that

$$[\hat{L}_y, \hat{L}^2] = 0 \tag{5.91}$$

$$[\hat{L}_z, \hat{L}^2] = 0. \tag{5.92}$$

It can also be shown that $\hat{L}^2$ and the components of angular momentum also all commute with the Hamiltonian:

$$[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_x] = [\hat{H}, \hat{L}_y] = [\hat{H}, \hat{L}_z] = 0, \tag{5.93}$$

meaning that the eigenfunctions of $\hat{H}$ are also simultaneously eigenfunctions of $\hat{L}^2$ and *one* component of angular momentum, conventionally taken to be $\hat{L}_z$. This is a **maximal set of mutually commuting operators**, a set of operators where each one commutes with all others.

5.4.3 Eigenvalues of Angular Momentum

Let us find the eigenvalues of the $\hat{L}^2$ and $\hat{L}_z$ operators. Given that angular momentum is a quantity relating to rotations, it is reasonable to assume that it will act on the angular part of the wavefunction. For this reason, we will write out the angular momentum operators explicitly in terms of angular position coordinates.

In the position basis, we can write

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{5.94}$$

with similar results for $\hat{L}_y$ and $\hat{L}_z$. Using these and the chain rule, e.g.

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial z} + \frac{\partial}{\partial \phi}\frac{\partial \phi}{\partial z}, \tag{5.95}$$

we get the following results for angular momentum operators in the position basis:

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{5.96}$$

$$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \tag{5.97}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{5.98}$$

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{5.99}$$

So we were right to assume that no derivatives of r would appear in these operators.

Notice that equation 5.99 looks very similar to the angular equation for the hydrogen atom electron (equation 5.11). In fact, if we take the angular equation and multiply it by $-\hbar^2 Y_\ell^m(\theta, \phi)$, bearing in mind that $Y_\ell^m(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ since the spherical harmonics were the solution to the angular equation, we get

$$-\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) Y_\ell^m(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta, \phi), \tag{5.100}$$

where we have substituted λ^2 for $\ell(\ell+1)$. This looks like an eigenvalue equation, and in fact it looks exactly like what we would get if we acted $\hat{L}^2$ on a wavefunction:

$$\hat{L}^2 \psi = -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \psi, \tag{5.101}$$

therefore the eigenfunctions of $\hat{L}^2$ must be the spherical harmonics, which makes sense since they are the angular part of the eigenfunctions of the hydrogen Hamiltonian, and their eigenvalues are $\hbar^2 \ell(\ell+1)$.

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta, \phi). \tag{5.102}$$

This finally explains why ℓ is called the orbital angular momentum quantum number, as it determines the magnitude of the angular momemtum of an electron in a certain orbital. An electron in a state with a given ℓ will have orbital angular momentum with magnitude

$$L = \hbar\sqrt{\ell(\ell+1)}. \tag{5.103}$$

This implies that the angular momentum of the electron is forced to be *quantised*. Depending on the total energy the electron has, which is determined by the principal quantum number n, the angular momentum can only have a magnitude given by the eigenvalue equation above for the allowed values of ℓ. For example, if an electron is sitting in the 2nd excited state ($n = 3$), then the magnitude of its angular momentum can either be $\hbar$, $\sqrt{2}\hbar$, or $\sqrt{6}\hbar$.

The spherical harmonics are also eigenfunctions of $\hat{L}_z$, which we can calculate explicitly by writing

$$\hat{L}_z Y_\ell^m(\theta, \phi) = -i\hbar \frac{\partial}{\partial\phi} Y_\ell^m(\theta, \phi) \tag{5.104}$$

$$= -i\hbar \frac{\Theta(\theta)}{\sqrt{2\pi}} \frac{\partial}{\partial\phi} \left(e^{im\phi} \right) \tag{5.105}$$

$$= m\hbar \frac{\Theta(\theta)}{\sqrt{2\pi}} e^{im\phi} \tag{5.106}$$

$$= m\hbar Y_\ell^m(\theta, \phi). \tag{5.107}$$

So the allowed values of the z-component of angular momentum are

$$L_z = m\hbar. \tag{5.108}$$

If we consider again the electron in the 2nd excited state and suppose it has $\ell = 2$, the allowed values for the z-component of its angular momentum are $-2\hbar$, $-\hbar$, 0, $\hbar$, and $2\hbar$. So the magnetic quantum number m determines the alignment of the electron's angular momentum with the z-axis, the larger the magnitude of m, the more aligned they are. Note that L_z can never be as large as the total magnitude of angular momentum, i.e. the angular momentum can never point exactly along z. This is because if $L_z = L$, then we know that $L_x = L_y = 0$, which is not allowed! However, as ℓ gets larger, the maximum allowed value of L_z gets closer and closer to L.

5.4.4 Visualising the Allowed Values of Angular Momentum

We can visualise the allowed values of angular momentum for a given state in the 3D space of angular momentum with L_x, L_y, and L_z each on their own axis. The angular momentum vector has a fixed length determined by ℓ, and the different allowed values of m sweep out cones around the z-axis since the values of L_x and L_y are unknown.

Note that this does *not* imply that L_x and L_y are allowed to take on a continuous set of values, they are also quantised. The cones are simply a visual aid which denotes that the values of L_x and L_y are unknown.

The angle between $\boldsymbol{L}$ and the z-axis in this diagram can be written

$$\cos\theta = \frac{L_z}{L} = \frac{m\hbar}{\hbar\sqrt{\ell(\ell+1)}} = \frac{m}{\sqrt{\ell(\ell+1)}}. \tag{5.109}$$

The minimal angle occurs for maximal L_z, which occurs when $|m| = \ell$.

$$\cos\theta_{\min} = \frac{\ell}{\sqrt{\ell(\ell+1)}} < 1. \tag{5.110}$$

This implies that

$$\theta_{\min} > 0, \tag{5.111}$$

as we have seen, however as $\ell \to \infty$, we get

$$\cos\theta_{\min} \to 1 \quad \implies \quad \theta_{\min} \to 0, \tag{5.112}$$

which is what we expect from classical physics.