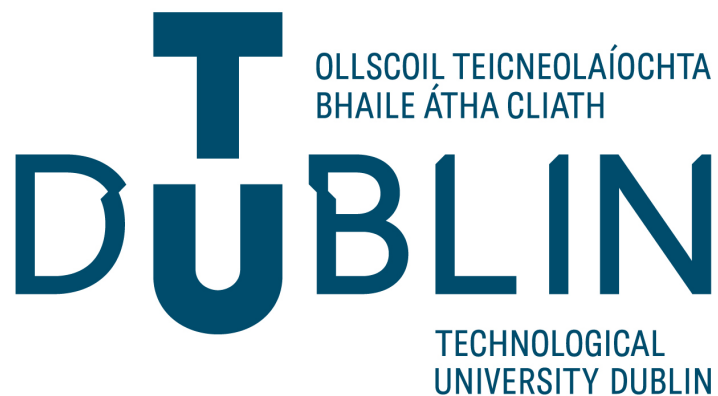


Equations of Quantum Mechanics

Michael Whelan 2021/2022



Project report submitted in partial fulfilment of the
examination requirements leading to the award of

BSc in Mathematical Sciences

Technological University Dublin

Supervised by

Prof. Rossen Ivanov

Acknowledgments

I would like to give a big thank you to my supervisor Prof. Rossen Ivanov for all his help on correcting and guiding me through this report.

I would like to thank Eliza for putting up with me all the way through writing this.

I would like to also thank my Mam and Dad.

Contents

1	Introduction	4
2	Principles of Quantum Mechanics	5
2.1	Hilbert Space	5
2.2	Operators	5
2.2.1	Ad-joint Operators	6
2.2.2	Hermitian Operators	8
2.2.3	Continuous Specrum	9
2.3	L^2 Norm	11
2.4	L^2 Functions	11
3	Schrödinger Equation	13
3.1	Wave Function	13
3.2	Derivation	15
4	Particle in a box	18
5	The Quantum Harmonic Oscillator	28
5.1	Solving the Schrödinger Equation	28
5.2	Probabilities and Distributions	39
6	Hydrogen Atom	44
6.1	Seperation of Variables	44
6.2	Further Separating the Angular Part	45
6.3	Solving the Φ Part	46
6.4	Solving the Θ part	47
6.5	Putting together the Angular parts	48
6.6	Solving the Radial Part	48
6.7	Putting together the wave function	49
7	Conclusion	51

1 Introduction

What is Quantum Mechanics? To answer that let us break down the words separately. 'Quantum' is the smallest amount or unit of something and 'mechanics' is mathematics dealing with motion and forces. So putting them together we get studying motion of the smallest units. Quantum Mechanics looks at the behaviour of sub-atomic particles such as the energy they produce or where they are at a given time. In this project we will focus mainly on the mathematical essence of Quantum Mechanics. We will begin explaining the basic principles and then reviewing Simple Harmonic motion in Classical Mechanics with the Harmonic Oscillator as an example. We will then focus on two examples A Particle in a Box and the Quantum Harmonic Oscillator in two-dimensions and The Hydrogen atom in three-dimensions where we will see some applications and how we use what we have learned in context. Our primary goal to learn about Quantum Mechanics from a mathematical point of view by using the Schrödinger equation and the theory of partial differential equations.

2 Principles of Quantum Mechanics

Throughout our examples we will be using many tools to solve our formulae. Here we will begin with some definitions and explanations. For this chapter we will use Dirac notation. In Dirac notation vectors are represented as $|v\rangle$ this is called a ket. A multiple of a vector by a complex number or scalar c is represented as $c|v\rangle$.

2.1 Hilbert Space

From our reading of (Vaughn 2005) A Hilbert space is a vector space H with an inner product $\langle f, g \rangle$ such that the norm defined by

$$|f| = \sqrt{\langle f, f \rangle} \quad (1)$$

turns H into a complete metric space. A complete metric space is a metric space in which every Cauchy sequence is convergent. A Cauchy is defined as a sequence a_1, a_2, \dots such that a metric $d(a_m, a_n)$ satisfies

$$\lim_{\min(m,n) \rightarrow \infty} d(a_m, a_n) = 0 \quad (2)$$

Examples of finite-dimensional Hilbert spaces include

1. The real numbers R^n with $\langle v, u \rangle$ the vector dot product of v and u .
2. The complex numbers C^n with $\langle v, u \rangle$ the vector dot product of v and the complex conjugate of u .

An example of an infinite-dimensional Hilbert space is L^2 , the set of all functions $f : R \rightarrow R$ such that the integral of f^2 over the whole real line is finite. In this case, the inner product is

$$\langle f, g \rangle = \int_{-\infty}^{\infty} f(x)g(x)dx \quad (3)$$

2.2 Operators

If we are studying a quantum system that system could consist of for example a single electron. Then an operator is a mathematical object that we can apply to this quantum system or to be specific the wave function of this quantum system. In real life this is the equivalent to making a measurement. For example we will talk briefly about the position operator.

The position operator is denoted at \hat{x} . If we were to make a measurement of where our electron is in space, mathematically this is the equivalent to writing

$$\hat{x}|\psi\rangle = x|\psi\rangle \quad (4)$$

Other operators include the momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad (5)$$

and the Hamiltonian operator

$$\hat{H} = i\hbar \frac{\partial}{\partial t} \quad (6)$$

The Hamiltonian in most cases is the measurement for the total energy of the system because it accounts for kinetic energy and potential energy. (Bowers 2020)

2.2.1 Ad-joint Operators

For any operator A we can define it's ad-joint A^\dagger as

$$\langle\psi|A^\dagger|\phi\rangle = \langle\phi|A|\psi\rangle^* \quad (7)$$

While operators in quantum mechanics usually act towards the right, ad-joint operators act to the left. This is known as the Hermitian conjugate. The Hermitian conjugate changes between bra-states and ket-states and now also their operators and ad-joints.

$$|\psi\rangle \iff \langle\psi| \quad (8)$$

$$A \iff A^\dagger \quad (9)$$

This definition helps us to answer the question, how do we deal with an expression where an operator acts on a state? It will look something like this

$$A|\psi\rangle \iff A^\dagger\langle\psi| \quad (10)$$

Bra-states act as functionals on ket-states, yielding the inner product. From the properties of inner products in complex Hilbert Spaces we know that we can exchange the two states if we add a complex conjugation like so

$$\langle \phi | : \quad |\psi\rangle \mapsto \langle \phi | \psi \rangle = \langle \psi | \phi \rangle^* \quad (11)$$

Now we ask what is the bra-state of A times a ket? It will also act as a functional, yielding the inner product, where we can swap the states by adding a complex conjugate

$$\langle A\phi | : \quad |\psi\rangle \mapsto \langle A\phi | \psi \rangle = \langle \psi | A\phi \rangle^* \quad (12)$$

We can write the final term as

$$(A\phi | : \quad |\psi\rangle \mapsto \langle A\phi | \psi \rangle = \langle \phi | A^\dagger | \psi \rangle \quad (13)$$

What other properties can we take from ad-joint operators? If we have a finite-dimensional Hilbert space with basis functions $|\psi_n\rangle$ where $n = 1, 2, 3, \dots$. We can express any operator as $m \times n$ matrix.

$$\begin{pmatrix} A_{11} & A_{12} & \dots A_{1n} \dots \\ A_{21} & A_{22} & \dots A_{2n} \dots \\ A_{31} & A_{32} & \dots A_{mn} \dots \end{pmatrix} \quad (14)$$

Where those matrix elements are defined like

$$A_{mn} = \langle \psi_m | A | \psi_n \rangle \quad (15)$$

We will now investigate the matrix elements of the ad-joint of A .

$$A_{mn}^\dagger = \langle \psi_m | A^\dagger | \psi_n \rangle \quad (16)$$

By using the definition of ad-joint operators we can rewrite this as

$$A_{mn}^\dagger = \langle \psi_m | A^\dagger | \psi_n \rangle = \langle \psi_n | A | \psi_m \rangle^* \quad (17)$$

Therefore the $m \times n$ matrix element of A^\dagger is the same as the complex conjugated $m \times n$ matrix element of A

$$A_{mn}^\dagger = \langle \psi_m | A^\dagger | \psi_n \rangle = \langle \psi_n | A | \psi_m \rangle^* = A_{nm}^* \quad (18)$$

In matrix notation, Hermitian conjugation corresponds to transposed and complex matrices.

2.2.2 Hermitian Operators

If A is a Hermitian operator then it is the same as its ad-joint operator

$$A = A^\dagger \quad (19)$$

Which is defined as

$$\langle \psi | A^\dagger | \phi \rangle = \langle \phi | A | \psi \rangle^* \quad (20)$$

1. Their eigenvalues are real numbers so $a_n^* = a_n$.
2. Eigenvectors that belong to different eigenvalues are orthogonal to each other which we can express as

$$\langle a_m | a_n \rangle = \delta_{mn}.$$

Let us now prove these 2 statements. We start with the definition of the ad-joint operator, but since $A^\dagger = A$ we can also rewrite

$$\langle \psi | A^\dagger | \phi \rangle = \langle \phi | A | \psi \rangle^* = \langle A | \phi \rangle \quad (21)$$

We now can replace the arbitrary vectors ψ and ϕ with eigenvectors of A such that we have

$$\langle a_n | A | a_m \rangle^* = \langle a_n | A | a_m \rangle \quad (22)$$

If we let the operator act on its eigenstates we get the corresponding eigenvalue so now we have

$$[a_m \langle a_n | a_m \rangle]^* = a_n \langle a_m | a_n \rangle \quad (23)$$

The complex conjugate on the LHS of the equation which results in the complex conjugate of the eigenvalue a_m and the complex conjugate of an inner can be resolved by exchanging two states.

$$a_m^* \langle a_m | a_n \rangle = a_n \langle a_m | a_n \rangle \quad (24)$$

We can now distinguish two cases. First is $m = n$ we can cancel the inner products on both sides and we get

$$a_m^* = a_m \quad (25)$$

This means that the eigenvalues are all real numbers, which proves the first statement.

Secondly, if $m \neq n$, we must see if the eigenvalues a_m and a_n are different or if they are the same, in which case would degenerate eigenvalues. In the first case, if the eigenvalues a_m and a_n are different, the inner products have to be zero for the equation to be valid.

$$a_m^* \langle a_m | a_n \rangle = a_n \langle a_m | a_n \rangle \implies \langle a_m | a_n \rangle = 0 \quad (26)$$

Therefore, the eigenvectors have to be orthogonal which proves the second statement. If the eigenvalues a_m and a_n are the same, we can construct linear combinations of vectors. let's call them b_1 and b_2 .

$$|b_1\rangle = |a_m\rangle + |a_n\rangle \quad (27)$$

$$|b_2\rangle = |a_m\rangle - |a_n\rangle \quad (28)$$

This implies

$$\langle b_1 | b_2 \rangle = \langle a_m | a_m \rangle - \langle a_m | a_n \rangle + \langle a_n | a_m \rangle - \langle a_n | a_n \rangle \quad (29)$$

The first and last term will cancel. Next we can assume that the inner product of those two states is real, since we can always adjust the phase of one state such that the inner product becomes real. For a real inner product, we can exchange the states and the result is zero.

$$\langle b_1 | b_2 \rangle = \langle a_m | a_m \rangle - \langle a_m | a_n \rangle + \langle a_n | a_m \rangle - \langle a_n | a_n \rangle = 0 \quad (30)$$

Therefore, the new states b_1 and b_2 are orthogonal to each other and by construction also to all other states a_k .

$$\langle a_k | b_{1,2} \rangle = \langle a_k | a_m \rangle \pm \langle a_k | a_n \rangle = 0 \quad \text{and} \quad A |b_{1,2}\rangle = a_m |b_{1,2}\rangle \quad (31)$$

2.2.3 Continuous Spectrum

All we have been discussing so far is for a discrete spectrum. What about a continuous spectrum? What if instead of getting a discrete set of eigenstates and eigenvalues we get a continuous set of eigenstates and

eigenvalues. We will start as an example finding the eigenvalues and eigenfunctions of the momentum operator

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

$$-i\hbar \frac{d}{dx} f_p(x) = p f_p(x) \quad (32)$$

with p being our eigenvalue and $f_p(x)$ being our eigenfunction. The solution to this is

$$f_p(x) = A e^{ipx/\hbar} \quad (33)$$

This solution is not square-inferable and operator p has no eigenfunctions in Hilbert space. However, if we only consider real eigenvalues, we can define sort of orthonormality

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx \quad (34)$$

This gives us the Direc delta function

$$|A|^2 2\pi\hbar \delta(p - p') \quad (35)$$

Since the Fourier transform of Dirac delta function is

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk \quad (36)$$

We pick $A = \frac{1}{\sqrt{2\pi\hbar}}$ and get

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad (37)$$

We now have

$$\langle f_{p'} | f_p \rangle = \delta(p - p') \quad (38)$$

We call this equation Dirac orthonormality. These functions are complete in a sense that any square integrable function $f(x)$ can be written in the form

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{ipx/\hbar} dp \quad (39)$$

To summarise the continuous spectra eigenfunctions with real eigenvalues are Dirac orthonormalizable and complete. (Safronova 2015)

2.3 L^2 Norm

The l^2 -norm $|x|$ is a vector norm defined for a complex vector

$$\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} \quad (40)$$

By

$$|\mathbf{x}| = \sqrt{\sum_{k=1}^n |x_k|^2} \quad (41)$$

The " L^2 -norm" (denoted with an uppercase L) is reserved for application with a function $\phi(x)$

$$|\phi|^2 \equiv \phi \cdot \phi \equiv \langle \phi | \phi \rangle \equiv \int |\phi(x)|^2 dx \quad (42)$$

with $\langle f, g \rangle$ denoting an angle bracket (Weisstein 2005)

2.4 L^2 Functions

L^2 is a function where $f : X \rightarrow \mathbb{R}$ such that

$$|f|^2 = \int_X |f|^2 d\mu \quad (43)$$

The collection of L^2 functions on X is called $L^2(X)$ of L2-space, which is a Hilbert space.

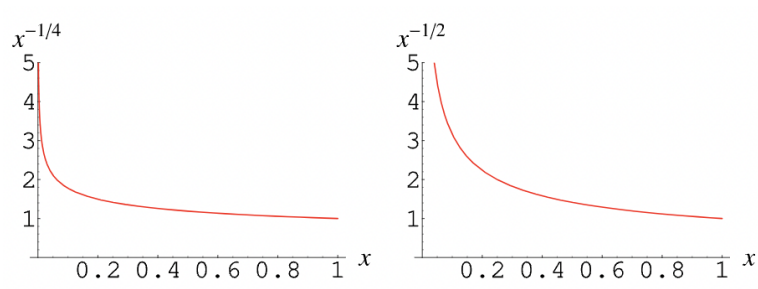


Figure 2.1: (Rowland 2022)

On the unit interval $(0, 1)$, the functions $f(x) = 1/x^p$ are in L^2 for $p < 1/2$. However, the function $f(x) = x^{-1/2}$ is not in L^2 since

$$\int_0^1 \left(x^{-1/2}\right)^2 dx = \int_0^1 \frac{dx}{x} \quad (44)$$

does not exist. More generally, there are L^2 -complex functions obtained by replacing the absolute value of a real number in the definition with the norm of the complex number. In fact, this generalizes to functions from a measure space X to any normed space (Rowland 2022)

3 Schrödinger Equation

3.1 Wave Function

In Quantum Mechanics we have equations to describe motion similar to Classical Mechanics. We will begin to derive Schrödinger's Equation but first we need to explain what a Wave Function is and take pieces of information from the Wave Function to derive Schrödinger's Equation.

"A wave function may be used to describe the probability of finding an electron within a matter wave. To do this, the wave function, which may include an imaginary number, is squared to yield a real number solution" (Helmenstine 2020). Let us take a basic wave function we will use this to describe the components of a wave.

$$\psi = e^{i(kx - \omega t)} \quad (45)$$

Where $i = \sqrt{-1}$. We know that

$$\psi = e^{i\alpha x} = \cos(\alpha x) + i \sin(\alpha x) \quad (46)$$

Let us consider the real part of the wave

$$\psi = \cos(kx - \omega t) \quad (47)$$

If we look at $\cos(kx)$ where $\lambda = \text{wavelength}$

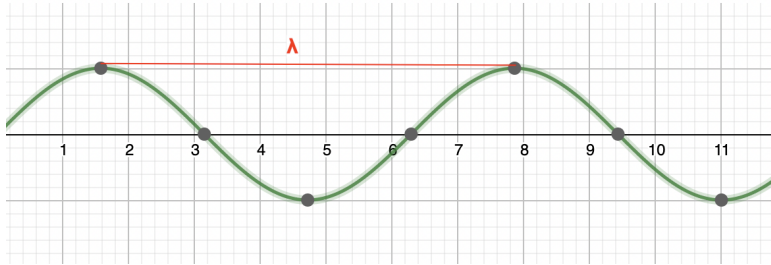


Figure 3.1:

$$k = \frac{2\pi}{\lambda} \quad (48)$$

We can rewrite $\cos(kx)$ as

$$\cos\left(\frac{2\pi}{\lambda}x\right) \quad (49)$$

This is known as a 'Standing Wave' it does not go anywhere.

If we now take $\cos(kx - \omega t)$ this is a travelling wave at velocity v to the right. The wave will reach its maximum amplitude when $kx - \omega t = 0$ because

$$\cos(kx - \omega t) = \cos(0) = 1 \quad (50)$$

This implies

$$kx = \omega t \quad (51)$$

$$\frac{x}{t} = \frac{w}{k} \quad (52)$$

and we know

$$\frac{x}{t} = \frac{Distance}{Time} = \frac{w}{k} = v \quad (53)$$

What is ω ? ω is the velocity in radians which is $2\pi f$ where f =frequency We now have

$$\omega = 2\pi f, \quad (54)$$

$$k = \frac{2\pi}{\lambda} \quad (55)$$

This implies

$$\frac{\omega}{k} = \frac{2\pi f}{2\pi} = f\lambda = v \quad (56)$$

Frequency is the number of waves that pass a particular point per second and the wavelength is each distance from peak to peak.

Planck's idea that the energy of the photon is quantised according to $E = hf$. The momentum of this photon is p

$$p = \frac{h}{\lambda} \quad (57)$$

Recall

$$k = \frac{2\pi}{\lambda} \quad (58)$$

Using the deBroglie Relationship where $\lambda = \frac{h}{p}$ implies

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h}p = \frac{p}{\hbar} \quad (59)$$

Furthermore $p = k\hbar$ gives us wavelength and momentum, $\omega = 2\pi f$ gives us frequency and $\frac{\omega}{k}$ gives us velocity v .

3.2 Derivation

Total Energy of a system with mass m in a field of potential U is expressed as

$$E = KE + PE \quad (60)$$

$$E = \frac{1}{2}mv^2 \quad (61)$$

We know

$$v = \frac{p}{m} \quad (62)$$

$$v^2 = \frac{p^2}{m^2} \quad (63)$$

$$(64)$$

We now have

$$E = \frac{p^2}{2m} + U \quad (65)$$

Here we will assume $U = 0$

Allow ψ to be our basic wave function again.

$$\psi = e^{i(kx - \omega t)} \quad (66)$$

Let us differentiate with respect to x holding time t constant.

$$\frac{d\psi}{dx} = ike^{i(kx - \omega t)} = ik\psi \quad (67)$$

Now we differentiate again

$$\frac{d^2\psi}{dx^2} = (ik)^2\psi \quad (68)$$

Recall $p = \frac{h}{\lambda}$ which implies $p = \frac{hk}{2\pi}$ where $\frac{h}{2\pi}$ the other version of Plank's Constant.

$$p = \hbar k \quad (69)$$

$$k = \frac{p}{\hbar} \quad (70)$$

Substituting back into Schrödinger's Equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi = -\left(\frac{p^2}{\hbar^2}\right)\psi \quad (71)$$

Multiply through by $-\hbar^2$

$$-\hbar^2 \frac{d^2\psi}{dx^2} = p^2\psi \quad (72)$$

Our Energy again is

$$E = \frac{p^2}{2m} \quad (73)$$

We are looking for an equation ψ in the form of

$$E\psi = \frac{p^2}{2m}\psi \quad (74)$$

$$(75)$$

We now consider the quantity p^2 as an eigenvalue of the operator $-\hbar \frac{d^2\psi}{dx^2}$. This is a generalisation that leads into the Schrödinger Equation.

$$p^2\psi = -\hbar \frac{d^2\psi}{dx^2} \quad (76)$$

Finally we have

$$E\psi = \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} \quad (77)$$

This is the time independent Schrödinger Equation as we treated time as a constant. Now let us derive the time dependent Schrödinger Equation.

We remind ourselves

$$E = \hbar\omega = hf \quad (78)$$

Using our basic wave function again

$$\psi = e^{i(kx - \omega t)} \quad (79)$$

We are now finding the derivative with respect to time t . ω will be considered as an eigenvalue of $\frac{\partial\psi}{\partial t}$ operator and ψ as an eigen function, next we replace the eigenvalue by the differentiation operator.

$$\frac{\partial\psi}{\partial t} = -i\omega\psi \quad (80)$$

But $E = \hbar\omega$ so

$$E\psi = \hbar\omega\psi \quad (81)$$

Then multiply by $-i$ and divide by \hbar

$$-\frac{i}{\hbar}E\psi = -i\omega\psi = \frac{\partial\psi}{\partial t} \quad (82)$$

So now

$$E\psi = -\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial \psi}{\partial t} \quad (83)$$

We can substitute $E\psi$ for $i\hbar \frac{\partial \psi}{\partial t}$ into the Schrödinger Equation which was

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi \quad (84)$$

And we get

$$-i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi \quad (85)$$

This is the time dependent Schrödinger Equation where time is treated as a variable. This illustrates that the wave function $e^{i(kx-\omega t)}$ satisfies the Schrödinger Equation.

The general solution turns out to be

$$\psi(x, t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)} \quad (86)$$

When $U=0$ $\omega k = \frac{\hbar k^2}{2m}$ depends on k . This is the situation for a free particle taht is not trapped in a potential which exhibits wave-like properties. This can be expressed as a Fourier Integral.

$$\Psi = \int e^{i(kx-\omega t)} A(k, \omega) dk d\omega = \int A(k, \omega) \psi dk d\omega \quad (87)$$

For some amplitude $A(k, \omega)$.

This is integration (or summation in the discrete case) over all possible momenta k . We considered k and ω as eigenvalues of appropriate operators which allows generalisation.

4 Particle in a box

Imagine a particle is stuck in a box where the walls are infinite.

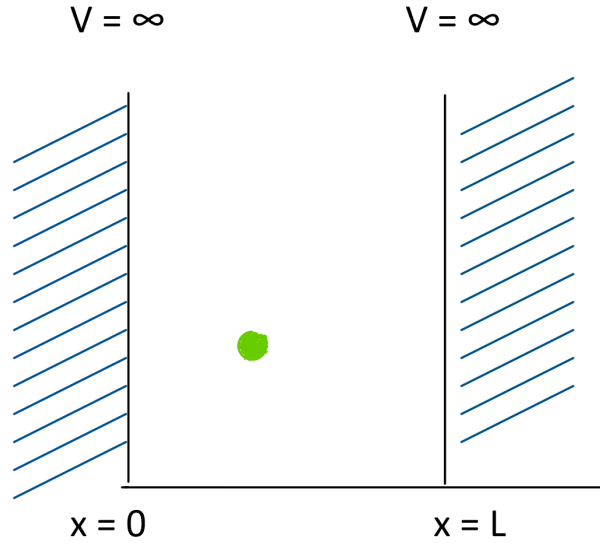


Figure 4.1:

The particle can only move in the x -axis and can only move between $x = 0$ and $x = L$. The potential at $x = 0$ is $V = \infty$ and the potential at L is also ∞ . The potential beyond $x = 0$ for all values less than $x = 0$ is infinity and the potential beyond $x = L$ for all positive values is infinity.

The potential between these two boundaries is zero where the particle can exist so the particle can exist so the particle is a free particle in the region between $x = 0$ and $x = L$.

We will start to tackle this problem by assuming the separation of variables (Fowler 2021).

$$\psi(x, t) = \psi(x)\varphi(t) \quad (88)$$

We will then convert the Schrödinger Equation from time dependent

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (89)$$

to the time independent

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (90)$$

The wave function is the solution of the general time dependent Schrödinger Equation.

$$\Psi = \text{Wavefunction} \quad (91)$$

This wave function contains the space and time dependence.

What is the relationship between the wave function and the eigenfunction? The wave function is a product of the eigenfunction and an expression that contains the time dependence.

$$\Psi(x, t) = \psi(x)e^{\frac{-iEt}{\hbar}} \quad (92)$$

This is the actual wave function solution of the Schrödinger. Let us recall equation (89) This contains the potential. What is the potential? We can say the potential can have two values. It can have infinite values for $x \geq L$ and $x \leq 0$ and zero values for $0 < x < L$ and greater than 0

$$V = \begin{cases} \infty & \text{for } x \geq L \text{ and } x \leq 0 \\ 0 & \text{for } 0 < x < L \end{cases}$$

The particle is restricted only in this particular region.

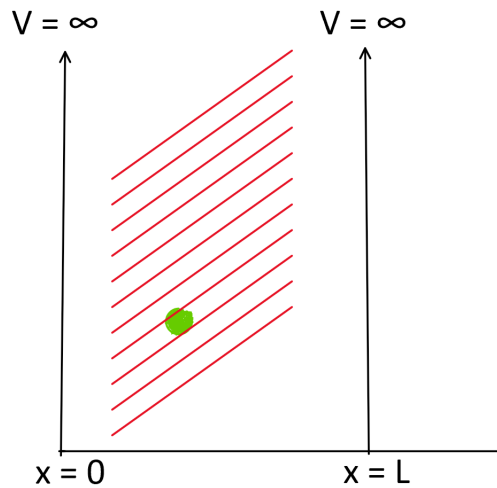


Figure 4.2:

So we only need to apply the Schrödinger Equation to this region. Beyond it, the Schrödinger Equation will only give us the solutions where it is equal to zero.

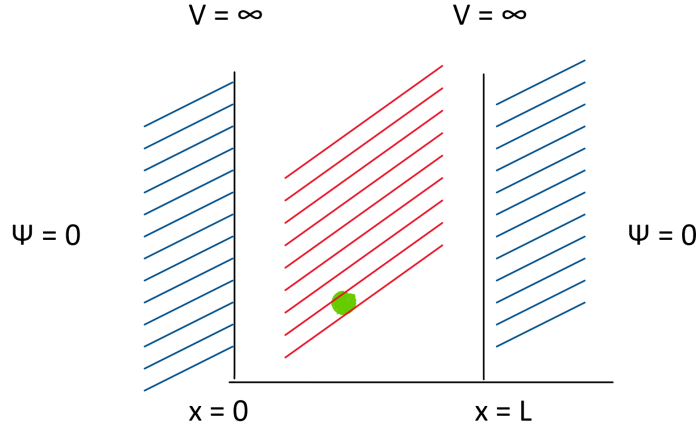


Figure 4.3:

The wave function does not exist beyond $x = L$ and $x = 0$ because the potential is infinite and the particle cannot penetrate through it (Sanny; & Moebs 2016).

In this region the potential is zero so now the equation becomes much simpler.

$$\frac{-\hbar}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (93)$$

$$\frac{-d^2\psi}{dx^2} = \frac{2mE}{\hbar} \psi \quad (94)$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad (95)$$

Let us assume

$$\frac{2mE}{\hbar^2} = k^2 \quad (96)$$

This implies

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (97)$$

Now substituting k into our formula we have

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad (98)$$

And the solution to this is

$$\psi = A \sin(kx) + B \cos(kx) \quad (99)$$

To find our A and B we need to apply some sort of boundary condition. The particle can only have a non-zero wave function solution in our region. We will assume $\psi(x=0)=0$ because at $x=0$ the potential is infinite so the wave function cannot exist. If we apply this in ψ we get

$$A \sin(k(0)) + B \cos(k(0)) = 0 \quad (100)$$

$$B \cos(k) = 0 \quad (101)$$

$$B = 0 \quad (102)$$

We can rewrite the equation as

$$\psi = A \sin(kx) \quad (103)$$

This is the new form of the eigenfunction solution but now we need A . Let us apply another boundary condition. If we apply the second boundary condition. We do this because the particle comes up against the impenetrable barrier where the potential is infinite, so wave functions automatically become 0. We can write the equation now as

$$\psi(x=L) = 0 \quad (104)$$

This implies

$$A \sin(kL) = 0 \quad (105)$$

A has to be a non-zero constant otherwise the wave function cannot exist. We can now say

$$A \sin(kL) = 0 \quad (106)$$

If we look at the sin function

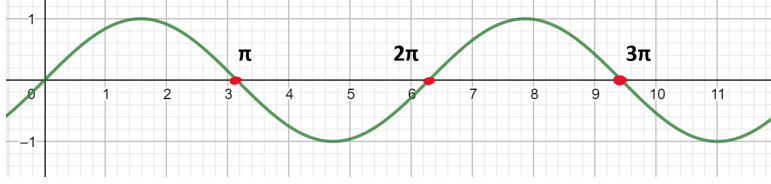


Figure 4.4:

Where $\theta = 0, \pm\pi, \pm2\pi, \pm3\pi...$

This implies $kL = 0, \pm\pi, \pm2\pi, \pm3\pi...$ Now $k = 0$ is not valid. If $k = 0$ then ψ will equal to zero. This is not possible because that would mean the particle has disappeared so now we have

$$kL = n\pi \quad (107)$$

We can rewrite

$$k_n = \frac{n\pi}{L} \quad (108)$$

Where $n = 1, 2, 3, 4, \dots$ We can now substitute this into our original wave function, we finally have the eigenfunction

$$\psi_n = A \sin\left(\frac{n\pi}{L}x\right) \quad (109)$$

Where $n = 1, 2, 3, 4, \dots$ We still need to find A . We can find A by normalising the wave function. It is not enough for the wave function to satisfy the Schrödinger Equation, it must satisfy another condition which is known as the "Born's Statistical Interpretation". This tells us that if you have a wave function solution, and you take it's complex conjugate and multiply it by the wave function and integrate between two points a, b

$$\int_a^b \Psi^* \Psi dx = P_{a,b} \quad (110)$$

This gives us the probability of finding the particle in between a, b . If we change a, b to $-\infty, +\infty$ we now have

$$\int_{-\infty}^{+\infty} \Psi^* \Psi dx = P_{+\infty, -\infty} \quad (111)$$

If we look at the probability of finding the particle from $-\infty$ to $+\infty$ which is the whole universe then the particle must exist somewhere and therefore we get

$$\int_{-\infty}^{+\infty} \Psi^* \Psi dx = 1 \quad (112)$$

All wave functions must satisfy this condition because otherwise we cannot use that wave function for a real and physical particle. In our case we will change the equation to

$$\int_0^L \Psi^* \Psi dx = 1 \quad (113)$$

However we haven't obtained the wave function yet.

Let us recall the wave function

$$\Psi(x, t) = \psi(x)e^{\frac{-iEt}{\hbar}} \quad (114)$$

This must satisfy the Born's Statistical Interpretation which will help us calculate the value of A .

We now have

$$\Psi(x, t) = A \sin\left(\frac{n\pi x}{L}\right) e^{\frac{-iE_n t}{\hbar}} \quad (115)$$

Now substituting

$$\int_0^L (A \sin\left(\frac{n\pi x}{L}\right) e^{\frac{-iEt}{\hbar}})(A \sin\left(\frac{n\pi x}{L}\right) e^{\frac{+iEt}{\hbar}}) dx = 1 \quad (116)$$

We now solve

$$A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \quad (117)$$

$$A^2 \int_0^L \frac{1}{2} \left(1 + \sin\left(\frac{2n\pi x}{L}\right)\right) dx = 1 \quad (118)$$

Separating the integrals

$$\frac{A^2}{2} \int_0^L dx + \frac{A^2}{2} \int_0^L \sin\left(\frac{2n\pi x}{L}\right) dx = 1 \quad (119)$$

Applying the limits

$$\frac{A^2}{2} [x]_0^L - \frac{A^2}{2} \left(\frac{L}{2n\pi}\right) \left[\cos\left(\frac{2n\pi x}{L}\right)\right]_0^L = 1 \quad (120)$$

$$\frac{A^2}{2} L - \frac{A^2 L}{4n\pi} \left[\cos\left(\frac{2n\pi L}{L}\right) - \cos\left(\frac{2n\pi(0)}{L}\right)\right] = 1 \quad (121)$$

$$\frac{A^2}{2} L - \frac{A^2 L}{4n\pi} (1 - 1) = 1 \quad (122)$$

$$\frac{A^2}{2} L = 1 \quad (123)$$

$$A^2 = \frac{2}{L} \quad (124)$$

Finally we have

$$A = \sqrt{\frac{2}{L}} \quad (125)$$

We now have

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (126)$$

Applying our wave function

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{\frac{-iE_n t}{\hbar}} \quad (127)$$

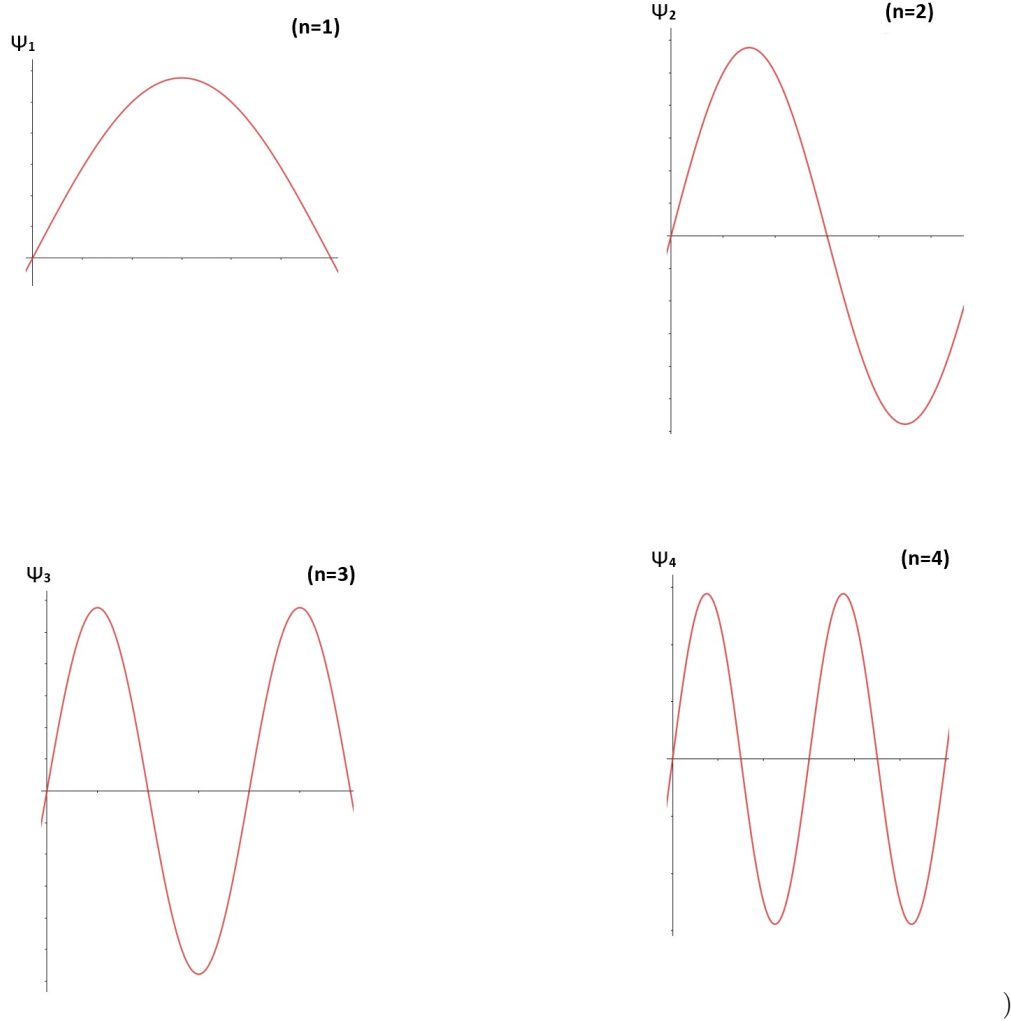


Figure 4.5:

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \quad (128)$$

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \quad (129)$$

$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) \quad (130)$$

$$\psi_4(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{4\pi x}{L}\right) \quad (131)$$

These are the wave functions. The first 4 of the infinite possible wave functions for this particular problem.

Let us now take a look at the probability associated with each wave function.

Recall $|\psi|^2$ = the probability of a wave function at a particular point. As we know you cannot have a negative probability. So after we take the modulus of ψ our graphs change.

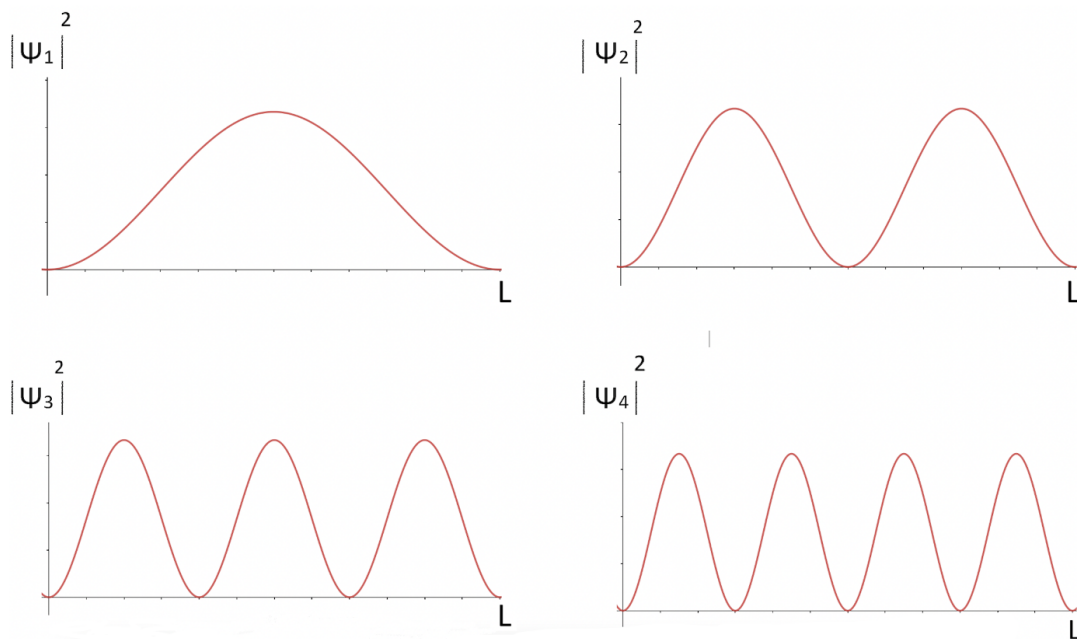


Figure 4.6:

The probability means if you take the measurements of a given wave function. Let us take the first one as an example.

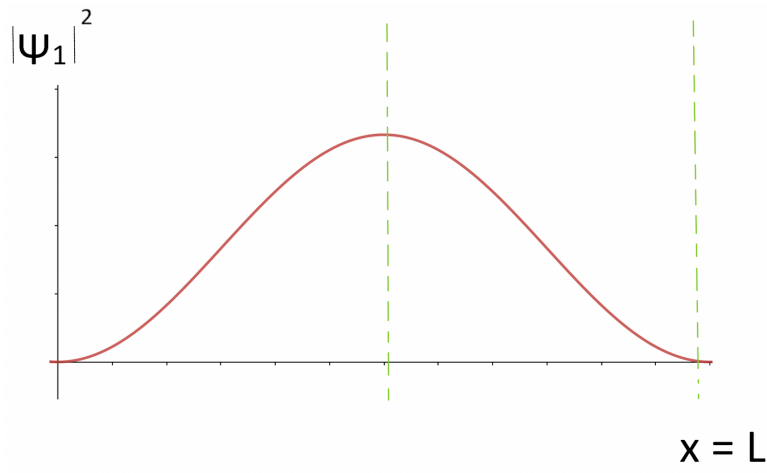


Figure 4.7:

From our understanding of (Landau & Lifschitz 1977), we will find the majority of the time the particle will be somewhere in the middle and the probability near the edges will be lower. Now we have captured our mathematical essence of the problem let us briefly discuss energy levels.

Let us recall

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (132)$$

and

$$k = \frac{n\pi}{L} \quad (133)$$

where $n = 1, 2, 3, \dots$

From here we know n can have many eigenvalues of the Hamiltonian. As we will see, E can also have many values. We can rewrite k as

$$\frac{2mE_n}{\hbar^2} = \frac{n^2\pi^2}{L^2} \quad (134)$$

We will say there is a subscript corresponding to n for all values of n . In other words there are different energies possible. We can now write

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad (135)$$

This is the expression for all possible energy levels of the particle.

This expression corresponds to discrete energy levels. What does this mean? In the quantum world, energies are restricted to only certain values so whatever energies are allowed by this equation, only those energies the particle can have. Let us look at what values are possible

$$n = 1 : E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \quad (136)$$

$$n = 2 : E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} \quad (137)$$

$$n = 3 : E_3 = \frac{9\pi^2 \hbar^2}{2mL^2} \quad (138)$$

There are only certain energy levels that are possible. There are infinite energy levels but not a continuous distribution. These energy levels are corresponding to ψ . So if the particle is in ψ_1 state, it will have energy level E_1 which is known as ground state. If the particle is in ψ_2 it will have E_2 and so on (Landau & Lifschitz 1977).

$$\Psi(x, t) = \sum c_n e^{\frac{-iE_n t}{\hbar}} \psi_n(x) \quad (139)$$

Is the general solution to the wave function. In general, you don't know for certain what energy the system has; you know only the probabilities for various states. But you always know that its energy must be one of the eigenstates of the Hamiltonian. In this general case, we say that the system is in a superposition of the eigenstates (Sanny; & Moebs 2016).

5 The Quantum Harmonic Oscillator

5.1 Solving the Schrödinger Equation

In the previous section we talked about briefly the Harmonic Oscillator which led us to the derivation of the Schrödinger Equation. We are now going to go into the Quantum Harmonic Oscillator in detail. As we know the Quantum world deals with tiny atoms and subatomic particles, do we are not looking at a macroscopic ball on a spring. We are now describing oscillations or vibrations around a point of stable equilibrium in the context of binding energies and electron orbitals. So these are oscillations but of a different nature, however they can be described using the same type of mathematics in the classical situation.

In the classical example we mentioned Hooke's Law as an extension of the harmonic motion This is typical in any mass-spring system. The quantum analog of this scenario could be that of an electron close to an attractive potential or an atom subjected to to a molecular potential that may look just like the harmonic oscillator within a certain limit.

We will follow the same procedures that we did when talking about the particle in a box. From our reading of (Dudik 2004) We know to find the Hamiltonian and then we will solve the time dependent Schrödinger Equation. When we learned about the classical harmonic oscillator we already know what our potential looks like and this will be a great starting point. Here is our potential.

$$V(x) = \frac{1}{2}kx^2 \quad (140)$$

Which is what we used for a mass on a spring. To translate this to the quantum world we need to swap the variable x for the position operator which looks like

$$V(\hat{x}) = \frac{1}{2}k\hat{x}^2 \quad (141)$$

Now we can solve the time dependent Schrödinger Equation. Let us recall the equation in general form.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \quad (142)$$

We can now plug in our potential in

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{1}{2} k \hat{x}^2 \psi(x) = E \psi(x) \quad (143)$$

Let us recall the form of the equation for the classical scenario

$$\frac{\partial^2 x}{\partial t^2} + \beta^2 x = 0 \quad (144)$$

We can put the other version in the same form if we subtract $E\psi$ from both sides and factor ψ out we now have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \left(\frac{1}{2} kx - E \right) \psi(x) = 0 \quad (145)$$

We can now see that where we have a second derivative of $\psi(x)$ with respect to x in one equation we have the second derivative of x with respect to time in the other, and where we have the bracket times ψ we have $\beta^2 x$ in the other.

We will multiply everything by -1 so we lose the negative sign and rearrange the terms in the brackets like so.

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \left(E - \frac{1}{2} kx^2 \right) \psi(x) = 0 \quad (146)$$

Now we will multiply through by $\frac{2m}{\hbar^2}$, we now have.

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar} \left(E - \frac{1}{2} kx^2 \right) \psi(x) = 0 \quad (147)$$

We will now let $\frac{2m}{\hbar^2} = \gamma$. Our equation now looks like

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \gamma \left(E - \frac{1}{2} kx^2 \right) \psi(x) = 0 \quad (148)$$

Now we distribute γ through.

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \gamma E \psi(x) - \gamma \frac{k}{2} x \psi(x) = 0 \quad (149)$$

We want to get rid of the constants and get the equation in the following form

$$\frac{\partial^2 \psi(X)}{\partial X^2} + \epsilon \psi(X) - X^2 \psi(X) = 0 \quad (150)$$

Where $X = \frac{x}{\alpha}$.

This is something we will be able to solve. We have changed lowercase x to capital X and we changed γE to ϵ where $X = \frac{x}{\alpha}$. Both ϵ and γ are new constants that have yet to be determined, which will allow to express the equation which we can easily then solve. We now need to find an equation for ψ of X instead of x , we also need a partial derivative operator with respect to X . We will now use the chain rule. We have

$$\frac{\partial}{\partial x} \psi(X) = \frac{\partial X}{\partial x} \frac{\partial}{\partial X} \psi(X) \quad (151)$$

We now need the derivative inside we then get

$$\frac{\partial}{\partial x} \psi(X) = \frac{\partial X}{\partial x} \frac{\partial}{\partial X} \psi(X) \quad (152)$$

Based on the relationship $X = \frac{x}{\alpha}$ we can replace X with $\frac{x}{\alpha}$

$$\frac{\partial}{\partial x} \psi(X) = \frac{\partial \frac{x}{\alpha}}{\partial x} \frac{\partial}{\partial X} \psi(X) \quad (153)$$

The derivative of this expression is

$$\frac{\partial}{\partial x} \psi(X) = \frac{1}{\alpha} \frac{\partial}{\partial X} \psi(X) \quad (154)$$

In the equation we are trying to get (150), we need the second partial derivative with respect to X . We will now square equation (154) we now have

$$\frac{\partial^2}{\partial x^2} \psi(X) = \frac{1}{\alpha^2} \frac{\partial^2}{\partial X^2} \psi(X) \quad (155)$$

We will now put this expression into our desired equation (150).

$$\frac{1}{\alpha^2} \frac{\partial^2}{\partial X^2} \psi(X) + \gamma E \psi(X) - \gamma \frac{k}{2} a^2 X^2 \psi(X) = 0 \quad (156)$$

We will now multiply by α^2 which leaves us with

$$\frac{\partial^2}{\partial X^2}\psi(X) + \gamma E a^2 \psi(X) - \gamma \frac{k}{2} a^4 X^2 \psi(X) = 0 \quad (157)$$

Now we will need to eliminate $\gamma \frac{k}{2} a^4$. We can do this by setting their product equal to one like so

$$\gamma \frac{k}{2} a^4 = 1 \quad (158)$$

From this we can find the expression for the α constant. We then get α on it's own.

$$\alpha = \left(\frac{2}{k\gamma} \right)^{\frac{1}{4}} \quad (159)$$

We now have simplified the Schrödinger Equation to this more manageable form.

$$\frac{\partial^2 \psi(X)}{\partial (X^2)} + \epsilon \psi(X) - X^2 \psi(X) = 0 \quad (160)$$

Where $X = \frac{x}{\alpha}$, $\alpha = \left(\frac{2}{k\gamma} \right)^{\frac{1}{4}}$ and $\epsilon = \gamma E \alpha^2$. Now let us write this a bit differently.

We will factor $\psi(X)$ out which gives us

$$\frac{\partial^2 \psi(X)}{\partial X^2} + (\epsilon - X^2) \psi(X) = 0 \quad (161)$$

To solve this we can look at limiting cases to infer partial solutions we can then generalise and get full solutions of the equation.

We will take one extreme case where

$$X \gg \epsilon \quad (162)$$

Under this assumption ϵ becomes negligible and the equation reduces to

$$\frac{\partial^2 \psi(X)}{\partial X^2} - x^2 \psi(X) = 0 \quad (163)$$

The solutions for this equation will look like

$$\psi(x) = ae^{-X^2/2} + be^{X^2/2} \quad (164)$$

The positive exponential $be^{X^2/2}$ can't be part of the solution because we would not be able to normalise. The reason for this is because exponentials with positive exponents grow indefinitely which would make it impossible for the wave function to integrate to 1. If we eliminate the positive term we are left with

$$\psi(x) = ae^{-X^2/2} \quad (165)$$

Again this solution only works when X is much larger than ϵ .

Now let us assume that the solution we found where a is the constant is not the solution we found. Instead let us assume the solution we found is

$$\psi(X) = g(X)e^{\frac{-X^2}{2}} \quad (166)$$

The reason for this is because when we initially solve the differential equation we are finding the shape of the solution at a certain limit. We want to delimit the possible types of solutions and looking at x as it goes to infinity is the first step

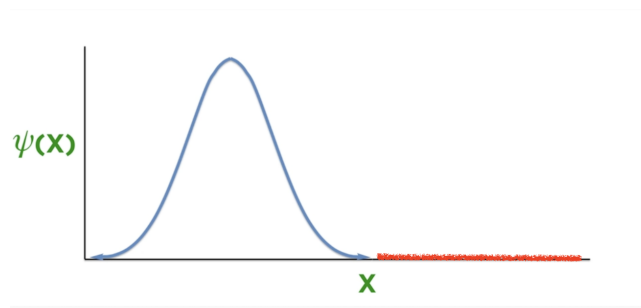


Figure 5.1:

The red region in figure 5.1 is easy to examine here there can only be two possibilities. One, the wave-function grows indefinitely or two, goes to zero. If it doesn't make sense to grow indefinitely the solution must contain a negative exponential. Look at figure 5.1, it's as if we are initially solving for $\psi(X)$ in a region where it does not depend on X . In the centre of the curve it does depend meaning that ψ changes a lot in this region as X

changes. We initially assumed we were solving in this limit of very large X and we found the exponential tail, but now we want the full solution which includes X dependence. To do this we can plug it into the Schrödinger Equation for the harmonic oscillator.

$$-\frac{\partial^2 [g(X)e^{-X^2/2}]}{\partial X^2} + (\varepsilon - X^2) g(X)e^{-X^2/2} = 0 \quad (167)$$

We now need to solve this which will require evaluating the second derivative from the first term. The first derivative will require the product rule, since we have the product. We have

$$\frac{\partial [g(X)e^{-X^2/2}]}{\partial X} = \frac{\partial g(X)}{\partial X} e^{-X^2/2} + g(X) \frac{\partial (e^{-X^2/2})}{\partial X} \quad (168)$$

We then bring $\frac{-2X}{2}$

$$\frac{\partial [g(X)e^{-X^2/2}]}{\partial X} = \frac{\partial g(X)}{\partial X} e^{-X^2/2} + g(X) \frac{-2X}{2} \frac{\partial (e^{-X^2/2})}{\partial X} \quad (169)$$

Which finally have

$$\frac{\partial [g(X)e^{-X^2/2}]}{\partial X} = \frac{\partial g(X)}{\partial X} e^{-X^2/2} - g(X) X e^{-X^2/2} \quad (170)$$

Now we must get the second derivative

$$\frac{\partial}{\partial X} \left(\frac{\partial g(X)}{\partial X} e^{-X^2/2} - g(X) X e^{-X^2/2} \right) \quad (171)$$

We can split this up and differentiate separate

$$\frac{\partial}{\partial X} \left(\frac{\partial g(X)}{\partial X} e^{-X^2/2} \right) - \frac{\partial}{\partial X} \left(g(X) X e^{-X^2/2} \right) \quad (172)$$

For the first term we get

$$\frac{\partial}{\partial X} \frac{\partial g(X)}{\partial X} e^{-X^2/2} + \frac{\partial g(X)}{\partial X} \frac{\partial}{\partial X} e^{-X^2/2} \quad (173)$$

$$= \frac{\partial^2 g(X)}{\partial X^2} e^{-X^2/2} = X \frac{\partial g(X)}{\partial X} e^{-X^2/2} \quad (174)$$

And now the second term we can write as

$$- \left(\frac{\partial g(X)}{\partial X} X e^{-X^2/2} + g(X) \frac{\partial(X)}{\partial X} e^{-X^2/2} + g(X) X \frac{\partial(e^{-X^2/2})}{\partial X} \right) \quad (175)$$

We then simplify

$$-X \frac{\partial g(X)}{\partial X} e^{-X^2/2} - g(X) e^{-X^2/2} + X^2 g(X) e^{-X^2/2} \quad (176)$$

We now have

$$= \frac{\partial^2 g(X)}{\partial X^2} e^{-X^2/2} - X \frac{\partial g(X)}{\partial X} e^{-X^2/2} - X \frac{\partial g(X)}{\partial X} e^{-X^2/2} - g(X) e^{-X^2/2} + X^2 g(X) e^{-X^2/2} \quad (177)$$

Which eventually equals

$$= \frac{\partial^2 g(X)}{\partial X^2} e^{-X^2/2} = 2X \frac{\partial g(X)}{\partial X} e^{-X^2/2} = g(X) e^{-X^2/2} + X^2 g(X) e^{-X^2/2} \quad (178)$$

We can now plug this into back into the Schrödinger Equation

$$\frac{\partial^2 g(X)}{\partial X^2} e^{-X^2/2} - 2X \frac{\partial g(X)}{\partial X} e^{-X^2/2} - g(X) e^{-X^2/2} + X^2 g(X) e^{-X^2/2} + (\varepsilon - X^2) g(X) e^{-X^2/2} = 0 \quad (179)$$

If we divide by $e^{-X^2/2}$ we get

$$\frac{\partial^2 g(X)}{\partial X^2} - 2X \frac{\partial g(X)}{\partial X} - g(X) + X^2 g(X) + (\varepsilon - X^2) g(X) = 0 \quad (180)$$

Expanding the bracket and simplifying we get

$$\frac{\partial^2 g(X)}{\partial X^2} - 2X \frac{\partial g(X)}{\partial X} = g(X) + \varepsilon g(X) = 0 \quad (181)$$

Then we factor $g(X)$ out of the two terms

$$\frac{\partial^2 g(X)}{\partial X^2} - 2X \frac{\partial g(X)}{\partial X} + (\varepsilon - 1)g(X) = 0 \quad (182)$$

This is as simple as we can get it.

This is the canonical linear homogeneous second-order ordinary differential equation and can be written as

$$w'' - 2zw' + \lambda w = 0 \quad (183)$$

Where w represents $g(X)$, z represents X and λ represents $(\varepsilon - 1)$. This equation is known as the Hermite equation. It's solutions are the Hermite polynomials.

$$g(X) = H_n(X) = (-1)^n e^{X^2} \frac{\partial}{\partial X^n} e^{-X^2} \quad (184)$$

We can find some of the Hermite polynomials by plugging in values for n . For example when $n = 0$ we have

$$H_0(X) = (-1)^0 e^{X^2} \frac{\partial}{\partial X^0} e^{-X^2} = 1e^{X^2} \frac{\partial}{\partial X^0} e^{-X^2} = 1e^{X^2} e^{-X^2} = 1(1) = 1 \quad (185)$$

When $n = 1$ we have

$$H_1(X) = (-1)^1 e^{X^2} \frac{\partial}{\partial X^1} e^{-X^2} = -1e^{X^2} \left(-2Xe^{-X^2} \right) = 2X \quad (186)$$

When $n = 2$ we have

$$H_2(X) = (-1)^2 e^{X^2} \frac{\partial^2}{\partial X^2} e^{-X^2} = 1e^{X^2} \left(-2e^{-X^2} + 4e^{-X^2} X^2 \right) = -2 + 4X^2 \quad (187)$$

It is clear that Hermite polynomials are regular polynomials that grow in order as n increases. In any case our solution for the wave function also contains a real negative exponential. We can now write

$$\psi_n(X) = H_n(X) e^{-x^2/2} \quad (188)$$

This is the mathematical representation of the eigenstates of a quantum particle in a harmonic potential.

We now need to make sure the wave function is normalised. Let us start with H_0 .

$$H_0 \longrightarrow \langle \psi(X) | \psi(X) \rangle = \int_{-\infty}^{\infty} \psi_0^*(X) \psi_0(X) dX \quad (189)$$

Which equals

$$\int_{-\infty}^{\infty} \left[H_0(X) e^{-X^2/2} \right]^* \left[H_0(X) e^{-X^2/2} \right] dX \quad (190)$$

We then plug in $H_0(X) = 1$

$$\int_{-\infty}^{\infty} \left[1 e^{-X^2/2} \right]^* \left[1 e^{-X^2/2} \right] dX = \int_{-\infty}^{\infty} e^{-X^2} dX = \sqrt{\pi} \quad (191)$$

The general solution for the harmonic potential is

$$\psi_n(x) = \frac{1}{\sqrt{2^n n! \pi^{1/4}}} H_n(x) e^{-x^2/2} \quad (192)$$

Once we know the normalisation factors we can find a solution for $\psi_0(X)$ which is

$$\psi_0(X) = \frac{1}{\langle \psi(X) | \psi(X) \rangle} e^{-X^2/2} = \frac{1}{\pi^{1/4}} e^{-X^2/2} \quad (193)$$

Then this expression for the general form of the normalisation factor for the wave function in the harmonic potential, with the Hermite polynomial.

We will now calculate the eigenenergies. For $n = 0$, let us set $H_0 = 1$. Plugging that into $\psi_0(x)$ we get

$$\psi_n(X) = H_n(X) e^{-\frac{X^2}{2}} \implies \psi_0(X) = e^{-\frac{X^2}{2}} \quad (194)$$

We can then plug this expression for $\psi_0(X)$ into the Schrödinger equation so now it looks like this

$$\frac{1}{\pi^{1/4}} \left(\frac{\partial^2 e^{-\frac{X^2}{2}}}{\partial X^2} + \varepsilon_0 e^{-\frac{X^2}{2}} - X^2 e^{-\frac{X^2}{2}} \right) = 0 \quad (195)$$

We first need to take the second derivative of $\frac{\partial^2 e^{-\frac{X^2}{2}}}{\partial X^2}$ which ends up being

$$\frac{\partial(-X e^{-\frac{X^2}{2}})}{\partial X} = -e^{-\frac{X^2}{2}} + X^2 e^{-\frac{X^2}{2}} \quad (196)$$

Now plugging this back into our whole equation we get

$$-e^{-\frac{X^2}{2}} + X^2 e^{-\frac{X^2}{2}} + \varepsilon_0 e^{-\frac{X^2}{2}} - X^2 e^{-\frac{X^2}{2}} = 0 \quad (197)$$

Dividing both sides by the exponential term we now have

$$-1 + X^2 + \varepsilon_0 - X^2 = 0 \quad (198)$$

We now simplify to get

$$\varepsilon_0 = 1 \quad (199)$$

Recall we had

$$\begin{aligned} \varepsilon &= \gamma E \alpha^2 \\ \alpha &= \left(\frac{2}{k\gamma} \right)^{\frac{1}{4}} \\ \gamma &= \frac{2m}{\hbar^2} \end{aligned}$$

Let's plug these expressions in place of γ, α and E

$$1 = \frac{2m}{\hbar^2} E_0 \left(\frac{2}{k\gamma} \right)^{\frac{1}{2}} \quad (200)$$

$$= \frac{2m}{\hbar^2} E_0 \left(\frac{2\hbar^2}{k2m} \right)^{\frac{1}{2}} \quad (201)$$

$$\frac{2m\hbar}{\hbar^2} E_0 \left(\frac{1}{km} \right)^{\frac{1}{2}} \quad (202)$$

We finally have

$$\frac{2}{\hbar} E_0 \left(\frac{m}{k} \right)^{\frac{1}{2}} = 1 \quad (203)$$

We can solve the energy E_0

$$E_0 = \frac{\hbar}{2} \sqrt{\frac{k}{m}} \quad (204)$$

If we define $\omega = \sqrt{\frac{k}{m}}$ this now becomes

$$E_0 = \frac{1}{2}\hbar\omega \quad (205)$$

This is one of the most important results in quantum mechanics. This tells us the ground state of the quantum harmonic oscillator has a non-zero energy. It is possible to work out the eigen energies for all eigenstates which are given by this equation.

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad (206)$$

If we compare this to the result for the classical harmonic oscillator.

$$E = \frac{1}{2}mv_0^2 \quad (207)$$

When the initial velocity of the particle is zero, the energy equals 0. But in the quantum case, the lowest allowed energy is inversely proportional to mass, given what omega represents. Although this is a non-zero value it is very small because $\hbar = 1.054 \times 10^{-34} \frac{m^2 kg}{s}$. However when a particle mass is very small this value becomes relevant.

5.2 Probabilities and Distributions

With the Schrödinger Equation solved we will interpret our results. We will start by looking at the wave functions. We will use the probability density function

$$P_0 = \langle \psi_0(X) | \psi_0(X) \rangle = \psi_0^*(X)\psi_0(X) \quad (208)$$

Again this function tells us the probability of finding the particle in a certain position. We will use this along with our ground state wave function.

$$\psi_0(X) = \frac{1}{\pi^{1/4}} H_0(X) e^{-X^2/2} \quad (209)$$

We found earlier that $H_0(X) = 1$. Now for the probability density function we need to find $\psi^*(X)\psi(X)$. Since there are no complex numbers in the expression ψ^* is the same as ψ so we now have

$$P_0 = \left(\frac{1}{\pi^{1/4}} \times 1 \times e^{-X^2/2} \right)^2 = \frac{1}{\pi^{1/2}} e^{-X^2} \quad (210)$$

This will take on a bell shape curve when we plot the PDF against position.

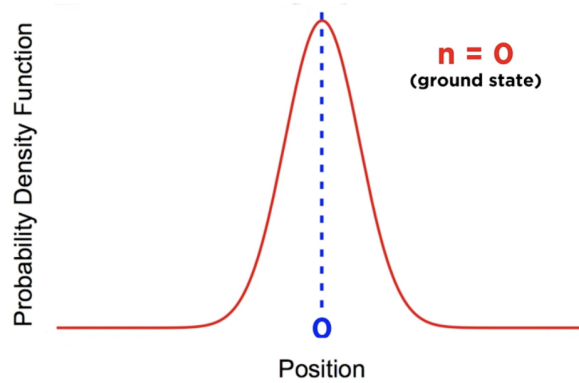


Figure 5.2: (Farina 2021)

This is centered around zero and as there is only one spike we can call this an odd function.

If we jump up to $n = 1$ we have the first excited state

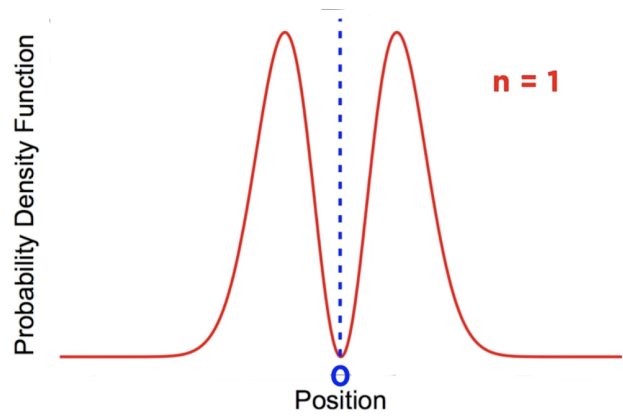


Figure 5.3: (Farina 2021)

The PDF is represented by P_1 . The particle cannot be found at $x = 0$. This function has two spikes so we call this an even function. If we now look at $n = 2$ we have

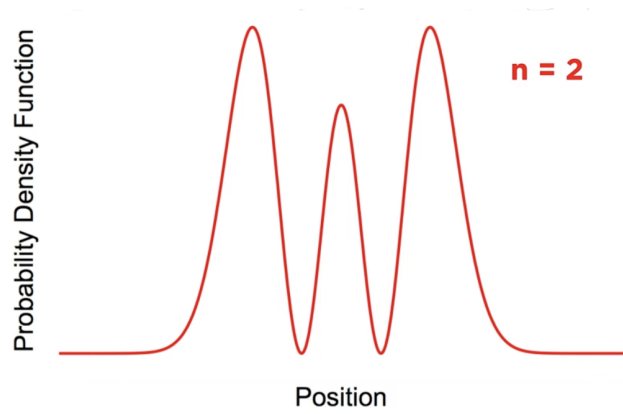


Figure 5.4: (Farina 2021)

Which again is an odd function. Finally for $n = 3$ we have

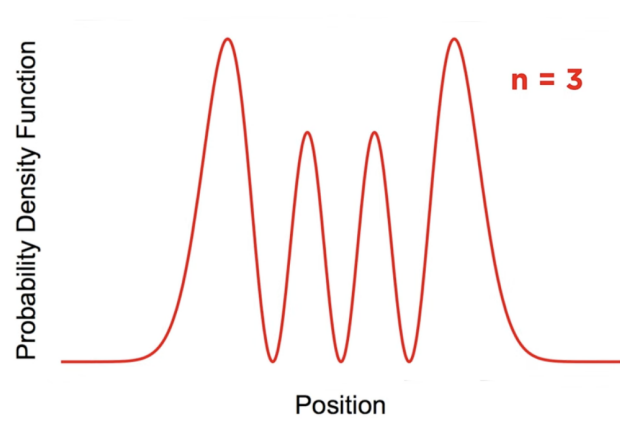


Figure 5.5: (Farina 2021)

Similar to the Particle in a Box where we found both odd and even solutions. This is a very common result for symmetric systems such as the harmonic oscillator. To see how these states are distributed. This is how the ground state would look if we plotted $P + E$ the PDF plus the eigenenergy of a particular eigenstate, together with harmonic potential.

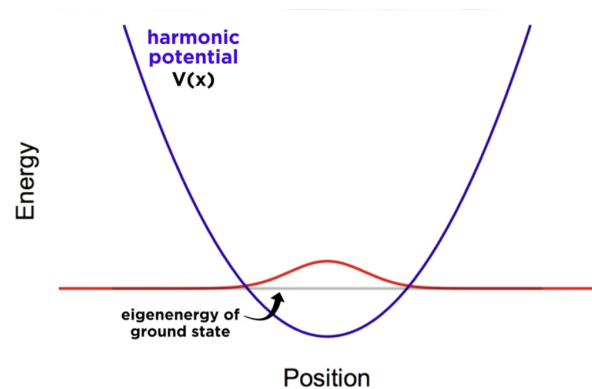


Figure 5.6: (Farina 2021)

The energy of the ground state is not zero as it is not at the bottom of the parabola. Then we plot the PDF $P(X)$ for the ground state where the boundary conditions dictate.

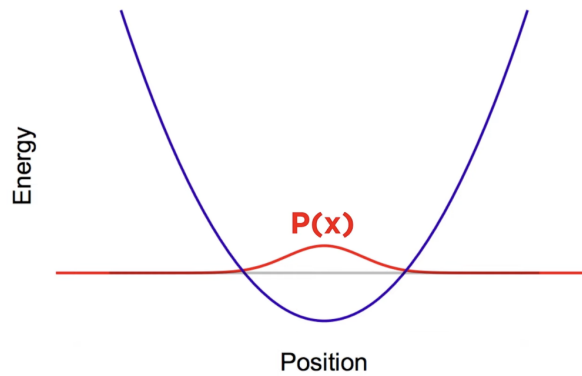


Figure 5.7: (Farina 2021)

The boundary conditions are given by the blue curve and that's why the red curve is within this region. The grey line represents the minimum of that wave function. Beyond the boundaries the PDF equals zero, and the particles is primarily localised in the centre. We can plot the other eigenstates the same way.

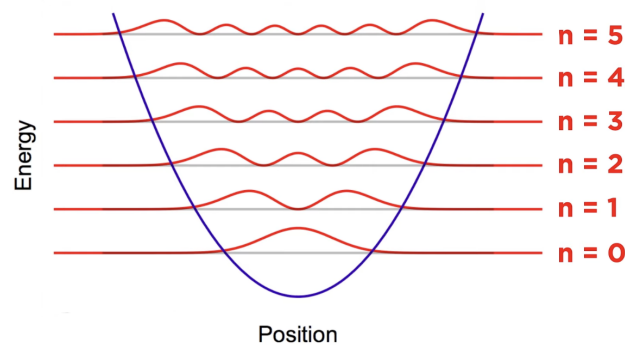


Figure 5.8: (Farina 2021)

Here we can see the first five excited states increasing in energy and we can see the particles can be found in different regions of the harmonic potential, but rarely outside, given that the probability density function drops to zero in each case.

Now even though the likelihood of finding the particle outside of $V(X)$ is extremely low, it is not zero since the tails of the functions extend to infinity. Because of these infinite tails a quantum particle has a no-zero probability.

We know that a particle in a quantum harmonic oscillator possess a set of quantised energies meaning it can't have energy from a continuous spectrum, and that these quantised energies are evenly spaced. Additionally the PDF functions tell us that the particle will be localised in certain positions along the x-axis, depending on the

eigenenergy that is possessed, and it will have a very low probability of being found in other locations.

6 Hydrogen Atom

One of the most famous problems in quantum mechanics is the Hydrogen Atom. What makes this problem more unique than the previous examples is this problem is in three dimensions where as the other previous ones was in two.

We will begin with the time time-independent Schrödinger equation

$$\hat{H}\psi = E\psi \quad (211)$$

For the hydrogen atom, the Hamiltonian is defined in spherical coordinates like so

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (212)$$

We will now define a few components of this equation.

- $\hbar = h/2\pi$ is the reduced Planck's constant.
- $\mu = \frac{m_p m_e}{m_p + m_e}$ is the reduced mass of the electron and proton.
- $\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$ is the Laplacian operator in spherical coordinates.
- e is the elementary charge, $1.602 \times 10^{-19} \text{C}$, e.g. positive for a proton, negative for an electron.
- $\epsilon_0 = 8.854187817 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$ is the vacuum permittivity.
- r is the radial position. Under the Born-Oppenheimer approximation, we assume the nucleus is fixed so that r becomes the radial distance of the electron from the nucleus.

6.1 Seperation of Variables

Firstly we must get the Shrodinger equation into a second order partial differential equation. We first plug in the Laplacian

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (213)$$

Next we let the equation equal to 0 and multiply by $-\frac{2\mu}{\hbar^2}$.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0 \quad (214)$$

We can assume the variables can separate in the form of $\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_l^{m_l}(\theta, \phi)$ Where R is the radial component and Y is the spherical component (Truong-Son 2016). We now have

$$\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) RY = 0 \quad (215)$$

Multiply through by $\frac{r^2}{RY}$

$$\overbrace{\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right)}^{\text{Radial Component}} + \overbrace{\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2}}^{\text{Angular Component}} + \overbrace{\frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right)}^{\text{Radial Component}} = 0 \quad (216)$$

These two functions now become equal to each other

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = - \left[\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] \quad (217)$$

Because the functions have different variables we must now let them equal to the same constant $-\lambda$.

$$- \left[\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \right] = -\lambda \quad (218)$$

$$\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -\lambda \quad (219)$$

These are now ordinary differential equations and we take them separately. Switch the signs of the radial part and multiply by R. We then subtract λR to get

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R - \lambda R = 0 \quad (220)$$

For the angular equation we get

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \lambda Y = 0 \quad (221)$$

6.2 Further Separating the Angular Part

The angular part is still a function of θ and ϕ so this needs to be separated further. We assume that $Y_l^{m_l}(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ and we repeat the same process as the previous part.

$$\frac{\Phi}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{\Theta}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} + \lambda \Theta \Phi = 0 \quad (222)$$

Next we multiply by $\frac{\sin^2 \theta}{\Theta \Phi}$

$$\overbrace{\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right)}^{\Theta} + \lambda \sin^2 \theta + \overbrace{\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}}^{\Phi} = 0 \quad (223)$$

Like before we want this to be equal to a separation constant -B. We can tidy up the equation

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \sin^2 \theta - B = 0 \quad (224)$$

Which implies

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + B = 0 \quad (225)$$

6.3 Solving the Φ Part

We will first multiply through by Φ so we have

$$\frac{d^2 \Phi}{d\phi^2} + B\Phi = 0 \quad (226)$$

And then solve as we normally would an ordinary differential equation, assuming

$$\Phi = e^{im_l \phi} \quad (227)$$

Finally getting a linear combination solution

$$\Phi(\phi) = c_1 e^{im_l \phi} + c_2 e^{-im_l \phi} \quad (228)$$

The wave function must be cyclic so $\Phi(0) = \Phi(2\pi)$. We must now eliminate some variables, to do this let $c_1 + c_2 = A$ and m_l to be negative.

$$\Phi(\phi) = (c_1 + c_2) e^{im_l \phi} = A e^{im_l \phi} \quad (229)$$

From Euler's relation

$$e^{i \cdot m_l \cdot 0} = \cos(0m_l) + i \sin(0m_l) = e^{i \cdot m_l \cdot 2\pi} = \cos(2\pi m_l) + i \sin(2\pi m_l) \quad (230)$$

This only holds for integer values of m_l which we define the magnetic quantum number

$$m_l = 0, \pm 1, \pm 2, \dots \quad (231)$$

The unnormalised ϕ component to the angular wave function is then

$$\Phi(\phi) \propto e^{im_l \phi} \quad (232)$$

6.4 Solving the Θ part

$B = m_l^2$ here too. We multiply by $\frac{\Theta}{\sin^2 \theta}$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) \Theta = 0 \quad (233)$$

Next we use a function of $\cos \theta$. Let

$$P(\cos \theta) := \Theta(\theta) \quad (234)$$

$$x := \cos \theta \quad (235)$$

This transformation changes the operator by the chain rule from $\frac{d}{d\theta}$ to

$$\frac{dx}{d\theta} \frac{d}{dx} = -\sin \theta \frac{d}{dx} \quad (236)$$

We now have

$$\frac{d}{dx} \left(\sin^2 \theta \frac{dP}{dx} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) P = 0 \quad (237)$$

We know $\sin^2 \theta = 1 - \cos^2 \theta = 1 - x^2$. We get

$$\frac{d}{dx} \left((1 - x^2) \frac{dP}{dx} \right) + \left(\lambda - \frac{m_l^2}{1 - x^2} \right) P = 0 \quad (238)$$

After rewriting in terms of x we get the ODE as a function of $\cos \theta$

$$(1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left(\lambda - \frac{m_l^2}{1-x^2} \right) P = 0 \quad (239)$$

This is called an associated Legendre-type differential equation. This is a known equation type with solutions called the Associated Legendre Polynomials $P_l^{|m_l|}(\cos \theta)$ (Truong-Son 2016).

We won't go into detail of these however after a few iterations of the polynomials we find

$$\lambda = l(l+1) \quad (240)$$

6.5 Putting together the Angular parts

We have two solutions $P_l^{|m_l|}(\cos \theta)$ and $\Phi(\phi)$ we can now find the spherical harmonics $Y_l^{m_l}(\theta, \phi)$

$$Y_l^{m_l} \propto P_l^{|m_l|}(\cos \theta) e^{im_l \phi} \quad (241)$$

We can look at some normalised spherical harmonics

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \quad (242)$$

$$Y_1^0 = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta \quad (243)$$

$$Y_1^1 = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{i\phi} \quad (244)$$

$$Y_1^{-1} = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{-i\phi} \quad (245)$$

6.6 Solving the Radial Part

Now we have λ

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R - l(l+1)R = 0 \quad (246)$$

To get this in standard form we factor our R and divide by r^2 .

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[\frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (247)$$

Here $R(r)$ takes the following unnormalized form, which utilizes the associated Laguerre Polynomials $L_{n+1}^{2l+1}\left(\frac{2r}{na_0}\right)$ as a function of the principal quantum number n and radial position r . The first few associated Laguerre polynomials are shown here (Truong-Son 2016).

$$\begin{aligned} n = 1, \quad l = 0, \quad L_1^1(x) &= -1 \\ n = 2, \quad l = 0, \quad L_1^2(x) &= -2!(2-x) \\ l = 1, \quad L_3^3(x) &= -3! \end{aligned}$$

6.7 Putting together the wave function

From the first substitution we had

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_l^{ml}(\theta, \phi) \quad (248)$$

Here are the first few normalised wave functions where we let $\sigma = r/a_0$

$$\begin{aligned} (n, l, m_l) = (1, 0, 0) : \quad \psi_{100} &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\sigma} \\ (n, l, m_l) = (2, 0, 0) : \quad \psi_{200} &= \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2} \\ (n, l, m_l) = (2, 1, 0) : \quad \psi_{210} &= \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos \theta \\ (n, l, m_l) = (2, 1, \pm 1) : \quad \psi_{21\pm 1} &= \frac{1}{\sqrt{64\pi}} \left(\frac{1}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin \theta e^{\pm i\phi} \end{aligned}$$

Finally, if we find to find the energy on any atomic orbital wave function we evaluate

$$E = \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi_{nlm_l}^*(r, \theta, \phi) \hat{H} \psi_{nlm_l}(r, \theta, \phi) r^2 dr \sin \theta d\theta d\phi \quad (249)$$

Our expression for our eigenvalues is

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2} \quad (250)$$

The graph describes physically what is happening.

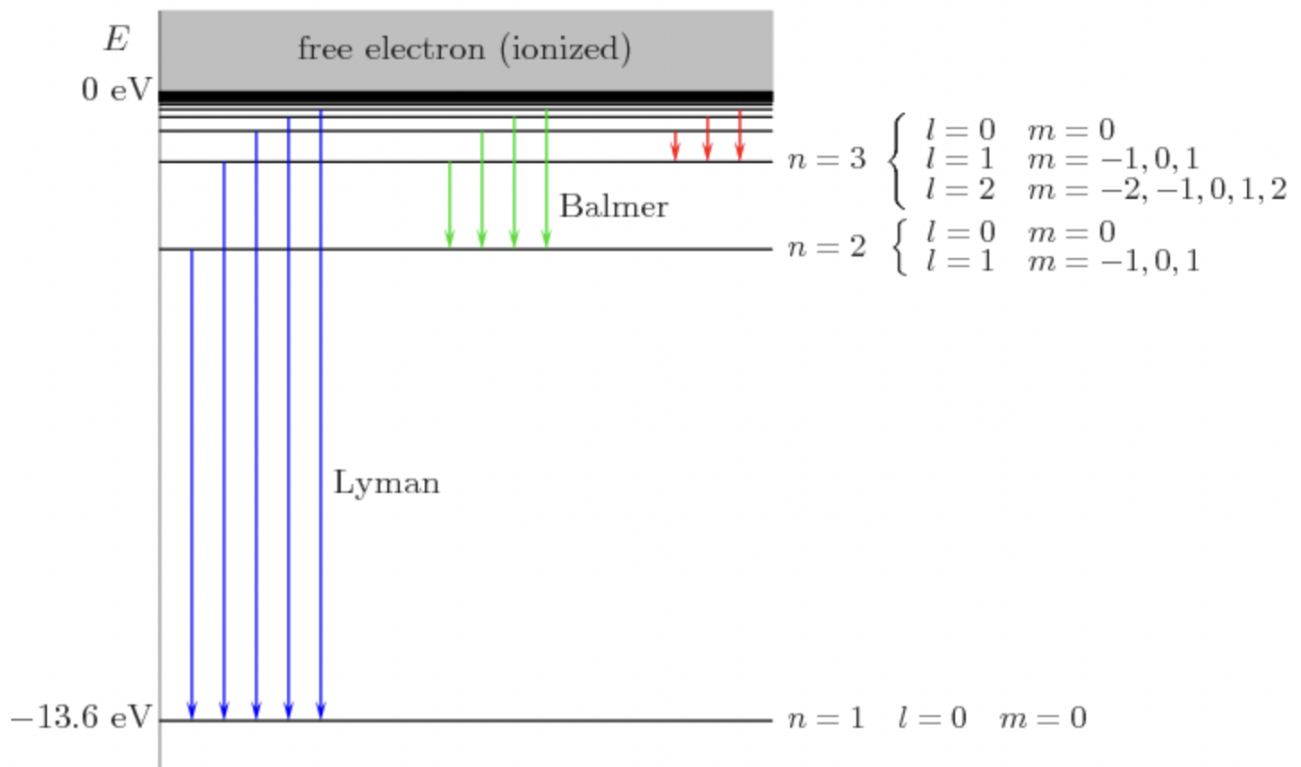


Figure 6.1: (van Dommelen 2018)

The energies are plotted in the form of energies in figure (6.1). The energy spectrum shows all the energy levels are negative. The hydrogen is defined to be zero from a large distance from the nucleus. The energy levels of the hydrogen atom have a maximum value. This means in a hydrogen atom the electron escapes if it's energy is greater than zero. This losing of an electron is called ionisation of the atom (van Dommelen 2018)

7 Conclusion

This is only a fraction of the field of Quantum Mechanics. There are many other applications and areas that can be explored but the aim here was to explore the mathematical equations of Quantum Mechanics. The theory at the beginning helped us understand some notation and terminology and we then used this in our examples of real world applications. While difficult, it is clear we achieved our goal from the beginning capturing the mathematical essence of quantum mechanics without going off on a tangent. With quantum mechanics being such a big branch of science it was very easy to go into much detail that drifted away from mathematics. The presented examples are particles in potential well. There are other problems, related to scattering from a barrier which have not been included in this study but maybe interesting to study in the future.

References

- Bowers, P. L. (2020), *Lectures in Quantum Mechanics A Primer for Mathematicians*, Cambridge University Press.
- Dudik, R. (2004), 'The Quantum Harmonic Oscillator '.
- URL:** http://physics.gmu.edu/~dmaria/590%20Web%20Page/public_html/qm_topics/harmonic/
- Farina, D. (2021), 'The Quantum Harmonic Oscillator Part 2: Solving the Schrödinger Equation '.
- URL:** <https://www.youtube.com/watch?v=l29vbExLSakt=1090s>
- Fowler, M. (2021), 'Particles in Two-Dimensional Boxes '.
- URL:** https://galileo.phys.virginia.edu/classes/252/2d_wells.html
- Helmenstine, A. (2020), 'What is a Wave Function?'.
- URL:** <https://www.thoughtco.com/definition-of-wavefunction-605790>
- Landau, L. & Lifschitz, E. (1977), *Quantum Mechanics Non-relativistic Theory*, Oxford: Pergamon Press.
- Rowland, T. (2022), ' L^2 - Function'.
- URL:** <https://mathworld.wolfram.com/L2-Function.html>
- Safronova, M. (2015), 'Eigenfunctions of hermitian operators '.
- URL:** <https://www.physics.udel.edu/~msafrono/424-2011/Lecture%2015.pdf>
- Sanny, S. J. L. J. & Moebis, W. (2016), *University Physics Volume 3*, OpenStax.
- Truong-Son (2016), 'Solve Schrödinger equation for hydrogen atom? '.
- URL:** <https://socratic.org/questions/solve-schr-dinger-equation-for-hydrogen-atom>
- van Dommelen, L. (2018), '4.3 The Hydrogen Atom '.
- URL:** https://web1.eng.famu.fsu.edu/~dommelen/quantum/style_a/hyd.html
- Vaughn, S. A. (2005), 'Hilbert Space '.
- URL:** <https://mathworld.wolfram.com/HilbertSpace.html>
- Weisstein, E. W. (2005), ' L^2 - Norm'.
- URL:** <https://mathworld.wolfram.com/L2-Norm.html>