

FYS2140 Guide - Quantum Physics

Gabriel Sigurd Cabrera

April 17, 2018

Contents

Introduction	4
1 Statistics	4
1.1 Expected Values	4
1.2 Variance	4
2 Waves	4
2.1 The Dispersion Relation	5
3 Bra-ket Notation	5
4 Schrödinger's Equation	6
4.1 Superposition of Waves	6
4.2 The Probabilistic Interpretation of Matter Waves	6
4.3 Normalization	7
5 Operators	7
5.1 Operators Applied	8
5.1.1 Finding the Expectation Value of Position	8
5.1.2 Finding the Expectation Value of Momentum	8
5.2 Ehrenfest's Theorem for Momentum	8
5.3 Hermitian Operators	9
5.4 The Hamiltonian Operator	9
6 Heisenberg's Uncertainty Principle	9
6.1 Commutators	10
6.1.1 The Canonical Commutation Relation	10
6.2 The General Uncertainty Principle	10

7	The Time-Independent Schrödinger Equation	10
7.1	Boundary Conditions	11
7.2	The Infinite Square Well	11
7.3	Harmonic Oscillator Potentials	12
7.3.1	Ladder Operators	12
7.3.2	Ground States	12
7.3.3	Energy	13
7.3.4	Dimensionless TISE	13
7.3.5	Analytical Solution	13
7.4	Bound and Unbound States	14
7.5	The Free Particle	14
7.6	Non-Normalizeable Free Particle Plane Wave Solutions	14
8	The Finite Well	15
8.1	Bound States	15
8.2	Reflection and Transmission	15
8.3	The Dirac Delta	16
8.4	Delta Potentials	16
9	The 5 Postulates of Quantum Mechanics	16
9.1	Postulate 1	17
9.2	Postulate 2	17
9.3	Postulate 3	17
9.4	Postulate 4	18
9.5	Postulate 5	19
10	Eigenstates	19
11	Useful Polynomials	19
11.1	Legendre Polynomials	19
11.1.1	Associated Legendre Polynomials	20
11.2	Laguerre Polynomials	20
12	Schrödinger's Equation in Spherical Coordinates	20
12.1	Separating Angle and Radial Distance	21
12.2	Angle and Azimuth	22
12.3	Solutions	22
12.3.1	Normalization of the Spherical Schrödinger Equation	22

12.3.2 The Radial Solution	23
12.3.3 Solving for the Hydrogen Atom	24
12.4 Quantum Numbers	25
12.5 Angular Momentum	25
12.5.1 Ladder Operators	27

Introduction

This booklet contains a summary of all the lecture notes from our FYS2140 - Quantum Physics course. At the beginning of each lecture, our professor would quickly repeat the most important details from the previous lecture; these notes are the source of the material in this pamphlet, and is intended as a quick reference in case the reader has (for example) forgotten a detail about an equation.

1 Statistics

In Quantum Mechanics, the laws of motion are governed by statistics; there are a multitude of values that we can never calculate with 100% certainty. Fortunately, we can still find the probability of such values by using basic statistical concepts.

1.1 Expected Values

The probability of finding a continuously distributed value in the range of $[x, x + dx]$ is given by the products of the probability density function $\rho(x)$ and the infinitesimal change dx .

$$\langle x \rangle = \int_{-\infty}^{\infty} x \rho(x) dx \quad (1)$$

Using the product $\rho(x)dx$, we can find the *expected value*¹ (or *expectation value*) of a given x via (1). This is a rather basic example however, as it is possible to find the expectation value for many different things.

1.2 Variance

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \quad (2)$$

In many cases, it is necessary to find the *variance*² σ_x of an expectation value $\langle x \rangle$ to be able to determine things such as standard deviation. To accomplish this, we can use (2).

2 Waves

$$\frac{\partial^2}{\partial t^2} \xi(x, t) = [c^2 \nabla^2 + V(x)] \xi \quad (3)$$

A particle can be described as a *complex wavefunction* Ψ (or for EM-waves ξ), which is itself a solution of a given *wave equation* [for example, the general EM-wave equation is shown in (3)]; the wavefunction we use to describe non-relativistic particles is called **Schrödinger's Equation**, and will be introduced later in this guide.

¹https://en.wikipedia.org/wiki/Expected_value#Absolutely_continuous_case

²<https://en.wikipedia.org/wiki/Variance#Definition>

$$A(x, t) = A_0 \cos(kx - \omega t + \varphi) \quad (4)$$

A localized particle can be described as the sum of a set of planewaves³ with different k values $k = \frac{2\pi}{\lambda}$, known as a *wavepacket*⁴; (4) is the generalized form of a plane wave.

2.1 The Dispersion Relation

$$\omega(k) = \frac{\hbar k^2}{2m} \quad (5)$$

The *De Broglie* dispersion relation⁵ [shown in (5)] is a useful value from which we can determine a wave's *phase velocity* v_f and *group velocity* v_g .

$$v_f = \frac{\omega}{k} \quad (6)$$

The **Phase Velocity** is essentially the velocity of our wave, and is shown in (6).

$$v_g = \frac{d\omega}{dk} \quad (7)$$

The **Group Velocity** is the particle's velocity, and is shown in (7).

Step-by-step If we wish to find our phase velocity or group velocity, we can follow the steps below to easily set up our equations (6) and (7):

1. Find $E(p)$
2. Replace E with $\hbar\omega$
3. Replace p with $\hbar k$
4. Solve for $\omega(k)$

3 Bra-ket Notation

When dealing with the wavefunction Ψ , it is possible to express certain concepts via the usage of *bras* and *kets* for a more elegant way of representing values.

$$\langle \Psi_i | \Psi_j \rangle = \int_{-\infty}^{\infty} \Psi_i^* \Psi_j dx \quad (8)$$

A complete bra-ket⁶ as seen on the left-hand side of (8), and is defined by the right-hand side. Within this bra-ket, the *bra* is represented by $\langle \Psi_i |$, while the *ket* is represented as $|\Psi_j\rangle$.

³https://en.wikipedia.org/wiki/Plane_wave#Mathematical_representations

⁴https://en.wikipedia.org/wiki/Wave_packet#Gaussian_wave_packets_in_quantum_mechanics

⁵https://en.wikipedia.org/wiki/Dispersion_relation#De_Broglie_dispersion_relations

⁶https://en.wikipedia.org/wiki/Bra%E2%80%93ket_notation

4 Schrödinger's Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(x) \right] \Psi \quad (9)$$

Schrödinger's equation⁷ is the wave equation that is used to describe the movement of particles in terms of a wavefunction $\Psi(x, t)$ – it is shown in its general form in (9). We can do many things with this equation and wavefunction, but this will be described later in detail.

4.1 Superposition of Waves

$$A(x, t) = A_0(k) e^{i(kx - \omega t)} \quad (10)$$

Since our wavefunction $\Psi(x, t)$ is a *wavepacket* (as discussed previously in Section 2), it is a superposition of many waves of the form shown in (10), with varying values of k .

$$\Psi(x, t) = \int_{-\infty}^{\infty} A_0(k) e^{i(kx - \omega t)} dk \quad (11)$$

If we want to construct our wavefunction, we can sum over all our waves for varying values of the wavenumber k , as seen in (11).

4.2 The Probabilistic Interpretation of Matter Waves

Using the knowledge we gained in Section 1, we can deduce that our wavefunction $\Psi(x, t)$ can actually be used as part of a probabilistic density function – one which can be used to determine all matter of properties, such as position, momentum, and energy (among others.)

$$P_{a,b}(t) = \int_a^b |\Psi(x, t)|^2 dx \quad (12)$$

We see in (12) that we can use the square of the absolute value of Ψ as our probabilistic density function.

$$\rho(x) = |\Psi(x, t)|^2 = \Psi^* \Psi \quad (13)$$

Since Ψ is usually complex, we can find our probability density function in two ways, as shown in (13).

$$\rho(x) = \langle \Psi | \Psi \rangle \quad (14)$$

If we wish to represent this probability density using bra-ket notation, we can use (14).

⁷https://en.wikipedia.org/wiki/Schr%C3%B6dinger_equation

4.3 Normalization

Due to the nature of statistics, it is impossible for a probability to ever be greater than 100% – in the case of physics, we often tend to drop the percentage sign and use the number 1 as a representation for 100%. Since this is the case, we should take care to make sure the integral of the probability density function $\Psi^*\Psi$ over infinity is always equal to one.

$$\langle\Psi|\Psi\rangle = \int_{-\infty}^{\infty} \Psi^*\Psi dx = 1 \quad (15)$$

To successfully normalize⁸ a wavefunction, we must begin by solving the equation shown in (15); once this has been integrated, there will most likely be a constant (let's call it A , and assume it is contained within Ψ from the start) on the left-hand side of the equation. The final step then is to solve for A and replace the A in $\Psi(x, t)$ with the new, normalized coefficient.

Two important things to bear in mind:

- Normalization is *independent* of time
- Normalization requires that $|\Psi| \rightarrow 0$ as $|x| \rightarrow \infty$

5 Operators

As mentioned in Section 1.1: Expected Values, we can integrate over a probability density equation to give us useful information about a variety of things. In quantum mechanics, we can for example use our wavefunction Ψ as a way to determine position and momentum⁹ by finding the expected values of their respective **operators**.

In the next few sections, we will use position and momentum as the basis for all other equations. For example, we will represent kinetic energy not as $E_K = \frac{1}{2}mv^2$, but rather as $E_K = \frac{p^2}{2m}$. This is helpful due to the fact that it allows us to simplify the way we calculate our expectation values¹⁰.

To understand how we will use position and movement as our **operators**¹¹, we must first define them.

Definition

$$\hat{x} = x \quad (16)$$

The operator for position \hat{x} is shown in (16).

$$\hat{p} = \frac{\hbar}{i}\nabla \quad (17)$$

The operator for momentum \hat{p} is shown in (17).

⁸https://en.wikipedia.org/wiki/Wave_function#Position-space_wave_functions

⁹These values cannot be known with 100% certainty however, for reasons that will be explained later

¹⁰We do not have any other tools with which to work at the moment, so it is best to build all our equations with the values we have access to, those being \hat{x} and \hat{p}

¹¹[https://en.wikipedia.org/wiki/Operator_\(physics\)#Operators_in_quantum_mechanics](https://en.wikipedia.org/wiki/Operator_(physics)#Operators_in_quantum_mechanics)

5.1 Operators Applied

$$\langle Q(\hat{x}, \hat{p}) \rangle = \int_{-\infty}^{\infty} \Psi^* Q\left(x, \frac{\hbar}{i} \nabla\right) \Psi dx \quad (18)$$

Let us now set up a general function Q of position and momentum; if we wish to determine the expectation value of Q , we can plug it into (18). Although this may seem a bit convoluted, in practice it could not be simpler – this is better understood via example.

5.1.1 Finding the Expectation Value of Position

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^* x \Psi dx \quad (19)$$

If we take the expectation value of x as an example, we can see from (19) that all we need to do is plug x in between our conjugates to find our result.

$$\langle x \rangle = \langle \Psi | x | \Psi \rangle \quad (20)$$

Equation (20) is equivalent to (19), using bra-ket notation – note the position of our operator's value.

5.1.2 Finding the Expectation Value of Momentum

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \frac{\hbar}{i} \nabla \Psi dx \quad (21)$$

To find the expectation value of p , we can simply plug the operator for momentum in between our conjugates, as seen in (21).

$$\langle p \rangle = \left\langle \Psi \left| \frac{\hbar}{i} \nabla \right| \Psi \right\rangle \quad (22)$$

If we wish to instead use bra-ket notation, we can once again place the value of our operator on the left side of the ket, as seen in (22).

5.2 Ehrenfest's Theorem for Momentum

In general, we know that momentum is the product of mass and velocity. In addition to this, we know that velocity is the first time derivative of position.

$$\langle p \rangle = m \langle v \rangle = m \nabla \langle x \rangle \quad (23)$$

We can use this relation to simplify finding the expectation value of momentum¹² in some cases via (23). An example of this being useful is in the case where $\langle x \rangle = \text{constant}$, since taking its derivative would give us zero and prevent us from needing to calculate another integral.

¹²https://en.wikipedia.org/wiki/Ehrenfest_theorem

5.3 Hermitian Operators

Let us begin with a postulate:

For all **observable** A , there exists a **Hermitian operator** \hat{A} .

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx = \int_{-\infty}^{\infty} (\hat{A} \Psi)^* \Psi dx \quad (24)$$

A useful property of a Hermitian operator is that it is a complex commutator with respect to our complex conjugates Ψ^* and Ψ , meaning that it can be moved left of Ψ^* in the particular way shown in (24).

$$\hat{A} \Psi = a \Psi \quad (25)$$

Another useful postulate:

The sole immediate result of an individual measurement of A will be the **eigenvalue** a of \hat{A}

This postulate naturally leads to the conclusion in (25).

$$\langle A \rangle = \langle \Psi | \hat{A} \Psi \rangle = \langle \hat{A} \Psi | \Psi \rangle \quad (26)$$

Finally, Hermitian operators play very nicely with bra-ket notation, as we see in (26).

5.4 The Hamiltonian Operator

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(x) \quad (27)$$

Oftentimes, it is necessary to simplify the notation in Schrödinger's equation – to do this, we can use the **Hamiltonian operator** \hat{H} , which is defined in (27). Note that \hat{H} represents one side of Schrödinger's equation without $\Psi(x, t)$, as seen previously in (9).

$$\hat{H} \psi = E \psi \quad (28)$$

In addition to this, note that this operator represents the amount of *energy* in the system, as it has an eigenvalue E .

6 Heisenberg's Uncertainty Principle

When measuring the position of a subatomic particle with high precision, it is not possible to measure its momentum with a similarly high precision. The reason for this is due to the fact that the instruments with which we measure this particle are themselves affecting the particle's behavior, leading to this *uncertainty*.

$$\sigma_p \sigma_x \geq \frac{\hbar}{2} \quad (29)$$

To mathematically model the limits of our measuring abilities, we can use equation (29), known as **Heisenberg's Uncertainty Principle**¹³.

6.1 Commutators

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (30)$$

Although not strictly related to the Heisenberg Uncertainty Principle, **commutators** are a useful tool that we use in several situations in quantum mechanics; a generalized example of a commutator is shown in (30)

6.1.1 The Canonical Commutation Relation

$$[x, p] = i\hbar \quad (31)$$

The commutator for our *canonical* variables is shown in (31).

6.2 The General Uncertainty Principle

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2 \quad (32)$$

In addition to Heisenberg's uncertainty principle, we have a more general version of the concept which can be used for all sorts of phenomena, quantum or not; it is shown in (32).

7 The Time-Independent Schrödinger Equation

$$\Psi(x, t) = \psi(x)\phi(t) = \psi(x)e^{-i\frac{E}{\hbar}t} \quad (33)$$

When solving Schrödinger's equation, we can sometimes assume that the wavefunction $\Psi(x, t)$ is separable into position-dependent and time-dependent factors, as we see in (33).

$$\Psi(x, t) = \sum_{n=1}^N c_n \Psi_n = \sum_{n=1}^N c_n \psi_n e^{-i\frac{E_n}{\hbar}t} \quad (34)$$

If we are dealing with a non-continuous (aka quantized) set of N individual solutions to our wavefunction, we can use (34) as a way to represent the general form of our $\Psi(x, t)$.

ψ is classified as a *stationary state*¹⁴, due to the fact that it is independent of time. In addition to this, we can also assume that the following is true for stationary states:

¹³https://en.wikipedia.org/wiki/Heisenberg%27s_uncertainty_principle

¹⁴https://en.wikipedia.org/wiki/Stationary_state

- The probability density and expectation values are constant in time
- The energy is 100% certain, such that $\sigma_E = 0$

Oftentimes, it is necessary to simplify the notation in Schrödinger's equation – to do this, we can use the **Hamiltonian operator** \hat{H} , which is defined in (27). Note that \hat{H} represents one side of Schrödinger's equation without $\Psi(x, t)$, as seen previously in (9).

$$E_n \psi_n = \hat{H} \psi_n \iff E_n \psi_n = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(x) \right] \psi_n \quad (35)$$

If we decide to simply work with $\psi(x)$ rather than $\Psi(x, t)$, we end up having to deal with the **Time-Independent Schrödinger Equation**¹⁵, or **TISE** for short. This is shown above in (35), with the Hamiltonian operator its equivalent written out in its complete notation.

$$\psi(x) = \sum_{n=1}^N c_n \psi_n \quad (36)$$

An important thing to note, however, is that using (35) is one of many steps needed to find ψ , since it is the sum of all quantized time-independent wavefunctions ψ_n , each with its own coefficient; this relationship is shown in (36).

7.1 Boundary Conditions

When using the the TISE, we have that:

- ψ **must** be continuous, with $\psi = 0$ when $|V(x)| \rightarrow \infty$
- $\nabla \psi$ **must** be continuous when $|V(x)| < \infty$

7.2 The Infinite Square Well

$$V(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases} \quad (37)$$

Say that we are given an *infinite square well* potential, as represented by (37)

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad (38)$$

The energy in the system is then given by (38).

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (39)$$

And the solution to the TISE is shown in (39).

¹⁵https://en.wikipedia.org/wiki/Schr%C3%B6dinger_equation#Time_independent

7.3 Harmonic Oscillator Potentials

Locally speaking, a large portion of potentials can be approximated by a **harmonic oscillator**¹⁶

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{1}{2}m\omega^2x^2\psi = E\psi \quad (40)$$

Given such a potential, we end up with a TISE of the form shown in (40).

7.3.1 Ladder Operators

$$\hat{a}_{\pm} = \frac{1}{\sqrt{\mp i\hat{p} + m\omega\hat{x}}} \quad (41)$$

Assuming still that we have quantized states ψ_n where $n \in \mathbb{N}$, wouldn't it be useful to be able to find ψ_{n+1} and ψ_{n-1} ? Using the **ladder operator**¹⁷ shown in (41) makes this possible.

$$[\hat{a}_-, \hat{a}_+] = \hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = 1 \quad (42)$$

Note that these operators are **non-Hermitian**¹⁸, and that their commutator is equal to 1, as shown in (42). In addition to this, they have the property that the product of the minus operator and the ground state is zero, such that $\hat{a}_-\psi_0 = 0$.

$$\psi_{n+1} = \frac{1}{\sqrt{n+1}}\hat{a}_+\psi_n \quad (43)$$

To increase our state, we can use (43).

$$\psi_{n-1} = \frac{1}{\sqrt{n}}\hat{a}_-\psi_n \quad (44)$$

To lower our state, we can use (44).

$$\psi_n = A_n\hat{a}_+^n\psi_0 \quad (45)$$

Given a ground state ψ_0 , we can find any state ψ_n by repeating (43) over and over until we reach our desired n ; to simplify this process, we can also perform this in one step, shown in (45).

7.3.2 Ground States

$$\psi_0 = Ce^{-\frac{m\omega}{2\hbar}x^2} \quad (46)$$

We can easily find the ground state ψ_0 for our time independent wavefunction ψ via the usage of (46).

¹⁶https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

¹⁷https://en.wikipedia.org/wiki/Ladder_operator#Harmonic_oscillator

¹⁸For a refresher on Hermitian operators, take a look at section 5.3

7.3.3 Energy

$$\hat{H} = \hbar\omega \left(\hat{a}_+ \hat{a}_- + \frac{1}{2} \right) \quad (47)$$

We can redefine the Hamiltonian operator in terms of our ladder operators, as shown in (47).

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \text{ for } n \in \mathbb{N} \quad (48)$$

Using our redefined \hat{H} , we can use its eigenvalue to find the energy E_n of a particular state via (48).

7.3.4 Dimensionless TISE

$$\frac{d^2\psi(\xi)}{d\xi^2} = (\xi^2 - K) \psi(\xi), \text{ for } \xi = \sqrt{\frac{m\omega}{\hbar}}x \text{ and } K = 2\frac{E}{\hbar\omega} \quad (49)$$

If we wish, we can rewrite our time-independent Schrödinger equation for a harmonic oscillator to be dimensionless (aka without units) by using the redefinition shown in (49).

$$\psi(\xi) = h(\xi) e^{-\frac{1}{2}\xi^2} \quad (50)$$

$$h(\xi) = \sum_j a_j \xi^j, \text{ with } a_{j+2} = \frac{2j - K + 1}{(j+2)(j+1)} a_j \quad (51)$$

The analytical solution to our HO TISE is then shown in (50), with its function $h(\xi)$ defined for us in (51). Since we can only find a_{j+2} using the above equations, it is obvious that we will be in need of two initial conditions, ie both a_0 and a_1 ; the solutions stemming from these are called *even* and *odd*, respectively.

Fortunately, we have a boundary condition stating that *either* a_0 or a_1 must be equal to zero, and that the series must end at $j_{\max} = n$ and $K = 2n + 1$, with n being the state of our current wavefunction ψ_n .

7.3.5 Analytical Solution

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\frac{1}{2}\xi^2} \quad (52)$$

The generalized analytical solution for the HO TISE can be found via the usage of a **Hermite Polynomial**¹⁹ in (52), where we assume that ξ is defined the same was as in (49).

¹⁹http://physics.gmu.edu/~dmaria/590%20Web%20Page/public_html/qm_topics/harmonic/

7.4 Bound and Unbound States

Assuming the reader has completed their earlier mechanics courses, we should all be familiar with the concept of *classical* bound and unbound states – a classical bound state is simply one where a particle or object cannot escape a potential well, either due to not having enough energy to get over a bump, or due to the fact that the well is infinitely deep. A classical unbound state is one where our object will fall endlessly (in one dimension, it's as though the object will move away forever into the infinity of the x-axis).

For quantum mechanics, we must change our perspective slightly – the difference here is that we must consider the possibility of **Quantum Tunneling**²⁰, whereby a particle may be able to get through a potential bump even though it is technically "in the way."

Mathematically speaking, a quantum bound state will always have an energy $E < V(\infty)$ and $E < V(-\infty)$; all other cases are considered unbound!

7.5 The Free Particle

Previously, we've dealt strictly with quantized energy, but only because we've been exclusively exposed to bound states! When dealing with *unbound* states (or *free particles*), we must consider that our energy is no longer restricted to specific values, and that we cannot simply use the solutions shown in the previous sections – instead, we will need to introduce the TISE wavefunction $\phi(k)$.

$$k \triangleq \frac{\sqrt{2mE}}{\hbar} \quad (53)$$

Note that we are indirectly defining ϕ as a function of energy, in the way shown in (53).

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \omega(k)t)} dk \quad (54)$$

Since we may no longer take a discrete sum over a variable n , we must instead integrate over our continuous k ²¹; this is given in (54).

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \Psi(x, 0) dx \quad (55)$$

Conversely, if we are given the initial condition for TDSE wavefunction $\Psi(x, 0)$, we can use it to our advantage and find our $\phi(k)$, as seen in (55).

7.6 Non-Normalizeable Free Particle Plane Wave Solutions

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx}, \text{ where } E = \frac{\hbar^2 k^2}{2m} \quad (56)$$

Even if our free particle plane wave solution is non-normalizeable, we can still use it as an approximation for a particle with a sharp energy, as shown in (56).

²⁰https://en.wikipedia.org/wiki/Quantum_tunneling

²¹Note that the definition of k contains an energy E , which as we've already discussed is no longer quantized, making k a continuous value as well

In addition to this, the direction in which a plane wave is moving depends on the sign before k in the exponent. A negative sign means it is moving in the direction $x \rightarrow -\infty$, with the positive implying a movement towards $x \rightarrow \infty$.

8 The Finite Well

Up to this point, we have been working mostly with *infinite* potential wells, which result in strictly bound states. Now that we are generalizing many of the aforementioned concepts for a *finite* potential well, we will be dealing both with bound and unbound states.

$$V(x) = \begin{cases} -V_0 & \text{for } -a \leq x \leq a \\ 0 & \text{otherwise} \end{cases} \quad (57)$$

A *finite* potential well, where there is a small potential drop in the range $\pm a$, has a potential of the form shown in (57). Given a finite potential well and a bound state, we can conclude that the system's energy is quantized.

8.1 Bound States

In general, we know that bound states have an energy $E < 0$ when we set the energy level based on the potential at $-a \geq x \geq a$. This also means that we have a symmetric potential, which can result in *symmetrical* and *anti-symmetrical* solutions.

Since we have three separate locations in mind (before the well, in the well, after the well) we must solve the TISE for all three locations. In essence, what we can do first is determine what Ψ and $\nabla\Psi$ is within the well, and then use their values on the edge of the well as the initial conditions for our two other locations.

Once this is done, we can find an equation for the quantized values of E , which must be solved numerically.

8.2 Reflection and Transmission

Since we are dealing with a finite well, we can no longer assume that our wavefunction is reflected perfectly when it hits one of the walls of the well – instead, we now must manually calculate what portion of the wave is **reflected**²² and what portion is **transmitted**²³.

$$R = \frac{|B|^2}{|A|^2} \quad (58)$$

$$T = \frac{|F|^2}{|A|^2} \quad (59)$$

For an incoming wave of the form Ae^{ikx} , we can find the reflected wave Be^{-ikx} via (58), and the transmitted wave via (59).

²²https://en.wikipedia.org/wiki/Reflection_coefficient

²³https://en.wikipedia.org/wiki/Transmission_coefficient

$$R(E) + T(E) = 1 \quad (60)$$

It is not possible for the sums of the reflected and transmitted wavefunctions to be greater than the original wavefunction, leaving us with (60) as a mathematical representation of the relation between R and T .

Generally, we can find these coefficients by using our aforementioned boundary conditions to solve for whatever variable is unknown.

Interestingly enough, the concept of **quantum tunneling** is essentially due to the fact that a portion of the wavefunction may be transmitted through a potential barrier, while a classical object would be unable to pass it.

8.3 The Dirac Delta

$$\delta(x) = \begin{cases} \infty & \text{for } x = 0 \\ 0 & \text{otherwise} \end{cases} \quad (61)$$

$$\int_{-\infty}^{\infty} \delta(x) dx = 1 \quad (62)$$

When dealing with a variety of natural phenomena, we will sometimes encounter situations where we have potential barriers (or wells) at specific points, but not elsewhere. For these kinds of situations, we may refer to the **Dirac delta function**²⁴, which is a misnomer, as it is not technically a function but rather a *distribution*. Nevertheless, it is defined in (61), with a valuable and important constraint defined in (62).

8.4 Delta Potentials

$$V(x) = -\alpha\delta(x) \quad (63)$$

It is important to note that we can have both bound and unbound states when dealing with a δ potential²⁵ [such as the one shown in (63)] depending on whether the total energy in the system is larger than zero or not (assuming that we set zero to be the energy outside the well.)

$$\Delta(\nabla\psi(x)) = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \nabla^2\psi dx \quad (64)$$

When dealing with δ potentials, $\psi(x)$ *must* be continuous – we may however choose to determine the measure of discontinuity in $\nabla\psi(x)$, which we can accomplish through (64).

9 The 5 Postulates of Quantum Mechanics

So far in this guide, we've been through a number of concepts – unbeknownst to us thus far, these ideas are all constructed upon a set of five basic postulates²⁶.

²⁴https://en.wikipedia.org/wiki/Dirac_delta_function

²⁵https://en.wikipedia.org/wiki/Delta_potential#Single_delta_potential

²⁶Similar but not identical to the mathematical concept of *axioms*

9.1 Postulate 1

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t}\Psi \quad (65)$$

The state of a system is based on the wavefunction $\Psi(x, t)$, which is a solution to the time-dependent Schrödinger equation (65), where \hat{H} is the system's *Hamiltonian operator*.

$\Psi(x, t)$ contains *all* the information about this system.

Comments

1. We can freely multiply Ψ with a constant – this is useful when taking normalization into account!

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i^* \psi_j dx \quad (66)$$

2. The solution to the Schrödinger equation can be represented by abstract vectors $|\psi\rangle$, which exist in a complex inner product space defined in (66). This is known as bra-ket notation (invented by Dirac), which are representative of vectors in a *Hilbert space*.

9.2 Postulate 2

For every observable Q , there exists a linear Hermitian operator \hat{Q} .

Comments

$$\hat{Q}(a\psi_i + b\psi_j) = a\hat{Q}\psi_i + b\hat{Q}\psi_j \quad (67)$$

1. Such operators being linear leads to the implication shown in (67).

$$\int_{-\infty}^{\infty} \psi_i^* \hat{Q}\psi_j dx = \int_{-\infty}^{\infty} (\hat{Q}\psi_i)^* \psi_j dx \iff \langle \psi_i | \hat{Q}\psi_j \rangle = \langle \hat{Q}\psi_i | \psi_j \rangle \quad (68)$$

2. Such operators are also Hermitian, as shown in (68).
3. The *canonical variables* are x and p , with $\hat{x} = x$, and $\hat{p} = \frac{\hbar}{i}\nabla$.
4. These operators are linear transformations for vectors in a vector space.

9.3 Postulate 3

$$\hat{Q}\psi_n = q_n\psi_n \iff \hat{Q}|\psi_n\rangle = q_n|\psi_n\rangle \quad (69)$$

After measuring an observable Q , the *only* possible result is the eigenvalue q_n of the operator \hat{Q} , such as in (69).

Comments

1. Immediately after the measurement of q_n , a system's state is equal to ψ_n – this is known as the collapse of a wavefunction.
2. The set $\{q_n\}$ is called the operator's spectrum; it can be *finite*, *countably infinite*, or *uncountably infinite*.
3. If multiple eigenstates²⁷ have the same eigenvalues, then the eigenvalue is *degenerate*²⁸. The number of states that are degenerate is called the *degree of degeneration* $d(n)$.

$$c_n = \int_{-\infty}^{\infty} \psi_n^* \psi dx = \langle \psi_n | \psi \rangle \quad (70)$$

4. The probability of measuring the n^{th} eigenvalue for a state $\psi = \sum c_n \psi_n$ is $|c_n|^2$, where $\sum |c_n|^2 = 1$; c_n can be found via Fourier's trick, shown in (70).

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \quad (71)$$

5. Operators whose commutator is equal to zero [seen in (71)] have the same eigenfunctions, and are called *compatible observable*²⁹.

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2 \quad (72)$$

6. Two incompatible commutators³⁰ follow the general uncertainty principle, shown in (72).

9.4 Postulate 4

$$\langle Q \rangle = \langle \psi | \hat{Q} \psi \rangle = \int_{-\infty}^{\infty} \psi^* \hat{Q} \psi dx \quad (73)$$

An ensemble of systems prepared in the state $|\psi\rangle$ will have an expectation value of the form shown in (73).

Comments

$$\sigma_Q^2 = \langle (Q - \langle Q \rangle)^2 \rangle = \langle Q^2 \rangle - \langle Q \rangle^2 \quad (74)$$

1. The variance is defined in (74)
2. If we have that $\sigma_Q = 0$, then Q is known with 100% certainty.

²⁷https://en.wikipedia.org/wiki/Introduction_to_eigenstates

²⁸https://en.wikipedia.org/wiki/Degenerate_energy_levels

²⁹https://en.wikipedia.org/wiki/Complete_set_of_commuting_observables

³⁰Intuitively, the idea of compatible operators is that some pairs of values can be known simultaneously and sharply. Incompatible operators can be visualized as two values (such as position and momentum) that cannot be known sharply when they are both measured simultaneously, leading to the inequality expressed in the general uncertainty principle.

9.5 Postulate 5

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle \quad (75)$$

If \hat{Q} is a Hermitian operator, and the set $\{|\psi_n\rangle\}$ is the set of *all* eigenstates for \hat{Q} , then (75) is a complete set.

Comment For continuous eigenvalues, we have that $\langle\psi_n|\psi_m\rangle = \delta_{mn}$.

10 Eigenstates

When performing a measurement on a system, the very fact that we've measured a particular value affects the system directly – in fact, the eigenvalue which we detect actually becomes the *eigenstate* of our system at the exact moment of measurement. We call this phenomenon the *collapse* of a wavefunction/state.

$$P_a = |c_a|^2 \quad (76)$$

$$|\psi\rangle = \sum c_a |\psi_a\rangle \quad (77)$$

If we wish to find the probability of measuring a particular eigenvalue a , we may use a combination of (76) and (77)

11 Useful Polynomials

When we begin dealing with quantum mechanics in 3-dimensions, some of our expressions can be simplified and generalized via the usage of different types of polynomial generator functions. These are the *Legendre Polynomials* P_l and *Laguerre Polynomials* L_q .

11.1 Legendre Polynomials

$$P_l \triangleq \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l \quad (78)$$

The Legendre Polynomial is defined in (78) for any arbitrary $l \in \mathbb{N}$; some examples are shown in Figure 1.

Figure 1: Several Legendre Polynomials

Polynomial Degree	Resulting Polynomial
$P_0(x)$	1
$P_1(x)$	x
$P_2(x)$	$\frac{1}{2}(3x^2 - 1)$
$P_3(x)$	$\frac{1}{2}(5x^2 - 3x)$

11.1.1 Associated Legendre Polynomials

$$P_l^m(x) \triangleq (1-x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx} \right)^{|m|} P_l(x) \quad (79)$$

In addition to the Legendre Polynomial, we have an *associated* Legendre Polynomial which is defined in (79) relative to the Legendre Polynomial.

11.2 Laguerre Polynomials

$$L_n(x) \triangleq e^x \frac{d^n}{dx^n} (x^n e^{-x}) \quad (80)$$

The Laguerre Polynomial is defined in (80) for any arbitrary $l \in \mathbb{N}$; some examples are shown in Figure 2.

Figure 2: Several Laguerre Polynomials

Polynomial Degree	Resulting Polynomial
$L_0(x)$	1
$L_1(x)$	$1 - x$
$L_2(x)$	$2 - 4x + x^2$
$L_3(x)$	$6 - 18x + 9x^2 - x^3$

12 Schrödinger's Equation in Spherical Coordinates

Now that we are moving into three dimensions, we will need to take several things into account – first of all, all positional derivatives *must* be gradients, so keep that in mind when repurposing one-dimensional equations for three. In the previous sections, we've strictly used gradients instead of $\frac{d}{dx}$ notation, so this should be relatively simple to implement, as long as one does not disregard our Jacobi factor (for example, when dealing with spherical coordinates, we must remember to include a factor $r^2 \sin(\theta)$ within a spherical integral.)

It is very common for us as physicists to work with central forces, such as a point charge emitting an electric field, so we will in this section assume that we are dealing with a potential $V(r)$; clearly,

this potential is dependent only on the radial distance from a point of origin, as it is independent of both angle and azimuth.

$$\Psi(r, \theta, \varphi, t) = \psi(r, \theta, \varphi) e^{\frac{-iE_n t}{\hbar}} \quad (81)$$

We've already used a separation of variables to solve Schrödinger's Equation in one-dimension, but this can also be accomplished in three-dimensions for a spherical coordinate system; as before, we may once again separate the time and position components of our equation as shown in (81).

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \quad (82)$$

Assuming we are then dealing with the spherical TISE for three dimensions, we can separate our equation into a radial component R , and an angular component Y , as seen in (82).

12.1 Separating Angle and Radial Distance

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2(\theta)} \frac{\partial^2 Y}{\partial \varphi^2} \right] + VRY = ERY \quad (83)$$

When we plug our separated variables R and Y into the TISE, we are left with a slightly modified variant of Schrödinger's Equation,³¹ shown above in (83). The reason for which we've done this is apparent when we take our next step, and separate (83) into two independent equations.

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) = l(l+1) \quad (84)$$

Firstly, we have an equation that is only dependent on the radial distance from the origin of the potential r ; this is called the **radial equation**, and is shown in (84).

$$\frac{1}{Y} \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2 Y}{\partial \varphi^2} \right) = -l(l+1) \quad (85)$$

Secondly, we also are left with an equation that doesn't depend on r , and instead depends only on θ and φ . This is known as the **angular equation**, and is shown above in (85).

$$l = 0, 1, 2, \dots, n-1 \quad (86)$$

The variable l is known as the azimuthal quantum number, and is limited to the values shown in (86). In this equation, n represents the energy level of our wavefunction, which varies depending on the given system.

³¹Note that we've implemented all the required Jacobi factors that arise from the spherical nature of our coordinate system

12.2 Angle and Azimuth

$$Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi) \quad (87)$$

We may also repeat the previous process, with the goal of having a separate equation for azimuth θ and angle φ , as shown above in (87).

$$\Phi \sin(\theta) \frac{d}{d\theta} \left(\sin(\theta) \frac{d\Theta}{d\theta} \right) + \Theta \frac{d^2\Phi}{d\varphi^2} = -l(l+1)\Phi\Theta \sin^2(\theta) \quad (88)$$

This time, we can supplement the radial equation directly by plugging in the separated functions Θ and Φ , giving us (88).

$$\frac{1}{\Theta} \left[\sin(\theta) \frac{d}{d\theta} \left(\sin(\theta) \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2(\theta) \Theta \right] = m^2 \quad (89)$$

Separating (88) gives us two parts – the first is dependent only on the azimuth θ , and is shown in (89).

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} = -m^2 \quad (90)$$

The second part of (88) is dependent only on the angle φ , and is shown in (90).

$$m = -l, -l+1, -l+2, \dots, l-2, l-1, l \quad (91)$$

The variable m shown in (89) and (90) is known as the magnetic quantum number, and is limited to the values shown in (91).

12.3 Solutions

$$\Theta = P_l^m(\cos(\theta)) \quad (92)$$

The solution to (89) for Θ is shown above in (92).

$$\Phi(\varphi) = e^{im\varphi} \quad (93)$$

The solution to (90) for Φ is shown above in (93).

$$Y_l^m(\theta, \varphi) = A P_l^m(\cos(\theta)) e^{im\varphi} \quad (94)$$

Combining these two equations gives us the **Spherical Harmonic**, shown in (94).

12.3.1 Normalization of the Spherical Schrödinger Equation

$$\int |\psi(\vec{r})|^2 d^3\vec{r} = \int_0^{2\pi} \int_0^\pi \int_0^\infty |R(r)|^2 |Y(\theta, \varphi)|^2 r^2 \sin(\theta) dr d\theta d\varphi = 1 \quad (95)$$

As previously, it is always in our interest to make sure we normalize our wavefunctions, as seen in (95)

$$\int_0^\infty |R(r)|^2 r^2 dr = 1 \quad (96)$$

$$\int_0^{2\pi} \int_0^\pi |Y(\theta, \varphi)|^2 \sin(\theta) d\theta d\varphi = 1 \quad (97)$$

When we are interested in normalizing our solutions to Schrödinger's equation in spherical 3-D form, it turns out that it is necessary to normalize the radial and angular equations separately, as shown in (96) and (97).

$$Y_l^m(\theta, \varphi) = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\varphi} P_l^m(\cos(\theta)) \quad (98)$$

$$\epsilon = \begin{cases} (-1)^m, & \text{for } m > 0 \\ 1, & \text{for } m \leq 0 \end{cases} \quad (99)$$

The normalized version of the spherical harmonic (aka the angular part of the solution to Schrödinger's equation) is shown above in (98), with ϵ defined in (99).

$$\int_0^\infty |u(r)|^2 dr = 1 \quad (100)$$

For the sake of simplicity, we will redefine our variables such that $u(r) \triangleq rR(r)$, and rewrite (96) into the form shown in (100).

12.3.2 The Radial Solution

$$V_{\text{eff}} = V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \quad (101)$$

To make further use of the redefinition $u(r) = rR(r)$, we should define an *effective potential* V_{eff} , shown in (101). The final addend in this equation $\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$ is known as the **centrifugal term**.

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + V_{\text{eff}} u = Eu \quad (102)$$

We can then rewrite the radial equation into a more pleasant form, seen in (102).

Although we cannot find a general solution for the radial equation in all cases, solving it for a specific set of parameters in a given system is possible – we will look at the solution for the Hydrogen atom, a system with a central stationary (or time-independent) potential.

12.3.3 Solving for the Hydrogen Atom

$$V = -\frac{k}{r}, \text{ with } k = \frac{e^2}{4\pi\epsilon_0} = 1.44 \text{ eVnm} \quad (103)$$

We can model the Hydrogen atom via usage of the *Coulomb Potential*, shown in (103).

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{k}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (104)$$

Using the Coulomb Potential, we have the radial equation shown in (104).

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \quad (105)$$

By redefining some values we can simplify (104), giving us (105). These redefinitions are:

$$a_0 = \frac{\hbar^2}{mk}, \kappa = \frac{\sqrt{-2mE}}{\hbar}, \rho_0 = \frac{2}{a_0\kappa}, \text{ and } \rho = \kappa x.$$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (106)$$

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)] v = 0 \quad (107)$$

Solving for $u(\rho)$ gives us (106). We will also need to find a solution for $v(\rho)$, for the differential equation shown in (107).

We will assume that $v(\rho)$ is a series of the form $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$.

$$c_{j+1} = \frac{2(j+l+1) - \rho_0}{j(j+1) + 2(l+1)(j+1)} c_j \quad (108)$$

Plugging our series into (107) gives us (108).

$$2(j_{\max} + l + 1) - \rho_0 = 0 \implies n \triangleq j_{\max} + l + 1 = \frac{1}{2}\rho_0, \text{ for } n = 1, 2, 3, \dots \quad (109)$$

Although our series is mathematically infinite, this is physically incorrect, and we must thus find a terminal expression for this series. If we assume our final element in the series is zero, we can set up a logical expression like in (109).

$$E_n = -\frac{\hbar^2}{2m_e a_0^2} \frac{1}{n^2} \quad (110)$$

Plugging in our original values leaves us with a very elegant solution (called **Bohr's Formula**), shown in (110).

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \quad (111)$$

Alternatively, we can find the wavefunction for the Hydrogen atom via the solutions for $R_{nl}(r)$, which will give us an equivalent result to Bohr's Formula!

$$\psi_{nlm}(\vec{r}, t) = R_{nl}(r)Y_l^m(\theta, \phi) \quad (112)$$

For context, (112) is the TISE we can construct using (111) and (98).

12.4 Quantum Numbers

In the previous subsection, we referenced several values n , l , and m (in particular, when dealing with the wavefunction ψ_{nlm}). We are already familiar with n , as it is the quantized energy level for a particle³².

According to Wikipedia, "as n increases, the number of electronic shells increases and the electron spends more time farther from the nucleus. As n increases, the electron is also at a higher potential energy and is, therefore, less tightly bound to the nucleus."³³

$$l = 0, 1, 2, \dots, n-1 \quad (113)$$

In addition to n , we have the **azimuthal quantum number** l , defined relative to n in (113).

According to Wikipedia, "the azimuthal quantum number is a quantum number for an atomic orbital that determines its orbital angular momentum and describes the shape of the orbital."³⁴

$$m = -l, -l+1, -l+2, \dots, l-2, l-1, l \quad (114)$$

Finally, we have our **magnetic quantum number** m , defined relative to l in (114).

According to Wikipedia, "the magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of orbital in space."³⁵

In contrast to one-dimensional problems, there is a potential for **degeneration**³⁶ to occur in multidimensional problems.

12.5 Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} \quad (115)$$

Angular momentum in its general form is defined in (115)

³²This is more formally known as the principle quantum number

³³https://en.wikipedia.org/wiki/Principal_quantum_number

³⁴https://en.wikipedia.org/wiki/Azimuthal_quantum_number

³⁵https://en.wikipedia.org/wiki/Magnetic_quantum_number

³⁶Degeneration is a term describing when several states each have the same energy eigenvalue

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \quad (116)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \quad (117)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \quad (118)$$

Each component of the angular momentum formula is shown in (116), (117), and (118).

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \quad (119)$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \quad (120)$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \quad (121)$$

The commutators for each combination of these operators are shown in (119), (120), and (121) – as we see, they do not commute.

$$[\hat{L}^2, \hat{L}_x] = 0 \quad (122)$$

$$[\hat{L}^2, \hat{L}_y] = 0 \quad (123)$$

$$[\hat{L}^2, \hat{L}_z] = 0 \quad (124)$$

On the other hand, the total angular momentum does commute!

$$\hat{L}_x = -i\hbar \left(-\sin(\phi) \frac{\partial}{\partial \theta} - \cos(\theta) \cos(\phi) \frac{1}{\sin(\theta)} \frac{\partial}{\partial \phi} \right) \quad (125)$$

$$\hat{L}_y = -i\hbar \left(\cos(\phi) \frac{\partial}{\partial \theta} - \cos(\theta) \sin(\phi) \frac{1}{\sin(\theta)} \frac{\partial}{\partial \phi} \right) \quad (126)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (127)$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right) \quad (128)$$

These operators can be written in spherical coordinates, seen in (125), (126), (127), and (128).

$$\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m \quad (129)$$

$$\hat{L}_z Y_l^m = \hbar m Y_l^m \quad (130)$$

L^2 and L_z have simultaneous eigenfunctions Y_l^m ³⁷; these are shown in (129) and (130).

12.5.1 Ladder Operators

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y \tag{131}$$

The ladder operator for spin is shown in (131).

³⁷Recall that this is known as the *spherical harmonic*, mentioned earlier in (94)