QUANTUM MECHANICS

Lecturer: Dr. Eugene A. Lim
Michaelmas 2012
Office : DAMTP B2.09
`http://www.damtp.cam.ac.uk/user/eal40/teach/QM2012/QMroot.html`

- ## *Introduction* : Quantum Mechanics with Qubits

  The Postulates of Quantum Mechanics for Qubits. Dynamics of Qubits.

- ## The Failure of Classical Mechanics and Wave-Particle Duality

  The Classical Wave Equation. Double Slit Experiment. Photoelectric Effect. Wave-Particle Duality.

- ## The Mathematics of Quantum Mechanics

  The Postulates of Quantum Mechanics. Operators. Eigenfunctions and Eigenvalues. Observables and Hermitian Operators.

- ## Schrödinger's Equation

  Dynamics of Non-relativistic Particles. Principle of Superposition. Probability Current. Free Particles. Degeneracies. Stationary States.

- ## Solving Schrödinger's Equation in One Dimension

  Quantization of bound states. Scattering and Tunneling. The Gaussian Wavepacket. Parity Operator.

- ## The Simple Harmonic Oscillator

  Quantization in Position Basis. *Quantization in Energy Basis.

- ## Commutators, Measurement and The Uncertainty Principle

  Expectation Values. Commutators and Measurements. Simultaneous Eigenfunctions. The Uncertainty Principle.

- ## The Hydrogen Atom

  The Bohr Model. Schrödinger's Equation in Spherical Coordinates. S-waves of Hydrogen Atom. Angular Momentum. The Full Spectrum of Hydrogen Atom.

- ## *Epilogue* : Love and Quantum Mechanics

  Entanglement. Teleportation.

Recommended Books

- S. Gasiorowicz, *Quantum Physics*, Wiley 2003.

- R. Shankar, *Principles of Quantum Mechanics*, Kluwer 1994.

- R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Volume 3, Addison-Wesley 1970.

- P. V. Landshoff, A. J. F. Metherell and W. G. Rees, *Essential Quantum Physics*, Cambridge University Press 1997.

- P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press 1967, reprinted 2003.

- J. J. Sakurai, J. Napolitano, *Modern Quantum Mechanics*, Addison-Wesley 2011

Acknowledgements

1 Introduction : Quantum Mechanics with Qubits

<div align="right">

This is Serious Thread.

―――――――――――――――――――

Serious Cat

</div>

When you studied Classical Mechanics in the Dynamics and Relativity lectures last year, you were told that a particle is an object of insignificant size. Then you spent eight weeks studying the dynamics of this particle and took an exam. One of the things you learned is to describe the *state* of the particle in terms of its position x and momentum p (and given its mass m, one can deduce its velocity $\dot{x} = p/m$), both which take definite real values at any given moment in time.

Let's think about a non-relativistic particle of mass m. In many of the problems and calculations, you often assumed that once you know information of these two variables $(x(t_0), p(t_0))$ of this particle at some initial time t_0, using Newton's Laws of Motion,

$$\frac{dp}{dt} = F \tag{1}$$

you can calculate and predict to any arbitrary accuracy the position and momentum $(x(t), p(t))$ of this particle at some later time $t > t_0$. In addition, it is implicit that one can at any time measure with arbitary accuracy the values of variables as we please.

In words we say that we "know the *state* of the particle" at any time t. The key phrases we have used in the above description is "Classical Mechanics" and "arbitrary accuracy". It turns out that, in *Quantum* Mechanics, one of the ideas that we have to abandon is the notion that we can "predict to any arbitrary accuracy" the position *and* momentum of any particle. In fact, it is worse than this: another notion we have to abandon is the idea of that we can *measure* with arbitrary accuracy both variables at the same time t. These two notions are not only those we will abandon of course, but giving these up already begs a bunch of questions: How do we describe the state of a particle, and how do we describe its dynamics?

Hence, in the study of how quantum particles move, or more generally how dynamical *systems* behave: rocks, electrons, Higgs Bosons, cats, you name it, we have to start with an entire new notion of how dynamical states of systems are *described* mathematically. Indeed, once we give up the notion of absolute knowledge about the state, we can start to introduce even more abstract states which has no classical analog such as the "spin" of an electron, and even more abstractly, how information is encoded in quantum mechanical systems.

In this first section of the lectures, we will use the simplest possible dynamical system – a system with only two possible states – as an introduction into the weird world of Quantum Mechanics. The goal of this introduction is to give you a broad overview of the structure of Quantum Mechanics, and to introduce several new concepts. Don't worry if you don't follow some of the details or you find that there are a lot of unexplained holes, we will go over the same ground and more in the coming lectures.

1.1 Classical Bit vs Quantum Qubit

As children of the computer revolution, you must be familiar with the idea of a *bit* of information. The bit is a system that can only has two possible states: 1/0 or up/down or on/off or dead cat/live cat etc. Let's use up/down for now. Such binary systems are also called (obviously) *two-state* systems. We can endow this bit with some set of physical rules which when acted upon the system, may change it from one state to another. For example, in Newton's Law of motion, the dynamics of (x, p) are described by Eq. (1). In words it means "When we act on the particle with a force described by $F(x)$ for an infinitisimal time dt, the value of p changes by Fdt". What kind of rules can we write down for a bit?

INPUT	OUTPUT
down	up
up	down

Table 1: A NOT gate

The set of rules for a bit can be something simple like a NOT gate. This rule simply flips an up to a down, and a down to an up. A NOT gate rule is shown in Table 1. Another rule we can write down is the "do nothing" gate, which just returns up if acted on up, and down if acted on down.

Mathematically, we can define the following column matrices to represent the up/down states

$$\chi_{\text{up}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \chi_{\text{down}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{2}$$

so a NOT gate can be described by the 2×2 matrix

$$\hat{P} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{3}$$

while a "do nothing" gate is obviously the identity

$$\hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4}$$

"Acting" then means usual matrix multiplication of the column vector from the left by the gate matrix

$$\text{result} = \text{gate matrix} \times \text{state}. \tag{5}$$

You can check that acting from the left with $\hat{P}$ and $\hat{I}$ on an up/down state gets you the right results, e.g. acting on up state with NOT gate yields a down state

$$\chi_{\text{down}} = \hat{P}\chi_{\text{up}}. \tag{6}$$

A bit is a classical quantity, so we can measure with arbitrary accuracy whether it is up or down. For example, a classical cat is either dead or alive (just check its pulse). We can also *predict* with arbitrary accuracy what would happen when we act on the bit with the rules: if we start with a up, acting on it with a NOT gate we predict that it will become a down (and then we can measure it to confirm that our prediction is true).

What about a quantum two-state system? Such a quantum state is called a *qubit*, for "quantum bit" obviously. What are the properties of a qubit and what kind of real physical system is modeled by one? You might have heard about the sad story of Schrödinger's Cat. The cat is put inside a closed box. There is a vial of poison gas in the box. A hammer will strike the vial if a certain amount of radioactivity is detected in the box, thus killing the cat. An observer outside the box has no way of finding out if this sad affair has occured without opening the box. Hence the cat is in the curious state of being both alive and dead at the same time according to the observer: the information about the deadness or aliveness of the cat is carried by a qubit.

You probably have realized that I have shoved a ton of things under a carpet of words here, and words are not well defined – there are many equally good ways to implement those words but Nature chose the path of Quantum Mechanics. Let's now be a bit more precise, and introduce the Postulates of Quantum Mechanics for two-state systems. We will elaborate on each of these postulates for more general cases in future lectures.
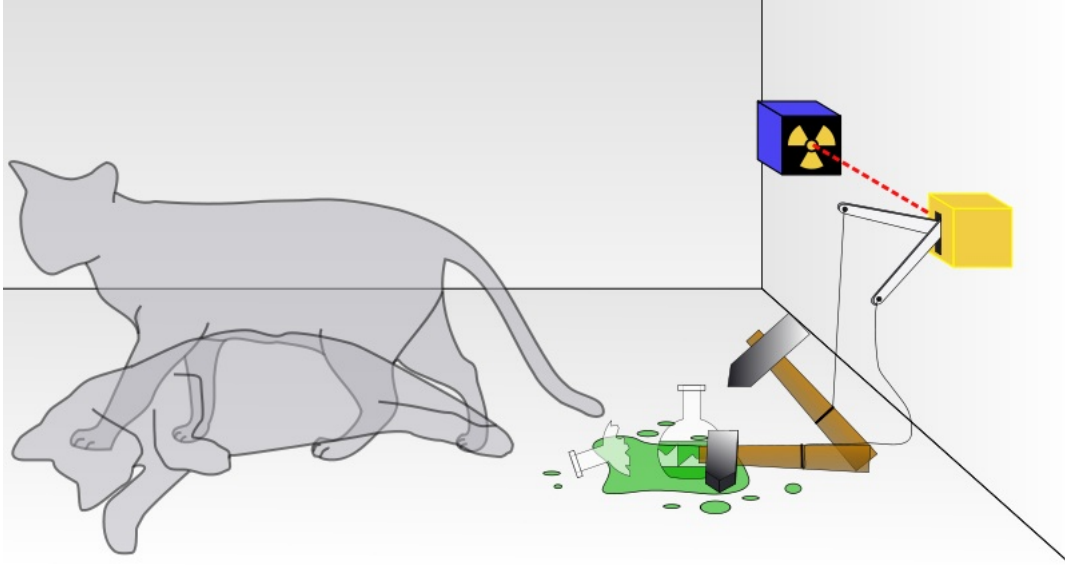
Figure 1: Schrödinger's Cat and its sad/happy fate. Stolen from Wikipedia.

Postulate 1 (State): A *qubit*, ψ, is described by the **state vector**

$$\psi = \alpha\chi_{\text{up}} + \beta\chi_{\text{down}} \ , \text{ where } \alpha, \beta \in \mathbb{C}. \tag{7}$$

α and β are called **probability amplitudes** for finding the up and down state, for reasons we will soon see. The important point here is that the coefficients α and β are *complex numbers* – this means that the information encoded in the state has been enlarged when compared to the binary classical bit[1]. Postulate 1 tells us that the state can be neither up nor down; it is some **linear superposition** between two possible states – hence the cat can be both dead and alive.

By convention, we normalize the state vector $(\psi^T)^*\psi = 1$, hence $|\alpha|^2 + |\beta|^2 = 1$, where the superscript T denotes transpose and $*$ denotes complex conjugation. The combination of these two operations is called **Hermitian Conjugation**, which we denote with a † i.e. for any complex matrix $\hat{A}$

$$(\hat{A}^T)^* \equiv \hat{A}^\dagger \tag{8}$$

This operation occurs so often in Quantum Mechanics that we will define the **inner product** (or "dot product") of two state vectors the following way. Given two state vectors ϕ and ψ, the inner product is then defined as

$$\phi \cdot \psi \equiv \phi^\dagger\psi. \tag{9}$$

Postulate 2 (Born's Rule): The *probability* of measuring an up/down state is the absolute square of the inner product of the desired outcome with the state, i.e.

$$\text{Probability of measuring up state} = |\chi_{\text{up}} \cdot \psi|^2 = |\alpha|^2, \tag{10}$$

$$\text{Probability of measuring down state} = |\chi_{\text{down}} \cdot \psi|^2 = |\beta|^2. \tag{11}$$

Note that since the qubit has to be in some state, the probability must add up to unity $|\alpha|^2 + |\beta|^2 = 1$ – this is the reason why the state vectors are normalized to one. More generally, state vectors must be **normalizable** to be valid quantum mechanical states. A note on jargon: note that probability amplitudes are complex, while probabilities are real.

---

[1]*Technically, the space in which a two-state quantum mechanically system live in is a S_2 sphere called the **Bloch Sphere** where the up/down state reside at the North and South poles of this sphere.*

Postulate 3 (Measurement): Once a measurement has been made and up/down has been obtained, the state vector ψ *collapses* into the measured state

$$\psi \xrightarrow{\text{measure}} \chi_{\text{up/down}}. \tag{12}$$

While Postulate 1 tells us that a qubit can be neither up nor down, Postulate 2 tells us the probability of measuring either of the two states. Postulate 3 then tells us that once the measurement has been made, follow up measurements will yield identical results (as long as we have not act on the state other than make a measurement). In particular, Postulate 3 implies that *the very act of measurement affects the system*. This is often called the **Collapse of the State Vector**.

So the story of the cat is now the following: the state of aliveness/deadness of the cat is carried by a qubit due to the quantum mechanical nature of radioactivity, and the probability of finding the cat to be dead or alive when we open the box is given by $|\alpha|^2$ or $|\beta|^2$. Once the box is opened, the cat's state will collapse into one of the two states depending on which is measured.

1.2   Operators on the State and Observables

Knowing how to describe a state is not enough of course; we want to know ultimately how states *evolve* with time. In the case of Classical Mechanics, the force $F(x)$ acts on a particle of mass m for an infinitesimal time dt to change the state $p \to p + F dt$. In Quantum Mechanics, we will soon discover that the equivalent law of motion for a quantum mechanical particle is given to us by Schrödinger's Equation which we will spend much of our time in these lectures studying. For now, however, let's abstract the notion of "acting on". Recall that a NOT gate Eq. (4) flips up/down to down/up. What happens when we act on the qubit ψ with the NOT gate? Viz.

$$\hat{P}\psi = \hat{P}\alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \hat{P}\beta \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{13}$$

$$= \alpha \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \beta \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{14}$$

i.e. we flip the probability amplitudes of measuring the up and down. Now $\hat{P}$ and $\hat{I}$ are very simple operations, and in classical information theory with bits, these are the only two possible actions you can act on a single bit. However, in the case of a qubit, the additional *complex* structure of the state vector allows for a much more varied kinds of actions – any 2×2 non-singular unitary matrix $\hat{O}$ with *complex* coefficients that takes ψ to another normalizable state ψ' is fine, i.e.

$$\psi' = \hat{O}\psi. \tag{15}$$

We will now introduce the high-brow word **operator**, i.e. $\hat{O}$ is an operator, and it operates on ψ to give us another state ψ' – it is a map from the space of all possible states to itself. As an aside, in these lectures, we will only deal with *linear* operators, which you will learn a lot about in your Linear Algebra class. Also, jargonwise we use "act" and "operate" interchangeably (although we don't use "actor".)

There is a special class of operators which corresponds to **observables**, i.e. things that we can measure, such as position and momentum of a particle. In the case of the qubit, the observable is the information of whether the state is up or down. How do we mathematically describe such an operator? This will lead us to Postulate 4. First, we introduce some more math – you may remember some of this from your IA class.

(Definition) Eigenvectors and Eigenvalues: If the operator $\hat{O}$ acting on state χ returns the state multiplied by some $\lambda \in \mathbb{C}$,

$$\hat{O}\chi = \lambda\chi \ , \ \lambda \in \mathbb{C} \tag{16}$$

then χ is called an **eigenvector** of $\hat{O}$ and λ its associate **eigenvalue**.

(Definition) Hermitian Matrices: Furthermore, suppose $\hat{O}$ obey

$$\hat{O} = \hat{O}^\dagger = (\hat{O}^T)^* \tag{17}$$

then $\lambda \in \mathbb{R}$ and $\hat{O}$ is a **Hermitian Matrix**. In other words: Hermitian Matrices have real eigenvalues.

Proof: From the definition of eigenvalues

$$\hat{O}\chi = \lambda\chi \tag{18}$$
$$\chi \cdot \hat{O}\chi = \lambda\chi \cdot \chi. \tag{19}$$

It is easy to show that $\chi \cdot \hat{O}\chi$ is also Hermitian, so

$$(\chi \cdot \hat{O}\chi)^\dagger = \chi \cdot \hat{O}\chi = \lambda^*\chi \cdot \chi \tag{20}$$

hence λ must be real.

We are now ready to state Postulate 4.

Postulate 4 (Observables): An operator associated with an observable $\hat{O}$ is Hermitian. The result of a measurement of such an observable on a state ψ yields one of the eigenvalues, and the state collapses (via Postulate 3) into its associated eigenvector.

Returning to the qubit, and we want to associate the result of such a measurement with 1 being up, and -1 being down[2]. One such operator (called a **Boolean operator**) is given by

$$\hat{N} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{21}$$

This operator is clearly Hermitian $\hat{N} = \hat{N}^\dagger$ and you can easily check that operating $\hat{N}$ on an up/down state returns the up/down state back with its associated eigenvalue ± 1

$$N\chi_{\text{up}} = 1 \times \chi_{\text{up}} \ , \ N\chi_{\text{down}} = -1 \times \chi_{\text{down}}, \tag{22}$$

i.e. the eigenvectors of $\hat{N}$ are the up/down states with their associated eigenvalues ± 1.

In the simple case of the qubit, it is clear that any state ψ can be described by some linear combination of the eigenvectors of $\hat{N}$, i.e. χ_{up} and χ_{down}, hence the space of eigenvectors is **complete**. You might also have noticed that the two eigenvectors are **orthonormal** to each other

$$\chi_{\text{up}} \cdot \chi_{\text{down}} = 0. \tag{23}$$

In fact, it can be shown that the eigenvectors of a Hermitian operator are complete and orthonormal to each other, but for the moment let us plow on. Here we emphasise that the physical act of measurement is *not* described by the mathematical act of operating on the state with a Hermitian operator, even though it is tempting to think that way!

* **Uncertainty Principle of the qubit** : One of the things that we have not gone into a lot of details in this introduction, is the notion of "measuring to arbitrary accuracy". We have asserted that one of the main idea of Quantum Mechanics of a single particle is that one cannot measure *both* its position x and momentum p to arbitrary accuracy at the same time. But this does not mean that we cannot measure the position x to arbitrary accuracy – we simply pay the price that we lose accuracy on the p measurement. This is the called the **Uncertainty Principle**, and we will formalize it in the coming lectures. However, you might ask, in the context of the qubit: can't we measure the up-ness or

---

[2]We can also do 0 and 1, but that would be confusing.

down-ness of a qubit to arbitrary accuracy? For example, once we open the box, the cat is dead – what is the price we pay for this accuracy? The answer to this paradox is to realize that the qubit actually has more than one Boolean operator. In fact it turns out that there exist a one (compact) parameter family of operators with eigenvalues ± 1, viz

$$\hat{N}_\theta = \begin{pmatrix} -\cos\theta & \sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}. \tag{24}$$

The *uncertainty principle of the qubit* pertains to the fact that one cannot measure, to arbitrary accuracy, the observables of all Boolean operators at the same time.*

1.3 Dynamics of a qubit

Finally, to close our whirlwind introduction to Quantum Mechanics, we turn to the dynamics of the qubit – we want to study its evolution. We want to still work with the eigenvectors of $\hat{N}$, so the time dependence is encoded in their *coefficients* $(\alpha(t), \beta(t))$, i.e.

$$\psi(t) = \alpha(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix}. \tag{25}$$

We have argued that operators act on states to give us another state. Colloquially, operators "do stuff to states". To give qubits dynamics, we can construct an operator $\hat{U}(t + \Delta t, t)$, let's call it the "wait for time Δt" operator, i.e.

$$\psi(t + \Delta t) = \hat{U}(t + \Delta t, t)\psi(t). \tag{26}$$

Physically, if $\Delta t = 0$, then $\hat{U}(t, t) = \hat{I}$ must be the identity. We can expand around this, to obtain

$$\hat{U}(t + \Delta t, t) = \hat{I} - \frac{i}{\hbar}\hat{H}(t)\Delta t + \dots \tag{27}$$

where $2\pi\hbar = h$ is the **Planck's Constant** and has the value 6.626×10^{-27} erg s (or 1.055×10^{-34} Joule s), while $\hat{H}$ is some Hermitian matrix with (possibly) time-dependent coefficients. Why $-i/\hbar$ and what is $\hbar$? Here we will cheat and simply say the reasons which will be a bit unmotivated

- $\hbar$ has dimensions, so we extract it out of $\hat{H}$ to get $\hat{H}$ to have the right dimensions of Energy.

- i is extracted so that $\hat{H}$ is Hermitian as it corresponds to an observable as we will see.

Rearranging Eq. (27) into something we are familiar with in calculus, and taking the limit of $\Delta t \to 0$

$$\lim_{\Delta t \to 0} \frac{\psi(t + \Delta t) - \psi(t)}{\Delta t} = -\frac{i}{\hbar}\hat{H}(t)\psi(t) \tag{28}$$

or

$$i\hbar \frac{d\psi}{dt} = \hat{H}(t)\psi(t). \tag{29}$$

This is known as the **Schrödinger's Equation** for a qubit. The Hermitian operator $\hat{H}(t)$ is called the **Hamiltonian**, because it is a generator of motion for $\psi(t)$. Note that it is first order in time derivative, unlike Newton's Law of motion, so a specification of $\psi(t_0)$ at some initial time t is all you need to evolve the system.

The Hamiltonian $\hat{H}(t)$ is time-dependent in general, but for most of the lectures we will consider the special and very important case of a time-independent $\hat{H}$.

Consider a simple Hamiltonian $\hat{H}$ of the following form

$$\hat{H} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}. \tag{30}$$

Since $\hat{H}\chi_{\text{up}} = E_1\chi_{\text{up}}$ and $\hat{H}\chi_{\text{down}} = E_2\chi_{\text{down}}$, $\chi_{\text{up/down}}$ are eigenvectors of $\hat{H}$ with eigenvalues E_1 and E_2. You might have learned from other courses (don't worry if you have not) that the Hamiltonian is also associated with the energies of the system – here E_1 and E_2 are the energy eigenvalues of $\hat{H}$. Since acting $\hat{H}$ on $\chi_{\text{up/down}}$ does not change $\chi_{\text{up/down}}$ but simply give us their energies, sometimes we also call the eigenvectors of $\hat{H}$ **Energy Eigenvectors**. This Hamiltonian is very simple, and we can easily find the solution to ψ

$$i\hbar\frac{d}{dt}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \tag{31}$$

or

$$\alpha(t) = \alpha(0)\exp\left[\frac{-iE_1 t}{\hbar}\right] \ , \ \beta(t) = \beta(0)\exp\left[\frac{-iE_2 t}{\hbar}\right]. \tag{32}$$

Since the probabilities of χ_{up} and χ_{down} in this case, $|\alpha(t)|^2$ and $|\beta(t)|^2$ do not evolve with time, we also call these states **Stationary States**. In particular, if we have started with the up/down state, we will stay in the up/down state forever.

This $\hat{H}$ is not very interesting as it is at the moment. We can make it more interesting by adding the NOT operator to it, and for simplicity, let's assume $E_1 = E_2 = E$ for the moment

$$\tilde{H} = \hat{H} - \epsilon\hat{P} = \begin{pmatrix} E & -\epsilon \\ -\epsilon & E \end{pmatrix}, \tag{33}$$

where ϵ is some real constant $|\epsilon| \ll E$. Physically, since the action of $\hat{P}$ is to flip an up state to a down state, one can think of this new operator $\tilde{H}$ as giving the dynamics to the qubit where it has a non-trivial chance of flipping states. (The condition $|\epsilon| \ll E$ ensures that the chance is small.)

Let's start with an up state at time $t_0 = 0$, i.e.

$$\psi(t_0) = \alpha(t_0)\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta(t_0)\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{34}$$

with $\alpha(t_0) = 1$ and $\beta(t_0) = 0$. The question is: *what is the probability of measuring the down state at some time $t > 0$?*

Using Schrödinger's Equation Eq. (29) and Eq. (25), we find the following pair of first order differential equations

$$i\hbar\frac{d\alpha}{dt} = E\alpha(t) - \epsilon\beta(t), \tag{35}$$

$$i\hbar\frac{d\beta}{dt} = E\beta(t) - \epsilon\alpha(t), \tag{36}$$

which we can solve, using the boundary conditions Eq. (34) to find the solutions[3]

$$\alpha(t) = e^{-iEt/\hbar}\cos\left(\frac{\epsilon t}{\hbar}\right), \tag{37}$$

$$\beta(t) = ie^{-iEt/\hbar}\sin\left(\frac{\epsilon t}{\hbar}\right). \tag{38}$$

Using Postulate 3, the probability of finding the down state at time $t > 0$ is then the amplitude square of the inner product of χ_{down} with $\psi(t)$,

$$P_{\text{down}} = |\chi_{\text{down}} \cdot \psi(t)|^2 = \sin^2\left(\frac{\epsilon t}{\hbar}\right). \tag{39}$$

The result is plotted in Fig. 2. In words, the presence of the $\epsilon\hat{P}$ operator in $\tilde{H}$ means that the probability

---

[3]Hint : define new variables $A(t) = \alpha(t) - \beta(t)$, $B(t) = \alpha(t) + \beta(t)$.
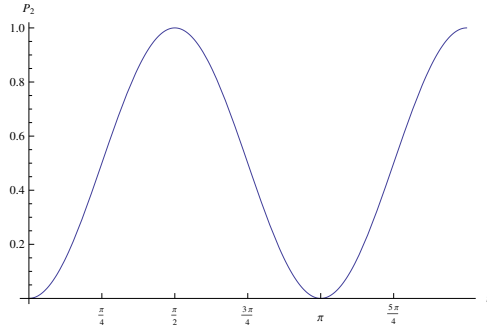
Figure 2: The probability of measuring the down state as a function of time in units of $\hbar/\epsilon$.

of measuring a down state oscillates with time.

We emphasise that it is the *probability* that is oscillating – say at time $t = 3\pi\hbar/\epsilon$, we have a 50-50 of measuring the state being up or down. Notice though, at $t = n\pi$ for $n = 0, 1, 2, \ldots$, there is *zero* probability of measuring the state being down. Hence sometimes you might hear people say "Quantum Mechanics mean that we cannot predict anything with certainty and hence it is not deterministic". That is certainly wrong – we can calculate the state vector to arbitrary accuracy, it is the notion of simultaneous measurements of *multiple incompatible observables* to arbitrary accuracy that is lost. But we are rushing ahead, so we leave this discussion for the future when we have developed the necessary mathematical tools to describe them.

1.4   Summary

Congratulations, you have just learned most of the structure of Quantum Mechanics! If this sounds too simple to be true – is Quantum Mechanics all about manipulating matrices and doing linear algebra – the secret answer is that yes it is true. Quantum Mechanics at its core is underlaid by linear algebra. Often, many people find Quantum Mechanics hard because *physically interpreting* the results is extremely counter-intuitive, and not because the calculational details are complicated.

In the coming lectures, we will abandon the qubit, and study the Quantum Mechanics of a single non-relativistic particle which is a more complex system than a qubit. When we do that however, do keep this first lecture in your mind – often you will find that a concept that is hard to understand in a particle system can be easily grasped when we strip everything down to a qubit. The study of the Quantum Mechanics of a non-relativistic particle, while seemingly a simple system, have remarkable explanatory power – indeed at the end of the lectures this very system reproduces the entire energy spectrum of the Hydrogen Atom.

Once we have done that, we will return to the qubit, and talk about love.

2 The Failure of Classical Mechanics and Wave-Particle Duality

This lecture is more qualitative than the rest of the class.

Very roughly speaking, in Classical Mechanics, one can describe motion in terms of either *particles* or *waves*. Classically, they are distinctly different things. In our every day life, we intuitively think of some things as particles (like bullets, cars, cats etc) while some other things as waves (sound waves, water waves, radio etc), because they seemingly behave very differently. In this lecture, we will show that quantum objects can neither be described as waves or particles, but has features of both.

You have studied particle motion under a system of Newtonian forces in your Dynamics and Relativity class in great detail – they obey Newton's Laws of Motion. Particles carry energy and momentum in infinitisimally *localized* small chunks, hence one often call them "point particles".

Waves, on the other hand, describe motion of entities which are spreaded out and *not localized*. Some common day examples are:

- Sound is carried by the compression and decompression of air, and the displacement of some parcel of air molecules from its original undisturbed position obeys the Wave Equation.

- Throw a pebble into a pond, and the disturbance caused by the pebble will caused a circular wave front to propagate outwards from the point of contact. The height of the water of the pond and its motion is described by waves.

- *Classical* Electric fields and Magnetic fields are described by waves. You will study this in great detail in the Part IB Electromagnetism class.

In the first two examples above, the waves are disturbances of some medium, while in the third example, electric and magnetic fields are waves themselves and do not need to propagate in a medium.

2.1 Wave Mechanics : The Wave Equation

Consider some function $f(x)$ that describe some pulse, with a maximum centered around the origin $f_{\max} = f(0)$ as shown in Fig. 3. This pulse for the moment is static since $f(x)$ is just a function of space and not time. Now, how do we give it motion? Suppose we want to describe the pulse traveling with constant velocity v to the right, in such a way that it preserves its original shape. At some time t later, the pulse is now centered around the location $x = vt$. Since we know that $f(0) = f_{\max}$, it is clear that a traveling pulse can be describe by the same function $f(x)$, but with the argument $x \to x - vt$, i.e. $f(x - vt)$. Similarly, a pulse with some other functional form $g(x)$ traveling to the left will be described by some function $g(x + vt)$. Let's call them *right-moving* and *left-moving* respectively.

Notice that the right moving pulse $f(x - vt)$ satisfies the differential equation

$$\left(v\frac{\partial}{\partial x} + \frac{\partial}{\partial t} \right) f(x - vt) = \hat{\mathcal{L}}_1 f(x - vt) = 0, \tag{40}$$

and the left moving pulse $f(x + vt)$ satisfies

$$\left(v\frac{\partial}{\partial x} - \frac{\partial}{\partial t} \right) g(x + vt) = \hat{\mathcal{L}}_2 g(x + vt) = 0. \tag{41}$$

Since the result of the action of any differential operator on zero is zero, we can operate $\hat{\mathcal{L}}_2$ on Eq. (40) and $\hat{\mathcal{L}}_1$ on Eq. (41) to get

$$\left(v\frac{\partial}{\partial x} + \frac{\partial}{\partial t} \right)\left(v\frac{\partial}{\partial x} - \frac{\partial}{\partial t} \right) f(x, t) = 0, \tag{42}$$

and

$$\left(v\frac{\partial}{\partial x} - \frac{\partial}{\partial t} \right)\left(v\frac{\partial}{\partial x} + \frac{\partial}{\partial t} \right) g(x, t) = 0, \tag{43}$$
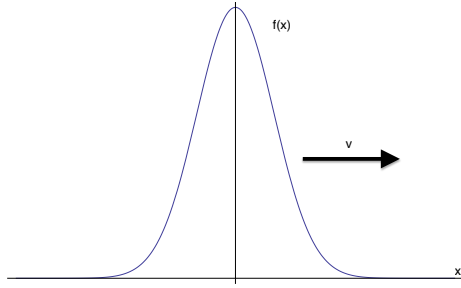
Figure 3: A pulse described by some function $f(x)$ moving with speed v to the right.

Figure 4: Circular waves caused by throwing a pebble into a pond.

or

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \frac{\partial^2 \psi}{\partial x^2}, \tag{44}$$

where $\psi(x,t) = f(x-vt) + g(x+vt)$. Notice that both f and g satisfies the *same* equation of motion Eq. (44), which is known imaginatively as the **Wave Equation**. Some features of the Wave Equation:

- Linearity: If ψ_1 and ψ_2 are both solutions of the Wave Equation, then so is $a\psi_1 + b\psi_2$ where $a, b \in \mathbb{C}$. This is known as the **Superposition Principle**.

- 2nd order in time derivative: As in Newton's Law of motion Eq. (1), the equation is second order in time derivative. This means that we need to specify two initial conditions $\psi(x,0)$ and $\dot{\psi}(x,0)$, as in particle dynamics.

There is a very special solution to the Wave Equation which will be important in our study called **plane waves**. These are solutions which are *periodic in space and time*

$$\psi(x,t) = A \exp\left[i\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{T}t\right)\right], \tag{45}$$

where λ is the *wavelength* and T is the *period*, and $A \in \mathbb{C}$ is known as the **amplitude** of the plane wave. The 2π's are annoying, so we often use the related quantities **wave number** $k \equiv 2\pi/\lambda$ and **angular frequency** $\omega = 2\pi/T$ instead, i.e.

$$\psi(x,t) = A \exp\left[i\left(kx - \omega t\right)\right]. \tag{46}$$

It is easy to show that Eq. (46) is a solution to the Wave Equation Eq. (44) provided that

$$v = \frac{\omega}{k}. \tag{47}$$

v is sometimes known as the **phase velocity** of the wave, and quantifies the propagation velocity of the wave.

Like particles, waves can carry energy and momentum. Since waves oscillate, we can define a quantity called **intensity**,

$$I = |\psi(x,t)|^2, \tag{48}$$

which is proportional to the time averaged (over the period) energy and momentum flow. Note that we have to put in the right constants to make the dimensions right, but let us ignore that for the moment.

In 3-dimensions, the Wave Equation is given by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \nabla^2 \psi, \tag{49}$$

while plane waves generalize simply from their 1 dimensional counterpart Eq. (46) to

$$\psi(\mathbf{x}, t) = A e^{i\mathbf{k}\cdot\mathbf{x} - i\omega t} \ , \ \omega = |\mathbf{k}|v \tag{50}$$

where $\mathbf{k}$ is known as the **wave vector**.

2.2   Two Slit Experiment with Waves and Particles

We assert early on that particles and waves are distinct entities, with different behaviors. A simple and famous experiment to illustrate the difference is the Two Slit experiment. In this section, we will talk about the results of this experiments with waves and particles, and then we will describe the results of an experiment with when quantum effects are important to show that quantum systems possess qualities of both.

2.2.1   Two Slit with Waves : Sound waves

One of the consequences of the Superposition Principle in wave behavior is **interference**, which you might have studied in high school. Since linearity implies that the sum of two solutions ψ_1 and ψ_2 to the Wave Equation is also a solution, if we add two identical plane waves in terms of A, λ and T but are off-phase by π, then the interference is destructive and the result is zero, i.e.

$$\psi(x, t) = A \exp\left[i\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{T}t\right)\right] + A \exp\left[i\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{T}t + \pi\right)\right] = 0. \tag{51}$$

Likewise, constructive interference can occur when the two plane waves are in phase.

Let us now discuss the Two Slit experiment with waves. Sound waves are described by displacement of the position of air molecules from their original "undisturbed" position due to a pressure difference. Let $\psi(\mathbf{x})$ the displacement of some parcel of air from its original position at $\mathbf{x}$. They obey the 2-D Wave Equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2}. \tag{52}$$

As the molecules "empty" out or "rush" back into space, this changes the local density which in turns changes the pressure. And this pressure inequality generates further motion of the molecules. Our ears pick up the motion of air, and the greater the amplitude of the motion of the air molecules, the greater the pressure and hence the louder we hear the sound. Human ears are sensitive to sound frequencies from 20 Hz to 20 kHz, so a good measure of the "loudness" would be to use Intensity Eq. (48) since our senses do not normally pick up stimuli changes of such high frequency.

Imagine a wall with two holes S_1 and S_2 separated by distance a, see Figure 5. On the left of the wall, is a mono-frequency sound source (say a piano playing the note middle C, $1/T = 261$ Hz) sufficiently far away such that by the time the sound waves arrive at the wall, we assume that the crests are parallel to the wall. First, we block the hole S_2. The incoming sound wave will come through S_1, and then propagate radially outward. Since it is radial, it is clear that the energy and hence the intensity of the sound waves is dissipated.

An observer then walk along parallel to the wall at a constant distance d. As expected, the closer she is to the open hole, the more intense the sound she hears, and she plots the intensity as a function of
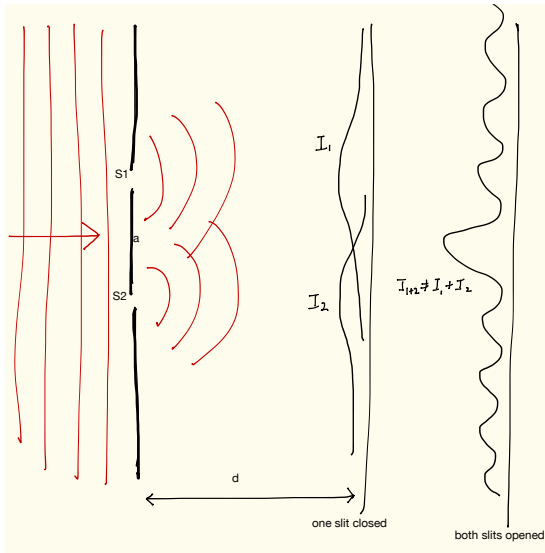
Figure 5: A double slit experiment with sound waves. The observer measures the left intensity plot when one of the slits is closed, and the right intensity plot when both slits are opened.

position and call it I_1. Similarly, she then closes S_1 and opens S_2, and the resulting intensity plot is I_2. Finally, she opens both S_1 and S_2, and make an intensity plot I_{1+2}. The plot she will obtain is the one on the right of Fig. 5, which is obviously $I_{1+2} \neq I_1 + I_2$.

This is because of the linearity of the wave solutions. Let ψ_1 describe the wave from S_1 and ψ_2 describe waves from S_2. With S_2 closed, the intensity is given by $I_1 = |\psi_1|^2$, and similarly for S_1. However, if both holes are opened, then both waves ψ_1 and ψ_2 will propagate towards the observer, and by linearity the $\psi = \psi_1 + \psi_2$. She then measures $I_{1+2} = |\psi_1 + \psi_2|^2 \neq |\psi_1|^2 + |\psi_2|^2$. The oscillatory pattern is easily explained by the fact that, depending on the distance of the observer from the S_1 and S_2, each wave will have arrived with a difference phase and hence can be constructive or destructive. You can easily show that the spacing between adjacent maxima of I_{1+2} is given by $\lambda d/a$.

2.2.2   Two Slit with Particles : Machine Gun

What about particles? We replace the peaceful piano playing middle C with a more violent machine gun. The machine fires equal mass bullets at equal velocities (and hence each bullet has equal kinetic energy). This machine gun is also designed such that it fires bullet at all directions at an equal rate. See Fig 6.

Since each bullet carries equal kinetic energy, the energy *flux* or intensity is then defined by the number of particles arriving per second at any given location x. As above, the intensity plots with one slit closed is given on the left of Fig. 6. When both slits are opened, it is not surprising that the total intensity $I_{1+2} = I_1 + I_2$, as expected since particles clearly do not exhibit wavelike behavior.

What about bullets hitting each other in mid-air, for example say a bullet hitting the edge of S_1 and gets deflected onto the path of another bullet coming through S_2, wouldn't this cause some form of "interference"? To eliminate this possibility, we can tune down the rate of the firing of the machine gun such that only one bullet is in the air at any time, and make the wall so thin that there is no chance of deflection off the inside of the hole. Then we will recover the result we asserted.

2.3   Is light particle-like or wave-like?

Now we want to repeat this experiment with light. Historically, this is known as the Young Two Slit Experiment and was credited in proving the wave nature of light in the 1800s.

The set up is again similar to Fig. 5, except that the incoming sound waves are now replaced by some monochromatic light source with frequency ω. Instead of an observer with ears, we set up a row of light
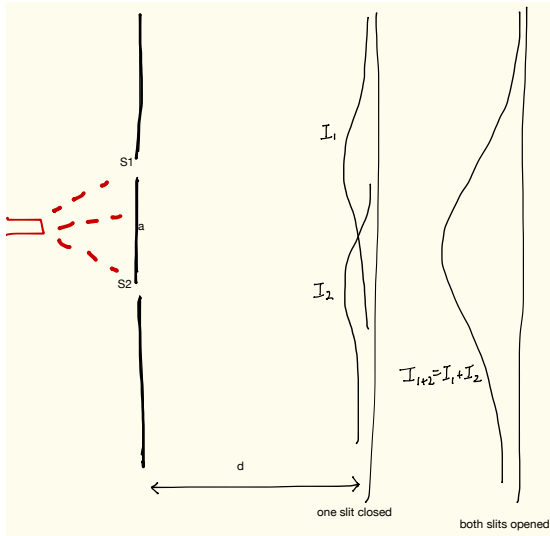
Figure 6: A double slit experiment with bullets. The observer measures the left intensity plot when one of the slits is closed, and the right intensity plot when both slits are opened.
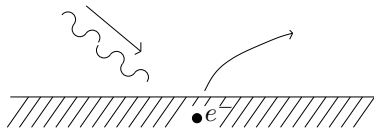

Figure 7: *The Photoelectric Effect.* The energy threshold required to expel an electron from a piece of metal is $E_0 > 0$. One can do this by shining a monochromatic light onto it. We can vary both the intensity I and the (angular) frequency $\omega = 2\pi c/\lambda$ of the light. We find that the liberation of an electron requires $\omega \geq \omega_0 = E_0/\hbar$ but is *independent* of I. On the other hand, the *rate* of electron emitted is $\propto I$.

detectors at a distance d from and parallel to the wall.

We then do the same experiment, do we see the wave pattern of Fig. 5 or the particle pattern of Fig. 6? You probably know the answer : it is the former. So light must be wave-like, as you will study in your Electromagnetism class, right?

But wait! Let us slowly dial down the intensity of the incoming light. At first, the intensity registered by the light detectors fall as expected. As we keep dialing down, a strange thing begins to happen – at some very low incoming intensity, the detectors are not being activated continuously. Instead, they are being activated *individually* – one detector goes off at location x_1, and then another goes off at some other location and so forth. It seems that light is coming in in *localized chunks*!

Perhaps an explanation is that at low intensity, light become particle-like? We can redo the experiment with a very low intensity such that the detectors are activated one at a time, and then plot out the number of times each detector is activated – and the result is still the same as in Fig. 5! So is light wave-like as it demonstrates interference behavior, or particle-like as it activates detectors locally?

The answer is of course, light has features of both. This is known as the **wave-particle duality** of light. Historically, while the Young Two Slit experiment is credited with "confirming" the wave-like nature of light, it is the **Photoelectric effect** (see Fig. 7) that shows that light also exhibits particle-like behavior – we call light particles **photons**.

To observe this effect, we take a piece of metal, and shine a monochromatic on it. We can change the frequency and the intensity of this light, and we observe that at certain frequenices, electrons will be emitted from this metal. Surprisingly, whether electrons are emitted or not depends *only on the frequency*, while the *rate* of emitted electrons depends on the incident intensity of light! Experimentally,

the frequency of the light required to liberate an electron is

$$\omega > \omega_0 = \frac{E_0}{\hbar} \tag{53}$$

where E_0 depends on the metal used. We have introduced Planck's constant $h = 2\pi\hbar$ in the previous lecture. Older books on quantum mechanics often like to use h, but we will use $\hbar$ in these lectures as most modern physicists now do.

This was puzzling to many people, until Einstein in his lunch break (1905) came up with the explanation with the crucial insight that if one thinks of light as localized bundles instead of a wave, the Photoelectric effect is completely natural. He stated that:

- A photon of frequency ω carries the energy

$$E = \hbar\omega, \tag{54}$$

  and the momentum

$$p = \hbar k. \tag{55}$$

- The energy and momentum of each photon is related to each other by

$$E = pc, \tag{56}$$

  where c is the speed of light. From your Dynamics class, relativistic kinematics imposes

$$E^2 = p^2 c^2 + m^2 c^4, \tag{57}$$

  so the photon is massless.

- Intensity of light corresponds to the *rate of photons emitted.*

- After liberation, conservation of energy implies that the electron has kinetic energy

$$E_K = \hbar\omega - E_0 = \hbar(\omega - \omega_0), \tag{58}$$

  which agrees well with experiments.

2.4   Everything is Quantum : De Broglie Waves

Is this strange behavior limited to light/photons? After all, light is massless so maybe it is special in some way. How about electrons, bullets, cats – do they exhibit wave-particle duality?

Historically, it was de Broglie who proposed that *all matter* exhibits this behavior. So for a particle moving at some momentum **p** possess a **de Broglie wavelength** given by

$$\lambda = \frac{2\pi\hbar}{|\mathbf{p}|}, \tag{59}$$

or sometimes simply $\mathbf{p} = \hbar\mathbf{k}$.

When he proposed this (it was his PhD thesis), there was no experiment that can test for this conjecture[4]. Indeed, for a bullet of mass 1g and moving at 1 cm/sec would have the de Broglie wavelength of

$$\lambda = \frac{2\pi\hbar}{p} \approx 10^{-26} \text{cm} \tag{60}$$

so any interference pattern would be impossible to see! But technology has moved on, and indeed there are now many experiments that verified this – *the entire Universe is quantum mechanical!* For those

---

[4]And hence demonstrating that the standard for theory PhDs in physics has not changed over the years.

who have taken Dr. Baumann's Concepts in Theoretical Physics class last term, he showed you a video of interference pattern of a two slit experiment done with electrons which conclusively demonstrated the wave-particle nature of matter in the Universe (the link to the `Youtube` video is on the course webpage).

Now we are in a conundrum – neither Newton's Law of motion of particles, and the Wave Equation of waves can describe things that exhibit wave-particle duality which inconveniently turns out to be everything.

What should we do?

3 The Mathematics of Quantum Mechanics

Previously we have introduced a two-state system to illustrate broadly the mathematical structure of Quantum Mechanics. Of course, the world is made out of more than just two-state qubits. In particular, qubits are *discrete* systems while most things we know and love are *continuous systems* – for example, how do we describe the position x and momentum p of a quantum mechanical object?

In this section, we will generalize what we have learned in the first lecture to how a non-relativistic particle move in a continuous coordinate space. As we move from discrete to continuous systems, we will take some liberties in the rigor of the mathematics – unfortunately we have limited time – but hopefully it will not be too much of a jolt to your senses.

3.1 Quantum Mechanics of a Particle

We started this class with the Classical equation of motion for a single particle, Newton's Law of motion Eq. (1) but then went off to discuss qubits. Let us now come back to the particle and ask "how do we describe a quantum mechanical particle?" We begin by restating the Postulates of Quantum Mechanics, but this time in the context of describing a particle.

Postulate 1 (State and Wavefunction): A particle is described by a **state** ψ. Furthermore, the **probability amplitude** of finding the particle at position $\mathbf{x}$ is given by a complex function $\psi(\mathbf{x})$

$$\psi \ : \ \mathbb{R}^3 \longrightarrow \mathbb{C}, \tag{61}$$

called the **wavefunction**. The space of ψ is the *space of all possible states in the system* called the **Hilbert Space**.

The wavefunction is **normalizable** or square integrable over all space $\mathbb{R}^3$

$$\int_{\mathbb{R}^3} \psi^*(\mathbf{x})\psi(\mathbf{x})dV = \int_{\mathbb{R}^3} |\psi(\mathbf{x})|^2 = \mathcal{N} < \infty. \tag{62}$$

Compare this to the state vector of the qubit in section 1.1. In the qubit, there are only two possible states up or down. But a particle can be anywhere in space, i.e. an infinite number of possible points. So instead of just two complex coefficients α and β describing the state, we have a continuous complex function which maps $\mathbb{R}^3$ (or $\mathbb{R}^n$ for an n-dimensional space) into $\mathbb{C}$.

We have intentionally introduced the notion of the state ψ as an individual entity, without conflating it with the wavefunction $\psi(\mathbf{x})$. In the high-brow way of thinking about quantum mechanics, $\psi(\mathbf{x})$ is really the (complex) *coefficient* of the state in the continuous and complete basis of $\mathbf{x}$. In words, we say that $\psi(\mathbf{x})$ *is the state ψ expressed in the $\mathbf{x}$ representation.* We can also represent ψ in the $\mathbf{p}$ *momentum representation.* We will discuss representations when we introduce Hermitian Operators – for the moment you can think of $\psi(\mathbf{x})$ as some complex function.

Having said all that, we will often interchange the words "wavefunction" and "state" in these lectures.

Postulate 2 (Born's Rule): The **probability** of finding the particle in some infinitisimal volume dV is given by

$$|\psi(\mathbf{x})|^2 dV. \tag{63}$$

It is nice to normalize total probability to unity so we normalize the wavefunction

$$\tilde{\psi}(\mathbf{x}) = \frac{1}{\sqrt{\mathcal{N}}}\psi(\mathbf{x}) \tag{64}$$

such that

$$\int_{\mathbb{R}^3} |\tilde{\psi}(\mathbf{x})|^2 dV = 1. \tag{65}$$

This means that

$$\rho(\mathbf{x}) \equiv |\tilde{\psi}(\mathbf{x})|^2 \in \mathbb{R} \tag{66}$$

is a **probability density function** in the usual sense. A little note on jargon: sometimes we sloppily call $|\psi(\mathbf{x})|^2$ the probability, which is nomenclaturely heinous but I hope you won't mind too much. We will also drop tildes to denote normalized wavefunctions from now on – it will be clear from the context which wavefunctions are normalized or not.

Since $\psi(\mathbf{x})$ is a scalar function, the probability density function is simply $\psi(\mathbf{x})^*\psi(\mathbf{x})$. Comparing this to the inner product of the qubit state we introduced way back in Eq. (9), we obviously do not need the transposition operation. To keep our notation consistent, we can also introduce the **inner product** of two wavefunctions ϕ and ψ

$$\boxed{\psi(\mathbf{x}) \cdot \phi(\mathbf{x}) \equiv \int_{\mathbb{R}^3} \psi^\dagger(\mathbf{x})\phi(\mathbf{x}) \ dV,} \tag{67}$$

where $\psi^\dagger$ denotes Hermitian Conjugation as before. Of course, if ψ is a scalar then this is simply usual conjugation. The scalar product of ψ with itself $\psi \cdot \psi = \int_{\mathbb{R}^3} |\psi(\mathbf{x})|^2 \ dV$ is called the **norm**, so normalized ψ has unit norm (doh).

In general, if $\phi(\mathbf{x})$ is the desired outcome, then the probability of measuring such an outcome given the wavefunction $\psi(\mathbf{x})$ is given by Born's Rule

$$\boxed{\text{Probability of measuring state } \phi(\mathbf{x}) \text{ in } \psi(\mathbf{x}) = \left| \int_{\mathbb{R}^3} \phi^\dagger(\mathbf{x})\psi(\mathbf{x}) \ dV \right|^2 = |\phi \cdot \psi|^2.} \tag{68}$$

We say $\int_{\mathbb{R}^3} \phi(\mathbf{x}) \cdot \psi(\mathbf{x}) \ dV$ is the probability amplitude of ϕ to be found in ψ – it measures the *overlap* of the two wavefunctions. You might note that the form Eq. (68) bears a lot more resemblance to the Born's Rule we encountered when we studied the qubit.

*From the viewpoint of Eq. (68), one can go super pedantic and write the probability amplitude $\psi(\mathbf{x})$ as

$$\psi(\mathbf{x}') = \int_{\mathbb{R}^3} \delta^3(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}) \ dV, \tag{69}$$

so Eq. (68) becomes

$$\text{Probability of measuring state } \delta^3(\mathbf{x} - \mathbf{x}') \text{ in } \psi(\mathbf{x}) = \left| \int_{\mathbb{R}^3} \delta^3(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}) \ dV \right|^2 = |\psi(\mathbf{x}')|^2 \tag{70}$$

recovering Eq. (63). This is cumbersome, but it allows us to be completely general about representation. You will study this in the Part II class Principles of Quantum Mechanics, but with snazzier notation than carrying all those integrals around.*

Equivalence class of states. If the wavefunctions are related to each other by a multiplicative non-zero complex number,

$$\psi_\alpha(\mathbf{x}, t) = \alpha\psi(\mathbf{x}, t) \ , \ \alpha \in \mathbb{C} - 0, \tag{71}$$

then both wavefunctions describe the same state. To check for this, we need to ensure that both wavefunctions will yield the same probability density function, viz:

Suppose $\psi(\mathbf{x}, t)$ is normalizable, then $\psi_\alpha(\mathbf{x}, t)$ also normalizable,

$$\int_{\mathbb{R}^3} |\psi_\alpha(\mathbf{x}, t)|^2 \ dV \quad = \quad |\alpha|^2 \int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \ dV = |\alpha|^2 \mathcal{N} < \infty. \tag{72}$$

Normalizing both wavefunctions

$$\tilde{\psi}_\alpha(\mathbf{x}, t) \quad = \quad \frac{\psi_\alpha(\mathbf{x}, t)}{\sqrt{|\alpha|^2 \mathcal{N}}} = \frac{\alpha}{|\alpha|} \tilde{\psi}(\mathbf{x}, t), \tag{73}$$

we see that the difference only depends on α through the complex phase $\alpha/|\alpha|$ and therefore yields the same probability density function,

$$\rho(\mathbf{x}, t) \quad = \quad |\tilde{\psi}_\alpha(\mathbf{x}, t)|^2 = |\tilde{\psi}(\mathbf{x}, t)|^2 \tag{74}$$

for all values of α.

Postulate 3 (Measurement): Once a measurement has been made, the wavefunction collapses into its *normalized* measured state ϕ

$$\psi \overset{\text{measure}}{\longrightarrow} \phi; \tag{75}$$

the very act of measurement has affected the wavefunction which would "jump" into its measured state.

This is often called **Collapse of the Wavefunction**. Why does a measurement "collapse" the wavefunction? One way to think about this is to consider the act of measurement – we would need an apparatus which must somehow *interact* with the system. For example, if we want to measure the position of a moving particle, we would need to *see* where it is, so we shine a light on it. The light bounces off the particle, and enter our eyes so we say "Aha, the particle is here." But the light has affected the particle in some way. In Feynman's words, *the disturbance is necessary for the consistency of the viewpoint [of making observations]*. But this does not mean we understand how or why the interaction occurs in such a way to "collapse" the wavefunction, since the apparatus themselves are made out of quantum mechanical things too. This is known as the **Measurement Problem**.

Let's think about this what it means to measure the position of the particle. If we have an amazingly accurate detector which can pinpoint the position of the particle, then once we found its position, say it is at position $\mathbf{x}_0$, then the wavefunction must collapses to something that will have support only at $\mathbf{x}_0$, i.e. a **Dirac Delta Function** $\psi(\mathbf{x}) \longrightarrow \delta^3(\mathbf{x} - \mathbf{x}_0)$ you have previously encountered in your IA class. Since the Dirac Delta is *not normalizable* so in principle it is not a valid wavefunction so we have to be a little bit more careful about calling it such. The root cause of this is that the probability of finding a particle *exactly* any point $\mathbf{x}_0$ is zero – since there is an infinite of points in a continuous space $\mathbb{R}^3$, the probability of finding the particle at any particular point cannot be finite.

Fortunately in practice, the best a detector can do is to pinpoint the position of the particle within some small but finite region ΔV. In this case, the wavefunction $\psi(\mathbf{x})$ then collapses into some other normalized wavefunction $\phi(\mathbf{x})$ which has support only around this region ΔV, i.e.

$$\int_{\Delta V} |\phi(\mathbf{x})|^2 \, dV \to 1. \tag{76}$$

3.2 Operators on the Wavefunction

Recall that in the qubit system, we can flip the states with the NOT gate. How do we "do stuff to the wavefunction"? Instead of complex matrices acting on vectors, we introduce **operators**. An operator $\hat{O}$ eats a complex valued function f and returns another such complex function, so it is a map from the space of ψ to itself, i.e.

$$g = \hat{O}f \ , \ \text{where} \ \ f, g : \mathbb{R}^3 \longrightarrow \mathbb{C}. \tag{77}$$

Fortunately, in Quantum Mechanics, we only deal with *linear* operators, so the corresponding map is also linear

$$\hat{O} \left[\alpha_1 f_1 + \alpha_2 f_2 \right] \quad = \quad \alpha_1 \hat{O} f_1 \ + \ \alpha_2 \hat{O} f_2 \tag{78}$$
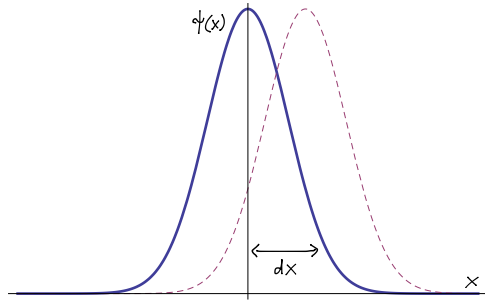
Figure 8: Translation of the (Real) part of the wavefunction $\psi(x)$ by dx.

for any complex-valued functions f_1 and f_2 and complex numbers α_1 and α_2.

In general, $g(\mathbf{x})$ is linearly independent from $f(\mathbf{x})$ – this corresponds to the operator having done something "physical" to the wavefunction. Let's see how this works in a physical situation.

Momentum Operator: Suppose we start with a wavefunction $\psi(x)$ in one-dimension. Since in classical dynamics, what momentum does is to generate *translations* in space x, in quantum theory we want to find an operator $\hat{T}$ which will *translate* $\psi(x)$ to the right by a tiny amount Δx, see fig 8, i.e.

$$\psi(x - \Delta x) = \hat{T}(x + \Delta x, x)\psi(x). \tag{79}$$

Since we know that if $\Delta x = 0$, $\hat{T}$ must simply be the trivial operator $\hat{1}$, we can expand around this to get

$$\psi(x - \Delta x) \approx (\hat{1} - \frac{i}{\hbar}\hat{p}\Delta x)\psi(x), \tag{80}$$

where $\hat{p}$ is some other operator. The factor $-i/\hbar$ is again convention which is required to both get dimensions right and for other reasons[5] – but it is a form which you have seen in the first lecture when we derived Eq. (29). Rearranging and taking the limit of $\Delta x \to 0$ as usual

$$\frac{i}{\hbar}\hat{p}\psi(x) = \lim_{\Delta x \to 0} \frac{\psi(x) - \psi(x - \Delta x)}{\Delta x} = \frac{\partial \psi}{\partial x} \tag{81}$$

or we can write down the operator $\hat{p}$ as

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{82}$$

$\hat{p}$ is called the **momentum operator** (in the x basis). We can generalize this to 3 dimensions easily

$$\boxed{\hat{\mathbf{p}} = -i\hbar\nabla.} \tag{83}$$

The action of the momentum operator $\hat{p}$ is to move the wavefunction by an infinitisimal amount in x space, just like its classical counterpart.

While many operators "do stuff" to states, there is a very important special class of operators which leave the state invariant which we will study next.

(Definition) Eigenvalues and Eigenfunctions: Suppose an operator $\hat{O}$ acting on $f(\mathbf{x})$ returns the same function multiply by some complex number λ,

$$\hat{O}f(\mathbf{x}) = \lambda f(\mathbf{x}), \tag{84}$$

then we say that $f(\mathbf{x})$ is an **eigenfunction** of $\hat{O}$ with **eigenvalue**[6] λ. Let's look at a couple of familiar examples.

---

[5] As a teaser, the reason we attach i is to ensure that the momentum operator corresponds to a physical observable, i.e. to make the operator Hermitian.

[6] Compare this to the words eigenvector and eigenvalue used in your Part IA Vectors and Matrices class.

Position Operator and its Eigenfunctions: In 3 dimensions, the position operator is the vector $\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$. The action of each of the component of the operator $\hat{x}_i$ on any wavefunction $\psi(\mathbf{x})$ returns the *variable* x_i

$$\hat{x}_i \psi(\mathbf{x}) = x_i \psi(\mathbf{x}) \ , \ \forall \ x_i \in \mathbb{R}. \tag{85}$$

It is clear that functions of $\hat{\mathbf{x}}$ behave the same way

$$F(\hat{\mathbf{x}})\psi(\mathbf{x}) = F(\mathbf{x})\psi(\mathbf{x}). \tag{86}$$

What about the eigenfunctions and eigenvalues of $\hat{\mathbf{x}}$? Working in one dimension for simplicity, we want to find the eigenfunction $u_X(x)$ with eigenvalue X (which is some number), i.e.

$$\hat{x}u_X(x) = xu_X(x) = Xu_X(x) \ , \ \forall \ X \in \mathbb{R}. \tag{87}$$

It turns out that this eigenfunction equation can be satisfied by the **Dirac-δ** , the continuous space version of the Kronecker-δ, which formally obeys the equation

$$x\delta(x - X) = X\delta(x - X). \tag{88}$$

We can check that this is true by multiplying both sides with some arbitrary function $f(x)$ and integrating over all space

$$\int_{-\infty}^{\infty} dx \ xf(x)\delta(x - X) = \int_{-\infty}^{\infty} dx \ Xf(x)\delta(x - X) = Xf(X). \tag{89}$$

In 3 dimensions, the eigenfunction for the position operator is generalized to $\delta^3(\mathbf{x} - \mathbf{X}) = \delta(x_1 - X_1)\delta(x_2 - X_2)\delta(x_3 - X_3)$.

Harking back to our discussion on Postulate 3, we argued physically that a particle with a definite position is described by a wavefunction that is the Dirac delta – now we see that such a wavefunction is an eigenfunction of the $\hat{\mathbf{x}}$ with the eigenvalue being the value of the position itself $\mathbf{x}$. As we said, Dirac deltas are not normalizable.

Momentum Operator and its Eigenfunctions: The eigenfunctions of $\hat{\mathbf{p}} = -i\hbar\nabla$, $u_{\mathbf{p}}(\mathbf{x})$, satisfies the eigenfunction equation

$$\hat{\mathbf{p}}u_{\mathbf{p}}(\mathbf{x}) = \mathbf{p}u_{\mathbf{p}}(\mathbf{x}) \tag{90}$$

or in differential form

$$-i\hbar\nabla u_{\mathbf{p}}(\mathbf{x}) = \mathbf{p}u_{\mathbf{p}}(\mathbf{x}), \tag{91}$$

with eigenvalue $\mathbf{p}$ (of course we can call it whatever we want, but as we will soon see it makes sense to call it "momentum $\mathbf{p}$"). We can directly integrate Eq. (91) to obtain

$$u_{\mathbf{p}}(\mathbf{x}) = A\exp\left(i\frac{\mathbf{p}\cdot\mathbf{x}}{\hbar}\right) \tag{92}$$

where $A \in \mathbb{C}$ is some arbitrary constant. Using de Broglie's relation $\mathbf{p} = \hbar\mathbf{k}$, we obtain

$$\boxed{u_{\mathbf{p}}(\mathbf{x}) = A\exp(i\mathbf{k}\cdot\mathbf{x})} \tag{93}$$

which is the time-independent part of the plane-wave solution Eq. (50). Hence we can conclude the following

- Plane wave solutions of wave vector $\mathbf{k}$ corresponds to a state of definite momentum $\mathbf{p} = \hbar\mathbf{k}$.

- *Non-normalizability*: The norm of any momentum eigenstate is infinity

$$u_{\mathbf{p}} \cdot u_{\mathbf{p}} = \int_{\mathbb{R}^3} |u_{\mathbf{p}}|^2 \ dV = \infty \tag{94}$$

so, like its position eigenstate friends, momentum eigenstates are also not normalizable.

- *Continuous Spectra.* Again like position eigenstates, the eigenvalues of $\hat{p}$ is a continuous variable. We say that $\hat{\mathbf{p}}$ has a *continuous spectrum*[7]. This means that to be pedantic, we should speak of the *probability density* of finding a particle of momentum $\mathbf{p}$ instead of probability, much like $|\psi(\mathbf{x})|^2$ is the probability density of finding a particle in position $\mathbf{x}$. We will postpone discussion of this until the next section.

***Duality of $\hat{x}$ and $\hat{p}$ operators.** What about the action of the position operator $\hat{x}$ on a momentum eigenfunction $u_p(x)$? Viz

$$\hat{x}u_p(x) = xu_p(x) = xA\exp\left(i\frac{px}{\hbar}\right). \tag{95}$$

Now it would be very tempting, but wrong, to think that by analogy to Eq. (83) we can write

$$\hat{x} = -i\hbar\frac{\partial}{\partial p} \quad \text{Wrong!} \tag{96}$$

The reason is simply that p in u_p is a number which labels u_p, not an argument of u. So the way to proceed is to apply a **Fourier Transform** to some wavefunction $\psi(x)$ to transform it to the $p = \hbar k$ basis

$$\psi(p) = \int dx \; \psi(x)e^{-ikx}. \tag{97}$$

Acting $\hat{x}$ on $\psi(p)$ yields

$$
\begin{aligned}
\hat{x}\psi(p) &= \int dx \; \hat{x}\psi(x)e^{-ipx/\hbar} \\
&= \int dx \; x\psi(x)e^{-ipx/\hbar} \\
&= \int dx \; \psi(x)\left(i\hbar\frac{\partial}{\partial p}\right)e^{-ipx/\hbar}
\end{aligned} \tag{98}
$$

or

$$\hat{x} = i\hbar\frac{\partial}{\partial p}. \tag{99}$$

In other words, the action of $\hat{x}$ on the *state* (as opposed to the wavefunction) ψ in the p basis is dual to the action of $\hat{p}$ on the *state* in the x basis.*

3.3   Hermitian Operators and Observables

Notice that the momentum $\mathbf{p}$ and the position $\mathbf{x}$ of a particle are **observables** – things that we can measure hence their eigenvalues are real. Operators associated with observables occupy a very special place in Quantum Mechanics. This leads us to Postulate 4.

Postulate 4 (Observables): An operator associated with an observable $\hat{O}$ is Hermitian. The result of a measurement of such an observable on a state ψ yields one of the eigenvalues, and the state collapses (via Postulate 3) into its associated eigenfunction.

If the operator is **Hermitian**, then its eigenvalues $\lambda \in \mathbb{R}$. You have seen Hermitian Matrices in the first lecture and also in your IA class previously. The extension of Hermiticity to function space is straightforward.

Hermitian Operators: A linear operator is said to be **Hermitian** if, for any pair of normalizable functions f, $g : \mathbb{R}^3 \to \mathbb{C}$ we have,

$$\boxed{\int_{\mathbb{R}^3} f^\dagger(\mathbf{x})\hat{O}g(\mathbf{x}) \; dV = \int_{\mathbb{R}^3} \left(\hat{O}f(\mathbf{x})\right)^\dagger g(\mathbf{x}) \; dV.} \tag{100}$$

---

[7]You can also say that $\hat{\mathbf{x}}$ has a continuous spectrum, which is technically correct but people will look at you in a funny way.

Recall that, for f and g to be normalizable, they must be square integrable

$$\int_{\mathbb{R}^3} |f(\mathbf{x})|^2 \, dV < \infty \quad , \quad \int_{\mathbb{R}^3} |g(\mathbf{x})|^2 \, dV < \infty, \tag{101}$$

which in turn requires that $f, g \to 0$ as $|\mathbf{x}| \to \infty$.

Properties of Hermitian Operators:

- Since f and g are arbitrary, we can drop them and write Eq. (100) in a more compact way

$$\hat{O} = \hat{O}^\dagger \tag{102}$$

  which you can compare to Eq. (17) Hermitian Matrices. Sometimes a Hermitian Operator is also called a **self-adjoint Operator**.

- The eigenvalues of Hermitian Operators are real and their eigenfunctions are orthonormal to each other.

  Proof (for non-degenerate discrete spectrum): Suppose $\hat{O}$ is a Hermitian operator with a discrete spectrum with eigenvalues $\{\lambda_n\}$ and their corresponding normalized eigenfunctions $\{u_n(\mathbf{x})\}$ for $n = 1, 2, 3, \ldots$. This means that

$$\hat{O} u_n(\mathbf{x}) = \lambda_n u_n(\mathbf{x}) \quad , \quad \int_{\mathbb{R}^3} |u_n(\mathbf{x})|^2 \, dV = 1. \tag{103}$$

  We further assume that the spectrum is **non-degenerate**

$$\lambda_n \neq \lambda_m \quad , \quad \forall \, n \neq m, \tag{104}$$

  which is to say that the eigenvalue of each eigenfunction is unique. (**Degeneracy** means that more than one eigenfunction has the same eigenvalue.)

  Consider two eigenfunctions u_m and u_n, and now using definition of Hermitian operators Eq. (100)

$$\int_{\mathbb{R}^3} u_m^\dagger(\mathbf{x}) \hat{O} u_n(\mathbf{x}) \, dV = \int_{\mathbb{R}^3} (\hat{O} u_m(\mathbf{x}))^\dagger u_n(\mathbf{x}) \, dV$$
$$\lambda_n \int_{\mathbb{R}^3} u_m^\dagger u_n(\mathbf{x}) \, dV = \lambda_m^* \int_{\mathbb{R}^3} u_m^\dagger u_n(\mathbf{x}) \, dV, \tag{105}$$

  hence we get the equality

$$(\lambda_n - \lambda_m^*) \int_{\mathbb{R}^3} u_m^\dagger u_n(\mathbf{x}) \, dV = 0. \tag{106}$$

  Now there are two cases:

  Case $m = n$: Eq. (106) becomes

$$(\lambda_n - \lambda_n^*) \int_{\mathbb{R}^3} u_n^\dagger u_n(\mathbf{x}) \, dV = (\lambda_n - \lambda_n^*) = 0 \quad , \quad (\text{Reality}) \tag{107}$$

  so $\lambda_n \in \mathbb{R}$.

  Case $m \neq n$: Eq. (106) becomes, using the reality condition,

$$(\lambda_n - \lambda_m) \int_{\mathbb{R}^3} u_m^\dagger u_n(\mathbf{x}) \, dV = 0, \tag{108}$$

  and by assumption of non-degeneracy $\lambda_m \neq \lambda_n$ then we have proven orthonormality

$$\int_{\mathbb{R}^3} u_m^\dagger u_n(\mathbf{x}) \, dV = 0 \quad , \quad (\text{Orthonormality}). \tag{109}$$

What if the eigenvalues are degenerate? In this case, the proof of Reality remains the same as shown above but the proof for orthonormality becomes more complicated, and beyond the scope of this lecture. The basic idea is that if $\hat{O}$ possess degenerate spectra, then there exist more than one basis of eigenfunctions which diagonalized $\hat{O}$. Consider a Hermitian operator $\hat{O}$ which possess two eigenfunctions u_n and u_m with the same eigenvalue $\lambda_m = \lambda_n = \lambda$, then for any $\alpha, \beta \in \mathbb{C}$ we have

$$\hat{O}(\alpha u_m + \beta u_n) = \alpha \lambda u_m + \beta \lambda u_n = \lambda(\alpha u_m + \beta u_n), \tag{110}$$

i.e. $(\alpha u_m + \beta u_n)$ is also an eigenfunction of $\hat{O}$. It is clear that since α, β are arbitrary, there exist a whole two-dimensional **subspace** spanned by u_m and u_n, each element in this subspace which are eigenfunctions of $\hat{O}$ with eigenvalue λ. This subspace is known as the *eigenspace of $\hat{O}$ with eigenvalue λ*.

- The eigenfunctions of Hermitian Operators are **Complete**. This means that any normalizable wavefunction $\psi(\mathbf{x})$ can be expanded as a linear sum of these eigenfunctions u_n. For a **discrete** spectrum

$$\boxed{\psi(\mathbf{x}) = \sum_{n=1}^{\infty} a_n u_n(\mathbf{x}),} \tag{111}$$

where $\{a_n\} \in \mathbb{C}$, and given by

$$\boxed{a_n = \int_{\mathbb{R}^3} u_n^\dagger \psi(\mathbf{x}) \, dV = u_n \cdot \psi.} \tag{112}$$

Proof:

$$
\begin{aligned}
\int_{\mathbb{R}^3} u_n^\dagger \psi(\mathbf{x}) \, dV &= \int_{\mathbb{R}^3} u_n^\dagger \sum_{m=1}^{\infty} a_m u_n(\mathbf{x}) \\
&= \sum_{m=1}^{\infty} a_m \int_{\mathbb{R}^3} u_n^\dagger(\mathbf{x}) u_m(\mathbf{x}) \, dV \tag{113} \\
&= \sum_{m=1}^{\infty} a_m \delta_{mn} = a_n. \tag{114}
\end{aligned}
$$

We can calculate the normalization integral of the wavefunction $\psi(\mathbf{x})$ as,

$$
\begin{aligned}
\int_{\mathbb{R}^3} \psi^\dagger(\mathbf{x}) \psi(\mathbf{x}) dV &= \int_{\mathbb{R}^3} \left(\sum_{n=1}^{\infty} a_n \, u_n(\mathbf{x}) \right)^\dagger \left(\sum_{m=1}^{\infty} a_m \, u_m(\mathbf{x}) \right) \, dV \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_n^* \, a_m \int_{\mathbb{R}^3} u_n^\dagger(\mathbf{x}) \, u_m(\mathbf{x}) \, dV \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_n^* \, a_m \, \delta_{mn} \\
&= \sum_{n=1}^{\infty} |a_n|^2 \tag{115}
\end{aligned}
$$

Thus for a *normalized* wavefunction $\psi(\mathbf{x})$ we have,

$$\sum_{n=1}^{\infty} |a_n|^2 = 1 \tag{116}$$

Consider Eq. (112). Postulate 4 says that each measurement will yield the eigenvalue of an observable while simultaneously collapsing the wavefunction into the associated eigenfunction. This

means that by Postulate 2, $|a_n|^2$ *is the probability of measuring the physical state associated with eigenfunction u_n.* a_n are then probability amplitudes. Eq. (116) then expresses the conservation of probability. (Compare this to Postulate 2 for the qubit way back in Lecture 1!)

For a **continuous** spectrum, the sum in Eq. (111) becomes an integral

$$\psi(\mathbf{x}) = \int \, dm \, C(m) u_m(\mathbf{x}) \, , \; C(m) \in \mathbb{C}. \tag{117}$$

where m labels the eigenfunctions and C some function of m. In continuous spectra, like position, the probability of finding the exact eigenvalue of m is zero, so we normally speak of the the probability density instead of probability. The probability of finding the state within some region dm is then $|C(m)|^2 dm$.

The orthogonality relation is then

$$\int_{\mathbb{R}^3} u_m^\dagger(\mathbf{x}) u_n(\mathbf{x}) \, dV = u_m \cdot u_n = |A|^2 \delta(m-n), \tag{118}$$

where the Kroneker delta has been replaced by the Dirac delta and A depends on how the eigenfunctions are normalized.

Completeness is an extremely powerful and useful calculational tool. The usual way of solving Quantum Mechanics problem is to first choose the observable(s) of the state ψ which possess *time-independent* eigenfunctions, and hence all the dynamics of ψ will be encoded in the coefficients. One then can think of the eigenfunctions u_n as "axes" and their coefficients $a_n(t)$ as pinpointing where the state is at any given time t, and the dynamic of the wavefunction can be seen as a trajectory through this space.

Example: (Momentum eigenfunctions): We have previously found the momentum eigenfunction Eq. (93). In one dimension this is, with $A = 1/2\pi$

$$u_p(x) = \frac{1}{2\pi} \exp(ikx) = \frac{1}{2\pi} \exp\left(i\frac{px}{\hbar}\right) \, , \; p = \hbar k \tag{119}$$

Since p is a continuous variable, the completeness relation is then

$$\psi(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(k) \exp(ikx) \, dk, \tag{120}$$

where $f(k)$ is some function of k and specify the *probability density amplitude* of finding a particle of momentum $p = \hbar k$. (You might recognize this as the Fourier Transform $f(k)$ of $\psi(x)$.) Orthogonality is

$$\begin{aligned} u_p(x) \cdot u_{p'}(x) &= \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \exp[i(k-k')x] \, dx \\ &= \frac{1}{2\pi} \delta(k-k'). \end{aligned} \tag{121}$$

When $p = p'$, we recover the fact that momentum eigenfunctions are not normalizable. This means that, formally, we should talk about probability densities of finding p particle, i.e. the probability of finding a particle of momentum p within $\hbar dk$ is

$$|f(k)|^2 \, dk. \tag{122}$$

We now look at some famous and important Hermitian operators.

- Position operator $\hat{\mathbf{x}}$: It is easy to see that the position operator $\hat{\mathbf{x}}$ and any function of the position operator $U(\hat{\mathbf{x}})$ is Hermitian. The eigenvalues of the position operator $\hat{\mathbf{x}}$ are the positions $\mathbf{x} \in \mathbb{R}^3$ themselves, which is a measurable quantity.

- Momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$: Check that it satisfies Eq. (100) by explicitly solving both sides for one of the component $\hat{p}_1$

$$
\begin{aligned}
\text{LHS of } Eq.(100) &= \int_{\mathbb{R}^3} f^{\dagger}(\mathbf{x})\hat{p}_1 g(\mathbf{x}) \, dV \\
&= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left[-i\hbar f^{\dagger}(\mathbf{x})\frac{\partial g}{\partial x_1} \right] \, dxdydz,
\end{aligned}
$$
(123)

and integrating by parts we get

$$
\begin{aligned}
\text{LHS of } Eq.(100) &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left[\left(-i\hbar\frac{\partial f}{\partial x_1} \right)^{\dagger} g(\mathbf{x}) \right] \, dxdydz \\
&= \int_{\mathbb{R}^3} (\hat{p}_1 f(\mathbf{x}))^{\dagger} g(\mathbf{x}) \, dV = \text{RHS of } Eq.(100).
\end{aligned}
$$
(124)

Here we used the fact that f and g both vanish as $|\mathbf{x}| \to \infty$ to drop the surface term arising after integration by parts. The other components of $\hat{\mathbf{p}}$ are Hermitian by an identical argument. The eigenvalues of $\hat{\mathbf{p}}$ as we have shown earlier are the values of the momenta themselves $\mathbf{p}$.

Recall when we derived the momentum operator earlier by expanding $\hat{T}(x + \Delta x, x) = 1 - \frac{i}{\hbar}\hat{p}\Delta x$, we have chosen to extract i out of the $\hat{p}$ – you will show in your Example sheet that if we chose to expand $\hat{T}$ as $\hat{T}(x + \Delta x, x) = 1 - \frac{1}{\hbar}\hat{\mathcal{P}}\Delta x$ instead, $\hat{\mathcal{P}}$ is not Hermitian.

- **The Hamiltonian Operator** $\hat{H}$: In Classical Mechanics, the energy of a particle of mass m and velocity $\mathbf{v}$ is given by the sum of its kinetic energy $m|\mathbf{v}|^2/2 = |\mathbf{p}|^2/2m$ and its potential energy $U(\mathbf{x})$, i.e.

$$
\text{Energy} = \frac{|\mathbf{p}|^2}{2m} + U(\mathbf{x}).
$$
(125)

In Quantum Mechanics, as you have seen with the position and momentum operator, what we have done is simply "give the classical quantities hats", i.e. $\mathbf{x} \to \hat{\mathbf{x}}$ and $\mathbf{p} \to \hat{\mathbf{p}}$. We can do the same here with the Energy, and hence obtain

$$
\boxed{\hat{H} \equiv \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + U(\hat{\mathbf{x}}).}
$$
(126)

This is known as the Hamiltonian operator for a particle of mass m. It's clear that $U(\hat{\mathbf{x}})$ is Hermitian, so now we need to show that $\hat{H}_{kin} = -(\hbar^2/2m)\nabla^2$ is Hermitian viz

$$
\begin{aligned}
\int_{\mathbb{R}^3} f^{\dagger}(\mathbf{x})H_{kin}g(\mathbf{x}) \, dV &= -\frac{\hbar^2}{2m}\int_{\mathbb{R}^3} f^{\dagger}(\mathbf{x})\nabla^2 g(\mathbf{x}) \, dV \\
&= -\frac{\hbar^2}{2m}\int_{\mathbb{R}^3} (\nabla^2 f)^{\dagger} g(\mathbf{x}) \, dV \text{ , by Green}'\text{s Identity} \\
&= \int_{\mathbb{R}^3} \left(\hat{H}_{kin}f(\mathbf{x}) \right)^{\dagger} g(\mathbf{x}) \, dV,
\end{aligned}
$$
(127)

where we have dropped the surface terms by imposing the vanishing of g, f at $|\mathbf{x}| \to \infty$. The eigenvalues of the Hamiltonian are energies E, which we just showed are real values

$$
\hat{H}u_E(\mathbf{x}) = Eu_E(\mathbf{x}),
$$
(128)

27

and the eigenstates are called **Energy Eigenstates** – you might have guessed this from the first lecture. The functional form of its Eigenfunctions depends on the exact form of the *potential $U(\hat{\mathbf{x}})$*, as is its spectrum which can be either continuous or discrete. We will be spending a lot of time studying this, so we will postpone further discussion.

- Angular Momentum Operator $\hat{\mathbf{L}}$: The Angular momentum operator classically is given by

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}, \tag{129}$$

and giving them hats we obtain the quantum mechanical Angular Momentum Operator

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = -i\hbar \mathbf{x} \times \nabla. \tag{130}$$

We will discuss the angular momentum operator in much greater detail in section 8.4.

3.4 Summary

We have elaborated on the Postulates first introduced in the first lecture, and covered a lot of ground in discussing the mathematical structure that underlies a quantum mechanical description of nature. What we have studied is applicable to any quantum system.

What about dynamics? If you have been reading ahead on many basic quantum mechanic books or even Prof. Nick Dorey's excellent notes (which these notes have shamelessly stolen from), you might have encountered Schrödinger's Equation for a particle much earlier. The usual story would then involve solving Schrödinger's Equation for a variety of potentials to gain intuition, before introducing the notion of operators. In these lectures, we have chosen to take a different tack – we have turned the story around, and introduced the mathematical structure of Quantum Mechanics before studying Schrödinger's Equation, which will be the subject of our next few coming lectures.

The hope of doing this upside-down approach is to quickly get to the gist of Quantum Mechanics without going through the sometimes (seemingly) mindless search for solutions of Schrödinger's Equation which can feel like solving PDEs instead of doing physics. With these mathematical tools, it might be easier for you to put everything that follows in context – perhaps even find solving Schrödinger's Equation fun this way! The downside (I think) is that we have introduced a lot of new concepts without much physical motivation. I hope that has not turned you off!

4 Schrödinger's Equation

In the first lecture, we worked out the dynamics of the qubit by introducing the "wait for some time Δt" operator $U(t + \Delta t, t)$, and then by expanding this operator around $\Delta t = 0$, we found Schrödinger's Equation for the qubit Eq. (29)

$$i\hbar \frac{d\psi}{dt} = \hat{H}(t)\psi(t). \tag{131}$$

We then endowed ψ with dynamics by adding in, at first a diagonal Hamiltonian Eq. (30) $\hat{H}$ and then with some more interesting dynamics by adding a NOT operator Eq. (33) $\tilde{H}$. We find that both Hamiltonians generate *different* kinds of motion for the qubit. The lesson here is that the dynamics of systems are *specified* – we do experiments to find out how things move, and then write down the Hamiltonians to describe their motion. There are literally an infinite number of Hamiltonians one can write down for any kind of systems, and most of them will not describe Nature.

4.1 Dynamics of Non-relativistic Particles

So what is the Hamiltonian for a particle? It was Schrödinger who wrote down the right Hamiltonian, although his derivation is suspect, all that matters is that he got the equation right – a lesson to be learned for budding physicists who insist on mathematical rigor. He wrote down

$$\boxed{i\hbar \frac{d}{dt}\psi(\mathbf{x}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{x}) \right] \psi(\mathbf{x}, t)} \tag{132}$$

which in our high-brow operator language is

$$\boxed{i\hbar \frac{d}{dt}\psi(\mathbf{x}, t) = \left[\frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + U(\hat{\mathbf{x}}) \right] \psi(\mathbf{x}, t)} \tag{133}$$

In other words, the Hamiltonian for a quantum mechanical particle of mass m is given by

$$\hat{H} \equiv \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + U(\hat{\mathbf{x}}), \tag{134}$$

which you have seen in the last lecture. Eq. (132) is the famous **Schrödinger's Equation** which describes the motion of a non-relativistic quantum mechanical particle. Sometimes this equation is written down as a Postulate, but in this lecture, we would like to take the more modern view where it is simply one of many Hamiltonians which turns out to be verified by experiments.

Some properties of Schrödinger's Equation:

- **Non-relativistic Free Particle Solution**: Schrödinger's Equation is first order in time t, so we need just one initial condition $\psi(0, \mathbf{x})$ and it is uniquely determined by Eq. (132). It is second order in $\mathbf{x}$, which suggests that it describes a non-relativistic particle in the following way.

  For a free particle, $U(\mathbf{x}) = 0$, the **Free Hamiltonian** is

$$\hat{H}_{\text{free}} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m}, \tag{135}$$

  so Eq. (132) becomes

$$i\hbar \frac{d}{dt}\psi(\mathbf{x}, t) = -\frac{\hbar^2}{2m}\nabla^2 \psi(\mathbf{x}, t), \tag{136}$$

29

which has the plane wave solution

$$\psi(\mathbf{x}, t) = A \exp(i\mathbf{k} \cdot \mathbf{x} - i\omega t) = u_{\mathbf{p}}(\mathbf{x}) \exp(-i\omega t), \tag{137}$$

where $u_{\mathbf{p}}$ is the momentum eigenfunction Eq. (93), so we obtain

$$\omega = \frac{\hbar|\mathbf{k}|^2}{2m}. \tag{138}$$

Using de Broglie Eq. (59) $\mathbf{p} = \hbar\mathbf{k}$ and $E = \hbar\omega$, we find

$$E = \frac{|\mathbf{p}|^2}{2m}, \tag{139}$$

which is exactly the correct **dispersion relation** for a free non-relativistic particle. Finally, since ψ is just the non-normalizable momentum eigenfunction $u_{\mathbf{p}}$ times some time dependent phase, it is also not normalizable.

From the solution Eq. (137), it is clear that the *momentum eigenfunctions $u_{\mathbf{p}}$ describe free particles with momentum (i.e. eigenvalue) $\mathbf{p}$*. In other words, the momentum eigenfunctions are also eigenfunctions of $\hat{H}_{\text{free}}$, i.e.

$$\hat{H}_{\text{free}} u_{\mathbf{p}} = E u_{\mathbf{p}}. \tag{140}$$

This is not surprising of course, since $\hat{H}_{\text{free}}$ is made up of just $\hat{\mathbf{p}}$. However, notice that for every energy E, there exist a large (for 3D, infinite) number of possible momentum eigenfunctions $u_{\mathbf{p}}$. That is to say, there exist a large **degeneracy** of momentum eigenvalues for every eigenfunction associated with eigenvalue E.

(Definition) Simultaneous Eigenfunctions: Suppose a wavefunction ψ obeys

$$\hat{O}_1\psi = \alpha\psi \; , \; \hat{O}_2\psi = \beta\psi \tag{141}$$

for any real values α, β, then we say that *ψ is a simultaneous eigenfunction of $\hat{O}_1$ and $\hat{O}_2$*. For example here, the momentum eigenfunctions $u_{\mathbf{p}}$ are eigenfunctions of both $\hat{H}_{\text{free}}$ and $\hat{\mathbf{p}}$.

As you will learn in section 7, operators which **commute** i.e. $\hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1 = 0$ will share at least one complete basis of eigenfunctions. Note that sometimes, simultaneous eigenfunctions of two operators can occur purely by accident and does not necessary form a complete basis.

- **Principle of Superposition**: Schrödinger's Equation is linear, and hence an important consequence of this linearity is that the sum of two wavefunctions is also a wavefunction, i.e.

$$\psi_3(\mathbf{x}, t) = \alpha\psi_1(\mathbf{x}, t) + \beta\psi_2(\mathbf{x}, t) \; , \; \forall \; \alpha, \beta \in \mathbb{C}. \tag{142}$$

Proof: It is clear that ψ_3 satisfies Eq. (132) if ψ_1 and ψ_2 do. The other condition to be a valid wavefunction is normalizability. Both ψ_1 and ψ_2 are normalizable, so

$$\int_{\mathbb{R}^3} |\psi_1|^2 \; dV = \mathcal{N}_1 < \infty \; , \; \int_{\mathbb{R}^3} |\psi_2|^2 \; dV = \mathcal{N}_2 < \infty. \tag{143}$$

For any two complex number z_1 and z_2, the triangle inequality states that

$$|z_1 + z_2| \le |z_1| + |z_2|, \tag{144}$$

and

$$(|z_1| - |z_2|)^2 \ge 0 \; \Rightarrow 2|z_1||z_2| \le |z_1|^2 + |z_2|^2. \tag{145}$$

Apply these relations with $z_1 = \alpha\psi_1$ and $z_2 = \beta\psi_2$ we get

$$\int_{\mathbb{R}^3} |\psi_3|^2 \ dV \quad = \quad \int_{\mathbb{R}^3} |\alpha\psi_1 + \beta\psi_2|^2 \ dV \tag{146}$$

$$\leq \quad \int_{\mathbb{R}^3} \left(|\alpha\psi_1| + |\beta\psi_2|\right)^2 \ dV \tag{147}$$

$$= \quad \int_{\mathbb{R}^3} \left(|\alpha\psi_1|^2 + 2|\alpha\psi_1||\beta\psi_2| + |\beta\psi_2|^2\right) \ dV \tag{148}$$

$$\leq \quad \int_{\mathbb{R}^3} \left(2|\alpha\psi_1|^2 + 2|\beta\psi_2|^2\right) \ dV \tag{149}$$

$$= \quad 2|\alpha|^2\mathcal{N}_1 + 2|\beta|^2\mathcal{N}_2 \ < \ \infty \qquad \square \tag{150}$$

4.2   Probability Current and Conservation of Probability

Consider a wavefunction which is normalized at $t = 0$,

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, 0)|^2 dV = 1. \tag{151}$$

Now allow ψ to evolve in time according to Schrödinger's Equation Eq. (132), and we want to see what the probability density function Eq. (66),

$$\rho(\mathbf{x}, t) = |\psi(\mathbf{x}, t)|^2 \tag{152}$$

does. Thus, from Eq. (151), $\rho(\mathbf{x}, 0)$ is a correctly normalized probability density. Differentiating ρ wrt time we get,

$$\frac{\partial\rho(\mathbf{x}, t)}{\partial t} = \frac{\partial}{\partial t}\left(|\psi|^2\right) = \frac{\partial\psi}{\partial t}\psi^\dagger + \psi\frac{\partial\psi^\dagger}{\partial t} \tag{153}$$

Now use Schrödinger's Equation Eq. (132) equation and its complex conjugate,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{x})\psi, \tag{154}$$

$$-i\hbar\frac{\partial\psi^\dagger}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^\dagger + U(\mathbf{x})\psi^\dagger \tag{155}$$

to eliminate time derivatives in Eq. (153) to obtain,

$$\frac{\partial\rho}{\partial t} \quad = \quad \frac{i\hbar}{2m}\left[\psi^\dagger\nabla^2\psi - \psi\nabla^2\psi^\dagger\right]$$

$$= \quad \frac{i\hbar}{2m}\nabla\cdot\left[\psi^\dagger\nabla\psi - \psi\nabla\psi^\dagger\right] \tag{156}$$

This yields the **conservation equation**,

$$\boxed{\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0} \tag{157}$$

where we define the **probability current**,

$$\boxed{\mathbf{j}(\mathbf{x}, t) = -\frac{i\hbar}{2m}\left[\psi^\dagger\nabla\psi - \psi\nabla\psi^\dagger\right].} \tag{158}$$

You will be asked to show that Eq. (158) is always a real quantity in the Example sheet – an eminently sensible result since probabilities are real quantities.

Consider a closed region $V \subset \mathbb{R}^3$ with boundary S, see Figure 9. The total probability $P(t)$ of finding the particle inside V is
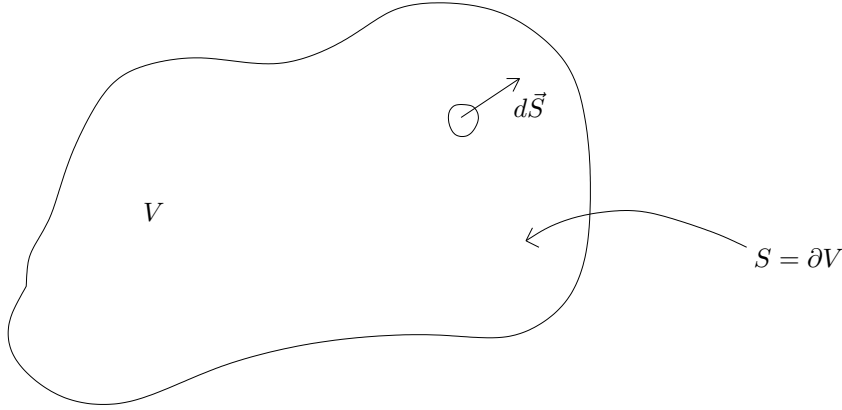
$$P(t) = \int_V \rho(\mathbf{x}, t) \ dV. \tag{159}$$

31

Figure 9: The rate of change of total probability $P(t)$ of finding the particle inside the volume V is equal to the total flux of $\mathbf{j}$ through the boundary S.

Taking the time derivative of Eq. (159), we get

$$\frac{dP(t)}{dt} = \int_V \frac{\partial \rho(\mathbf{x}, t)}{\partial t} \, dV = -\int_V \nabla \cdot \mathbf{j} dV = -\int_S \mathbf{j} \cdot \mathbf{dS} \tag{160}$$

where the last equality follows Gauss' Theorem. Eq. (160) tells us that rate of change of total probability $P(t)$ of finding the particle inside the volume V is equal to the total flux of $\mathbf{j}$ through the boundary S. Hence, probability can "leak" in and out of the boundary S, much like water[8].

4.3 Stationary States

We have so far found the solutions of Schrödinger's Equation Eq. (132)

$$\boxed{i\hbar \frac{d}{dt} \psi(\mathbf{x}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{x}) \right] \psi(\mathbf{x}, t)} \tag{161}$$

for the case of the free particles $U(\mathbf{x}) = 0$ and found that they are plane waves Eq. (137) and correspond to momentum eigenfunctions. In operator language, the momentum eigenfunctions $u_\mathbf{p}$ are eigenfunctions of the free Hamiltonian

$$\hat{H}_{\text{free}} u_\mathbf{p} = E u_\mathbf{p}. \tag{162}$$

What are the eigenfunctions for $\hat{H}$ when $U(\mathbf{x}) \neq 0$? Introducing the separation of variables

$$\psi_\omega(\mathbf{x}, t) = \chi_\omega(\mathbf{x}) \exp[-i\omega t], \tag{163}$$

or by using $E = \hbar\omega$, we get

$$\psi_E(\mathbf{x}, t) = \chi_E(\mathbf{x}) \exp\left[\frac{-iEt}{\hbar} \right], \tag{164}$$

where we have pedantically append the subscript E or ω on ψ to indicate that there exist a E-parameter family of solutions of this kind. Plugging Eq. (164) into Schrödinger's Equation Eq. (132) yields the **time-independent Schrödinger's Equation**

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \chi_E(\mathbf{x}) + U(\mathbf{x}) \chi_E(\mathbf{x}) = E \chi_E(\mathbf{x})} \tag{165}$$

---

[8]*In your Electromagnetism (or even if you have taken fluids dynamics), you may have seen a similar equation to Eq. (157) where the same equation is called the **continuity equation**.

or in operator language

$$\hat{H}\chi_E(\mathbf{x}) = E\chi_E(\mathbf{x}). \tag{166}$$

In other words, Eq. (165) is an eigenfunction equation for the full Hamiltonian $\hat{H}$, and $\chi_E(\mathbf{x})$ is its eigenfunction.

- Since their probability density $\rho(\mathbf{x}, t) = |\psi_E(\mathbf{x}, t)|^2 = |\chi_E(\mathbf{x})|^2$ is *time-independent*, we call $\psi_E(\mathbf{x}, t)$ (or more loosely $\chi_E(\mathbf{x})$) **Stationary States**.

  A note on jargon: when solving the time-independent Schrödinger's Equation, we often refer to $\chi(x)$ as the wavefunction.

- ψ_E are *states of definite energy* so are also known as **Energy Eigenstates**. The set of all stationary states $\{\psi_E\}$ of some Hamiltonian is called its **Energy Spectrum**. The spectrum can be **discrete**, **continuous**, or a combination of both.

- Typically χ_E are normalizable only for some allowed values of E, i.e. the spectrum of some Hamiltonian can contain both normalizable and non-normalizable eigenfunctions. We will encounter examples of this in section 5.

- Using the Principle of Superposition, the general solution of *time-dependent* Schrödinger's Equation is then the linear superposition of the stationary states (for discrete spectra)

$$\psi(\mathbf{x}, t) = \sum_{n=1}^{\infty} a_n \chi_{E_n}(\mathbf{x}) \exp\left[\frac{-iE_n t}{\hbar}\right] \ , \ a_n \in \mathbb{C} \tag{167}$$

where $\chi_{E_n}(\mathbf{x})$ are eigenfunctions of $\hat{H}$ with eigenvalues E_n, i.e. they solve Eq. (165) with $E = E_n$. a_n are complex coefficients. In general it is not a stationary state and hence does not have definite energy. On the other hand, we can ask "what is the probability of measuring a state with energy E_m at time t?". Using Eq. (68),

$$
\begin{aligned}
\text{Probability of measuring } \chi_{E_m}(\mathbf{x}) \text{ in } \psi(\mathbf{x}, t) &= \left| \chi_{E_m}(\mathbf{x}) \cdot \sum_{n=1}^{\infty} a_n \chi_{E_n}(\mathbf{x}) \exp\left[\frac{-iE_n t}{\hbar}\right] \right|^2 \\
&= \left| a_n \int_{\mathbb{R}^3} \sum_{n=1}^{\infty} \chi_{E_m}^{\dagger}(\mathbf{x}) \chi_{E_n}(\mathbf{x}) \, dV \right|^2 \\
&= \left| a_n \int_{\mathbb{R}^3} \delta_{mn} \chi_{E_m}^{\dagger}(\mathbf{x}) \chi_{E_n}(\mathbf{x}) \, dV \right|^2 \\
&= \left| a_m \int_{\mathbb{R}^3} \chi_{E_m}^{\dagger}(\mathbf{x}) \chi_{E_m}(\mathbf{x}) \, dV \right|^2 \\
&= |a_m|^2, \tag{168}
\end{aligned}
$$

where we have used the Orthonormality of eigenfunctions in line three, and the fact that χ_{E_m} is normalized in line four. Hence, the coefficients a_n are the probability amplitudes of measuring a state with energy E_n.

- For continuous spectra, the Principle of Superposition becomes an integral, i.e. a sum over all possible energy eigenstates become an integral over all possible energies

$$\psi(\mathbf{x}, t) = \int_0^{\infty} dE \, C(E) \chi_E(\mathbf{x}) \exp\left[\frac{-iE_n t}{\hbar}\right] \ , \ C(E) \in \mathbb{C}, \tag{169}$$

where $C(E)$ is a smooth funtion of E. As in all continuous spectra (like free momentum eigenstates or position eigenstates), we speak of the probability density of finding the state

$$\rho_E = |C(E)|^2 \tag{170}$$

and the probability of finding the state within some region E to $E + \Delta E$ is

$$P = \int_{E}^{E+\Delta E} \rho_E \, dE, \tag{171}$$

as usual.

4.4 Summary

We finally introduced Schrödinger's Equation. We show that it possess a natural basis, the Stationary States which have definite energy. The amplitude square of the coefficients of this basis $|a_n|^2$ tell us the probability of finding the particle in state with energy E_n. And we don't even have to find the actual functional form of the eigenfunctions $\chi_E(\mathbf{x})$ to do be able to calculate these probabilities!

Of course, the probability of finding a state with specific energy is not the same as calculating the probability of *finding where the particle is*. To do that, we have to actually solve Schrödinger's Equation to find the functional form of the wavefunction. This is our task for the next section.

5 Solving Schrödinger's Equation in One Dimension

Except for the original Star Wars$^{\text{TM}}$ Trilogy, the middle portion of all Trilogies is always boring[9]. And so, in our lectures on Quantum Mechanics, we arrive at the sagging middle.

In this section, we solve Schrödinger's Equation for a wide variety of potentials $U(x)$ in one dimension. So unfortunately we will spend some time mangling with partial differential equations, which may or may not be your favorite cup of caffeinated beverage. Having said that, solving this equation will illustrate some of the features of Quantum Mechanics of which we have been making assertions about so far, and some which you may have heard about.

- Section 5.1 : Quantization of Energy States

- Section 5.2 : Scattering. Transmissivity and Reflectivity

- Section 5.3 : Tunneling

- Section 5.4 : The Gaussian Wave Packet and Minimum Uncertainty

- Section 5.5 : Parity Operator

- Section 5.6 : Bound and Unbounded States

Note : in this section we will almost exclusively be working in the Stationary States basis, i.e. χ_E of the Hamiltonian, so we will drop the subscript E from χ and ψ. When there is an ambiguity, we will restore it. Also, sometimes we refer to $\chi(x)$ as the "wavefunction", although technically we are really solving for the eigenfunctions of the Hamiltonian.

5.1 Quantization of Energy Eigenstates : The Infinite Potential Well

Consider the **infinite potential well** (Fig 10)

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

Using Stationary States Eq. (164) in one dimension

$$\psi(x,t) = \chi(x) \exp\left[\frac{-iEt}{\hbar}\right],$$
(172)

we obtain the time-independent Schrödinger's Equation

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U(x)\chi = E\chi.$$
(173)

We now look at the behavior of $\chi(x)$ inside and outside the well.

- **Outside Well**:

$$U(x) = \infty \Rightarrow \chi(x) = 0$$
(174)

otherwise $E = \infty$ from (173). Thus, as in classical physics, there is zero probability of finding the particle outside the well.

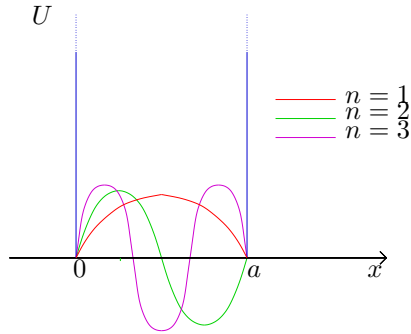[9]The prequels of Star Wars are the exception: they are all terrible.

Figure 10: A few lowest energy eigenfunctions of the infinite square well.

- **Inside Well**:

$$U(x) = 0 \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} = E\chi \tag{175}$$

It is a bother to carry around all the constants in Eq. (175), so we define

$$k = \sqrt{\frac{2mE}{\hbar^2}} > 0, \tag{176}$$

with a note to emphasise the fact that k depends on the eigenvalue E, and we get

$$\frac{d^2\chi}{dx^2} = -k^2\chi. \tag{177}$$

Eq. (177) has the general *oscillatory* solution

$$\chi(x) = A\sin(kx) + B\cos(kx) \tag{178}$$

with two arbitrary complex constants A and B which depends on the boundary conditions (since Eq. (177) is second order in x).

To find A and B we match solutions at the boundaries $x = 0$, $x = a$ by imposing continuity:

$$\chi(0) = \chi(a) = 0 \tag{179}$$

so $\chi(0) = 0 \Rightarrow B = 0$ and $\chi(a) = 0 \Rightarrow A\sin(ka) = 0$ with $ka = n\pi$, for $n = 1, 2, 3, \ldots$ which implies a set of solutions

$$\chi_n(x) = \begin{cases} A_n\sin\left(\frac{n\pi x}{a}\right) & , \quad 0 < x < a \ , \ n = 1, 2, 3, \ldots \\ 0 & , \qquad\qquad \text{otherwise} \end{cases}$$

Since the eigenfunctions χ_n are discrete, it turns out that they are *normalizable*. Applying the normalizing condition

$$\int_{-\infty}^{+\infty} |\chi_n|^2 \ dx = |A_n|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) \ dx = \frac{|A_n|^2 a}{2} = 1, \tag{180}$$

so we get

$$|A_n| = \sqrt{\frac{2}{a}} \ , \ \forall \ n. \tag{181}$$

Note that while A_n can be a complex number it will not matter since it is a irrelevant phase in this case. Hence the energy eigenfunctions of the infinite square well is a *discrete* series of sin functions labeled by n (Fig. 10). An eigenfunction labeled by n has $n - 1$ zero crossings, called **nodes**.

Some properties:

- **Quantization of Energy Levels**: Since n is a discrete spectrum, this means that *a quantum particle inside a infinite square well can only take specific, quantized, values of E*, unlike in Classical Mechanics. The energy levels are found by using Eq. (176)

$$E = E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \ , \ \text{for } n = 1, 2, \dots \tag{182}$$

The difference between two energy levels $E_{n'}$ and E_n is

$$\Delta E = E_{n'} - E_n = \frac{\hbar^2 \pi^2}{2ma^2}(n'^2 - n^2). \tag{183}$$

- **Ground State has non-zero Energy**: Also, unlike Classical mechanics, the *lowest energy state is non-zero*

$$E_1 = \frac{\hbar^2 \pi^2}{2ma^2} > 0. \tag{184}$$

The lowest energy state of any system is called its **Ground State** or **Vacuum State**.

- **Odd/Even Solutions and Parity Operator** If we draw a vertical line through $x = a/2$ and imagine it to be a mirror, the eigenfunctions alternate signs under **reflection** on this mirror in the following way

$$\text{Even} \ : \ \chi_n(x) = \chi_n(a - x) \ , \ n = 1, 3, 5, \ \dots \tag{185}$$

while

$$\text{Odd} \ : \ \chi_n(x) = -\chi_n(a - x) \ , \ n = 2, 4, 6, \ \dots \tag{186}$$

i.e. the eigenfunctions χ_n naturally fall into **Even** and **Odd** sets. We hasten to apologize for the unfortunate fact that even n are odd eigenfunctions and *vice versa*.

We can be precise about what we mean by reflection by defining the **Parity Operator** $\hat{P}$ whose action is to change the sign of the argument of a state around an axis. In the above example, the axis is $x = a/2$, so the $\hat{P}$

$$\hat{P}\psi(x) = \psi(a - x). \tag{187}$$

It is clear that the eigenfunctions χ_n are also (simultaneous) eigenfunctions of $\hat{P}$

$$\hat{P}\chi_n = (-1)^{n+1}\chi_n, \tag{188}$$

with eigenvalues $+1$ for even eigenfunctions and -1 for odd eigenfunctions.

We will discuss the Parity Operator in section 5.5, but can you see why the eigenfunctions are also Parity eigenfunctions?

5.2   Scattering : Transmissivity and Reflectivity

Consider the **Step Potential** (Fig 11)

$$U(x) = \begin{cases} 0 & , \quad x < 0 \quad \text{Region I} \\ \\ U_0 & , \quad x > 0 \quad \text{Region II} \end{cases}$$

Consider the behavior of a particle sent from the left of the plot with energy E. Classically, we know the answer simply: if $E > U_0$ then the particle goes over the barrier and if $E < U_0$ the particle is reflected back. What happens quantum mechanically? To find out, we have to solve Schrödinger's Equation.
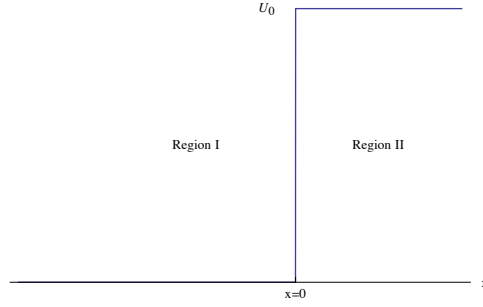
Figure 11: The step potential.

Again, using Stationary states, the time-independent Schrödinger's Equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2} + U(x)\chi = E\chi. \tag{189}$$

Like the previous problem, we consider the solutions independently in Regions I and II. There are two cases, when $E > U_0$ and when $E < U_0$.

- **Case 1:** $E > U_0$: *Region I*: $U = 0$, Eq. (173) becomes

$$\frac{-\hbar^2}{2m}\frac{d^2\chi}{dx^2} = E\chi, \tag{190}$$

and defining as usual $k = \sqrt{2mE/\hbar^2} > 0$, we get

$$\frac{d^2\chi}{dx^2} = -k^2\chi \tag{191}$$

which we can write the solution Eq. (177) as before when we consider the infinite potential well. However, let's write it in a more physically motivated way as follows

$$\chi(x) = \underbrace{e^{ikx}}_{\text{incoming}} + \underbrace{Ae^{-ikx}}_{\text{reflected}}, \tag{192}$$

where A quantifies the amplitude of a reflected wave[10]. In other words, we set up the incoming *right moving* wave $\exp(ikx)$ (secretly we have imposed boundary conditions), and we want to calculate how much of the wave is reflected back as *left moving* $\exp(-ikx)$. They are called right/left moving as they are eigenfunctions of the momentum operator $\hat{p}$ with $\pm\hbar k$ eigenvalues respectively.

You can think of this as a probability current heading in the $+x$ direction

$$
\begin{aligned}
j_I &= \frac{-i\hbar}{2m}\left(\chi^\dagger\frac{d\chi}{dx} - \frac{d\chi^\dagger}{dx}\chi\right) \\
&= \frac{\hbar k}{m}(\underbrace{1}_{j_{\text{inc}}} - \underbrace{|A|^2}_{j_{\text{ref}}})
\end{aligned}
\tag{193}
$$

where j_{inc} is the current carried by the right moving wave and j_{ref} the left moving wave. If $|A| = 1$ then the total current is zero, i.e everything is reflected back.

Region II: $U = U_0$, Eq. (173) becomes

$$\frac{-\hbar^2}{2m}\frac{d^2\chi}{dx^2} = (E - U_0)\chi, \tag{194}$$

---

[10]Some books call this the reflectivity, and gave it a name R.

38

since $E > U_0$, let's define

$$q = \sqrt{\frac{2m(E - U_0)}{\hbar^2}} > 0, \tag{195}$$

so we get

$$\frac{d^2\chi}{dx^2} = -q^2\chi, \tag{196}$$

which is also oscillatory. Since there is no left-moving wave (again secretly imposing boundary conditions), the general solution is

$$\chi(x) = \underbrace{Be^{iqx}}_{\text{transmitted}}, \tag{197}$$

where B quantifies the amplitude of a transmitted wave. The current can be calculated as usual, and it is

$$j_{II} = j_{\text{trans}} = \frac{\hbar q}{m}|B|^2. \tag{198}$$

We want to now solve A, B as functions of k, q by matching solutions at $x = a$. Since $U(x)$ is discontinuous but finite, this can get a bit tricky. We will use the following result:

Continuity of χ at Discontinuous potential: *Suppose $U(x)$ is discontinuous but finite at $x = a$, then $\chi(a)$ and $d\chi/dx|_{x=a}$ are continuous, but $d^2\chi/dx^2|_{x=a}$ is discontinuous.*

Proof: From Schrödinger's Equation, since $U(a)$ is discontinuous, $d^2\chi/dx^2|_{x=a}$ is also discontinous. Now integrate the time-independent Schrödinger's Equation over the interval $[a - \epsilon, a + \epsilon]$,

$$\int_{a-\epsilon}^{a+\epsilon} dx \, \frac{-\hbar^2}{2m} \frac{d^2\chi}{dx^2} = \int_{a-\epsilon}^{a+\epsilon} dx \, (E - U(x))$$
$$\left.\frac{d\chi}{dx}\right|_{a+\epsilon} - \left.\frac{d\chi}{dx}\right|_{a-\epsilon} = -\frac{2m}{\hbar^2} \int_{a-\epsilon}^{a+\epsilon} dx \, (E - U(x)). \tag{199}$$

Taking the limit of $\epsilon \longrightarrow 0$, the RHS of Eq. (199) vanishes, so this implies

$$\lim_{\epsilon \to 0} \left[\left.\frac{d\chi}{dx}\right|_{a+\epsilon} = \left.\frac{d\chi}{dx}\right|_{a-\epsilon} \right], \quad \text{Continuity of first derivative} \tag{200}$$

which also implies that $\chi(a)$ is continuous. $\square$.

Using our result above, we can then continuity conditions at the boundary $x = 0$ to get

$$\chi(x = 0) \Rightarrow 1 + A = B, \tag{201}$$

and

$$\lim_{\epsilon \to 0} \left[ik(e^{-ik\epsilon} - Ae^{ik\epsilon}) = iqBe^{ik\epsilon} \right] \Rightarrow ik(1 - A) = iqB. \tag{202}$$

Using the two equations Eq. (201) and Eq. (202), we can solve for R and T

$$A = \frac{k - q}{k + q} \,, \; B = \frac{2k}{k + q}. \tag{203}$$

Now if $E \gg U_0$, $q \to k$ and hence $A \to 0$ and $B \to 1$, i.e. if the incoming wave is very energetic, everything is transmitted and nothing is reflected as we expect classically.

Although A and B are real quantities here, this is not always the case. And don't fall into the temptation of comparing the absolute amplitudes of A and B as the wavefunctions are not normalizable! The right way to think about this is to compare probability currents,

$$\textbf{Reflectivity} \,, \quad R = \frac{j_{\text{ref}}}{j_{\text{inc}}} = \left(\frac{k-q}{k+q}\right)^2 \tag{204}$$

$$\textbf{Transmissivity} \,, \quad T = \frac{j_{\text{trans}}}{j_{\text{inc}}} = \frac{4kq}{(k+q)^2} \tag{205}$$

So as $E \gg U_0$, then $q \to k$, and $R = 0$ and $T = 1$ as expected. Note that even when $E > U_0$, there is a non-zero chance of particles being reflected, unlike the classical case.

We can check for the conservation of probability, using equation Eq. (157), which in one dimension is

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0. \tag{206}$$

For Stationary States, ρ is independent of time, so then this becomes

$$\frac{\partial j}{\partial x} = 0 \Rightarrow j_I = j_{II}, \tag{207}$$

and using the results we have

$$\frac{\hbar k}{m}(1 - |R|^2) = \frac{\hbar q}{m}|T|^2. \tag{208}$$

- **Case 2:** $E < U_0$: The results in Region I is as before, but for Region II, we define

$$\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} > 0, \tag{209}$$

so Schrödinger's Equation becomes

$$\frac{d^2 \chi}{dx^2} = \kappa^2 \chi. \tag{210}$$

This equation has the solution

$$\chi(x) = Ce^{\kappa x} + De^{-\kappa x}. \tag{211}$$

The growing mode C is non-normalizable, so we set $C = 0$ hence the final solution is

$$\chi(x) = De^{-\kappa x} \tag{212}$$

i.e. the wavefunction decays as it penetrates the barrier. Note that we can simply use our previous solution, and substitute $q \to i\kappa$, to find the coefficients

$$A = \frac{k - i\kappa}{k + i\kappa} \ , \ D = \frac{2k}{k + i\kappa}. \tag{213}$$

The current in Region II vanishes

$$j_{II} = j_{\text{trans}} = \frac{-i\hbar}{2m}\left(\chi^\dagger \frac{d\chi}{dx} - \frac{d\chi^\dagger}{dx}\chi\right) = 0, \tag{214}$$

meaning that *no particle is transmitted*. What about the reflectivity? Since $|A|^2 = 1$,

$$j_{\text{ref}} = j_{\text{inc}}, \tag{215}$$

the reflectivity is unity.

*Now you may feel a bit uncomfortable – the wavefunction inside the barrier, even though exponentially small, *does not vanish*. Does this mean that, via Born's Rule, we should have a small but non-vanishing probability of finding the particle? How do reconcile the fact that the probability current is zero yet there is non-zero wavefunction inside the barrier? To resolve this paradox will take us too far afield, but we can do a "word calculus" version of it.

If we follow Born's Rule logic, then there is a finite probability of finding a particle with negative kinetic energy – corresponding to the fact that the "momentum" of the particle is imaginary. But nobody has seen a negative kinetic energy particle before, so this must not be the answer[11]. Physically, to observe such a particle, we need to shine a light on it and then collect the scattered light to deduce the location of the particle. To fix the exact location of the particle, we need the wavelength λ of the light to be much smaller than the characteristic penetration depth of the wavefunction, but this means collision of the light particle with the particle will give it sufficient energy, $2\pi\hbar/\lambda \gg (U - E)$ to kick it out of the barrier!*

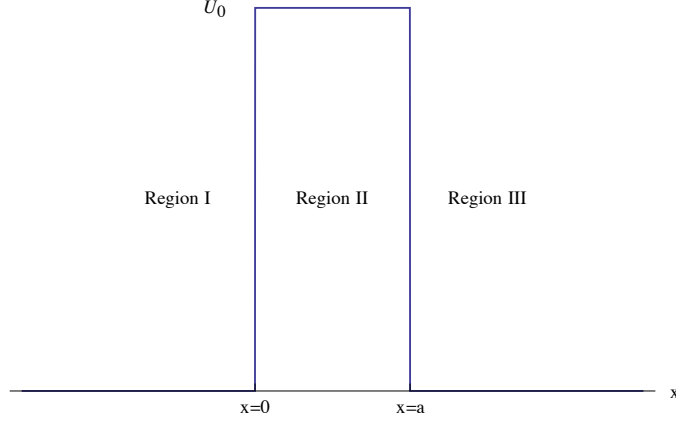[11] Physicists give them a name, *ghosts*, because nobody has seen them before.

Figure 12: The barrier potential.

5.3 The Barrier Potential : Tunneling

In the previous step potential, we see that even if $E < U_0$, the wavefunction penetrates into the barrier, and decay exponentially as long as the barrier remains in place. Now, what happens, if after some distance a, the potential drops again to zero Fig. 12 ? The wavefunction decays exponentially until it hits $x = a$, and then suddenly it is no longer suppressed by the potential and is free to propogate. Physically, this means that there is a no-zero probability of finding a particle on the right side of the barrier – we say that the particle has *tunneled* through the barrier, and this phenomenon is knonw as **Tunneling**. We will consider the case when $E < U_0$. As before, we define the variables

$$k = \sqrt{\frac{2mE}{\hbar^2}} > 0 \ , \ \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} > 0, \tag{216}$$

and as should be familiar to you, we write down the following ansatz

$$\chi(x) = \begin{cases} \exp(ikx) + A\exp(-ikx) & x < 0 & \text{Region I} \\ B\exp(-\kappa x) + C\exp(\kappa x) & 0 < x < a & \text{Region II} \\ D\exp(ikx) & x > a & \text{Region III} \end{cases}$$

At boundary $x = 0$, continuity conditions imply

$$1 + A = B + C \ , \ ik(1 - A) = \kappa(-B + C), \tag{217}$$

whilat at $x = a$, we get

$$B\exp(-\kappa a) + C\exp(\kappa a) = D\exp(ika) \ , \ \kappa(-B\exp(-\kappa a) + C\exp(\kappa a)) = ikD\exp(ika). \tag{218}$$

We then do a bunch of tedious algebra to solve for A, B, C and D. Since we are interested in the transmitted current, we look for D which has the following horrible form

$$D = \frac{2k\kappa e^{-ika}}{i(k^2 - \kappa^2)\sinh(\kappa a) + 2k\kappa\cosh(\kappa a)}. \tag{219}$$

The incident and transmitted flux are then

$$j_{\text{inc}} = \frac{\hbar k}{m} \ , \ j_{III} = j_{\text{trans}} = \frac{\hbar k}{m}|D|^2 \tag{220}$$

hence the transmissivity is

$$\begin{aligned} T &= \frac{j_{\text{trans}}}{j_{\text{inc}}} = |D|^2 \\ &= \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa a) + 4k^2\kappa^2} > 0, \end{aligned} \tag{221}$$

41

i.e. the transmissivity is positive and non-zero. There is a chance that you will find a particle of momentum $p = \hbar k$ on the right side of the barrier $x > a$.

5.4 The Gaussian Wavepacket

In the previous problems, you may have felt a bit uncomfortable that we are using momentum eigenstates

$$u_p = Ae^{ikx} \tag{222}$$

as "particle states", even though we have argued forcefully in the section 3 that such states are not normalizable. Your discomfort is well-founded – indeed in realistic situations, say when we want to do an experiment by sending a particle into a barrier and check whether it tunnels or not, what we do is to set up the particle whose position we "roughly" know, say at x_0. A good model of such a set-up is to specify the probability density of the particle to be a Gaussian at some fixed time $t_0 = 0$, i.e.

$$\rho(x, t_0) \propto \exp\left[\frac{-(x - x_0)^2}{2\tilde{\sigma}^2}\right], \tag{223}$$

where $\tilde{\sigma}^2$ is the **dispersion**[12] of the particle, i.e. it measures how "spread out" the particle is. Those who have studied statistics might recall that the above probability density means that the particle can be found within $x_0 \pm \tilde{\sigma}$ is 66%. Of course, the Gaussian is square integrable, so this wavefunction is normalizable. The question we want to ask now is: *if we set this system up and let it evolves freely, i.e.* $U(x) = 0$, *what happens to it?*

As before, we want to work in the Stationary State basis. But since we are interested in *time evolution*, we will keep the time dependence. From Eq. (164), and using $E = p^2/2m = \hbar^2 k^2/2m$ for a free particles and $\chi(x) = \exp(ikx)$ this becomes

$$\psi_k(x, t) = \exp(ikx)\exp\left(\frac{-i\hbar k^2 t}{2m}\right), . \tag{224}$$

Since the spectrum for free particles is continuous, we can construct any arbitrary real space wavefunction by an integral Eq. (169),

$$\psi(x, t) = \int_{-\infty}^{\infty} dk\; C(k)\exp(ikx)\exp\left[\frac{-i\hbar k^2 t}{2m}\right] \tag{225}$$

where $C(k)$ is some smooth function. What $C(k)$ should we choose such that we obtain the probability density Eq. (223) which possess some average momentum $p_0 = \hbar k_0$? Now we cheat a little, and assert that this corresponds to the choice

$$C(k) = \exp\left[-\frac{\sigma}{2}(k - k_0)^2\right], \tag{226}$$

which (not surprisigly) is also a Gaussian in k-space with a dispersion of $2\sigma^{-1/2}$. Now we want to evalute the integral Eq. (225). Collecting the terms proportional to k^2 and k in the exponential,

$$\psi(x, t) = \int_{-\infty}^{\infty} dk \exp[-\underbrace{\left(\frac{\sigma}{2} + \frac{i\hbar t}{2m}\right)}_{\alpha/2} k^2 + \underbrace{(\sigma k_0 + ix)}_{\beta} k \underbrace{-\sigma k_0^2/2}_{\delta}]. \tag{227}$$

and completing the square we get

$$\psi(x, t) = \int_{-\infty}^{\infty} dk \exp\left[-\frac{1}{2}\alpha\left(k - \frac{\beta}{\alpha}\right)^2 + \frac{\beta^2}{2\alpha} + \delta\right] \tag{228}$$

$$= \exp\left[\frac{\beta^2}{2\alpha} + \delta\right]\int_{-\infty}^{\infty} dk \exp\left[-\frac{1}{2}\alpha\left(k - \frac{\beta}{\alpha}\right)^2\right]. \tag{229}$$

---

[12]In statistics, this is known as the **variance** but we will follow standard jargon.
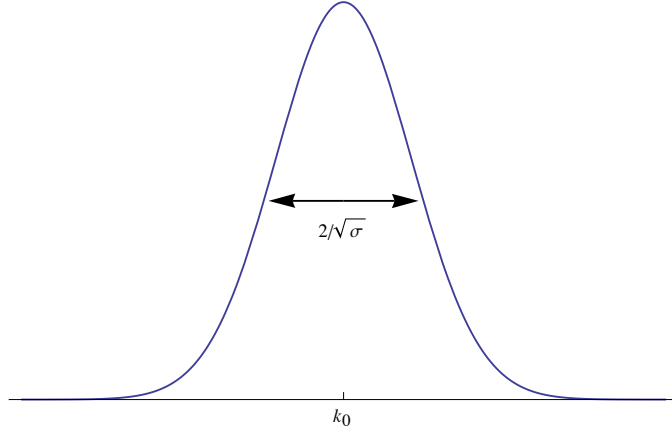
Figure 13: The Gaussian Wavepacket in k-space with mean momentum $\langle p \rangle = \hbar k_0$.

The integral is a usual Gaussian Integral[13], and gives $\sqrt{2\pi/\alpha}$ so we finally get the wavefunction

$$\psi(x,t) = \sqrt{\frac{2\pi}{\alpha}} \exp\left[\frac{\beta^2}{2\alpha} + \delta\right]. \tag{230}$$

This wavefunction is not normalized, so let's normalized is by setting $\tilde{\psi} = \psi/\sqrt{\mathcal{N}}$, where

$$
\begin{aligned}
\mathcal{N} &= \int_{-\infty}^{\infty} dx\ |\psi|^2 \\
&= \left(\frac{4\pi}{\sigma^2 + \hbar^2 t^2/m^2}\right) \int_{-\infty}^{\infty} dx\ \exp\left[-\frac{\sigma}{|\alpha|^2}\left(x - \frac{k_0 \hbar t}{m}\right)^2\right] \\
&= 2\pi\sqrt{\frac{\pi}{\sigma}}
\end{aligned}
\tag{231}
$$

where again we have used the Gaussian integral.

The properly normalized probability density function is then

$$|\tilde{\psi}(x,t)|^2 = \frac{1}{\pi}\sqrt{\frac{\sigma}{\sigma^2 + \bar{x}^2/k_0^2}} \exp\left[\frac{-\sigma(x - \bar{x}(t))^2}{\sigma^2 + \bar{x}^2/k_0^2}\right] \tag{232}$$

where the *mean position* is moving with a constant velocity

$$\bar{x}(t) = \frac{\hbar k_0}{m}t = \frac{p_0}{m}t. \tag{233}$$

This is consistent with our classical intuition that the particle move with velocity $\dot{x} = p_0/m$. At $t = 0$, we recover the promised Gaussian Wavepacket in position space we wrote down earlier Eq. (223).

However, more interestingly, the effective dispersion

$$\tilde{\sigma}(t) = \sqrt{\frac{1}{2}\left(\sigma + \frac{\bar{x}^2}{\sigma k_0^2}\right)} > \tilde{\sigma}(0) \tag{234}$$

is also increasing! In other words, not only is the Gaussian wave is moving, it is also *spreading*, becoming more and more **delocalized**. Since the dispersion measures the uncertainty in the location of the particle, the particle's position is becoming more and more uncertain. In fact, it can be shown that the Gaussian Wavepacket is the state of *minimum uncertainty*.

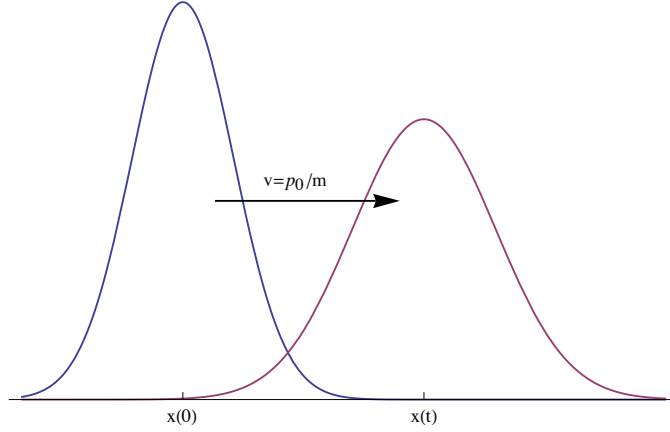[13]Gaussian Integral is $\int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\pi/a}$.

Figure 14: The probability density function $\rho(x, t)$ in x-space, with its mean $\bar{x}(t)$ moving at velocity p_0/m. The dispersion of the particle increases with time, and hence the particle's position become less certain.

Minimum Uncertainty Wavepacket: From our discussion of the momentum eigenfunctions in section 3 and continuous spectrum, we showed that the probability density of momentum is Eq. (122), i.e.

$$\rho(p, t) = |C(k)|^2 \propto \exp\left[\frac{-\sigma(p - p_0)^2}{\hbar^2}\right] \tag{235}$$

which is a Gaussian with dispersion $\sigma_p = \sqrt{\hbar^2/2\sigma}$. Then the product of the two dispersions yield

$$(\Delta x)^2(\Delta p)^2 = \tilde{\sigma}^2 \sigma_p^2 = \frac{\hbar^2}{4}\left(1 + \frac{\hbar^2 t^2}{m^2 \sigma^2}\right) \geq \frac{\hbar^2}{4} \tag{236}$$

which is to say that at $t = 0$, our knowledge of the wavepacket in *both* the position and momentum is at the *minimum but is non-zero*. You might have seen this relation before, and it is called the **Heisenberg Uncertainty Relation**. Since we have secretly used Schrödinger's Equation when we wrote down the Stationary States as basis and used Born's Rule to interprete the results, it is a consequence of quantum mechanical nature of the particle. We will discuss this in much greater detail in section 7.

5.5 Parity Operator

When we consider the infinite potential in section 5.1, we showed that its energy eigenfunctions naturally subdivided into odd and even states. We also introduced the **Parity Operator** whose action is to change the sign of the argument of a state around an axis. In 1 dimension, this is simple (taking the axis $x = 0$ for simplicity)

$$\hat{P}\psi(x) = \psi(-x). \tag{237}$$

In higher dimensions, we have to specify which of the spatial arguments we want to flip as they are *different* operations. For example in 2 dimensions

$$2 \text{ dimensions} : \hat{P}_x f(x, y) = f(-x, y) \ , \ \hat{P}_y f(x, y) = f(x, -y) \tag{238}$$

are two different operators: $\hat{P}_x$ flips around $x = 0$ while $\hat{P}_y$ flips around $y = 0$.

In 3 dimensions, and an operator which flip all arguments would have the form

$$\hat{P}f(\mathbf{x}) = f(-\mathbf{x}), \tag{239}$$

44

Figure 15: Parity Operators: Alice discovering that the Wonderland is not what it cut out to be.

so all the points go through the origin to its diagrammatic opposite position – such an operation is sometimes called an **inversion**.

Some properties of the Parity Operator:

- $\hat{P}$ *is Hermitian.* (You will be asked to show this in the Example Sheet.)

- $\hat{P}^2 = 1$. Proof is trivial : $\hat{P}\hat{P}f(x) = \hat{P}f(-x) = f(x)$ $\square$.

- Eigenfunctions and Eigenvalues of $\hat{P}$: Let λ be an eigenvalue of $\hat{P}$ and $\phi(x)$ is its eigenfunction so

$$\hat{P}\phi(x) = \lambda\phi(x) = \phi(-x) \tag{240}$$

  and now, applying $\hat{P}$ on both sides from the left, we get

$$\hat{P}^2\phi(x) = \lambda^2\phi(x) = \phi(x) \tag{241}$$

  and hence $\phi_\pm(x)$ eigenfunctions of $\hat{P}$ with eigenvalues $\lambda = \pm 1$. We call ϕ_+ *parity even* and ϕ_- *parity odd* solutions.

- **Simultaneous eigenfunctions of $\hat{H}$ and $\hat{P}$**: Other than the infinite potential well, what other potentials $U(x)$ also admit parity eigenfunctions? Consider the time-independent Schrödinger's Equation with eigenfunction $\chi(x)$

$$\hat{H}\chi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\chi(x) + U(x)\chi(x) = E\chi(x),. \tag{242}$$

  If we flip the coordinate $x \to -x$ in Eq. (242), $\partial^2/\partial x^2$ remains invariant, and so *if* the potential is invariant under the same reflection $U(x) = U(-x)$, then it's clear that $\chi(-x)$ is also an eigenfunction of $\hat{H}$ with eigenvalue E and $\chi(-x) = \pm\chi(x)$. We say that $U(x)$ is **symmetric** under reflection $x \to -x$, and that $\chi(x) = \pm\chi(-x)$ is symmetric/**antisymmetric** under $x \to -x$.

  In other words, if $U(x)$ obeys the same symmetry[14] as the Parity Operator, then eigenfunctions of the associated Hamiltonian $\hat{H}$ are also eigenfunctions of $\hat{P}$. Of course, there exist a large degeneracy in the eigenfunctions of $\hat{P}$.

---

[14]In slicker language we will introduce in section 7, we say that $\hat{P}$ and $\hat{H}$ commute.
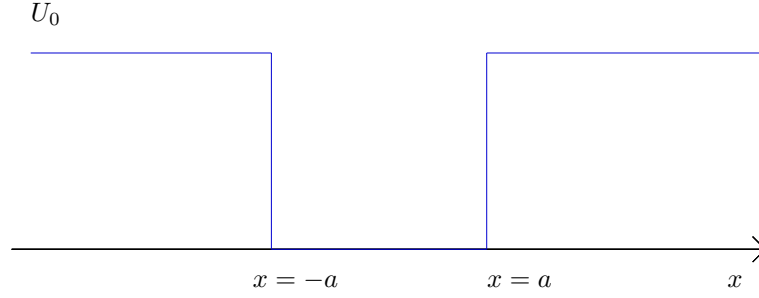
U_0

$x = -a$ $x = a$ x

Figure 16: The finite potential well. The Hamiltonian of this potential possess both bound and unbounded states.

5.6   Bound and Unbound States : The Finite Potential Well

Consider the **finite potential well** (Fig 16)

$$U(x) = \begin{cases} 0 & , \quad -a < x < a \\ \\ U_0 & , \quad \text{otherwise} \end{cases}$$

Bound and Unbounded States: It is clear from our discussion on the step potential in section 5.2, if the energy of the states $E \le U_0$, then the wavefunction have exponentially decaying solutions in Regions I and III. In other words, they don't propagate outside Region II and hence are "trapped" inside the well. We call such states **bound states**. In general, bound states (like the infinite potential well case) are *discrete*. If, on the other hand, $E > U_0$, even in Region I and III the wavefunction propagates and hence is **unbounded**.

Consider the bounded case $E \le U_0$. We define the constants as usual

$$k = \sqrt{\frac{2mE}{\hbar^2}} > 0 \ , \ \kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} > 0. \tag{243}$$

Region II: Schrödinger's Equation becomes

$$\frac{d^2\chi}{dx^2} = -k^2\chi \tag{244}$$

which has solutions

$$\chi_{II}(x) = A\cos(kx) + B\sin(kx). \tag{245}$$

This potential is clearly symmetric under $x \to -x$, so there must exist even and odd solutions. It is clear that $A\cos(kx)$ is the even solution and $B\sin(kx)$ is the odd solution.

Consider the *even* solution, so setting $B = 0$ we have

$$\chi_{II}(x) = A\cos(kx). \tag{246}$$

Regions I and III : The solution are

$$\text{Region I} \ : \ \chi_I(x) = Ce^{\kappa x} + \cancel{Ee^{-\kappa x}} \tag{247}$$

where we drop the F term as it is not normalizable, i.e. $\int_{-\infty}^{-a} \exp(-\kappa x) \ dx = -\infty$ and similarly

$$\text{Region III} \ : \ \chi_{III}(x) = De^{-\kappa x} + \cancel{Ge^{\kappa x}}. \tag{248}$$
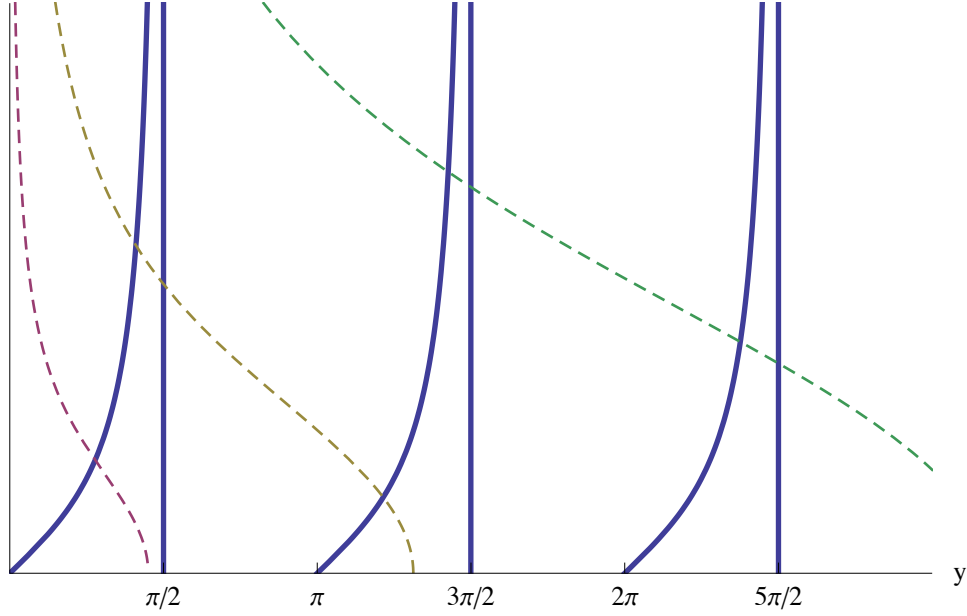
46

Figure 17: Bounded even solutions of the finite potential well. The thick line is $\tan y$ while the dotted lines are $\sqrt{(\lambda - y^2)/y}$ with increasing λ to the right. The crossings between lines indicates a possible solution. One can see that as we increase the width a^2 of the potential, or the depth U_0, there are more bounded solutions.

Since $\chi(x)$ is even, we know that $\chi(x) = +\chi(-x)$, so $C = D$. Imposing continuity at $x = a$, we get

$$A \cos(ka) = D \exp(-\kappa a) \ , \ \ -kA \sin(ka) = -\kappa D \exp(-\kappa a). \tag{249}$$

Combining all these equations, we find the transcendental equation

$$k \tan(ka) = \kappa \tag{250}$$

which cannot be solved in closed form, but we can plot out the solution to see its features. Define

$$\lambda = \frac{2mU_0 a^2}{\hbar^2} > 0 \ , \ y = ka, \tag{251}$$

then Eq. (250) becomes

$$\tan y = \frac{\sqrt{\lambda - y^2}}{y} \tag{252}$$

which we plot in Fig. 17. From this figure, we can see

- As the width a and depth U_0 increases, the number of solutions grow.

- Bounded states have *discrete energy spectrum* as advertised

$$E_n = \frac{\hbar^2 y_n^2}{2ma^2} \tag{253}$$

where y_n is a solution to the Eq. (252) with n labeling each crossing, and from fig 17 we see that

$$(n-1)\pi < y_n < \left(n - \frac{1}{2}\right)\pi. \tag{254}$$

- Again there exist a non-zero probability density in the classical forbidden Regions I and III.
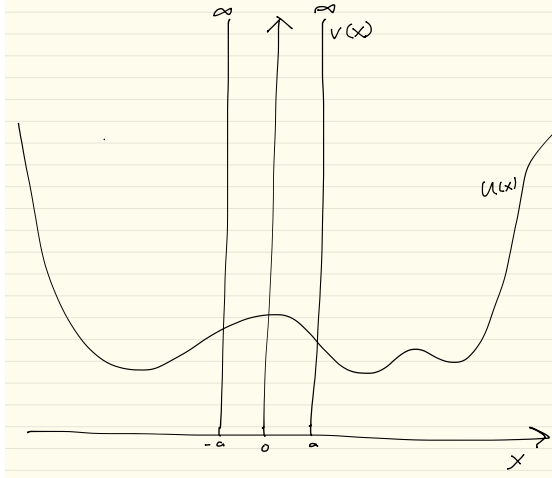
47

Figure 18: A potential $U(x)$ which supports at least one bound state, and the superimposed infinite potential walls $V(x)$.

You will be asked to look for odd solutions of the finite potential well in Example Sheet 1. There you will find that, for sufficiently shallow potential, there may exist *no* odd bound states. This means that the lowest energy bound (ground) state is then *even*. You might have noticed, from our discussion in the infinite well potential and solving the delta function potential in Example sheet 1, that the ground state has the uncanny habit of being even. Is there an underlying deep reason this is so? The answer is yes – this is the consequence of the following Theorem which will now prove.

*Theorem (Ground state in 1D): The Ground state has no nodes, and is unique in 1 dimension.

"Uniqueness" here means that there exist no other state with no nodes. Before we begin, we assert (but not prove) that bound state solutions to the time-independent Schrödinger's Equation are real modulo a possible complex phase[15]. Hence nodes here refers to zero crossings on the real axis, thus we will work with real eigenfunctions from now on.

Proof: We will prove this theorem in three steps.

- **Step 1**: $\exists$ *a bound state with no nodes.*

  Suppose we have an arbitrary potential $U(x)$ (not necessarily symmetric) which can support at least one bound state. We now modify this potential by *adding* an infinite square well potential $V(x)$ "wall" centered around $x = 0$, with width $\pm a$, see fig. 18. As we take $a \to \infty$, the "walls" go to infinity and hence the potential returns to $U(x)$. On the other hand, if we take $a \to 0$, the modified potential looks more and more like an infinite square well potential with width $2a$. In this latter limit, we know from our study of the infinite square well potential, there exist a solution with no nodes

  $$\lim_{|a| \to 0} \chi_0(x) \to A \cos\left(\frac{\pi x}{2a}\right). \tag{255}$$

  Note that while it is the ground state in the infinite square well potential, at this stage we have not proven that fact for arbitrary potential $U(x)$. Without loss of generality we take $\chi_0(x) > 0$.

  Now, consider the shape of $\chi_0(x)$ as we begin to widen the "walls" by gradually taking $a \to \infty$. As we do that, $\chi_0(x)$ begins to deform and approach its *true* state given the potential $U(x)$. Suppose now, in this process, $\chi_0(x)$ develop at least one node. Since normalizability imposes the fact that $\chi_0(\pm a) = 0$, there are now two possibilities on the derivative $\chi_0'(\pm a)$ at the boundaries (see fig. 19):

---

[15]One way to see this is that the wavefunction must decay at infinity to be normalizable.

Case 1 : $\chi_0'(\pm a)$ changes sign in at least one of the boundary, hence $\chi_0'(\pm a) = 0$, but since $\chi_0(\pm a) = 0$ this implies that $\chi_0(x) = 0$ everywhere since Schrödinger's equation is 2nd order and hence if there exist a point where $\chi_0' = \chi_0 = 0$ then it must be trivial everywhere.

Case 2 : $\chi_0'(\pm a)$ does not change sign at the boundaries. This means that there must exist at least one node, $|y| < |a|$. Let's consider the case $y < 0$. It is clear that $\chi'(-a) < 0$ and $\chi'(y) > 0$, but as we take $-a \to y$, continuity of the derivatives[16] imply that $\chi_0'(y) \to \chi_0'(-a)$. But this means that the only possibly solution must be $\chi_0'(y \to -a) = 0$, and hence again $\chi_0(x)$ is trivial.

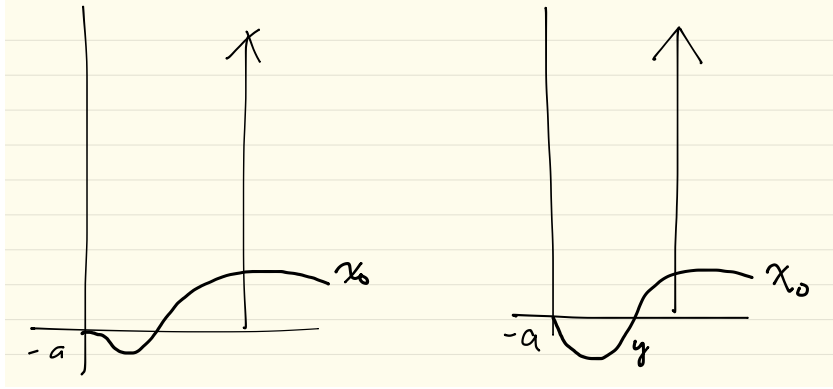Figure 19: The behavior of χ_0 at the boundaries. For Case 1 (left plot), χ_0 changes sign at $x = -a$ while for Case 2 (right plot), χ_0 does not change sign at $x = -a$.

- **Step 2**: *Uniqueness of Bound state with no nodes.*

  Suppose $\phi(x)$ is another state with no nodes (which may or may not be degenerate with $\chi_0(x)$). Without loss of generality let $\phi(x) > 0 \; \forall \; x$, then via orthonormality

  $$\phi(x) \cdot \chi_0(x) = \int_{-\infty}^{\infty} \phi(x)\chi_0(x) \; dx = 0 \tag{256}$$

  but since $\chi_0(x) > 0$ and $\phi(x) \geq 0$, the only solution is $\phi(x) = 0$, i.e. the trivial state.

- **Step 3**: *Bound state with no nodes is the lowest energy state.*

  Let E_0 be the energy eigenvalue for χ_0, i.e. $\hat{H}\chi_0 = E_0\chi_0$. Consider the eigenfunction $\phi(x)$ which possess at least one node, with eigenvalue E, i.e. $\hat{H}\phi = E\phi$. Without loss of generality, we consider $\phi(-\infty) \to 0_+$, i.e. it approaches $-\infty$ from the positive side. Suppose now its first node from $-\infty$ occurs at x_1, see fig. 20. We can construct a quantity

  $$\begin{aligned}
  E_0 \int_{-\infty}^{x_1} \chi_0\phi \; dx &= \int_{-\infty}^{x_1} \hat{H}\chi_0\phi \; dx \\
  &= \int_{-\infty}^{x_1} \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\chi_0\phi \; dx \\
  &= \int_{-\infty}^{x_1} \chi_0 \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\phi \; dx - \frac{\hbar^2}{2m}\left[\chi_0'(x)\phi(x) - \chi_0(x)\phi'(x)\right]\Big|_{-\infty}^{x_1} \tag{257}
  \end{aligned}$$

  where we have integrate by parts twice from the 2nd to 3rd line and kept the boundary terms. But now $\phi(-\infty) = \chi_0(-\infty) = 0$ by the normalizability condition, and $\phi(x_1) = 0$ since it is a node, this leaves us with

  $$E_0 \int_{-\infty}^{x_1} \chi_0\phi \; dx = \int_{-\infty}^{x_1} \chi_0\hat{H}\phi \; dx + \frac{\hbar^2}{2m}\chi_0(x_1)\phi'(x_1) \tag{258}$$

---

[16]Notice that this is true even if there exist a delta function potential at y – the reason is of course at y, $\chi_0(y) = 0$ is a node and hence the delta function term vanishes.
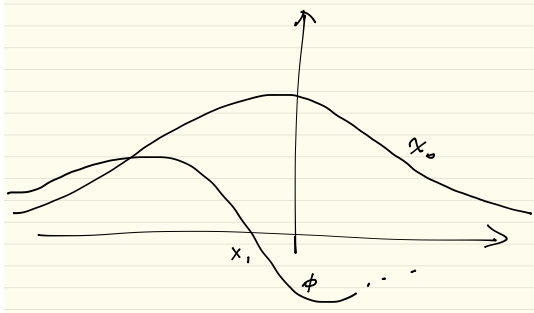
Figure 20: Some eigenfunction $\chi_0(x)$ which has no nodes with energy E_0 and some other eigenfucntion ϕ which possess at least one nodes, and with energy E.

or, using $\hat{H}\phi = E\phi$,

$$(E_0 - E)\underbrace{\int_{-\infty}^{x_1} \chi_0\phi \; dx}_{>0} = \frac{\hbar^2}{2m}\underbrace{\chi_0(x_1)\phi'(x_1)}_{<0}.$$ (259)

But since $\chi_0 > 0$ and $\phi(x < x_1) > 0$ so the integral is positive definite, and $\phi'(x_1) < 0$ as it must to cross the real axis from the positive plane, we obtain the inequality

$$E > E_0$$ (260)

and hence our proof of the Theorem is complete. $\square$

We can carry this proof through to see further that for a non-degenerate and discrete energy spectra, the n-th energy state must have $n - 1$ nodes. Since the ground state has no nodes, in a potential which has reflection symmetry, it must be even. However, this theorem holds even when the potential is not reflection symmetric. The general proof to this Theorem can be found in a standard text-book on Sturm-Liouville theory which you may actually have to study for your Methods class!*

6 The Simple Harmonic Oscillator

Hopefully, by now you are experts in solving Schrödinger's Equation in 1 dimension for a wide variety of potentials. All this is practice for what we will tackle next: the most important of all the 1-dimensional potential, the Simple Harmonic Oscillator. It is so important that it deserves its own section.

The Harmonic Oscillator is one of the most studied Classical Mechanics system – it is the prototype for many commonly occuring systems such as the pendulum (and hence accurate clocks), vibration in mechanical systems, A/C current that powers your computer, earthquakes and more.

In Quantum Mechanics, it is even more crucial. Classically, any system fluctuating by small amounts around near a configuration of stable equilibrium can be modeled by a Harmonic Oscillator – as you might have studied in the perturbations of an orbit around a planet in your Dynamics and Relativity class. This is also true in Quantum Mechanics. In Quantum *Field* Theory, particles are exactly such fluctuations around some stable equilibrium of fields, hence the importance of the quantization of the Harmonic Oscillator cannot be understated. If you like, you are made out of Simple Harmonic Oscillators.

6.1 Quantization of the Harmonic Oscillator in Position Basis

You might note the appended "in the Position Basis" in the title to this section. As it turns out, the method by which we will quantize the Harmonic Oscillator is not the most elegant. In modern treatments, quantization of the Harmonic Oscillator is done in the energy basis *– which we will discuss later but will not be examined.*

The potential for the Harmonic Oscillator is quadratic in x

$$U(x) = \frac{1}{2}m\omega^2 x^2, \tag{261}$$

so the Hamiltonian is

$$\hat{H}_{\text{SHO}} \equiv \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2. \tag{262}$$

In Classical Mechanics, the particle motion is described by Newton's Law of Motion Eq. (1), and the solution is the oscillator around $x = 0$,

$$x(t) = A\sin(\omega t + \delta) \tag{263}$$

with period $T = 2\pi/\omega$.

In Quantum Mechanics, the particle motion is described by Schrödinger's Equation. Using Stationary States as usual we get

$$\frac{-\hbar^2}{2m}\frac{d^2\chi}{dx^2} + \frac{1}{2}m\omega^2 x^2\chi = E\chi, \tag{264}$$

and as usual we seek the Eigenfunctions and Eigenvalues of χ. To simplify notation, we defined rescaled variables

$$y = \sqrt{\frac{m\omega}{\hbar}}x \ , \ \epsilon = \frac{2E}{\hbar\omega}, \tag{265}$$

so Eq. (264) becomes

$$\chi'' + (\epsilon - y^2)\chi = 0, \tag{266}$$

where primes denote derivative wrt y, i.e $' = d/dy$.

Consider the solution at two limits $y \to \infty$ and $y \to 0$:

- *Case $y \to \infty$*: In this case, we can drop the $\epsilon\chi$ term, and Eq. (266) becomes

$$\chi'' = y^2\chi, \tag{267}$$

which has the solution

$$\chi = A y^m e^{-y^2/2}. \tag{268}$$

Check :

$$\begin{aligned}
\chi'' &= A y^{m+2} e^{\pm y^2/2} \left[1 \pm \frac{2m+1}{y^2} + \frac{m(m-1)}{y^4} \right] \\
&\overset{y \to \infty}{\longrightarrow} A y^{m+2} e^{\pm y^2/2} = y^2 \chi.
\end{aligned} \tag{269}$$

Since we want the wavefunction to be normalizable, we choose $y^m \exp[-y^2/2]$.

- *Case $y \to 0$*: In this case, Eq. (266) becomes

$$\chi'' + \epsilon \chi = 0, \tag{270}$$

which has the familiar solution

$$\chi = A \cos(\sqrt{\epsilon} y) + B \sin(\sqrt{\epsilon} y). \tag{271}$$

Expanding around $y = 0$, we get (with c some constant)

$$\chi \overset{y \to 0}{\longrightarrow} A + cy + \mathcal{O}(y^2). \tag{272}$$

Inferring from the two solutions in the two limits above Eq. (268) and Eq. (272), the full solution must have the form

$$\chi(y) = f(y) \exp\left(-\frac{y^2}{2} \right) \tag{273}$$

where $f(y) \to A + cy$ as $y \to 0$, and $f(y) \to y^m$ as $y \to \infty$.

Plugging the ansatz Eq. (273) back into Eq. (266), we get

$$f'' - 2yf' + (\epsilon - 1)f = 0. \tag{274}$$

This is a 2nd order equation with a regular point at $y = 0$ and has a power law solution,

$$f(y) = \sum_{n=0}^{\infty} a_n y^n \tag{275}$$

which we proceed to plug back into Eq. (274). And now

$$f'' = \sum_{n=0}^{\infty} n(n-1)a_n y^{n-2} = \sum_{n=0}^{\infty} (n+1)(n+2)a_{n+2} y^n \tag{276}$$

which we can always do by shifting $n \to n+2$, so

$$f'' - 2yf' + (\epsilon - 1)f = \sum_{n=0}^{\infty} \left[(n+1)(n+2)a_{n+2} - 2na_n + (\epsilon - 1)a_n \right] y^n = 0 \tag{277}$$

is satisfied when we set

$$(n+1)(n+2)a_{n+2} - 2na_n + (\epsilon - 1)a_n = 0. \tag{278}$$

The above is a *recurrence relation*:

$$a_{n+2} = \frac{(2n - \epsilon + 1)}{(n+1)(n+2)} a_n. \tag{279}$$

Hence given two values a_0 and a_1, Eq. (279) will generate all values of a_n. Recalling that the potential is reflection symmetric around $x = 0$, it will have parity odd and even solutions. As it turns out, a_0 will generate *even* solutions

There are now two possibilities:

- The series Eq. (275) terminates, i.e. $\exists N > 0$ such that $a_n = 0 \ \forall \ n > N$.

- The series Eq. (275) does not terminate, i.e. $\nexists N > 0$ such that $a_n = 0 \ \forall \ n > N$.

It will turn out that the second possiblity does not lead to normalizable wavefunctions. To see that, we check for growth of the coefficients as $n \to \infty$, as they control the growth of the power law solutions

$$\frac{a_{n+2}}{a_n} \overset{n \to \infty}{\longrightarrow} \frac{2}{n}. \tag{280}$$

Consider the asymptotic behavior of the coefficients of the discarded $\exp(y^2/2)$ solution way back when we consider $y \to \infty$ solutions:

$$\exp(y^2) = \sum_{m=0}^{\infty} \frac{y^{2m}}{m!} \equiv \sum_{n=0}^{\infty} b_n y^n. \tag{281}$$

The coefficients are $b_n = (n/2)!$ for even $n = 2m$ and zero for odd $n = 2m + 1$, so the even series is

$$\frac{b_{n+2}}{b_n} = \frac{2}{n+2} \overset{n \to \infty}{\longrightarrow} \frac{2}{n} \tag{282}$$

which is the same as Eq. (280) for the power series solution.

Hence the series must terminate (first possibility), i.e. $\exists$ an integer $N > 0$ such that $a_{n+2} = 0$ with $a_N \neq 0$. Using Eq. (279), this give us the **Quantization Condition**

$$2N - \epsilon + 1 = 0 \ , \ \epsilon = 2N + 1 \ , \ \text{for } N = 0, 1, 2, 3, \ldots \tag{283}$$

So if ϵ is one of these special integer values, the series truncate and the wavefunction becomes normalizable. Now since $\epsilon = 2E/\hbar\omega$, the energy spectrum of the Harmonic Oscillator is then

$$\boxed{E_N = \left(N + \frac{1}{2}\right)\hbar\omega}. \tag{284}$$

Like the infinite well potential, the *lowest energy state* or Ground state has non-zero energy, $E = (1/2)\hbar\omega$. The energy levels are also equally spaced $\Delta E = E_{n+1} - E_n = \hbar\omega$ – reminiscence of the quantization of photon energy $E = \hbar\omega$.

Finally, we can find the wavefunctions. For *each* value of N, we generate using the recurrent relationship Eq. (279) a truncated series of a_n's. Choosing $a_0 = a_1 = 1$ (we need to renormalize the wavefunctions at the end), and alternative even/odd series:

- $N = 0$, $\epsilon = 1$, then

$$
\begin{aligned}
a_0 &= 1 \\
a_2 &= \frac{0 - 1 + 1}{2} a_0 = 0.
\end{aligned}
\tag{285}
$$

- $N = 1$, $\epsilon = 3$, then

$$
\begin{aligned}
a_1 &= 1 \\
a_3 &= \frac{2 - 3 + 1}{6} a_1 = 0.
\end{aligned}
\tag{286}
$$

- $N = 2$, $\epsilon = 5$, then

$$
\begin{aligned}
a_0 &= 1 \\
a_2 &= \frac{0 - 5 + 1}{2} a_0 = -2 \\
a_4 &= \frac{4 - 5 + 1}{12} a_2 = 0.
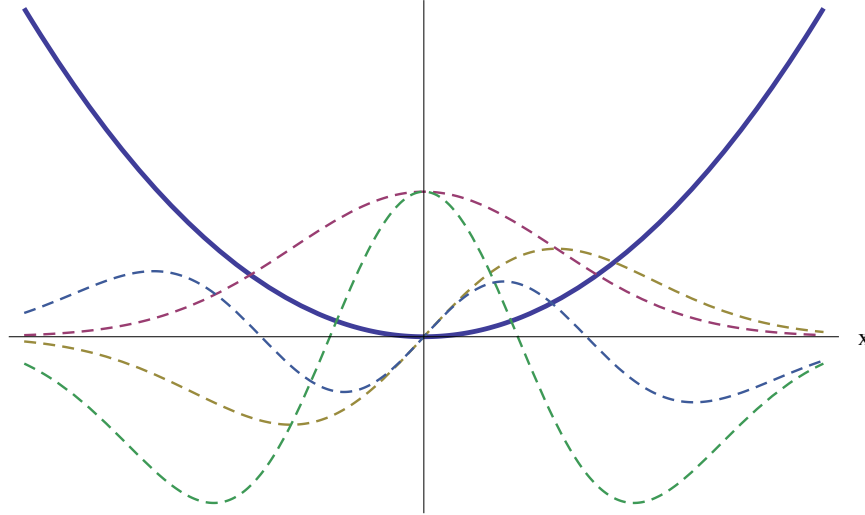\end{aligned}
\tag{287}
$$

Figure 21: The Simple Harmonic Oscillator. The thick line is the potential $U(x) = (1/2)m^2\omega^2 x^2$, while the dashed lines are the wavefunctions for the $N = 0, 1, 2, 3$ energy eigenstates.

- $N = 3$, $\epsilon = 7$, then

$$
\begin{aligned}
a_1 &= 1 \\
a_3 &= \frac{2 - 7 + 1}{2} a_1 = -\frac{2}{3} \\
a_5 &= \frac{6 - 7 + 1}{15} a_3 = 0.
\end{aligned}
\tag{288}
$$

And you can have fun calculating the rest – it is like a video game with increasing level of difficulty so don't get addicted. We can tabulate the results for the first few energy eigenstates.

N	E_N	$\chi_N(x)$	Parity	Nodes
0	$\frac{1}{2}\hbar\omega$	$e^{-y^2/2}$	$+1$	0
1	$\frac{3}{2}\hbar\omega$	$ye^{-y^2/2}$	-1	1
2	$\frac{5}{2}\hbar\omega$	$(1 - 2y^2)e^{-y^2/2}$	$+1$	2
3	$\frac{7}{2}\hbar\omega$	$\left(y - \frac{2}{3}y^3\right)e^{-y^2/2}$	-1	3

$$\tag{289}$$

The first few wavefunctions are plotted in fig. 21.

Finally, before we finish, we make a couple of remarks:

- There are no unbounded states in the Harmonic Oscillator. Can you see why?

- All the energy eigenstates have positive energies. You will be asked to prove this in an Example sheet.

6.2 *Quantization of the Harmonic Oscillator in Energy Basis

This section requires knowledge of commutator relationship to be studied in section 7, and it is not required study for this lecture course. But it is so pretty, and so powerful, that I am going to be put it here to show you why no practicing physicists ever quantized the Harmonic Oscillator the way we just did in Position Basis.

You have learned that position and momentum operator obey the commutator relationship

$$[\hat{x}, \hat{p}] = i\hbar. \tag{290}$$

54

We will now introduce the at first mysteriously named **raising and lowering operators**, which is some linear combination of the $\hat{x}$ and $\hat{p}$ operators

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\omega\hbar}}\hat{p} \tag{291}$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\omega\hbar}}\hat{p}, \tag{292}$$

so that they satisfy the new commutator relationship (if you have done Hamiltonian Classical Mechanics, this looks very much like a Canonical Transformation)

$$[\hat{a}, \hat{a}^\dagger] = 1. \tag{293}$$

You can then show that the Harmonic Oscillator Hamiltonian $\hat{H}$ Eq. (262) becomes

$$\frac{\hat{H}_{\text{SHO}}}{\hbar\omega} = \left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right). \tag{294}$$

From now onwards, we are going to do something that physicists like to do: set the units of energy $\hbar\omega = 1$. So now everytime you see "5", you should think "$5\hbar\omega$".

Given the Hamiltonian operator in these strange operators, we want to find the eigenstates and eigenvalues, so we want to solve the eigenfunction equation

$$\hat{H}_{\text{SHO}}\chi_E = E\chi_E \tag{295}$$

which is nothing mysterious. But wait! Notice that we have sneakily dropped the argument (x) from $\chi_E(x)$. Indeed, we are now going to ignore position from now. Using the commutator relation Eq. (293), we can then do some commutator algebra (again see section 7) to see that the following commutator relations hold

$$[\hat{a}, \hat{H}_{\text{SHO}}] = \hat{a} \ , \ [\hat{a}^\dagger, \hat{H}_{\text{SHO}}] = -\hat{a}^\dagger. \tag{296}$$

Now, let's see some trickery. Operate $\hat{H}_{\text{SHO}}$ on $(\hat{a}\chi_E)$ we find

$$\hat{H}_{\text{SHO}}\hat{a}\chi_E = (\hat{a}\hat{H}_{\text{SHO}} - [\hat{a}, \hat{H}_{\text{SHO}}])\chi_E = (E-1)(\hat{a}\chi_E) \tag{297}$$

where we have *commuted* $\hat{H}_{\text{SHO}}$ *through* $\hat{a}$ using Eq. (296). But the resulting equation imply that the state $\hat{a}\chi_E$ is also an eigenstate of $\hat{H}_{\text{SHO}}$ with eigenvalue $E - 1$! Hence this further imply that acting on χ_E with $\hat{a}$ (with some yet undetermined constant C_E)

$$\hat{a}\chi_E = C_E\chi_{E-1} \tag{298}$$

lowers the energy of the state χ_E by one unit! This is why we call $\hat{a}$ a **lowering operator**. You can guess what $\hat{a}^\dagger$ does (Exercise : show it)

$$\hat{a}^\dagger\chi_E = C_{E+1}\chi_{E+1}, \tag{299}$$

i.e it *raises* the energy by one unit so it is called the **raising operator**.

But notice that *the energy raised and lowered are in quantized units of one*, i.e. in units of $\hbar\omega$. This is exactly what we previously found in Eq. (284). Now using the fact that the energy eigenvalue of the Hamiltonian must be positive, this means that we cannot infinitely lower the energy of the state, and there must exist a **Ground State** where the lowering operator **annihilates** it

$$\hat{a}\chi_0 = 0. \tag{300}$$

What is the energy of this state? We have one last bit of magic:

$$
\begin{aligned}
\hat{a}\chi_0 &= 0 \\
\hat{a}^\dagger \hat{a}\chi_0 &= 0 \\
\left(\hat{H}_{\text{SHO}} - \frac{1}{2}\right)\chi_0 &= 0
\end{aligned}
\tag{301}
$$

or

$$
\hat{H}_{\text{SHO}}\chi_0 = \frac{1}{2}\chi_0
\tag{302}
$$

which tells us that the Ground State has energy $(1/2)\hbar\omega$ which is exactly what we found in the previous section!

Since there is no upper limit on the energies, we can keep applying $\hat{a}^\dagger$ on χ_E to raise its energy, and hence generating the spectrum

$$
\boxed{E_N = \left(N + \frac{1}{2}\right)\hbar\omega}
\tag{303}
$$

which we will get after acting on χ_0 N times with $\hat{a}^\dagger$.

Notice that we didn't even have to calculate the wavefunction in position space to find the spectrum. In real world applications, often time the things that we care about (and can easily measure) is the energy spectrum of any system. You can of course find the wavefunction of the particle using operator methods as we just did, but for this you will have to wait for next year's Part II class.

6.3 Summary

In this short section, you studied the mother of all quantum systems: the Simple Harmonic Oscillator. You find that the spectrum is bounded, quantized and have equal spacing of $\hbar\omega$. You learned to solve Schrödinger's Equation using power series method, and found normalizability of the wavefunctions play a crucial role in deciding what states are allowed[17].

You will see many similarities in the techniques used in this section when we confront the Hydrogen Atom. But before we do that, we will segue into more formal mathematics.

---

[17]This is a lesson often forgotten by practicing physicists when inventing new theories!

7 Commutators, Measurement and The Uncertainty Principle

*A black cat went past us, and then
another that looked just like it.*

Neo

In this section, we return from the wilderness of solving differential equations to more formal mathematics. In particular, we want to study the notion of measurement, and **simultaneous measurements of observables** that we alluded to way back in the introduction. There we have been careful to say that we cannot measure with arbitrary accuracy the position *and* momentum of a particle at the same time. Then when we study the Gaussian Wavepacket in section 5.4, we saw that the product of the dispersions of its position and momentum has the minimum value

$$(\Delta x)^2 (\Delta p)^2 \geq \frac{\hbar^2}{4}, \tag{304}$$

which we proceed to argue should be interpreted as our inability to measure p and x to arbitrary accuracy at the same time. In this section, we will show that non-commuting observables will lead to the Heisenberg Uncertainty Principle – one of the pillars of Quantum Mechanics.

7.1 Pure Ensembles and Expectation Values

Postulate 3 tells us that the measurement of an observable $\hat{O}$ in some state $\psi = \sum_{n=1}^{\infty} a_n u_n$ yields the eigenvalue λ_n with some probability $|a_n|^2$. The state then collapses into u_n. This is all fine and good in theory, the question is: how do we test for this fact?

The way to do this, is to make *many repeated measurements of identically prepared states*, and plot out a histogram of the results, e.g. we measure λ_1 6 times, λ_2 32 times, λ_3 8 times etc. And then compare this to our theoretical prediction. Of course the more identically prepared states there are, the better our experiment will test the theoretical prediction. Such a set of identically prepared states is called a **Pure Ensemble**.

Given a pure ensemble, and a set of measurements, we can also ask what is the *average* value of all the the measured eigenvalues. In the limit of a very large number of measurements, this is called the **Expectation Value**, which is defined to be

$$\boxed{\langle O \rangle_\psi = \psi(\mathbf{x}) \cdot (\hat{O}\psi(\mathbf{x})) = \int_{\mathbb{R}^3} \psi^\dagger(\mathbf{x})\hat{O}\psi(\mathbf{x}) \, dV.} \tag{305}$$

We can show that this exactly is the average value of the measured eigenvalues

$$\int_{\mathbb{R}^3} \psi^\dagger(\mathbf{x})\hat{O}\psi(\mathbf{x}) \, dV \;=\; \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \int_{\mathbb{R}^3} a_m^* a_n u_m^\dagger(\mathbf{x})\hat{O}u_n(\mathbf{x}) \, dV$$

$$=\; \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \lambda_n a_m^* a_n u_m^\dagger \int_{\mathbb{R}^3} u_m^\dagger(\mathbf{x})u_n(\mathbf{x}) \, dV$$

$$=\; \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \lambda_n a_m^* a_n \delta_{mn} \;,\; \text{and hence}$$

$$\langle O \rangle_\psi \;=\; \sum_{n=1}^{\infty} \lambda_n |a_n|^2. \tag{306}$$

It is trivial to show that the expectation value of a Hermitian operator is purely real.

Some examples:

- Expectation of $\hat{x}$,

$$
\begin{aligned}
\langle \hat{x} \rangle_\psi &= \int dx \ \psi^\dagger(x)\hat{x}\psi(x) \\
&= \int dx \ x|\psi(x)|^2 \\
&= \int dx \ x\rho(x),
\end{aligned}
\tag{307}
$$

which is the same as the classical notion of finding the expectation value of x given probability distribution of $\rho(x)$.

- Expectation of $\hat{p}$,

$$
\begin{aligned}
\langle \hat{p} \rangle_\psi &= -i\hbar \int dx \ \psi^\dagger(x)\frac{d}{dx}\psi(x) \\
&= -\frac{i\hbar}{4\pi^2} \int dx \int dk \int dk' \ f^\dagger(k')e^{-ikx}\frac{d}{dx}f(k)e^{ikx} \\
&= -\frac{i\hbar}{4\pi^2} \int dk \int dk' \ f^\dagger(k')(2\pi\delta(k-k'))(ik)f(k) \\
&= \frac{1}{2\pi} \int dk \ \hbar k|f(k)|^2,
\end{aligned}
\tag{308}
$$

which is the same as the classical notion of finding the expectation value of x given probability distribution of $|f(k)|^2$, in agreement with Eq. (122).

7.2   Commutators and Simultaneous Measurement

What do we mean by "measuring both things at the same time"?

In Classical Mechanics, this simply means that we can set up two different detectors, say X (for x measurement) and P (for p measurement). To make simultaneous measurements, we press the buttons both at the same time or even with some slight difference in time (to account for experimental error). It doesn't matter which detectors "goes first", we will get the more or less the same answer.

In Quantum Mechanics, Postulate 3 tells us that the very act of measurement *collapses* the wavefunction, so now it *matters which detector goes first!* Given a wavefunction $\psi(x)$, if X goes first then the following sequence of events occurs

$$
\psi(x) \xrightarrow{X} \phi_{x_0}(x) \xrightarrow{P} u_{p_0}(x)
\tag{309}
$$

where $\phi_{x_0}(x)$ is a highly localized function around the measured value x_0 as discussed previously, and $u_{p_0}(x)$ is some highly localized function around the measured value p_0. On the other hand, if P goes first then

$$
\psi(x) \xrightarrow{P} u_{p'_0}(x) \xrightarrow{X} \phi_{x'_0}(x).
\tag{310}
$$

Since $\phi_{x_0} \neq \psi(x)$ and $u_{p'_0}(x) \neq \psi(x)$ in general, the measured pair of values will be *different – the first measurement has destroyed some information regarding the second observable!* This is the root reason of why there exist an uncertainty relation in Quantum Mechanics.

We can now ask: *under what conditions will the order of the measurements not matter?* Say if we have two observables, $\hat{O}_A$ and $\hat{O}_B$, then we want

$$
\psi(x) \xrightarrow{O_A} \phi(x) \xrightarrow{O_B} \chi(x),
\tag{311}
$$

and

$$
\psi(x) \xrightarrow{O_B} \phi(x) \xrightarrow{O_A} \chi(x),
\tag{312}
$$

to give the same observed eigenvalues of $\hat{O}_A$ and $\hat{O}_B$. By inspection, it is clear that this will occur if ϕ *is an eigenfunction of both $\hat{O}_A$ and $\hat{O}_B$, and hence so is χ.*

To formalize all these words, we will introduce some new mathematics.

(Definition) Commutator: The Commutator of two operators $\hat{O}_A$ and $\hat{O}_B$ is defined by

$$\boxed{[\hat{O}_A, \hat{O}_B] = \hat{O}_A\hat{O}_B - \hat{O}_B\hat{O}_A.} \tag{313}$$

This definition means that

$$[\hat{O}_A, \hat{O}_B] = -[\hat{O}_B, \hat{O}_A]. \tag{314}$$

We now have two possibilities that describe the situation on measurements above:

- **Commuting Observables and Simultaneous Eigenfunctions**: Suppose now $\hat{O}_A$ and $\hat{O}_B$ are two observables. Suppose, further that the wavefunction $\psi(x)$ is a *simultaneous eigenfunction $\hat{O}_A$ and $\hat{O}_B$* with eigenvalues a and b

$$\hat{O}_A\psi(x) = a\psi(x) \ , \ \hat{O}_B\psi(x) = b\psi(x) \tag{315}$$

then

$$[\hat{O}_A, \hat{O}_B]\psi(x) = (\hat{O}_A\hat{O}_B - \hat{O}_B\hat{O}_A)\psi(x) = ab - ba = 0, \tag{316}$$

which is to say, "$\hat{O}_A$ and $\hat{O}_B$ commute". We can write this relation in operator form by dropping ψ

$$\boxed{\textbf{Commuting Observables} \ : [\hat{O}_A, \hat{O}_B] = 0.} \tag{317}$$

As have seen in the above example, commuting observables can be measured simultaneously. We call such observables **Compatible Observables** or **Commuting Observables**. Physically, this means that $\hat{O}_A$ and $\hat{O}_B$ have definite eigenvalues in ψ.

Now, let's state an extremely important theorem.

Theorem (Simultaneous Basis of Eigenfunctions) : Suppose $\hat{O}_A$ and $\hat{O}_A$ commute, then they share (at least) a basis of simultaneous eigenfunctions.

Proof: We will prove this Theorem for the special case where *at least* one of the operator is non-degenerate. Assuming $\hat{O}_A$ is non-degenerate, so it possess a set of eigenfunctions $\{\psi_{a_i}\}$ with distinct eigenvalues $\{a_i\}$. By the eigenvalue equation

$$\hat{O}_A\psi_{a_i} = a_i\psi_{a_i}, \tag{318}$$

and operating from the left with $\hat{O}_B$,

$$\hat{O}_B\hat{O}_A\psi_{a_i} = a_i\hat{O}_B\psi_{a_i} \tag{319}$$

and using commutativity $[\hat{O}_A, \hat{O}_B] = 0$,

$$\hat{O}_A(\hat{O}_B\psi_{a_i}) = a_i(\hat{O}_B\psi_{a_i}) \tag{320}$$

which is to say that $\hat{O}_B\psi_{a_i}$ is also an eigenfunction of $\hat{O}_A$ with eigenvalue a_i. But since $\hat{O}_A$ is non-degenerate, $\hat{O}_B\psi_{a_i}$ must be the same eigenfunction as ψ_{a_i} up to a (for the moment possibly complex) number λ (recall that there exist an equivalence class of wavefunctions see Eq. (71)) as ψ_{a_i}, i.e.

$$\hat{O}_B\psi_{a_i} = \lambda\psi_{a_i}. \tag{321}$$

But this is nothing but an eigenvalue equation for $\hat{O}_B$ and we identify λ as its eigenvalue, which by Hermiticity is real. Since every eigenfunction of $\hat{O}_A$ is also an eigenfunction of $\hat{O}_B$, it is clear that

$\{\psi_{a_i}\}$ forms a complete basis for *both* operators. In this special case where $\hat{O}_A$ is non-degenerate, there is only one such basis. $\square$

The proof for the case where both operators are degenerate is much more involved. Those interested can see Shankar (pg 45).

Since ψ_{a_i} is also an eigenfunction of both $\hat{O}_A$ and $\hat{O}_B$, and we can also give it a b label $\psi_{a,b}$, and we say that $\psi_{a,b}$ are **Simultaneous Eigenfunctions** of $\hat{O}_A$ and $\hat{O}_B$.

Example: Harking back to section 4.1, recall that $\hat{\mathbf{p}}$ and $\hat{H}_{\text{free}}$ share the same Eigenfunctions $u_{\mathbf{p},E}(\mathbf{x})$ where now we have democratically label the eigenfunction without prejudice to any operator:

$$\hat{H}_{\text{free}}u_{\mathbf{p},E}(\mathbf{x}) = Eu_{\mathbf{p},E}(\mathbf{x}) \ , \ \hat{\mathbf{p}}u_{\mathbf{p},E}(\mathbf{x}) = \mathbf{p}u_{\mathbf{p},E}(\mathbf{x}). \tag{322}$$

We will see another case of degeneracy and simultaneous eigenfunctions when we discuss Angular Momentum in section 8.4.

Example : Recall the Parity operator in 1 dimension has the action $\hat{P}\psi(x) = \psi(-x)$. Now consider a Hamiltonian $\hat{H} = \hat{p}^2/2m + U(x)$ where the potential $U(x) = U(-x)$ is reflection invariant. Then $\hat{P}$ and $\hat{H}$ commute

$$[\hat{P},\hat{H}] = 0. \tag{323}$$

Proof: Recall from Eq. (187) that for a reflection symmetric potential $U(x)$, if $\chi_E(x)$ is an eigenfunction of $\hat{H}$ with energy E, then so is $\chi_E(-x)$, then

$$
\begin{aligned}
[\hat{P},\hat{H}]\chi_E(x) &= \hat{P}\hat{H}\chi_E(x) - \hat{H}\hat{P}\chi_E(x) \\
&= \hat{P}E\chi_E(x) - \hat{H}\chi_E(-x) \\
&= E(\chi_E(-x) - \chi_E(-x)) = 0
\end{aligned} \tag{324}
$$

and by Completeness of the eigenfunctions of $\hat{H}$, the proof is complete. $\square$

Conservation Laws: In Classical Mechanics, some observables are *conserved under time evolution* if the potential $U(\mathbf{x})$ has some symmetry. For example, if $U(\mathbf{x}) = f(r)$ is spherically symmetric, then we know that the total angular momentum $\mathbf{L}$ is conserved. In Quantum Mechanics, conservation laws are expressed as the *vanishing of the observable with the Hamiltonian*, i.e. if $\hat{O}$ commutes with $\hat{H}$

$$[\hat{O},\hat{H}] = 0 \tag{325}$$

then the observable is conserved under time evolution. In the above example with Parity, you can see from the many examples in section 5 that if a state has a definite parity, then this parity is conserved under time evolution as long as the Potential is symmetric under reflection.

- **Non-commuting Observables**: The definition for non-commuting observables $\hat{O}_A$ an $\hat{O}_B$ is simply

$$\boxed{\text{non} - \textbf{Commuting Observables} \ : [\hat{O}_A,\hat{O}_B] \neq 0.} \tag{326}$$

In words, we say that "$\hat{O}_A$ and $\hat{O}_B$ do not commute".

As you can easily prove to yourself, non-commuting observables do not share eigenfunctions, hence from the example at the start of this section this means that observations of one will now affect the observations of the other.

An example of this is our favorite pair of observables $\hat{\mathbf{p}}$ and $\hat{\mathbf{x}}$. Acting on some generic state $\psi(\mathbf{x})$ we find

$$[\hat{x}_i,\hat{x}_j]\psi(\mathbf{x}) = (x_ix_j - x_jx_i)\,\psi(\mathbf{x}) = 0 \tag{327}$$

while

$$[\hat{p}_i, \hat{p}_j]\psi(\mathbf{x}) \;=\; (-i\hbar)^2 \left[\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} - \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i} \right]\psi(\mathbf{x}) \;=\; 0 \tag{328}$$

using the symmetry of mixed partial derivatives. Finally,

$$
\begin{aligned}
[\hat{x}_i, \hat{p}_j]\psi(\mathbf{x}) &= \left[x_i\left(-i\hbar\frac{\partial}{\partial x_j}\right) - \left(-i\hbar\frac{\partial}{\partial x_j}\right)x_i \right]\psi(\mathbf{x}) \\
&= -i\hbar\left[x_i\frac{\partial f}{\partial x_j} - \frac{\partial}{\partial x_j}(x_i\psi) \right] \\
&= -i\hbar\left[x_i\frac{\partial\psi}{\partial x_j} - \psi\frac{\partial x_i}{\partial x_j} - x_i\frac{\partial\psi}{\partial x_j} \right] \\
&= i\hbar\delta_{ij}\psi(\mathbf{x}).
\end{aligned}
\tag{329}
$$

We obtain the **Canonical Commutator Relationships** for $\hat{x}_i$ and $\hat{p}_i$

$$\boxed{[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}} \;,\; \boxed{[\hat{x}_i, \hat{x}_j] = 0} \;,\; \boxed{[\hat{p}_i, \hat{p}_j] = 0} \tag{330}$$

As we will see in the next section, non-commuting observables lead to the Uncertainty Principle.

*__Canonical Quantization__: In the lectures, we have derived Eq. (330) from our definitions of $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$, working in the position basis. However, if we take away the basis, we can *impose* the canonical commutator relations, i.e. specifying Eq. (330) as the starting point for Quantum Mechanics and then deriving the position (or any other) basis operators from there. This is the more usual "modern" view, although our approach of deriving the momentum operator from the properties of translation is, in the view of some, more general.*

7.3   Non-commuting Observables and The Uncertainty Principle

As we told the story at the start of this section, if two observables $\hat{O}_1$ and $\hat{O}_2$ do not commute, then the order of the measurements matter. Indeed, since say when the measurement associated with observable $\hat{O}_1$ is made, the wavefunction collapses into one of its eigenstate, some of the information associated with $\hat{O}_2$ is "lost" so to speak. In this section, we will quantify this.

(Definition) Uncertainty Operator: The uncertainty of a state ψ with respect to an observable $\hat{O}$ is defined as

$$\boxed{\Delta\hat{O} = \hat{O} - \langle\hat{O}\rangle_\psi.} \tag{331}$$

This operator has the following properties

- $\Delta\hat{O}$ **is Hermitian**. *Proof*: As $\hat{O}$ is an observable, it must be Hermitian, and since $\langle\hat{O}\rangle_\psi$ is just a number, $\Delta\hat{O}$ must also be Hermitian. □

- **Dispersion**: The expectation value of $(\Delta\hat{O})^2$ of a state ψ is known as the dispersion, and has the following form

$$
\begin{aligned}
\langle(\Delta\hat{O})^2\rangle_\psi &= \langle\hat{O}^2 + \langle\hat{O}\rangle_\psi^2 - 2\hat{O}\langle\hat{O}\rangle_\psi\rangle_\psi \tag{332} \\
&= \langle\hat{O}^2\rangle_\psi + \langle\hat{O}\rangle_\psi^2 - 2\langle\hat{O}\rangle_\psi\langle\hat{O}\rangle_\psi \tag{333}
\end{aligned}
$$

or

$$\boxed{\langle(\Delta\hat{O})^2\rangle_\psi = \langle\hat{O}^2\rangle_\psi - \langle\hat{O}\rangle_\psi^2} \tag{334}$$

i.e. the dispersion of $\hat{O}$ is the "expectation of the square minus the square of the expectation", which is consistent with the classical notion of a dispersion of an ensemble.

Furthermore, if χ is a normalized eigenfunction of $\hat{O}$ then $\langle \Delta \hat{O}^2 \rangle_\chi = 0$. Proof is by direct application of Eq. (334):

$$
\begin{aligned}
\langle \hat{O}^2 \rangle_\chi &= \chi \cdot (\hat{O}^2 \chi) = \lambda^2 \text{ and} \\
\langle \hat{O} \rangle_\chi^2 &= (\chi \cdot (\hat{O} \chi)) = \lambda^2
\end{aligned}
\tag{335}
$$

so

$$
\langle \hat{O}^2 \rangle_\chi - \langle \hat{O} \rangle_\chi^2 = 0 \quad \square.
\tag{336}
$$

- Since the expectation value of any operator is just a number, it is easy to prove that for any two non-commuting observables $\hat{O}_A$ and $\hat{O}_B$

$$
[\Delta \hat{O}_A, \Delta \hat{O}_B] = [\hat{O}_A, \hat{O}_B].
\tag{337}
$$

In other words, if the state χ_A is an eigenstate of $\hat{O}_A$ then the uncertainty is zero and we measure it with probability 1, which is a trivial statement. What is *non-trivial* is that if $\hat{O}_B$ is another observable which does not commute with $\hat{O}_A$, then its uncertainty in any simultaneous measurement on χ_A will be infinite! We now state the general form of the **Uncertainty Principle**:

Uncertainty Principle: For any given two observables $\hat{O}_A$ and $\hat{O}_B$, then the following uncertainty relation holds for any state ψ

$$
\boxed{\langle \Delta \hat{O}_A^2 \rangle_\psi \langle \Delta \hat{O}_B^2 \rangle_\psi \geq \frac{1}{4} |\langle [\hat{O}_A, \hat{O}_B] \rangle_\psi|^2.}
\tag{338}
$$

In the case when $\hat{O}_A = \hat{x}$ and $\hat{O}_B = \hat{p}$, then using the canonical commutator relation $[\hat{x}, \hat{p}] = i\hbar$, we get the original famous **Heisenberg Uncertainty Principle**

$$
\langle \Delta \hat{x}^2 \rangle \langle \Delta \hat{p}^2 \rangle \geq \frac{\hbar^2}{4}
\tag{339}
$$

which you have already seen derived using the Gaussian wavepacket in section 5.4.

We want to prove the Uncertainty Principle Eq. (338) in a snazzy operator way[18]. To do this, we require 2 useful lemmas.

Lemma 1 (The Schwarz inequality): For any two normalized states ψ and ϕ, then[19]

$$
(\psi \cdot \psi)(\phi \cdot \phi) \geq |\psi \cdot \phi|^2.
\tag{340}
$$

Proof: For any complex number λ and any two normalized states ψ and ϕ, we can construct a state

$$
\Phi = \psi + \lambda \phi
\tag{341}
$$

and then

$$
\Phi \cdot \Phi \geq 0 \,\, \forall \,\, \lambda
\tag{342}
$$

since Φ is just another state and its norm must be ≥ 0 but $\leq \infty$ if both ψ and ϕ are normalizable. If we now set

$$
\lambda = -(\phi \cdot \psi)/(\phi \cdot \phi)
\tag{343}
$$

and plug it into Eq. (342), we get Eq. (340). $\square$

---

[18]See Prof. Nick Dorey's notes for a perhaps more direct way.
[19]This inequality is analogous to the vector space inequality $|\mathbf{a}|^2 |\mathbf{b}|^2 \geq |\mathbf{a} \cdot \mathbf{b}|^2$ which you might have seen before.

Lemma 2: An **anti-Hermitian operator** is defined to be a *linear* operator which obey the relationship

$$\int_{\mathbb{R}^3} f^\dagger(\mathbf{x}) \hat{C} g(\mathbf{x}) \, dV = - \int_{\mathbb{R}^3} \left(\hat{C} f(\mathbf{x}) \right)^\dagger g(\mathbf{x}) \, dV.$$

(344)

or more compactly

$$\hat{C} \equiv -\hat{C}^\dagger.$$

(345)

The expectation values of anti-Hermitian operator is purely imaginary. *Proof*: Suppose $\chi(\mathbf{x})$ is a normalized eigenfunction of $\hat{C}$ with eigenvalue λ, then taking expectation values of both $\hat{C}$ and $\hat{C}^\dagger$

$$\langle \hat{C} \rangle_\chi = \int_{\mathbb{R}^3} \chi^\dagger(\mathbf{x}) \hat{C} \chi(\mathbf{x}) \, dV = \lambda, \quad \text{and}$$

$$\langle \hat{C}^\dagger \rangle_\chi = \int_{\mathbb{R}^3} \chi^\dagger(\mathbf{x}) \hat{C}^\dagger \chi(\mathbf{x}) \, dV$$

(346)

$$= \int_{\mathbb{R}^3} (\hat{C}\chi(\mathbf{x}))^\dagger \chi(\mathbf{x}) \, dV = \lambda^*,$$

(347)

and using Eq. (344) we see that $\lambda + \lambda^* = 0$ and since $\lambda \in \mathbb{C}$, all its eigenvalues are purely imaginary. Using the Completeness property of linear operators, we can expand any state ψ in this basis so it follows that the expectation value $\langle \hat{C} \rangle_\psi$ is purely imaginary. $\square$

We are now ready to prove Eq. (338).

Proof (Uncertainty Principle): Given a state Ψ, then operating on this state with the uncertainty operators $\Delta \hat{O}_A$ and $\Delta \hat{O}_B$ yield

$$\psi = \Delta \hat{O}_A \Psi \ , \ \phi = \Delta \hat{O}_B \Psi$$

(348)

where ψ and ϕ are some other states. Using Hermiticity of $\Delta \hat{O}_A$, we see that

$$\psi \cdot \psi = \int_{\mathbb{R}^3} (\Delta \hat{O}_A \Psi(\mathbf{x}))^\dagger \Delta \hat{O}_A \Psi(\mathbf{x}) \, dV$$

$$= \int_{\mathbb{R}^3} \Psi(\mathbf{x})^\dagger \Delta \hat{O}_A^2 \Psi(\mathbf{x}) \, dV = \langle (\Delta \hat{O}_A)^2 \rangle_\Psi$$

(349)

where we have used the Hermiticity of $\Delta \hat{O}_A$ in the 2nd line. Similarly we can calculate $\phi \cdot \phi = \langle (\Delta \hat{O}_B)^2 \rangle_\Psi$ and $\psi \cdot \phi = \langle \Delta \hat{O}_A \Delta \hat{O}_B \rangle_\Psi$.

Using Lemma 1, we then take the expectation value around the state Ψ to get

$$(\psi \cdot \psi)(\phi \cdot \phi) \geq |\psi \cdot \phi|^2$$

$$\implies \langle (\Delta \hat{O}_A)^2 \rangle_\Psi \langle (\Delta \hat{O}_B)^2 \rangle_\Psi \geq |\langle \Delta \hat{O}_A \Delta \hat{O}_B \rangle_\Psi|^2.$$

(350)

We are halfway through the proof – our next task is to evaluate the RHS of Eq. (350). First we note that the following identiy holds

$$\Delta \hat{O}_A \Delta \hat{O}_B = \frac{1}{2} \left(\Delta \hat{O}_A \Delta \hat{O}_B + \Delta \hat{O}_A \Delta \hat{O}_B \right)$$

$$= \frac{1}{2} \left(\Delta \hat{O}_A \Delta \hat{O}_B - \Delta \hat{O}_B \Delta \hat{O}_A + \Delta \hat{O}_B \Delta \hat{O}_A + \Delta \hat{O}_A \Delta \hat{O}_B \right)$$

$$= \frac{1}{2} [\Delta \hat{O}_A, \Delta \hat{O}_B] + \frac{1}{2} (\Delta \hat{O}_A \Delta \hat{O}_B + \Delta \hat{O}_B \Delta \hat{O}_A).$$

(351)

But the commutator $[\Delta \hat{O}_A, \Delta \hat{O}_B] = [\hat{O}_A, \hat{O}_B]$ is *anti-Hermitian*

$$([\hat{O}_A, \hat{O}_B])^\dagger = (\hat{O}_A \hat{O}_B - \hat{O}_B \hat{O}_A)^\dagger = \hat{O}_B \hat{O}_A - \hat{O}_A \hat{O}_B = -[\hat{O}_A, \hat{O}_B]$$

(352)

while the last term on Eq. (351) is Hermitian

$$(\Delta \hat{O}_A \Delta \hat{O}_B + \Delta \hat{O}_B \Delta \hat{O}_A)^\dagger = \Delta \hat{O}_B \Delta \hat{O}_A + \Delta \hat{O}_A \Delta \hat{O}_B.$$

(353)

Hence the RHS of Eq. (350) becomes, using Lemma 2 for the expectation value of $[\hat{O}_A, \hat{O}_B]$,

$$|\langle \Delta\hat{O}_A \Delta\hat{O}_B \rangle_\Psi|^2 = |\underbrace{\frac{1}{2}\langle [\hat{O}_A, \hat{O}_B] \rangle}_{\text{Imaginary}} + \underbrace{\frac{1}{2}\langle (\Delta\hat{O}_A \Delta\hat{O}_B + \Delta\hat{O}_B \Delta\hat{O}_A) \rangle}_{\text{Real}}|^2$$

$$= \frac{1}{4}\left|\langle [\hat{O}_A, \hat{O}_B] \rangle\right|^2 + \frac{1}{4}\left|\langle (\Delta\hat{O}_A \Delta\hat{O}_B + \Delta\hat{O}_B \Delta\hat{O}_A) \rangle\right|^2 \qquad (354)$$

and since the last term can only make the inequality stronger, the proof is complete. $\square$

7.4 Summary

In this section, we study the notion of simultaneous observations and elaborated on how some observables are inherently incompatible with each other and the measurement of one will destroy information of the other(s). Such incompatibility is encoded in mathematical language as non-commutativity of the operators associated with the observables.

We then show that the Postulates of Quantum Mechanics lead us to the Uncertainty Principle – which is a powerful *consequence* of Postulate 3 (collapse of a wavefunction after a measurement), restricting our ability to extract information out of a wavefunction. How much information is "destroyed" by the collapse is given by the amount of non-commutativity of the observables as indicated by Eq. (338). Returning to $\hat{x}$ and $\hat{p}$, their commutator is $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$, i.e. the amount of "lost information" is proportional to the Planck's Constant $\hbar$, which sets the scale of Quantum Mechanics. Since Classically, no information is "lost" in any measurement, the "Classical Limit" of a quantum theory can be recovered by taking the limit $\hbar \to 0$.

This section marks the end of our formal development of Quantum Mechanics.

8 The Hydrogen Atom

Finally, we will put everything that we have learned together to investigate the Hydrogen Atom, the capstone of our lectures.

8.1 The Hydrogen Atom Historically and Experimentally

Historically, it is the observations of the *quantized nature of the spectral lines* of the Hydrogen atom and the failure of classical mechanics to explained it that led to the Quantum revolution.

Take a tube of Hydrogen gas, run an electric current through it, and after some time light will be emitted from this tube of Hydrogen gas. We put this light through a spectrometer, and observe what are the frequencies of the light, as in fig. 22. What we see is, instead of a continuous spectrum, the spectra of the Hydrogen atom is organized in discrete lines. In addition, the lines are not in random places, but follow a certain order as shown in fig. 23.
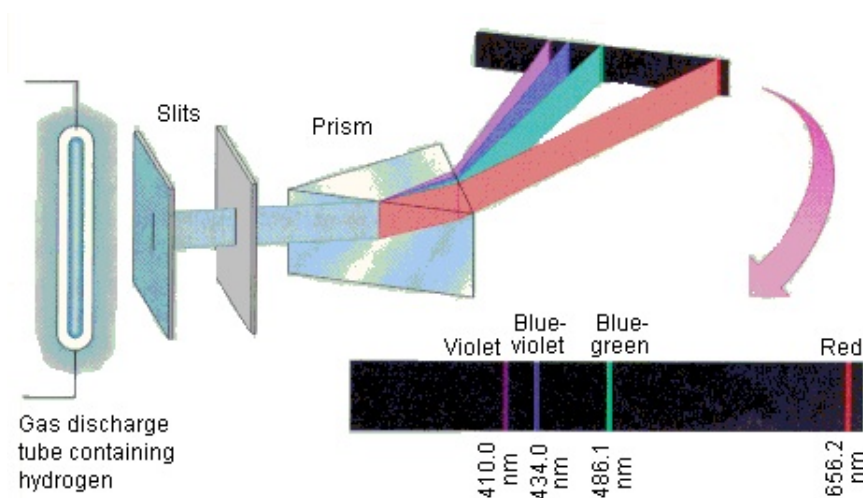

Figure 22: A spectrometer reveals the quantized nature of the Hydrogen emission lines. Picture stolen from the internet.

So the historical scientists looked at the frequencies ν of the spectrum, found that they obey an intriguing relation

$$\nu_{mn} = R_0 c \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \tag{355}$$

where $R_0 = 1.097 \times 10^{-7} m^{-1}$, called the **Ryberg Constant** and n, m are integers.

Furthemore, classical electrodynamics (which was well known by that time, thanks to Maxwell) predict that an electron orbiting around an electric field generated by the proton will *emit electromagnetic waves*, and hence lose energy. This means that the electron should have fallen into the proton – and it was a great puzzle why it was stable.

Bohr Model: Neils Bohr in 1913 proposed an *ad-hoc* solution to this situation. He suggested that first, electron move around the proton in circular orbits with radius r as described by Classical Mechanics.
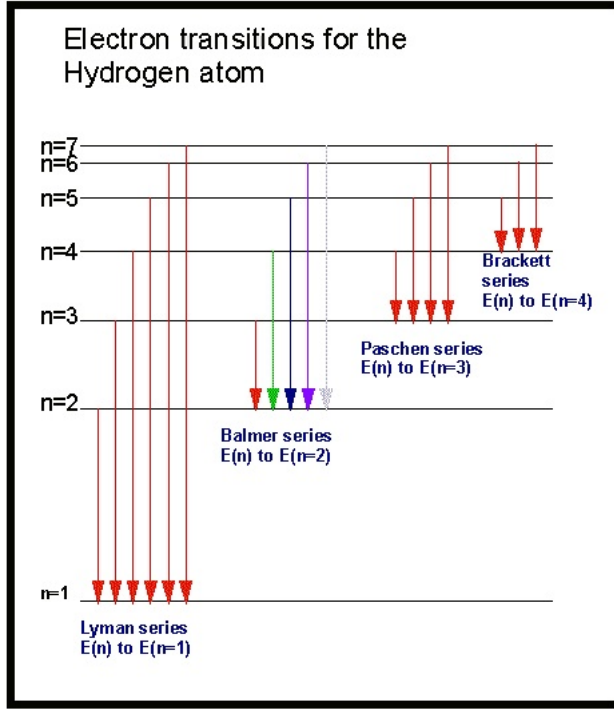
Figure 23: The frequencies and energies of emitted light of the Hydrogen Atom. Historically, before Bohr and Quantum Mechanics showed up, scientists did not know why only certain frequencies are permitted, and why they are organized in this nature. Instead of figuring it out, they decided to give the lines their own names.

So with Coulomb's Force

$$F = -\frac{e^2}{4\pi\epsilon_0 r^2} \tag{356}$$

where ϵ_0 is the permittivity constant. Then Newton's Law Eq. (1) implies that

$$F = -\frac{m_e v^2}{r} \tag{357}$$

and using the classical definition of angular momentum

$$J = m_e v r \tag{358}$$

we can solve for r

$$r = \frac{4\pi\epsilon_0 J^2}{m_e e^2}. \tag{359}$$

Classically, J can take on any continuous positive value $J \geq 0$, hence so can r. This means that the energy spectrum

$$
\begin{aligned}
E &= \text{Kinetic Energy} + \text{Potential Energy} \\
&= \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} \\
&= -\frac{m_e e^4}{32\pi^2\epsilon_0 J^2} \tag{360}
\end{aligned}
$$

is continuous.

Bohr *postulated* that, in addition to such rules, the angular momentum is *quantized* and obey the following additional rule

$$J = n\hbar , \; n = 1, 2, 3, \cdots \tag{361}$$

where $\hbar$ is the Planck's constant (known by 1900), then the radius and Energy spectra becomes quantized:

$$E_n = \frac{-m_e e^4}{32\pi^2\epsilon_0 \hbar^2} \times \frac{1}{n^2} = -E_R \frac{1}{n^2} \tag{362}$$

and

$$r_n = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2} = n^2 r_B \tag{363}$$

where $r_B = (4\pi\epsilon_2\hbar^2)/(m_e e^2)$ is known as the **Bohr Radius** and is about 0.528 angstroms, and the Ryberg Energy $E_R = m_e e^4/(32\pi^2\epsilon_0^2\hbar^2)$ is 13.6 eV (the energy required to eject an electron from a proton).

Since spectral lines correspond to transitions between the energy levels of the electron, and by conservation of energy must obey

$$2\pi\hbar\nu_{mn} = E_m - E_n \tag{364}$$

or

$$\nu_{mn} = \frac{m_e e^4}{64\pi^3\epsilon_0^2\hbar^3 c}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{365}$$

which also explains the Ryberg as a bonus (as you can check by plugging in all the numbers)

$$\frac{m_e e^4}{64\pi^3\epsilon_0^2\hbar^3 c} = R_0. \tag{366}$$

This was a great success at that time[20], but it is of course not satisfying: *why does the electron only orbit the proton in such discrete momenta and why only circular orbits?* The attempt to *derive* these rules led ultimately to the birth of Quantum Mechanics.

In these lectures, we will describe the Hydrogen Atom as a particle moving around a central spherically symmetric potential, i.e. the Coulomb potential $U(r) = -e^2/(4\pi\epsilon_0 r)$ where e is the electron charge, and that this particle obey Schrödinger's Equation Eq. (132). This is an approximation, but a very good one – indeed we will show that we can derive the entire spectrum and degeneracies of the Hydrogen Atom that is more than good enough for government work. On the other hand, we will now state from the get-go what we have ignored just for completeness (you don't have to know them for the Exams).

- *Non-relativistic Approximation.* The "classical" velocity of the electron around the proton is roughly 2×10^6 m/s, which is about 1% the speed of light. This means that *relativistic* effects will have a small but testable effect. Recall that Schrödinger's Equation describe a *non-relativistic* particle, so this relativistic correction is not modeled.

- *Electron spin.* A point particle has no **spin** – it is a point whichever direction you look at it. However, a real electron is not a point particle, and hence possesses a definite spin. Spins are observable quantities, so mathematically are Hermitian Operators. It turns out that an electron can only have two possible spin states, "up" or "down" – such a particle is called a **spin-1/2** (pronounced "spin one-half") particle. The spin of an electron, as its name imply, add to the angular momentum of the electron-proton system. Since we modeled the electron as a point particle, this is not included in our discussion.

- *Static proton.* The proton mass is $M_{p^+} = 1.67 \times 10^{-24}$ g, while the electron mass is $m_e = 9.1 \times 10^{-28}$ g, i.e. the mass of the proton is about a thousand times more than that of an electron. While it is a good approximation then to model the electron as going around a static potential, in reality, the proton itself is affected by presence of the electron. We will ignore this effect.

8.2 Schrödinger's Equation in Spherical Coordinates

Before we study the Hydrogen Atom, let us work on our mathematical muscles by considering **Spherical Symmetric** Potentials. We will be old-fashioned, and look for solutions of the wavefunctions in

---

[20]What Bohr did at that time would be considered *phenomenology* these days – making stuff up without trying too hard to explain the underlying theory, yet another lesson for budding physicists about what is really important.
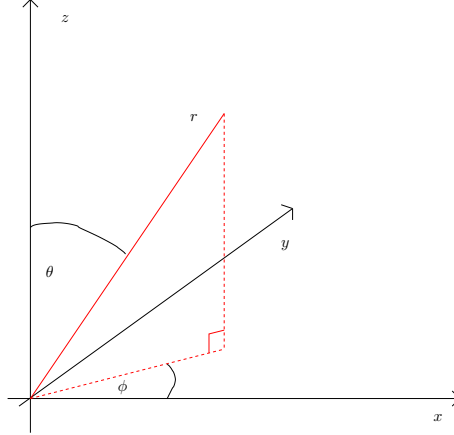
Figure 24: Spherical Coordinates.

coordinate basis[21], but instead of in Cartesian coordinates we will work in spherical coordinates fig. 24

$$
\begin{aligned}
x &= r \cos\phi \sin\theta \\
y &= r \sin\phi \sin\theta \\
z &= r \cos\theta \\
r &= \sqrt{x^2 + y^2 + z^2}.
\end{aligned}
\tag{367}
$$

The domain of the coordinates obey

$$
0 \le r \le \infty \; , \; 0 \le \theta \le \pi \; , \; 0 \le \phi < 2\pi
\tag{368}
$$

noting that the θ coordinate picks up both the poles at π and 0 as it runs from pointing in the $+z$ to the $-z$ directions.

Using the Chain Rule, we can rewrite the Laplacian ∇^2 in spherical coordinates as, for some function $f(r,\theta,\phi)$

$$
\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial \phi^2}.
\tag{369}
$$

The time-independent Schrödinger's Equation in 3 dimensions is

$$
-\frac{\hbar^2}{2m}\nabla^2 \chi_E(\mathbf{x}) + U(\mathbf{x})\chi_E(\mathbf{x}) = E\chi_E(\mathbf{x}),
\tag{370}
$$

so under a coordinate transformation to spherical coordinates this become, dropping the subscript E for now

$$
\boxed{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \chi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \chi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \chi}{\partial \phi^2}\right] + U(r,\theta,\phi)\chi = E\chi.}
\tag{371}
$$

The solution $\chi(r,\theta,\phi)$ can depend on all the coordinates of course.

For the rest of the class, we will specialize to spherically symmetric potential, so

$$
U(r,\theta,\phi) \to U(r).
\tag{372}
$$

---

[21]There is an equivalent energy-basis method akin to section 6.2, those interested may come and talk to me!

Spherical Symmetric Solutions (S-Waves): As practice, let us look for spherically symmetric solutions

$$\chi(r, \theta, \phi) \rightarrow \chi(r) \tag{373}$$

which are called **S-waves** – "S" for **S**pherically symmetric of course. The Laplacian in this case become the more manageable

$$\nabla^2 \chi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \chi}{\partial r} \right) = \frac{2}{r} \frac{\partial \chi}{\partial r} + \frac{\partial^2 \chi}{\partial r^2}, \tag{374}$$

so Schrödinger's Equation becomes

$$-\frac{\hbar^2}{2m} \left(\frac{2}{r} \frac{\partial \chi}{\partial r} + \frac{\partial^2 \chi}{\partial r^2} \right) + U(r)\chi(r) = E\chi(r), \tag{375}$$

where $0 \leq r \leq \infty$. Normalizability implies

$$
\begin{aligned}
\int_{\mathbb{R}^3} |\chi(r)|^2 \, dV &= \underbrace{\int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos\theta)}_{4\pi} \int_0^{\infty} dr \, r^2 |\chi|^2 \\
&= 4\pi \int_0^{\infty} dr \, r^2 |\chi|^2 \leq \infty
\end{aligned}
\tag{376}
$$

so this means that

$$
\begin{aligned}
\chi(r) &\longrightarrow 0 \quad \text{as} \quad r \rightarrow \infty \\
\chi(r) &\longrightarrow \text{finite} \quad \text{as} \quad r \rightarrow 0.
\end{aligned}
\tag{377}
$$

We now employ a trick, noting that

$$\frac{2}{r} \frac{\partial \chi}{\partial r} + \frac{\partial^2 \chi}{\partial r^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\chi) \tag{378}$$

so we can do a change of variables

$$S(r) \equiv r\chi(r) \tag{379}$$

where S stands for S-waves of course, such that Eq. (375) is now the familiar form

$$-\frac{\hbar^2}{2m} \frac{\partial^2 S}{\partial r^2} + U(r)S = ES. \tag{380}$$

This is simply a Schrödinger's Equation in 1 dimension r which you have spent many hours solving before, but with several differences

- $\chi(r)$ is finite at $r = 0$, hence $\chi(r) = S(r)/r \xrightarrow{r \rightarrow 0}$ finite. Using the L'Hopital rule

$$\lim_{r \rightarrow 0} \frac{S(r)}{r} = \lim_{r \rightarrow 0} \frac{dS/dr}{1} \tag{381}$$

so the condition on $\chi(0)$ requires $S'(r) \rightarrow$ finite and $S(r) = 0$.

- Normalizability condition Eq. (376).

- It is defined on $0 \leq r < \infty$.

The last condition, $0 \leq r < \infty$ provide us with a neat trick to find the solutions: we can assume that we are solving for the domain $-\infty < r < \infty$ assuming a potential with reflection symmetry $U(r) = U(-r)$, and then take only **odd** solutions (which obey the boundary condition $S(0) = 0$.) So now we can simply copy our solutions from all our hard work solving 1-D Schrödinger's problems with reflection symmetry, take the odd solutions and we are done!

Example: **Spherically Symmetric Harmonic Oscillator**

$$U(r) = \frac{1}{2}m\omega^2 r^2 \tag{382}$$

so we can just copy the spectrum from Eq. (284)

$$E_N = \left(N + \frac{1}{2}\right)\hbar\omega \tag{383}$$

and take the $N = 1, 3, 5, \ldots$ solutions.

8.3 S-waves of the Hydrogen Atom

We are now ready to take our first steps into finding the spectrum of the Hydrogen atom. The Hydrogen atom consists of a proton and an electron. Placing the proton at the origin of the spherical coordinate system, and by the assumptions we laid out at the end of section 8.1 the proton is fixed and not moving. It generates an electric field corresponding to the **Coulomb Potential**

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \tag{384}$$

As you may have learned in your Dynamics and Relativity class, the negative sign in front of the potential indicates that it is **attractive**, and we define the energy of the particle at rest at $r \to \infty$ to be $E = 0$. This means that the energy of the particle at $r < \infty$ will be *negative*.

Let's begin with Schrödinger's Equation Eq. (371) which we will rewrite as

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\Psi)\right] - \frac{1}{2mr^2}\underbrace{\left[\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]}_{-\hat{\mathbf{L}}^2\Psi} - \frac{e^2}{4\pi\epsilon_0 r}\Psi = E\Psi \tag{385}$$

where we have defined the **Total Angular Momentum Operator**

$$\hat{\mathbf{L}}^2 = -\left[\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{386}$$

In general the solution depends on all the coordinates $\Psi(r, \theta, \phi)$. Now we will assert that the general solution to a spherically symmetric potential $U(r)$ is of the following *separable form*

$$\boxed{\Psi_{nlm}(r, \theta, \phi) = \chi_{E_{n,l}}(r)Y_{l,m}(\theta, \phi)} \tag{387}$$

where $Y_{l,m}(\theta, \phi)$ is known as **Spherical Harmonics**. At the moment the indices (n, l, m) Eq. (387) look mysterious to you – they are called **quantum numbers**, with the names

n	**Principal/Energy**	$n = 1, 2, 3, \ldots$
l	**Total Angular Momentum**	$l = 0, 1, 2, \ldots, n-1$
m	**Magnetic Angular Momentum**	$-l \le m \le l$

Recalling the discussion on Simultaneous Eigenfunctions in section 7.2, in Eq. (322) where we have labeled the simultaneous eigenfunctions with the labels $\mathbf{p}$ and E to indicate their degeneracy, we similarly have labeled the quantum number (n, l, m) to indicate the degeneracy in the Energy, Total Angular Momentum and Magnetic Angular Momentum respectively. Also note that the radial wavefunction $\chi_{E_{n,l}}(r)$ depends on l – it will become clear[22] why this is so when we tackle the full spectrum of the Atom in section 8.6

---

[22]Apologies if this is very mysterious – I will offer a physical argument here: the actual shape of the radial wavefunction depends on the angular momentum of the particle, just as in classical physics the radial component of the trajectory depends on the angular momentum *if the total energy of the particles are the same.*

We will have a lot more to say about Angular Momentum in section 8.4, and what the indices are, and prove that Eq. (387) is indeed the most general normalizable solution. For now, we will look for solutions where $Y_{l,m}(\theta, \phi) = $ constant. This mean that we will look for S-wave solutions such that $\hat{\mathbf{L}}^2 \Psi_{nlm}(r) = 0$. At the risk of confusing you even further, we are going to look for solutions where $l = 0$, $m = 0$ – don't worry if you don't understand now.

We begin by making our equation look nicer by rescaling the coordinates

$$\epsilon = \frac{32\pi^2 \epsilon_0^2 \hbar^2}{m_e e^4} E \ , \ \zeta = \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} r, \tag{388}$$

such that they are in units of $\zeta = r/r_B$ Bohr Radii, and $\epsilon = E/E_R$ the Rydberg Energy. So not only we make the equation look nicer, we have given physical meaning to the coordinates.

In these units Schrödinger's Equation become

$$\frac{\partial^2 (\zeta \chi)}{\partial \zeta^2} + \left(\epsilon + \frac{2}{\zeta}\right) \zeta \chi = 0, \tag{389}$$

and we can again do the change of variables to the S S-wave (see Eq. (379))

$$S(\zeta) = \zeta \chi \tag{390}$$

so we get an even more simplified equation

$$\frac{\partial^2 S}{\partial \zeta^2} + \left(\epsilon + \frac{2}{\zeta}\right) S = 0. \tag{391}$$

Following our experience with the Harmonic Oscillator, we look for solutions where the wavefunction $S \to 0$ at $\zeta \to \infty$, so we suppress it with an exponential and try the following ansatz

$$S(\zeta) = g(\zeta) \exp(-\alpha \zeta) \tag{392}$$

where α is a real constant to be determined. We plug this into Eq. (391) to get

$$\frac{\partial^2 g}{\partial \zeta^2} - 2\alpha \frac{\partial g}{\partial \zeta} + \left(\frac{2}{\zeta} + \epsilon + \alpha^2\right) g = 0 \tag{393}$$

and now choosing $\alpha^2 = -\epsilon$ we get

$$\frac{\partial^2 g}{\partial \zeta^2} - 2\alpha \frac{\partial g}{\partial \zeta} + \frac{2}{\zeta} g = 0. \tag{394}$$

This equation has a power series solution

$$g(\zeta) = \sum_{k=1}^{\infty} a_k \zeta^k, \tag{395}$$

note that it starts at $k = 1$ not $k = 0$! Now, we plug this ansatz back into Eq. (393)

$$\sum_{k=1}^{\infty} k(k-1) a_k \zeta^{k-2} - \sum_{k=1}^{\infty} 2\alpha k a_k \zeta^{k-1} + \sum_{k=1}^{\infty} 2 a_k \zeta^{k-1} = 0 \tag{396}$$

which we can then do same trick as we did in the Simple Harmonic Oscillator by shifting the sum of the first term

$$\sum_{k=1}^{\infty} k(k-1) a_k \zeta^{k-2} = \sum_{k=1}^{\infty} k(k+1) a_{k+1} \zeta^{k-1} \tag{397}$$

to get the recurrence relation

$$a_{k+1} = \frac{2(\alpha k - 1)}{k(k+1)} a_k. \tag{398}$$

There are now two possibilities

- The series Eq. (395) terminates – $\exists\, n > 0$ such that $a_k = 0\ \forall\ k \geq n$

- The series Eq. (395) does not terminate – $\nexists\, n > 0$ such that $a_k = 0\ \forall\ k \geq n$

As you probably can guess, if the series does not terminate then it is divergent. Take the ratio at $k \to \infty$

$$a_{k+1} = \frac{2\alpha}{k} a_k \Rightarrow a_{k+1} \approx \frac{(2\alpha)^k}{k!} \tag{399}$$

which are the coefficients for the series expansion of $\exp(2\alpha\zeta)$, so $S(\zeta) \propto \exp(\alpha\zeta)$ and is clearly not physical as it blows up at $\zeta \to \infty$.

To terminate the series, there must exist some value $k = n$ in Eq. (398) such that the numerator is zero – this can be arrange by choosing the **Quantization Condition** for the Hydrogen atom

$$n = \frac{1}{\alpha} \to n^2 = -\frac{1}{\epsilon}. \tag{400}$$

Recalling that ϵ are in units of $E_R = m_e e^4/(32\pi^2 \epsilon_0^2 \hbar^2)$, the spectrum is then

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \tag{401}$$

which is exactly what was observed and predicted by the Bohr Model.

Finally, we can generate the wavefunctions in the usual way by using the recursion relation Eq. (398) to calculate the coefficients a_k for each n

$$\chi_n = \frac{e^{-\zeta/n}}{\zeta} \sum_{k=1}^{n} a_k \zeta^k. \tag{402}$$

The first three polynomials are given below

$$\begin{aligned}
\chi_1(\zeta) &= \exp(-\zeta) \\
\chi_2(\zeta) &= \left(1 - \frac{\zeta}{2}\right)\exp(-\zeta/2) \\
\chi_3(\zeta) &= \left(1 - \frac{2\zeta}{3} + \frac{2}{27}\zeta^3\right)\exp(-\zeta/3).
\end{aligned} \tag{403}$$

and the (unnormalized) wavefunctions are plotted in fig. 25.

We can normalize the eigenfuntions in the usual way. For example for χ_1,

$$\int_{\mathbb{R}^3} |\chi_1|^2\ dV = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) \int_0^\infty d\zeta\ \zeta^2 \exp[-2\zeta] = \pi \tag{404}$$

so the normalized eigenfunction is $\tilde{\chi}_1 = \sqrt{1/\pi}\chi_1$.

8.4 Angular Momentum Operators

In Classical Mechanics, the angular momentum $\mathbf{L}$ of a particle around a point O is the cross product of its distance $\mathbf{x}$ from O and its momentum $\mathbf{p}$

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}. \tag{405}$$

If furthermore, this particle is traveling about a spherically symmetric potential $U(\mathbf{x}) = U(r)$ around the origin O, then $\mathbf{L}$ *is a constant of motion*. Given the momentum
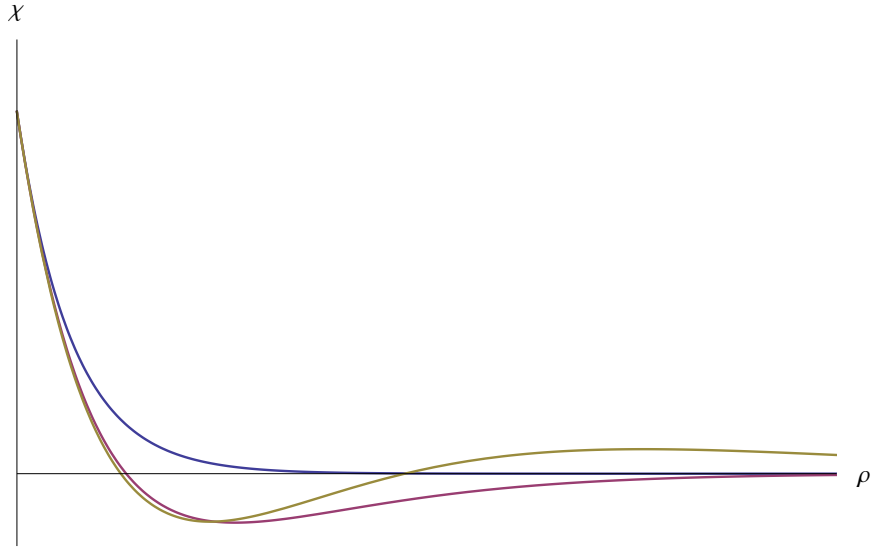
$$\mathbf{p} = m\mathbf{v} \tag{406}$$

Figure 25: The unnormalized wavefunctions for the first 3 S-states $(l, m = 0)$ of the Hydrogen atom. The number of nodes per wavefunction is simply n.
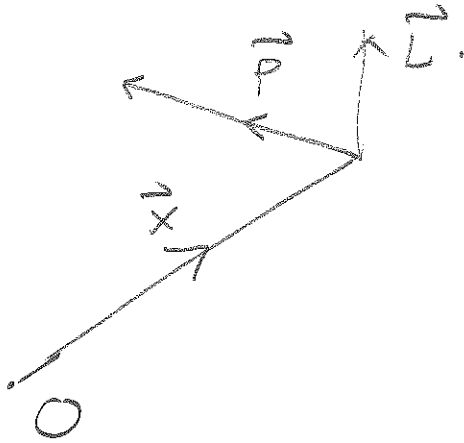

Figure 26: Classical Angular Momentum.

then

$$
\begin{aligned}
\frac{d\mathbf{L}}{dt} &= m\frac{d\mathbf{x}}{dt} \times \mathbf{v} + m\mathbf{x} \times \frac{d\mathbf{v}}{dt} \\
&= 0 + m\mathbf{x} \times \frac{\mathbf{F}}{m}
\end{aligned}
\tag{407}
$$

where we have used Newton's Law Eq. (1). But $\mathbf{F} \parallel \mathbf{x}$ for spherically symmetric potential about O, so the last term vanishes and hence $\mathbf{L}$ is conserved. This means that the *total angular momentum* $\mathbf{L^2}$ is just a number.

In Quantum Mechanics, when we discussed position and momentum, we "promote" the variables into operators, i.e.

$$
\mathbf{x} \to \hat{\mathbf{x}} \ , \ \mathbf{p} \to \hat{\mathbf{p}}.
\tag{408}
$$

We have seen in section 3.3 with the Hamiltonian operator $\hat{H}$ that we can similarly carry this through for the classical Hamiltonian by "giving variables hats". It turns out that, we can do exactly the same

73

for the **Angular Momentum operator**[23]

$$\boxed{\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = \hat{\mathbf{x}} \times (-i\hbar\nabla)}. \tag{409}$$

In component form $\hat{\mathbf{x}} = (\hat{x}, \hat{y}, \hat{z})$ and $\hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$, so

$$\hat{\mathbf{L}} = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x). \tag{410}$$

In coordinate basis,

$$\hat{L}_x = -i\hbar\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -i\hbar\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = -i\hbar\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right).$$

- **$\hat{\mathbf{L}}$ is Hermitian**: Check for $\hat{L}_x$: for any two functions $\phi(\mathbf{x})$ and $\psi(\mathbf{x})$, for $\hat{L}_x$

$$
\begin{aligned}
\int_{\mathbb{R}^3} \phi^\dagger(\mathbf{x})\hat{L}_x\psi(\mathbf{x})\ dV &= \int_{\mathbb{R}^3} \phi^\dagger(\mathbf{x})(-i\hbar)\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right)\psi(\mathbf{x})\ dV \\
&= -\int_{\mathbb{R}^3}(-i\hbar)\left[\frac{\partial}{\partial z}(\phi^\dagger\hat{y}) - \frac{\partial}{\partial y}(\phi^\dagger\hat{z})\right]\psi(\mathbf{x})dV + \cancel{\text{boundary terms}} \\
&= \int_{\mathbb{R}^3}(-i\hbar)^*\left[\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right]\phi^\dagger\psi\ dV \\
&= \int_{\mathbb{R}^3}\left(\hat{L}_x\phi(\mathbf{x})\right)^\dagger\psi(\mathbf{x})\ dV
\end{aligned}
\tag{411}
$$

which proves its Hermiticity. We have used the fact that the order of the partial differention with respect to the coordinates not matter (or we can also say that $\hat{p}_x$ commute with $\hat{p}_y$.) The algebra is similar for $\hat{L}_y$ and $\hat{L}_z$.

- They do not commute with each other. These are the **Angular Momentum Canonical Commutator Relationships**

$$\boxed{[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z\ ,\ [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x\ ,\ [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y} \tag{412}$$

Since they do not commute, this means that unlike the Classical case where we can measure $\mathbf{L}$ to arbitrary accuracy, *we cannot simultaneously obtain to arbitray accuracy all the three components of the Angular Momentum in Quantum Mechanics!* This non-commutativity has its root cause in the non-commutativity of $\hat{x}$ and $\hat{p}$ – to measure $\mathbf{L}$ to arbitrary accuracy, we need to measure $\mathbf{x}$ and $\mathbf{p}$ to arbitrary accuracy, but as we learned from the Uncertainty Principle, this is not possible in Quantum Mechanics since the measurement of one affect the other.

We want to derive the commutators Eq. (412) from the commutator relations for $\hat{x}$ and $\hat{p}$, but before we begin crunching through the algebra, let us also introduce some **Operator Identities**, which would be useful for many applications. For any three operators $\hat{A}$, $\hat{B}$ an $\hat{C}$, the following identities hold:

$$
\begin{aligned}
\text{Identity 1}\ \ [\hat{A} - \hat{B}, \hat{C}] &= \hat{A}\hat{C} - \hat{B}\hat{C} - \hat{C}\hat{A} + \hat{C}\hat{B} \\
&= [\hat{A}, \hat{C}] - [\hat{B}, \hat{C}]
\end{aligned}
\tag{413}
$$

---

[23]*The Angular Momentum operators are generators of rotation and can be "derived" in a similar way to the way we derived the Momentum operator, see Eq. (79), so we do not have to make this ansatz if we want to be rigorous.*

$$\text{Identity 2 } [\hat{A}, \hat{B}\hat{C}] \quad = \quad \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A}$$
$$= \quad \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A}$$
$$= \quad [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \tag{414}$$

And if $[\hat{A}, \hat{C}] = [\hat{B}, \hat{C}] = 0$, then Identity 3 holds

$$\text{Identity 3 } [\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} = \hat{C}[\hat{A}, \hat{B}]. \tag{415}$$

Finally, we have an important identity (which you should try to prove yourself)

$$\text{Jacobi Identity } [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0. \tag{416}$$

Armed with these identities, we can now calculate

$$[\hat{L}_x, \hat{L}_y] \quad = \quad [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z]$$
$$= \quad [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{z}\hat{p}_y,] \text{ using Identity 1} \tag{417}$$

The first term yields

$$[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] = \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] \tag{418}$$

since $\hat{p}_x$ commutes with $\hat{y}$, $\hat{z}$, $\hat{p}_z$ and $\hat{y}$ commutes with $\hat{z}$, $\hat{p}_x$, $\hat{p}_z$, and using Identity 3. Similarly, the last term is

$$[\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z]. \tag{419}$$

Meanwhile the middle two terms are zeroes because all the terms inside the commutator commute with each other, hence we get

$$[\hat{L}_x, \hat{L}_y] \quad = \quad \hat{x}\hat{p}_x \underbrace{[\hat{p}_z, \hat{z}]}_{-i\hbar} + \hat{x}\hat{p}_y \underbrace{[\hat{z}, \hat{p}_z]}_{i\hbar}$$
$$= \quad i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \tag{420}$$
$$= \quad i\hbar\hat{L}_z, \tag{421}$$

where we have used the canonical commutator relations for $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$. The calculation for $\hat{L}_y$ and $\hat{L}_z$ are similar.

We can also write down the **Total Angular Momentum Operator $\hat{\mathbf{L}}^2$** in analogy to the Classical counterpart

$$\boxed{\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2} \tag{422}$$

Properties of the $\hat{\mathbf{L}}^2$:

- **$\hat{\mathbf{L}}^2$ is Hermitian**: Since $\hat{L}_x$ is Hermitian, $\hat{L}_x^2$ must also be Hermitian and the same for $\hat{L}_y$ and $\hat{L}_z$. Hence $\hat{\mathbf{L}}^2$ is also Hermitian.

- It commutes with all the Angular Momentum operators

$$\boxed{[\hat{L}_x, \hat{\mathbf{L}}^2] = 0} \ , \quad \boxed{[\hat{L}_y, \hat{\mathbf{L}}^2] = 0} \ , \quad \boxed{[\hat{L}_z, \hat{\mathbf{L}}^2] = 0.} \tag{423}$$

Proof: Show for $\hat{L}_x$ term by term (via Identity 1)

$$[\hat{L}_x, \hat{L}_x^2] = 0 \tag{424}$$

$$[\hat{L}_x, \hat{L}_y^2] \quad = \quad [\hat{L}_x, \hat{L}_y]\hat{L}_y + \hat{L}_y[\hat{L}_x, \hat{L}_y] \text{ by Identity 2}$$
$$= \quad i\hbar(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z) \tag{425}$$

and similarly

$$\begin{aligned} [\hat{L}_x, \hat{L}_z^2] &= [\hat{L}_x, \hat{L}_z]\hat{L}_z + \hat{L}_z[\hat{L}_x, \hat{L}_z] \quad \text{by Identity 2} \\ &= -i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y). \end{aligned} \tag{426}$$

Totalling them up

$$[\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] = 0. \tag{427}$$

The calculation is identical for $\hat{L}_y$ and $\hat{L}_z$. $\square$.

Index Notation: Sometimes it does get tiresome writing the components of $\hat{\mathbf{L}}$ out each time. So let us introduce some slick notation. We assign the labels (x_1, x_2, x_3) to the Cartesian coordinates (x, y, z). So for any two 3 dimensional vectors $\mathbf{A}$ and $\mathbf{B}$, $A_1 = A_x$, and so $\mathbf{A} = A_i$. The dot product is then $\mathbf{A} \cdot \mathbf{B} = \delta_{ij}A_iA_j$.

We also introduce the **Levi-Civita Symbol** ϵ_{ijk},

$$\epsilon_{ijk} = \begin{cases} +1 & \text{for even no. interchange of indices} \\ -1 & \text{for odd no. interchange of indices} \end{cases} \tag{428}$$

so $\epsilon_{213} = -1$, $\epsilon_{231} = +1$, etc. Using this notation, cross products can be written as

$$\mathbf{A} \times \mathbf{B} = \epsilon_{ijk}A_jB_k. \tag{429}$$

So now we can write $\hat{\mathbf{L}}$ in the super compact form

$$\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k. \tag{430}$$

In this notation, then the canonical commutator relations are

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \ , \ [\hat{x}_i, \hat{x}_j] = 0 \ , \ [\hat{p}_i, \hat{p}_j] = 0, \tag{431}$$

while the Angular Momentum canonical commutators is

$$\boxed{[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k.} \tag{432}$$

We can then show

$$\begin{aligned} [\hat{L}_i, \hat{x}_l] &= \epsilon_{ijk}\hat{x}_j\hat{p}_k\hat{x}_l - \epsilon_{ijk}\hat{x}_l\hat{x}_j\hat{p}_k \\ &= \epsilon_{ijk}\hat{x}_j(\hat{x}_l\hat{p}_k - i\hbar\delta_{lk}) - \epsilon_{ijk}\hat{x}_l\hat{x}_j\hat{p}_k \ , \ \text{using } [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \\ &= -i\hbar\epsilon_{ijl}\hat{x}_j \\ &= i\hbar\epsilon_{ilj}\hat{x}_j \end{aligned} \tag{433}$$

and similarly

$$\begin{aligned} [\hat{L}_i, \hat{p}_l] &= \epsilon_{ijk}\hat{x}_j\hat{p}_k\hat{p}_l - \epsilon_{ijk}\hat{p}_l\hat{x}_j\hat{p}_k \tag{434} \\ &= \epsilon_{ijk}\hat{x}_j\hat{p}_k\hat{p}_l - \epsilon_{ijk}(\hat{x}_j\hat{p}_l - i\hbar\delta_{jl})\hat{p}_k \ , \ \text{using } [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \\ &= i\hbar\epsilon_{ilk}\hat{p}_k. \tag{435} \end{aligned}$$

You can practice your index juggling kungfu to derive the following relation

$$[\hat{L}_i, \hat{x}_j^2] = 2i\hbar\epsilon_{ijk}\hat{x}_j\hat{x}_k \tag{436}$$

so this implies that

$$[\hat{L}_i, \hat{\mathbf{x}}^2] = 0. \tag{437}$$

And similarly for momentum

$$[\hat{L}_i, \hat{p}_j^2] = 2i\hbar\epsilon_{ijk}\hat{p}_j\hat{p}_k \tag{438}$$

implies

$$[\hat{L}_i, \hat{\mathbf{p}}^2] = 0. \tag{439}$$

8.5 Eigenfunctions and Eigenvalues of Angular Momentum Operators

With all this algebra done and relations derived, we are now ready to state an important result.

Simultaneous Eigenfunctions of the Hydrogen Atom: *Given a Coulomb potential, there exist a basis of simultaneous eigenfunctions of* $\hat{H}$, $\hat{\mathbf{L}}^2$ *and any one of the* $\{\hat{L}_x, \hat{L}_y, \hat{L}_z\}$ *observables.*

Proof: Recall that the Hamiltonian for the Hydrogen Atom is

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\hat{r}) = \frac{\hat{\mathbf{p}}^2}{2m} + U(\sqrt{\hat{x}^2 + \hat{y}^2 + \hat{z}^2}), \tag{440}$$

and hence using the commutators we derived above Eq. (437) and Eq. (439), it clearly commutes with $\hat{\mathbf{L}}$

$$[\hat{H}, \hat{\mathbf{L}}] = 0 \tag{441}$$

and via Identity 2, also commutes with $\hat{\mathbf{L}}^2$

$$[\hat{H}, \hat{\mathbf{L}}^2] = 0. \tag{442}$$

Also via Eq. (423)

$$[\hat{\mathbf{L}}, \hat{\mathbf{L}}^2] = 0. \tag{443}$$

However, since $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, i.e. the angular momentum operators do not commute with each other, we have to choose a direction via Eq. (443). By convention we choose $\hat{L}_z$. Hence we have three *mutually commuting operators* $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z\}$, and hence they share a complete basis of eigenfunctions. $\square$

Harking back to section 8.3, we stated that the eigenfunction is Eq. (387)

$$\Psi_{nlm}(r, \theta, \phi) = \chi_{E_n}(r)Y_{l,m}(\theta, \phi) \tag{444}$$

and we have introduced the rather mysterious indices (n, l, m). Now it is clear that the indices label the eigenvalues of the three mutually commuting observables $\hat{H}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. In section 8.3 we found the S-waves solution of Ψ_{nlm}, so $Y(\theta, \phi) =$ constant. In this section, we will now solve for non-spherically symmetric solutions, and explain the meaning of l and m.

For non-spherically symmetric wavefunctions $Y(\theta, \phi)$ is not a constant. Since $[\hat{L}_z, \hat{\mathbf{L}}^2] = 0$, we know there exists a *simultaneous basis of eigenfunctions* such that

$$\hat{L}_z Y_{l,m}(\theta, \phi) = m\hbar Y_{l,m}(\theta, \phi), \tag{445}$$

and

$$\hat{\mathbf{L}}^2 Y_{l,m}(\theta, \phi) = l(l+1)\hbar^2 Y_{l,m}(\theta, \phi). \tag{446}$$

Here the **Magnetic Angular Momentum** $m\hbar$ and the **Total Angular Momentum** $l(l+1)\hbar^2$ are eigenvalues of $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ respectively and the $\hbar$ convention to ensure that l and m are dimensionless numbers. For the moment, the $l(l+1)$ looks unmotivated – you could replace it with λ if you like but we are anticipating the answer.

First, we want to write the $\hat{\mathbf{L}}$ in spherical coordinates

$$\hat{L}_x = i\hbar\left(\cos\phi\cot\theta\frac{\partial}{\partial\phi} + \sin\phi\frac{\partial}{\partial\theta}\right)$$

$$\hat{L}_y = i\hbar\left(\sin\phi\cot\theta\frac{\partial}{\partial\phi} - \cos\phi\frac{\partial}{\partial\theta}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

where we have picked the coordinate systems such that the $\hat{L}_z$ has the simplest looking form – this is the reason why we have chosen $\hat{L}_z$ to be the 3rd commuting observable because it simplifies the calculation.

The Total Angular Momentum operator has been derived way back in Eq. (386)

$$\hat{\mathbf{L}}^2 = -\left[\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{447}$$

Let's solve for the eigenfunctions. We will drop the (l,m) subscript from $Y(\theta,\phi)$ for now since we are going to pretend we don't know the answer yet:

- **Magnetic Angular Momentum** m: A choice of Y which satisfies Eq. (445) is $Y(\theta,\phi) = A(\theta)e^{im\phi}$ for some arbitrary $A(\theta)$, so

$$\hat{L}_z Y(\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}A(\theta)e^{im\phi} = m\hbar Y(\theta,\phi). \tag{448}$$

The wavefunction should be the same if we spin it around by 2π, i.e. $Y(\theta,\phi) = Y(\theta,\phi+2\pi)$, hence this means that

$$e^{2\pi im} = 1 \;\Rightarrow\; m \in \mathbb{Z} \tag{449}$$

i.e. m is *quantized*[24].

- **Total Angular Momentum** l: We want to solve

$$\hat{\mathbf{L}}^2 Y(\theta,\phi) = l(l+1)\hbar^2 Y(\theta,\phi). \tag{450}$$

Using Eq. (386) and $Y(\theta,\phi) = A(\theta)e^{im\phi}$ we get

$$-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A(\theta)}{\partial\theta}\right) + \frac{m^2\hbar^2}{\sin^2\theta}A(\theta) = l(l+1)\hbar^2 A(\theta), \tag{451}$$

with the condition

$$\boxed{-l \le m \le l \;,\; l(l+1) > 0 \;,\; l = 0,1,2,3,\dots} \tag{452}$$

This equation is called the **Associated Legendre equation** which has solutions in closed form. We won't go into the details of solving it. Note that l *is also quantized* and the limits on m per l means that *for each l there is a $2l+1$-fold degeneracy.*

The *non-singular* and hence normalizable solutions are labeled by l and m and is generated by

$$A(\theta) = (\sin\theta)^{|m|}\frac{d^{|m|}}{(d\cos\theta)^{|m|}}P_l(\cos\theta) = P_{l,m}(\theta) \tag{453}$$

where $P_l(\cos\theta)$ are **Legendre Polynomials**.

The combination $A(\theta)e^{im\phi} = Y_{l,m}(\theta,\phi)$ are called **Spherical Harmonics**. In its full glory (you don't have to remember this), the normalized wavefunction is

$$Y_{l,m}(\theta,\phi) = (-1)^m\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}P_{l,m}(\cos\theta)e^{im\phi}. \tag{454}$$

Here are some normalized eigenfunctions of $Y_{l,m}(\theta,\phi)$ for the first few modes

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \;,\; Y_{1,1} = -\sqrt{\frac{3}{8\pi}}e^{i\phi}\sin\theta$$

$$Y_{1,0} = \sqrt{\frac{3}{8\pi}}\cos\theta \;,\; Y_{2,2} = \sqrt{\frac{15}{32\pi}}e^{2i\phi}\sin^2\theta.$$

Some properties of Spherical Harmonics:

---

[24]*We have been a bit too fast in assuming that the wavefunction must be the same after 2π rotation – we have been thinking classically. Recall that we said in the first lecture, there exist observables which has no classical counterpart. In this case, some wavefunctions return to be "the same" after a 4π rotation. So the condition becomes $e^{4\pi im} = 1$ or m can take also half-integers. Such wavefunctions, in a 2π rotation, returns to the same wavefunction with a minus sign. Particles with such weird wavefunctions are called spin-1/2 particles, and in fact electrons are such particles, but we have chosen to ignore it for the moment as we explained at the start of this lecture*.

- The **Orthonomality condition** is an integral over all the sphere S_2,

$$\int_{S_2} d\Omega \, Y_{l,m}(\theta, \phi)^* Y_{l',m'}(\theta, \phi) = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) d\theta \, Y_{l,m}(\theta, \phi)^* Y_{l',m'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}. \quad (455)$$

- **Completeness**: For *any* function of two angles (θ, ϕ), we can express it as a double sum over (l, m)

$$f(\theta, \phi) = \sum_{l=0}^{l=\infty} \sum_{m=-l}^{m=l} C_{l,m} Y_{l,m}(\theta, \phi) \, , \, C_{l,m} \in \mathbb{C}. \quad (456)$$

- **Degeneracy**: For each value $l = 0, 1, 2, 3, \ldots$, m can take $m = -l, -l+1, \ldots, 0, 1, \ldots, +l$ possible values hence there is a $2l + 1$-fold degeneracy.

8.6 The Full Spectrum of the Hydrogen Atom

We are now ready to calculate the full spectrum and its associated eigenfunctions of the hydrogen atom. We begin by rewriting the time-independent Schrödinger's Equation in spherical coordinates Eq. (385)

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\Psi_{nlm})\right] + \frac{\hat{\mathbf{L}}^2}{2mr^2}\Psi_{nlm} - \frac{e^2}{4\pi\epsilon_0 r}\Psi_{nlm} = E\Psi_{nlm} \quad (457)$$

where we have replaced all the angular derivatives with the handy Total Angular Momentum operator $\hat{\mathbf{L}}^2$

$$\hat{\mathbf{L}}^2 = -\left[\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad (458)$$

and given the eigenfunction Ψ_{nlm} its rightful indices (n, l, m)

$$\Psi_{nlm}(r, \theta, \phi) = \chi_{E_{n,l}}(r) Y_{l,m}(\theta, \phi). \quad (459)$$

Previously when we calculated S-waves solution in section 8.3 we have dropped the $\hat{\mathbf{L}}^2 \Psi_{nlm}$ term in the calculation. This corresponds to $Y_{l,m}$ which is independent of ϕ and θ, i.e. a constant. By looking at the definition for the Spherical Harmonics Eq. (454), we see that this term correspond to the $Y_{0,0}$ term. Hence the solutions we have in section 8.3 corresponds to the Ψ_{n00} i.e. $(n, l = 0, m = 0)$ eigenfunctions.

Now want to calculate the rest of the spectrum where $l \neq 0$ and $m \neq 0$. Restoring the $\hat{\mathbf{L}}^2 \Psi_{nlm}$ term, and using its eigenvalue equation Eq. (446) we get

$$\hat{\mathbf{L}}^2 \Psi_{nlm} = \chi_{E_{n,l}}(r) \hat{\mathbf{L}}^2 Y_{l,m}(\theta, \phi) = \chi_{E_{n,l}}(r)[l(l+1)\hbar^2] Y_{l,m}(\theta, \phi) \quad (460)$$

and plugging this back into Eq. (457) we get

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\Psi_{nlm})\right] + \frac{l(l+1)\hbar^2}{2mr^2}\Psi_{nlm} - \frac{e^2}{4\pi\epsilon_0 r}\Psi_{nlm} = E\Psi_{nlm}. \quad (461)$$

All our hard work in the previous section has paid off – the horrible looking angular derivatives have been replaced by a benign looking term *which looks like an extra l-dependent term in the potential*

$$\text{Effective Potential} \quad U_{\text{eff}} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2}. \quad (462)$$

This extra term scales like $1/r^2$ and has *positive* sign compared to the Coulomb potential, so it is *repulsive* and dominates at small r but decays faster than the Coulomb potential at large r, see fig. 27. Hence the effect of angular momentum on the electron is to push its wavefunction to a large r – this is eminently sensible.
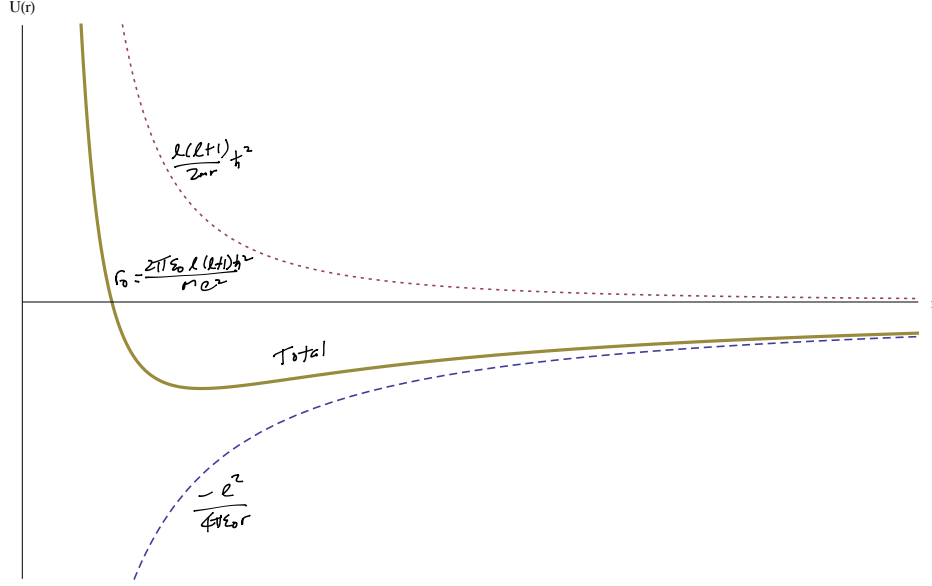
Figure 27: The effective potential for the Hydrogen Atom is a sum of the Coulomb term and a contribution from the angular momentum.

From Eq. (461), since, $Y_{l,m}(\theta, \phi)$ is independent of r, we can now drop the $Y_{l,m}(\theta, \phi)$ to get

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\chi_{E_{n,l}})\right] + \frac{l(l+1)\hbar^2}{2mr^2}\chi_{E_{n,l}} - \frac{e^2}{4\pi\epsilon_0 r}\chi_{E_{n,l}} = E\chi_{E_{n,l}}. \tag{463}$$

We will drop the subscript $E_{n,l}$ to simply notation from now on.

This is just a 2nd order ODE in r, and we follow the exact same steps as in section 8.3. First we rescale the energy and radius to the Ryberg energy and the Bohr Radius

$$\epsilon = \frac{32\pi^2\epsilon_0^2\hbar^2}{m_e e^4}E \ , \ \zeta = \frac{m_e e^2}{4\pi\epsilon_0\hbar^2}r, \tag{464}$$

to get

$$\frac{\partial^2(\zeta\chi)}{\partial\zeta^2} + \left(\epsilon + \frac{2}{\zeta} - \frac{l(l+1)}{\zeta^2}\right)\zeta\chi = 0. \tag{465}$$

Comparing this to the S-wave case Eq. (389) we have acquired an extra $l(l+1)/\zeta^2$ in the potential. Again, we can do the change of variables trick

$$R(\zeta) = \zeta\chi \tag{466}$$

to get the even more simplified equation

$$\frac{\partial^2 R}{\partial\zeta^2} + \left(\epsilon + \frac{2}{\zeta} - \frac{l(l+1)}{\zeta^2}\right)R = 0. \tag{467}$$

Pluging in the usual ansatz for normalizable wavefunctions

$$R(\zeta) = g(\zeta)\exp(-\alpha\zeta) \tag{468}$$

we obtain

$$\frac{\partial^2 g}{\partial\zeta^2} - 2\alpha\frac{\partial g}{\partial\zeta} + \left(\frac{2}{\zeta} - \frac{l(l+1)}{\zeta^2} + \epsilon + \alpha^2\right)g = 0. \tag{469}$$

Choosing $\alpha^2 = -\epsilon$ – note that this implies that $E < 0$ which is completely sensible since the potential is negative – we get,

$$\frac{\partial^2 g}{\partial\zeta^2} - 2\alpha\frac{\partial g}{\partial\zeta} + \left(\frac{2}{\zeta} - \frac{l(l+1)}{\zeta^2}\right)g = 0. \tag{470}$$

So far we have been following what we have done in solving the S-waves solution. Now we can try the power law solution

$$g(\zeta) = \sum_{k=1}^{\infty} a_k \zeta^k. \qquad (471)$$

This gets us

$$\sum_{k=1}^{\infty} k(k-1)a_k\zeta^{k-2} - \sum_{k=1}^{\infty} 2\alpha k a_k \zeta^{k-1} + \sum_{k=1}^{\infty} 2a_k \zeta^{k-1} - l(l+1)\sum_{k=1}^{\infty} a_k \zeta^{k-2} = 0 \qquad (472)$$

where we have acquired an extra $l(l+1)$ dependent term at the end compared to Eq. (396). Shfting the first term as usual

$$\sum_{k=1}^{\infty} k(k-1)a_k\zeta^{k-2} = \sum_{k=1}^{\infty} k(k+1)a_{k+1}\zeta^{k-1} \qquad (473)$$

and shifting the last term in the following way by taking out the first term in the sum

$$-l(l+1)\sum_{k=1}^{\infty} a_k\zeta^{k-2} = -l(l+1)\left(\frac{a_1}{\zeta} + \sum_{k=1}^{\infty} a_{k+1}\zeta^{k-1}\right) \qquad (474)$$

the differential equation becomes

$$\sum_{k=1}^{\infty} \left[(k(k+1) - l(l-1))a_{k+1} - 2\alpha k a_k + 2a_k\right]\zeta^{k-1} - l(l+1)\frac{a_1}{\zeta} = 0. \qquad (475)$$

From Eq. (475), we can see that a_1 is the only term proportional to $1/\zeta$ and hence $a_1 = 0$ (this also makes sense physically – the wavefunction must not blow up at $\zeta = 0$), hence setting the other terms to zero we finally get the recurrence relation

$$a_{k+1} = \frac{2(\alpha k - 1)}{k(k+1) - l(l+1)} a_k. \qquad (476)$$

Again, it is fruitful to compare this to the S-waves relation Eq. (398) – the extra $l(l+1)$ term in the potential has ended up as an extra term in the denominator of the relation.

It is clear that the series must terminate to be convergence since at $k \to \infty$ the recurrence relation has the same form as the S-waves case. To terminate the series, we apply the Quantization Condition i.e $\exists\, n > 0$ such that for $a_k = 0\ \forall\ k \geq n$, leading to

$$n = \frac{1}{\alpha} \to n^2 = -\frac{1}{\epsilon}. \qquad (477)$$

But wait! The extra $l(l+1)$ term in the denominator also gives an *extra* condition: $k \neq l$ else a_{k+1} becomes infinite! Combining this fact that we have set $a_1 = 0$, this means that $a_1 = a_2 = a_3 = \cdots = a_l = 0$. The series' non-vanishing terms then starts from a_{l+1}, a_{l+2} and so forth until a_n.

Putting all these together, this means that for any l there are many solutions for $g_{En,l}$ where $n \geq l+1$, each with energy using Eq. (477)

$$E_n = -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}. \qquad (478)$$

This explains our seemingly mysterious labeling of $\chi_{E_{n,l}}$ with l – the radial wavefunction depends on both the principal quantum number n and l.

Thus we have solved for the wavefunctions which for any given (n, l, m) subject to $n \geq l+1$ and $-l \leq m \leq l$

$$\boxed{\Psi_{nlm} = \chi_{E_{n,l}}(r)Y_{l,m}(\theta, \phi)} \qquad (479)$$

and using Eq. (466) and Eq. (468)

$$\chi_{E_{n,l}}(r) = e^{-\zeta/n} \sum_{k=l+1}^{n} a_k \zeta^{k-1}. \tag{480}$$

Degeneracy of the Full Hydrogen Spectrum

We now summarize the degeneracy of the Hydrogen Spectrum, which pictorially can be plotted as fig. 28:

- The energy spectrum is the same as the Bohr Model.

- For each Principal value of n, there exists a n-fold degeneracy in $l = 0, 1, \ldots, n-1$ Total Angular Momentum modes with associated radial wavefunctions $\chi_{E_{n,l}}$.

- For each Total Angular Momentum value of l, there exists a $2l+1$-fold degeneracy in $m = -l, -l+1, \ldots, 0, 1, \ldots, l$ in Magnetic Angular Momentum modes, with angular wavefunctions $Y_{l,m}(\theta, \phi)$.

- Total degeneracy per level n is
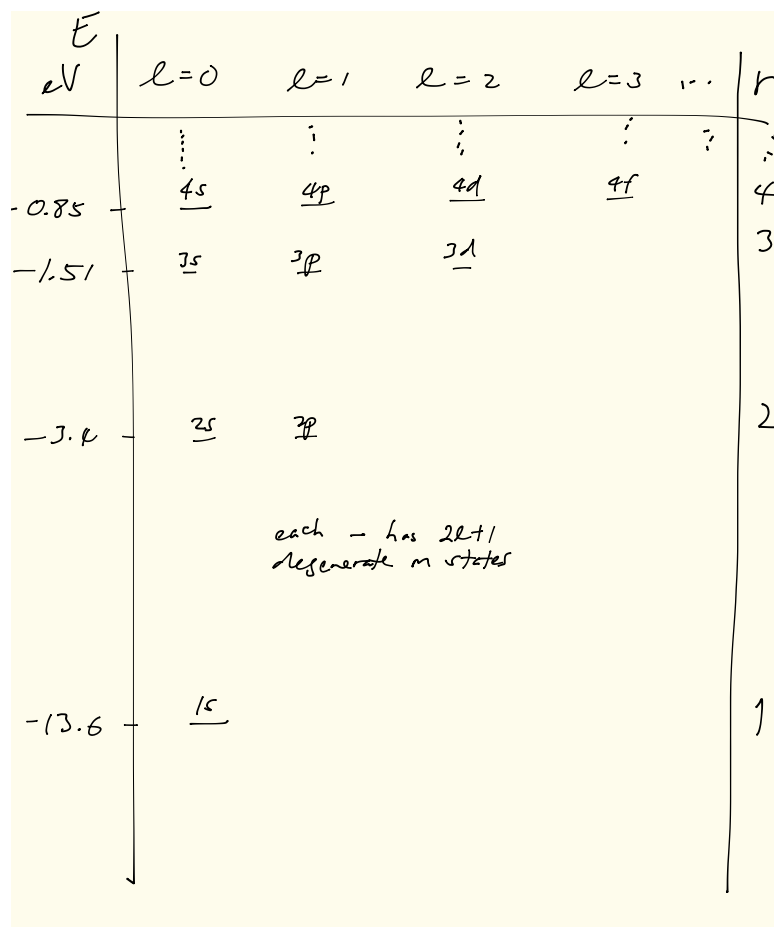
$$D(n) = \sum_{l=0}^{n-1} (2l+1) = n^2. \tag{481}$$

Figure 28: The full spectrum the Hydrogen atom. The l quantum numbers are historically labeled s, p, d, f, etc. The left hand column is the energy required to eject the electron into infinity, in units of Electron Volts (eV). For each (n, l) pair there is a $2l + 1$ degenereacy in the m Magnetic Angular Momentum numbers. Due to the spin-1/2 nature of electrons, for each degeneracy electrons can also take an "up" or "down" state – this we do not study in this class.

9   *Epilogue : Love and Quantum Mechanics

> *'cause I'll die if I saw you, and*
> *I'll die if I didn't see you there.*

> John Mayer

In these lectures, we have been dealing with *states of singular things* by which we mean a single particle, a single up/down state, a single cat etc. However, the weirdness of quantum mechanics is best demonstrated when we have more than one thing, and those things are *entangled* – roughly speaking their wavefunctions overlap and interact in non-trivial way.

Let's now go back to our old friend, the qubit. Before we begin, let's introduce some cool new notation. A state ψ can be represented by

$$\psi \equiv |\psi\rangle \tag{482}$$

The $|\rangle$ is called a **ket**. For the purpose of this lecture, think of it simply as a funky symbol for a column vector. The Hermitian conjugate of the ket is

$$\psi^\dagger \equiv \langle\psi| \tag{483}$$

where $\langle|$ is called a **bra**. So the dot product of two states ψ_1 and ψ_2

$$\psi_1^\dagger \psi_2 = \psi_1 \cdot \psi_2 \equiv \langle\psi_1|\psi_2\rangle \tag{484}$$

makes a **bra-ket**. Let's also shorten our notation for the up and down states with arrows

$$|\uparrow\rangle \equiv \chi_{\text{up}} \ , \ |\downarrow\rangle \equiv \chi_{\text{down}}. \tag{485}$$

and their Hermitian Conjugates

$$\langle\uparrow| \equiv \chi_{\text{up}}^\dagger \ , \ \langle\downarrow| \equiv \chi_{\text{down}}^\dagger. \tag{486}$$

So in this notation, the qubit is represented by

$$|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle. \tag{487}$$

The probability amplitude of measuring an up and down state, via Postulate 2 is then achieved by "completing the braket[25]"

$$\langle\uparrow|\psi\rangle = \langle\uparrow|(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) = \alpha \tag{488}$$

where we have used $\langle\uparrow|\uparrow\rangle = 1$ and $\langle\uparrow|\downarrow\rangle = 0$.

9.1   Entanglement : The Einstein-Podolsky-Rosen Paradox

You are experts in working with a single qubit, but how do we describe the state of two different qubits, ψ_1 and ψ_2?

If they are physically separate states, we can describe them simply as a pair of qubits

$$|\psi_1\rangle = \alpha_1|\uparrow\rangle + \beta_1|\downarrow\rangle \ , \ |\psi_2\rangle = \alpha_2|\uparrow\rangle + \beta_2|\downarrow\rangle \tag{489}$$

so the measurement of one does not affect the other. However, there is another possible way in which they can interact – as **product states** in the following way

$$|\Psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle \tag{490}$$

---

[25]In this notation the wavefunction that you studied in this lectures is $\psi(x) = \langle x|\psi\rangle$, i.e. it is an amplitude.

where $\otimes$ is the product of two matrices. In its full amazingly ugly glory this is

$$|\psi_1\rangle \otimes |\psi_2\rangle = \begin{pmatrix} \alpha_1 \begin{pmatrix} \alpha_2 \\ \beta_2 \end{pmatrix} \\ \beta_1 \begin{pmatrix} \alpha_2 \\ \beta_2 \end{pmatrix} \end{pmatrix} \tag{491}$$

which you can see how unwieldy these are so we won't ever use this notation. Instead, we write

$$\begin{aligned} |\Psi\rangle &= \alpha_1\alpha_2|\uparrow\rangle_1|\uparrow\rangle_2 + \alpha_1\beta_2|\uparrow\rangle_1|\downarrow\rangle_2 + \beta_1\alpha_2|\downarrow\rangle_1|\uparrow\rangle_2 + \beta_1\beta_2|\downarrow\rangle_1|\downarrow\rangle_2 \\ &= \alpha_1\alpha_2|\uparrow\uparrow\rangle + \alpha_1\beta_2|\uparrow\downarrow\rangle + \beta_1\alpha_2|\downarrow\uparrow\rangle + \beta_1\beta_2|\downarrow\downarrow\rangle \end{aligned} \tag{492}$$

where we have dropped the $\otimes$ for simplicity, and then collect the product states into the kets, i,e. $|\uparrow\rangle_1|\uparrow\rangle_2 \equiv |\uparrow\uparrow\rangle$ – it is clear that the first arrow denotes qubit 1 and the second arrow denotes qubit 2. Since we have not specified α_i and β_i, we can collect all the coefficients

$$|\Psi\rangle = A|\uparrow\uparrow\rangle + B|\uparrow\downarrow\rangle + C|\downarrow\uparrow\rangle + D|\downarrow\downarrow\rangle \ , \ A, B, C, D \ \in \ \mathbb{C} \tag{493}$$

which is the most general two qubit state – it is a linear combination of these four possible states, but with complex amplitudes A, B, C, D. If you like, you can normalize the state so that the probabilities add up to one

$$|A|^2 + |B|^2 + |C|^2 + |D|^2 = 1. \tag{494}$$

Classically, if you are given 2 bits with binary states 0 and 1, then there are four possible combinations $(00, 01, 10, 11)$ you can make with them, so this is not surprising.

But as in the single qubit, the complex nature of the coefficients makes things more interesting quantum mechanically. Suppose we have the following normalized state

$$|\Psi\rangle = \sqrt{\frac{1}{2}}|\uparrow\downarrow\rangle + \sqrt{\frac{1}{2}}|\downarrow\uparrow\rangle. \tag{495}$$

We are given a detector that can make measurement on a *single* qubit. Let's use it on the first qubit. According to Postulate 2, the probability of measuring an $\uparrow$ state is

$$\begin{aligned} \text{Probability of measuring } \uparrow_1 &= \left| \langle\uparrow|(\sqrt{\frac{1}{2}}|\uparrow\downarrow\rangle + \sqrt{\frac{1}{2}}|\downarrow\uparrow\rangle) \right|^2 \\ &= \left| \sqrt{\frac{1}{2}}\langle\uparrow_1|\uparrow_1\rangle \otimes |\uparrow\rangle_2 \right|^2 = \frac{1}{2} \end{aligned} \tag{496}$$

where we have restored the $\otimes$ in the last line to show that the $\langle\uparrow|_1$ only "completed its braket" with the $|\uparrow\rangle_1$ ket state.

But now according to Postulate 3, once a measurement is made, the state collapsed to its measured state, which in this case is $|\uparrow\downarrow\rangle$. In other words the following sequence of events has occured

$$|\Psi\rangle \overset{|\uparrow\rangle_1}{\to} |\uparrow\downarrow\rangle, \tag{497}$$

which hopefully by now you are not surprised – the 2nd qubit has jumped to its $\downarrow$ state. A state such as Eq. (495) is called an **Entangled State** – measurement of one qubit will affect the other. The following are examples of entangled states

$$|\Psi\rangle = \sqrt{\frac{1}{2}}|\uparrow\downarrow\rangle - i\sqrt{\frac{1}{2}}|\downarrow\uparrow\rangle \tag{498}$$

$$|\Psi\rangle = \sqrt{\frac{1}{4}}|\uparrow\uparrow\rangle - \sqrt{\frac{3}{4}}|\downarrow\downarrow\rangle. \tag{499}$$

Not all product states are entangled – the following is not an entangled state

$$\begin{aligned}
|\Psi\rangle &= \sqrt{\frac{1}{2}}|\uparrow\uparrow\rangle + \sqrt{\frac{1}{2}}|\uparrow\downarrow\rangle \\
&= \sqrt{\frac{1}{2}}|\uparrow\rangle_1 \otimes (|\uparrow\rangle_2 + |\downarrow\rangle_2)
\end{aligned} \tag{500}$$

since measurement of either qubits do not alter the probability amplitudes of the other.

Einstein-Podolsky-Rosen Paradox: A long time ago, Einstein with his buddies Podolsky and Rosen, were in great angst about this. They propose the following *gedenken* experiment: prepare the state[26] as in Eq. (495), and keep the two qubits in two unopened boxes. Now, send one qubit to Alice at one end of the universe, and the other qubit to Bob at the other end of the universe.

Now Alice wants to open her box. At this stage, $|\Psi\rangle$ is "uncollapsed", so her probability of finding an $\uparrow$ in her box is 1/2 as we just calculated above. If she now opens the box, and found an $|\uparrow\rangle$ state, then Bob will open his box and find his state to be $|\downarrow\rangle$ with probability 1. This is just a story version of the calculation we did above, but EPR were very upset because it seems to imply that information has traveled at the instance Alice opened her box to Bob's qubit in his box instantly. But there is no paradox – the states are *correlated* in such a way that measurement of one imply the other.

In honor of our angst-ridden physicists, nowadays we call the entangled state Eq. (495) an **EPR pair**.

9.2 Teleportation : The Quantum Love Letter

In the late 1990s, Alice and Bob broke up after an intense relationship. However, like many breakups where both sides still care, their breakup was ambivalent. Alice wasn't sure Bob was the person she wanted, and Bob just wanted to find some space to work through some personal issues. In their final night together, they gave each other a box, and inside each box is a qubit state with the eigenstates

$$\text{I love you} = |\uparrow\rangle \ , \ \text{I love you not} = |\downarrow\rangle, \tag{501}$$

and left with their qubit states entangled as an EPR state

$$|\Phi\rangle = \sqrt{\frac{1}{2}}|\downarrow\downarrow\rangle + \sqrt{\frac{1}{2}}|\uparrow\uparrow\rangle \tag{502}$$

just like their feelings for each other. They put their boxes in safe places, went on with their lives, and drifted apart.

Years later, Alice was cleaning out her closet when she discovered the box and her heartstrings were tugged by the memories of Bob. She felt that she *has* to send Bob a message, but her feelings are still ambivalent, and she doesn't know whether she still love Bob or not. Her feelings are in fact in the following quantum state

$$|\chi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle. \tag{503}$$

She wanted to send this state to Bob, without collapsing it – how is she going to do this? It seems hopeless – she cannot describe the state to Bob because then she must make an observation on $|\chi\rangle$. That would require her to apply Postulate 3 and collapse the wavefunction – does she love Bob or not – and hence resolving her ambivalence.

But wait! She remembered that Bob's qubit in his box is entangled with the qubit she now holds in her own box. Perhaps she can use the fact that her qubit is still entangled with Bob's qubit to send the message? In fact, she can and we will describe how she can use this entanglement to **teleport** her

---

[26]Which one can do by making a hydrogen atom emit a pair of photons in such a way that they conserve angular momentum.

message $|\chi\rangle$ to Bob – at the cost of requiring her to tell Bob what she needs him to do to his qubit to reconstruct $|\chi\rangle$.

To do that, Alice needs a few operators. The first operator we have already seen, is the NOT operator

$$\hat{P} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{504}$$

She also needs the $\hat{Z}$ operator

$$\hat{Z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{505}$$

which flips the sign of the coefficient of the $|\downarrow\rangle$ coefficient, i.e.

$$\hat{Z}|\chi\rangle = \alpha|\uparrow\rangle - \beta|\downarrow\rangle, \tag{506}$$

and the **Hadamard** operator (this is not the Hamiltonian – we are following standard quantum computation notation)

$$\hat{H} = \sqrt{\frac{1}{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \tag{507}$$

which "rotates" the states in the following way

$$\hat{H}|\chi\rangle = \alpha\frac{|\downarrow\rangle + |\uparrow\rangle}{\sqrt{2}} + \beta\frac{|\downarrow\rangle - |\uparrow\rangle}{\sqrt{2}}. \tag{508}$$

Finally she needs a two-qubit operator, called the CNOT (for Controlled NOT) $\hat{C}$ operator. This operator does the following: it checks the first qubit of a two qubit state, and if the first qubit is $\downarrow$ it flips the second qubit, and if the first qubit is $\uparrow$ it keeps the second qubit as it is. In other words the CNOT operator uses the first qubit to "control" whether or not to NOT the second qubit. Mathematically, CNOT has the following action

$$\hat{C}|\uparrow\downarrow\rangle = |\uparrow\downarrow\rangle \ , \ \hat{C}|\uparrow\uparrow\rangle = |\uparrow\uparrow\rangle \ , \ \hat{C}|\downarrow\downarrow\rangle = |\downarrow\uparrow\rangle \ , \ \hat{C}|\downarrow\uparrow\rangle = |\downarrow\downarrow\rangle. \tag{509}$$

(You can check that all these operators are unitary.)

With these tools, Alice now do the following things. First she take her message state $|\chi\rangle$ and entangle it with her own qubit in the box, but since that qubit is entangled with Bob's qubit, the following triply entangled states now result

$$\begin{aligned} |\Psi\rangle &= |\chi\rangle \otimes |\Phi\rangle \\ &= \sqrt{\frac{1}{2}}\alpha|\uparrow\rangle(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) + \sqrt{\frac{1}{2}}\beta|\downarrow\rangle(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle), \end{aligned} \tag{510}$$

where we have used the convention that the first qubit is Alice's $|\chi\rangle$ state, the second is her qubit of the EPR pair, and the third is Bob's qubit.

Since she only access to her own qubit in the box, and $|\chi\rangle$, she acts on this pair with the CNOT operator to obtain (using braces to indicate the target of the $\hat{C}$ action)

$$\begin{aligned} |\Psi_1\rangle &= \hat{C}\sqrt{\frac{1}{2}}\left[\alpha\underbrace{|\uparrow\rangle|\uparrow\rangle}|\uparrow\rangle + \alpha\underbrace{|\uparrow\rangle|\downarrow\rangle}|\downarrow\rangle + \beta\underbrace{|\downarrow\rangle|\uparrow\rangle}|\uparrow\rangle + \beta\underbrace{|\downarrow\rangle|\downarrow\rangle}|\downarrow\rangle\right] \\ &= \sqrt{\frac{1}{2}}\alpha|\uparrow\rangle(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) + \sqrt{\frac{1}{2}}\beta|\downarrow\rangle(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) \end{aligned} \tag{511}$$

where $|\Psi_1\rangle$ is now the new entangled state.

Finally, she takes her feelings $|\chi\rangle$ state, and act on it with the Hadamard operator to get

$$|\Psi_2\rangle = \frac{1}{2}\alpha(|\uparrow\rangle + |\downarrow\rangle)(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) + \frac{1}{2}\beta(|\uparrow\rangle - |\downarrow\rangle)(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle). \qquad (512)$$

Now, let's regroup the kets in the following way (which we can do since $\otimes$ is associative)

$$|\chi\rangle|\text{Alice's Qubit Bob's Qubit}\rangle \to |\chi\text{Alice's Qubit}\rangle|\text{Bob's Qubit}\rangle, \qquad (513)$$

and rearrange Eq. (512) to get

$$|\Psi_2\rangle = \frac{1}{2}|\uparrow\uparrow\rangle(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) + \frac{1}{2}|\uparrow\downarrow\rangle(\alpha|\downarrow\rangle + \beta|\uparrow\rangle) + \frac{1}{2}|\downarrow\uparrow\rangle(\alpha|\uparrow\rangle - \beta|\downarrow\rangle) + \frac{1}{2}|\downarrow\downarrow\rangle(\alpha|\downarrow\rangle - \beta|\uparrow\rangle). \quad (514)$$

Notice that in Eq. (514) we have grouped up all four possible outcomes of Alice's measurements on the two qubits in her hand and sneakily brought the unknown coefficients α and β into Bob's unmeasured qubit!

Alice now makes a measurement on both her qubits, and she will obtain one of the four possible outcomes

Alice's Measurement	Bob's Resulting Qubit State
$\uparrow\uparrow$	$\alpha|\uparrow\rangle + \beta|\downarrow\rangle$
$\uparrow\downarrow$	$\alpha|\downarrow\rangle + \beta|\uparrow\rangle$
$\downarrow\uparrow$	$\alpha|\uparrow\rangle - \beta|\downarrow\rangle$
$\downarrow\downarrow$	$\alpha|\downarrow\rangle - \beta|\uparrow\rangle$

Now all she needs to send her ambivalent, Quantum Love Letter, is to tell Bob what to do with his qubit depending on what she measured:

Alice's Measurement	Instructions to Bob
$\uparrow\uparrow$	Keep Your State as It is
$\uparrow\downarrow$	Act on it with a $\hat{P}$
$\downarrow\uparrow$	Act on it with a $\hat{Z}$
$\downarrow\downarrow$	Act on it with a $\hat{P}$ then $\hat{Z}$

You can check yourself that the final qubit that Bob now holds in his hands after following Alice's instructions is

$$|\text{Bob's Final Qubit}\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle = |\chi\rangle \qquad (515)$$

which is exactly the ambivalent quantum state $|\chi\rangle$ that Alice wanted Bob to receive!

This weird and remarkable quantum effect is called **Quantum Teleportation** – we have teleported a quantum state from one place (Alice) to another (Bob). Of course, the teleportation is not instantaneous as Alice still has to tell Bob what to do and the instructions travel at the usual slow pace of the speed of light. This effect was discovered by Bennett, Brassard, Crepeau, Jozsa[27], Peres and Wooters in 1993.

Far from being science fiction, Quantum Teleportation has been achieved experimentally using single photons and nuclear spins – some of the technology requiring fine control over fragile single quantum states were awarded the Nobel Prize this year[28]. Now it is an increasing competitive technical race to see which research group can teleport further in one leap.

---

[27]Prof. Richard Jozsa is teaching you Methods this year.
[28]2012 Nobel Prize in Physics were awarded to David Wineland and Serge Haroche.

Postscript

All these are irrelevant for our quantum-crossed lovers. After receiving the unexpected message and instructions from Alice, Bob found that he has left his old box at his old family home as he has moved from New York to London. He bought a ticket immediately, and flew to New York and dug out his box from a dank basement in Harlem, NYC. He acted on his qubit following Alice's instructions, and now in his hand he holds $|\chi\rangle$ – Alice's unresolved quantum feelings.

Should he make an observation and collapse the state vector, and finally, after all these years, find out whether Alice loves him or not?