QUANTUM MECHANICS- PART I

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Note the following pages contain mostly unedited and uncorrected notes of my lectures from 2-7 June 2014. You may use it, but discretion advised.

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Chapter 1

Historical Introduction

Quantum mechanics is in part a mathematical frame work to describe and predict the behaviour of particles/systems on a microscopic scale. A successful theory should predict the result of measurements. Quantum mechanics (QM) is spectacularly successful in this sense. It is probably the most successful theory measured against known facts. Quantum physics is therefore the fundamental framework of all of physics while Classical physics is a reliable approximation which is more intuitive at scales that we deal with in every day life. Logically it may even appear that we should therefore start with foundations of quantum physics as the basis of every phenomena we know. As we shall see during these lectures, even the mathematical framework is rather simple. [1]

Purely from a mathematical point of view, we understand the basis of QM very well- we know the basic axioms, parts and how they are put together and even why it works so well. However, there is disagreement among the thinkers of QM on what kind of microscopic world it describes. For example, Roger Penrose says " what ever the reality may be, one has to explain how one perceives the world to be. QM does not do this. One must incorporate some thing additional into QM- not contained in the standard rules of QM at present". This view is held by many others, and is expressed from time to time.

A diametrically opposite view, an operational one from Stephen Hawking, would be to ignore the reality altogether. "I don't demand that a theory correspond to reality since I don't know what it is". One is only concerned with results- that it should predict the results of measurements. QM does this very successfully- while you may want to ponder over these questions exemplified by the problem of a cat being alive or dead, here we briefly discuss the origins and lay the foundations for some useful applications.

We shall leave these philosophical questions aside and develop QM from an operational point of view. We begin with the old quantum theory which provided a set of thumb rules, not necessarily a consistent framework, but showed a definite departure from the intuitive approach of classical mechanics. These seeming inconsistencies vanish once the mathematical framework of quantum mechanics is established. So much

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[1] Much of the material in the initial chapters follow approximately the treatment given in the book– Introduction to Quantum Mechanics by P.T. Mathews, McGraw Hill, 1968.

so, some modern text books in quantum mechanics may even skip any discussion of the old quantum theory. However, to appreciate the enormous progress achieved by the formulation of quantum mechanics, we think it is necessary to know the concepts that led to its development.

1.1 Old quantum theory

Before we introduce the revolutionary ideas that lead to the formulation of QM, let us first review of our basic ideas in classical mechanics.

In Newtonian mechanics, which describes the dynamics of moving bodies, matter is regarded as made up of point particles. The dynamics or time evolution of these particles is described by Newton's Laws:

$$\vec{F} = \frac{d\vec{p}}{dt} = m\frac{d^2\vec{r}}{dt} \tag{1.1}$$

where $\vec{p}$ is the momentum and $\vec{F}$ is the applied force. When the mass is constant, the force is related to the product of mass and acceleration. The basic attributes of a particle are its mass which is a constant, its position and momentum (Energy). The state of the system at a given time is completely specified once its position and momentum are given. These states may be described as points in phase-space. The Newton's laws describe how these phase points or the state of the system move in phase space as a function of time.

An important point to note here is that the equation of motion or the laws of classical mechanics involve quantities the we directly measure like velocity, position etc. It is deterministic- that is if at some time t the state of the system is completely specified, then we just have to know its past and its future. We just know how to compute the solutions which today the computers do with good efficiency. Any aspect of indeterminacy arises purely from the accuracy to which the initial conditions are specified. Intuition is developed on these lines from experience like when a fielder on a cricket field judges where the ball would fall!!

Combined with the Newton's law of gravity, the classical mechanics describes phenomena all the way from a small system to the motion of planets, stars and galaxies. The motion of a free particle, of mass m, is described in terms of its energy, E and momentum $\vec{p}$

However, this description was not suitable in classical optics. Even during the time of Newton the phenomenon of interference and diffraction of light were well known. Though Newton thought of light as made up of corpuscles, the corpuscular theory could not explain the phenomenon of interference or diffraction which required the description of light in terms of wave optics. Maxwell's electromagnetic theory provided the basis for complete explanation of known optical phenomena using light as an electromagnetic wave. The electro-magnetic phenomena are best described in terms of electric and magnetic fields, obeying Maxwell's equations. In free space the fields satisfy the wave equation

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\vec{E}(\vec{r}) = 0, \tag{1.2}$$

where c is identified with the velocity of propagation of waves. Similar wave equation can be written for the magnetic field $\vec{B}$. It was Maxwell's inspired guess that the velocity of the wave propagation should be identified with the velocity of light.

As mentioned before the properties of interference and diffraction required the wave nature of light. A typical wave in free space is represented by a function of the form

$$\psi(\vec{r}) = e^{-i(\omega t - \vec{k}.\vec{r})}, \tag{1.3}$$

where the angular frequency $\omega = 2\pi\nu$ and the modulus of wave vector $k = |\vec{k}| = 2\pi/\lambda$. Here ν and λ are the usual frequency and wave length. The function ψ, the so called wave function, is a solution of the wave equation provided the following condition is satisfied

$$\frac{\omega^2}{c^2} - k^2 = 0 \Longrightarrow \omega = kc; \quad k = |\vec{k}|. \tag{1.4}$$

So here is the classical picture of the world- end of 19th century- that matter is made up of point particles described by energy and momentum $(E, \vec{p})$; radiation is described by waves of a given frequency and wave vector $(\omega, \vec{k})$. The foundations of are kept apart with different sets of laws, particle mechanics and wave mechanics.

The first real problem came with the phenomenon called "Black-body Radiation".

The blackbody radiation: The concept of blackbody was introduced by Kirchoff- a system that absorbs all electromagnetic radiation incident upon it. A black body is also an ideal emitter- when in thermal equilibrium emits electromagnetic radiation whose spectrum is determined by the temperature alone. This subject has been discussed in great detail both in the history of quantum physics and else where. Let us recall the essential points:

The phenomenon concerns the thermodynamics of exchange of energy between radiation and matter. Classically such an exchange of energy has to be continuous. A radiation of any frequency ω can transfer any amount of energy upon absorption. The precise amount depends on the intensity of radiation. Based on this the derived formula, Raleigh- Jeans formula, for the energy density turns out to be wrong.

The correct thermodynamic formula for the energy density given Planck is obtained with the assumption that the energy exchange is discrete and takes place in units of $\hbar\omega = h\nu$, where $h = 2\pi\hbar = 6.62 \times 10^{-34}\ Joule - sec.$ is Planck's constant- it is one of the universal constants. Planck's derivation of the formula involved classical arguments with the important caveat that the energy exchange takes place in discrete amounts depending on the frequency. While it was unsatisfactory, it was a phenomenological success.

Planck's hypothesis may be restated by saying that the radiation of frequency ω behaves like a beam of particle (photons) each carrying energy

$$E = \hbar\omega. \tag{1.5}$$

Since the energy exchange can only occur by the absorption or emission of individual particles, the unit of energy exchanged is $\hbar\omega$. Since the these particles, photons, travel at the speed of light its rest mass $m = 0$ according to special theory of relativity. Thus we have the energy-momentum dispersion relation

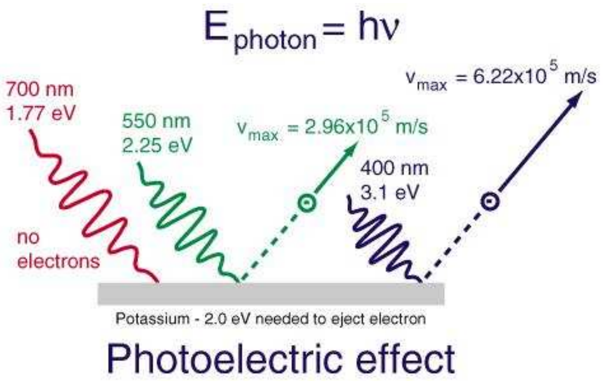
$$E = \hbar\omega = pc \Longrightarrow p = \hbar|\vec{k}|, \tag{1.6}$$

where p is the modulus of the momentum of the photon and using the relation $\omega = |\vec{k}|c$. We thus arrive at the fundamental equations that connect the particle and wave parameters of the electromagnetic field:

$$\boxed{\textbf{Particle:} \qquad \begin{matrix} E = \hbar\omega \\ \vec{p} = \hbar\vec{k} \end{matrix} \qquad \textbf{:Wave}}$$

The energy and momentum are intrinsically the properties of a particle while the frequency and wave vector are intrinsic properties of a wave. The relation above hypothesised by Planck connect the two.

The Photo-electric effect: Einstein in one of his classic papers in 1905 interpreted the observed photo-electric effect in way that it provided the basis for Planck's hypothesis in a simple manner. In 1887, Heinrich Hertz observed that when monochromatic light is incident on the surface of a metal, some times the electrons are emitted. The maximum kinetic energy of the electrons so emitted was independent of the intensity of radiation but depended only on the frequency of light. While the rate of emission of photoelectrons depends on the intensity, the kinetic energy was not.

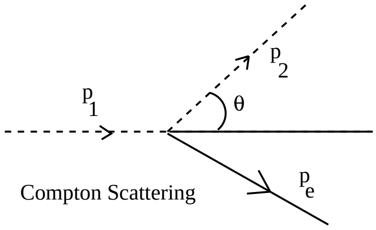


Einstein gave a simple explanation using Planck's idea of discrete energy exchange, summarised in the energy-balance equation

$$\hbar\omega = W + T, \tag{1.7}$$

where W is called the work function which is a property of the metal and T is the kinetic of the electron. From our modern perspective it is easy to understand the equation–the electrons are bound by an attractive potential in a metal, the work function W is the energy required to over come this potential. The energy transferred by a photon hitting an electron should be greater than this W to free the electron. If the energy of the photon is greater than W, the difference is the kinetic energy of the electron. This explanation is entirely in terms of particle interpretation of radiation.

The Compton effect: A better appreciation of the particle nature of radiation can be gleaned from Compton scattering. It is an example of inelastic scattering of light in which the wavelength of the scattered light is different from the incident radiation first observed by Arthur Compton in 1923. This is important because the effect can not be explained purely by assuming the radiation as waves.



Compton Scattering

In a simple analysis of the Compton scattering, we have in the particle picture photons scattering of atomic electrons (assumed to be at rest initially). We may ask what is the wave length of the scattered photon- does it change or remain the same? Secondly what is the rate of scattering at a particular angle. The first question may be answered by looking at the kinematics while the second one requires dynamics which we have not yet specified.

Energy-momentum conservation implies

$$\begin{aligned} \vec{p_1} &= \vec{p_2} + \vec{p}_e, \\ cp_1 + mc^2 &= cp_2 + \sqrt{c^2 p_e^2 + m^2 c^4} \end{aligned} \tag{1.8}$$

where $\vec{p}_{1,2}$ are the momenta of the initial and final photons and $\vec{p}_e$ is the momentum of the recoil electron. Denoting the angle of scattering of the photon as θ, we may combine, by eliminating the electron momentum, the above equations as

$$mc(p_1 - p_2) = 2 p_1 p_2 \sin^2 \theta/2. \tag{1.9}$$

Until now we have used the particle picture of radiation. Since the wavelength of the radiation is $\hbar/p$, the change in the momentum given above may be written as

$$\lambda_1 = \lambda_2 - 2\lambda_e \sin^2 \theta/2 \tag{1.10}$$

where $\lambda_e = \hbar/mc$ is a constant that depends only on the electron mass. Thus the change in the wavelength of the radiation is simply a function of the scattering angle alone. This is precisely what was observed by Compton. Note that we measure the wavelength of the scattered radiation which is entirely a property of the wave, but the change in wave length as observed may be entirely explained by assuming radiation as photons with well defined energy and momentum. The marked duality between the wave picture and particle picture of radiation is evident.

de Broglie and Matter waves: While the observation of photoelectric effect and Compton effect revealed the particle aspects of radiation, what about the matter itself? Classically all matter is regarded as made up of particles, often regarded as, albeit approximately, point particles. It was suggested by de Broglie that the relations

$$E = \hbar\omega, \quad \vec{p} = \hbar\vec{k}$$

should apply equally well to electrons (or particles in general).

Just as radiation is represented by a wave propagating in free space by $e^{-i\omega t+i\vec{k}.\vec{r}}$, the matter waves may be represented by

$$e^{-\frac{i}{\hbar}(Et-\vec{p}.\vec{r})}.$$

where the wave is characterised by particle parameters E, p. This was a revolutionary idea which puts both matter and radiation on par– wave particle duality is taken to be a very general principle.

This wave particle duality was immediately confirmed by the experiments of Davisson and Germer who showed that a beam of electrons reflected from the surface of nickel crystal formed diffraction patterns, similar to the light that forms diffraction pattern upon reflection from a grating.

Bohr's hypothesis: More than hundred years ago Rutherford showed that an atom, say hydrogen, has a structure in which the electron/s are revolving around a heavy positively charged nucleus some what similar to the planets going round the Sun. In both cases the potential is $1/r$, where r is the radial distance. However, the electrons are negatively charged. Therefore, according to electromagnetic theory, the accelerating charge should continuously radiate thereby losing energy and ultimately fall into the nucleus in about 10^{-10} seconds. Atoms can not be stable in the classical theory.

Obviously this can not hold since atoms are stable in general nor was there emission of continuous radiation. Furthermore, Balmer studied radiation from hydrogen as early as 1885. He showed that the emitted radiation frequencies were discrete. He observed that the dominant observed lines satisfied the empirical relation

$$\omega_n = N(\frac{1}{2^2} - \frac{1}{n^2}); \quad n = 3, 4, 5, \cdots \tag{1.11}$$

Bohr came up with a semiclassical theory of atoms that provided a set of thumb rules to explain the stability of the atoms and the observed discreteness of Balmer lines which may be summarised in two statements:

- The magnitude of angular momentum of the electron occurs in integer units of $\hbar$, that is
$$l = \hbar n; \quad n = 1, 2, ...$$
This results in discrete value of energy E_n.

- Radiation occurs when an electron makes discontinuous transitions from one orbit to another. Once the electron reaches the lowest orbit, there is no further radiation possible. Hence the Bohr atom in its lowest possible energy level is stable.

$$\hbar\omega_{nn'} = |E_n - E_{n'}|. \tag{1.12}$$

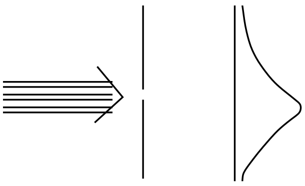
Consider an electron moving in a circular orbit of radius a. Its angular momentum is given by
$$l = ma^2\omega = \hbar n.$$

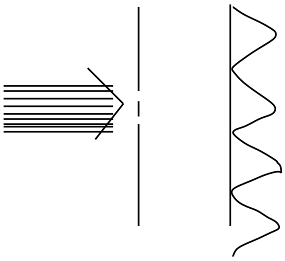
Classical stability equation implies
$$mv^2/a = ma\omega^2 = e^2/a^2$$
where e is electronic charge in MKS units. Solving these equations, by eliminating ω, we have
$$\begin{aligned} a_n &= \left(\frac{\hbar^2}{me^2}\right) n^2 = a_0 n^2 \\ E_n &= \frac{ma_n^2\omega^2}{2} - \frac{e^2}{a_n} = -\frac{e^2}{2a_0 n^2} \end{aligned} \tag{1.13}$$

Therefore the rules enunciated by Bohr not only account for the stability but also explain the Balmer lines.

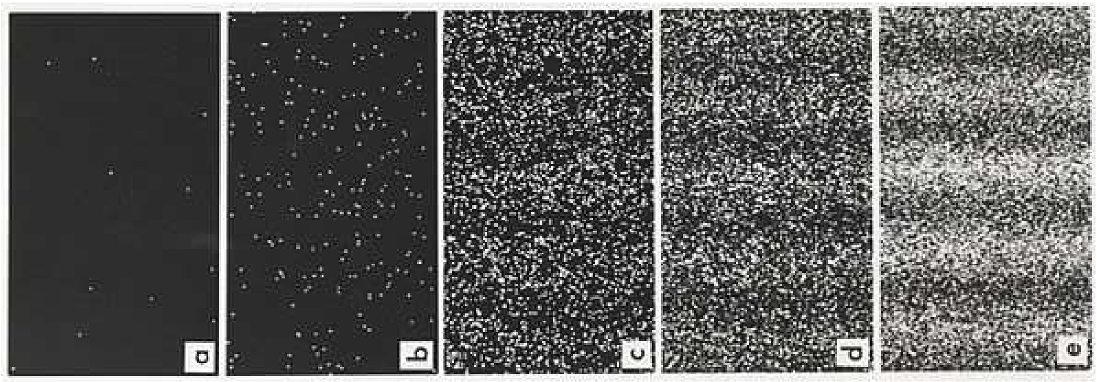
Some Remarks: We now come to the last of the important developments before Quantum Mechanics was born. Conceptually this is different from the other evidences for quantum behaviour that are listed above. We go back to the formula derived by Planck. While the idea of Planck regarding quantisation enabled him to derive th distribution formula for black body radiation as a function of temperature and frequency, it was based on the classical arguments. This unhappy situation was resolved by Bose when he derived the Planck's distribution formula based entirely on a new counting procedure for photons. Immediately Einstein extended his arguments to material particles.

Some recent developments: In the last few decades the wave particle duality has been demonstrated even more convincingly by a class of experiments: The classic Young's double slit experiment to produce interference patterns has been redone by sending in particles (both photons and electrons), one at a time with delay. When only a single slit is exposed the particles detected on a screen form a single bright patch as expected from their particle nature. However, when both slits are open, an interference pattern emerges after sufficiently large number of particles are sent in.





These experiments therefore directly demonstrate the wave-particle duality of matter and radiation. This interference phenomenon is demonstrated to occur with photons, electrons, atoms and some molecules.



In summary, we have reviewed the origins of quantum theory where a set of ad-hoc thumb-rules, completely at variance with the classical theory of matter and radiation, were proposed to explain the phenomena:

- Planck proposed quantisation of the energy of radiation through blackbody energy density.
- Particle aspect of radiation- confirmed by photoelectric effect, compton effect.
- Wave nature of matter, de Broglie's hypothesis, confirmed by Davisson-Germer experiment through electron diffraction.
- Quantisation of angular momentum and energy by Bohr to explain Balmer series. Confirmed by the experiments of Franck-Hertz experiment.

The development of quantum mechanics, as we shall see in the next few lectures, gives a consistent picture where the above ad-hoc rules appear as natural consequence and in which the wave-particle duality is an essential part. It provides for the description of all phenomena at all scales, though on a macroscopic scale it tends to the classical description which we know works fine.

It should be noted however, that we rely on quantum mechanics formalism to obtain answers, though for all practical purposes we give up the notion of reality as picturised by classical mechanics in terms of unique, deterministic, trajectories. In fact we have to give up the notion of classical determinism.

Chapter 2

Operators and Observables

> There is a limit to the fineness of our powers of observation and smallness of the accompanying disturbance- a limit which is inherent in the nature of things, and can never be surpassed by improved technique—Paul Dirac.

In this chapter, we discuss the principles of quantum mechanics and its formulation, in a simple form without using the full power of the mathematical abstraction. We have already discussed the origins of wave-particle duality inherent in natural phenomena as gleaned through old quantum theory. This emerges naturally in the mathematical formulation of quantum mechanics. The state of a system in quantum mechanics is described differently from classical mechanics. The observables in quantum mechanics are described by linear operators. They are not only linear but also Hermitian. This correspondence between operators and observables is subtle. Below, we discuss this connection through examples.

We first discuss briefly the notion of operators as a prelude to developing quantum mechanics. This is done using ordinary differentials as that is what we need later.

2.1 Operators

We denote operators with a 'hat'- for example $\hat{O}$ is an operator. The operators could be functions too. For example,

$$\hat{O}(x) = x, \tag{2.1}$$

where x is simply position coordinate, or it could be a differential operator, like this

$$\hat{O}(\partial/\partial x) = \frac{\partial}{\partial x}. \tag{2.2}$$

By convention the operators act on the right. Later we will also introduce the operators that act on the right through conjugation. The operator may be also of the form $\hat{O}(x, \partial/\partial x)$. Suppose

$$\hat{O}(x, \partial/\partial x) = \frac{\partial}{\partial x}.x \quad , \tag{2.3}$$

where the *rhs* is a sequence of two operations, multiplication by x first and then differentiation with respect to x, thus if $f(x)$ is any function of x, we have

$$\hat{O}(x, \partial/\partial x)f(x) = \frac{\partial}{\partial x}.xf(x) = (1 + x\frac{\partial}{\partial x})f(x) \tag{2.4}$$

using the rule for differentiation. So formally we write

$$\frac{\partial}{\partial x}.x = (1 + x\frac{\partial}{\partial x}) \tag{2.5}$$

which is an "operator equation". If

$$\hat{A}f(x) = (\hat{B} + \hat{C})f(x) \tag{2.6}$$

then

$$\hat{A} = (\hat{B} + \hat{C}). \tag{2.7}$$

In general the operator acts on a function (or state) and returns another function. However, to each operator $\hat{O}$, there may belong a set of numbers a_n and a set of functions $u_n(x)$ such that

$$\hat{O}u_n(x) = a_n u_n(x). \tag{2.8}$$

The operator returns the same function apart from multiplication by a number. We refer to a_n as an eigenvalue and u_n is the corresponding eigenfunction. Thus the eigenfunction remains unaltered by the operation of the operator apart from multiplication by a number. Often in quantum mechanics we are interested in cases where these numbers are real- the operators corresponding to such eigenvalues are called Hermitian. For example consider $\hat{O} = -i\partial/\partial x$. The eigenvalue equation may be written as

$$-i\frac{\partial}{\partial x}u_n(x) = a_n u_n(x), \tag{2.9}$$

The solution is in general of the form

$$u_n(x) = e^{ia_n x}.$$

which is a solution for any arbitrary a_n. We impose a boundary condition to find the particular set of a_n. Let u_n be periodic over a range L. Then

$$u_n(x + L) = u_n(x) \implies u_n(x) = e^{ia_n x}; \quad a_n = \frac{2n\pi}{L}. \tag{2.10}$$

In the limit $L \to \infty$ the eigenvalues become continuous. Thus the eigenvalues depend upon the boundary condition imposed.

An important property of the operators is that they may not necessarily commute, that is the order of operation when reversed may not yield the same result. Consider two operations $\hat{A}, \hat{B}$. The commutator of these two operators is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{2.11}$$

In general

$$[\hat{A}, \hat{B}] = \hat{C} \tag{2.12}$$

where $\hat{C}$ is a new operator. For example

$$[x, \partial/\partial x] = -1 = -[\partial/\partial x, x] \tag{2.13}$$

as can be easily verified.

2.2 Observables

In classical mechanics, described by Newtonian dynamics, it is implicitly assumed that the process of observation does not the alter or disturb the system appreciably. We in fact neglect this. Now consider the situations where in these disturbances are not negligible with the following formulation:

- To each observation (say energy, momentum or position) we have a set of numbers which belong to the particular observation. An apparatus A acting on the system may return a particular value of the measurement leaving the system unchanged. It may also alter or disturb the system.

- Two different observations A, B could be done in different orders: Observation A followed by B denoted by BA, or B followed by A denoted by AB. For reasons that will be obvious soon, we use the same notation for observations as for operators but without a hat. Classically they may yield the same result since the system is unaltered after an observation. However when the disturbance is not negligible after an observation, we have

  $$AB \neq BA, \ \textit{or} \ AB - BA \neq 0$$

  the non-zero value of this must be related to the unavoidable disturbance. (with hind-sight gained from old quantum theory we may guess that this unavoidable disturbance must be proportional to $\hbar$).

The properties of observations bear remarkable resemblance to the properties of the operators. We thus make a very general assumption that observations may be represented by operators, there being a unique operator for each observation like energy, position and momentum etc. This however puts a restriction on the nature of some operators–the observables are represented by real numbers which therefore requires the operators representing such observables should be Hermitian (Hermitian operators have real eigenvalues). We may state this a a fundamental theorem in quantum mechanics:

> The observable quantities in quantum mechanics are represented by Hermitian operators.

It is a simple but powerful statement.

2.3 The formalism

The operators in quantum mechanics act on the *state function* of the system, not the system itself, yielding either a new state function or a number corresponding to some measurement leaving the state function unchanged. Often the function that represents the state of the system is also called the *wave function* in a reference to its historical origins.

Let us make this more precise by the following assumptions:

1. If the system is in an eigenstate of the operator $\hat{O}$, $u_n(x)$, then the result of observation is always an eigenvalue a_n.

2. Otherwise, the possible results of an observation $\hat{O}$ are the corresponding eigenvalues a_n.

3. When the system is not represented by an eigenstate of the operator, the result of repeated observations on a system in an arbitrary state $\psi(x)$, which is in general a complex valued function, is given by the average

$$\langle a_\psi \rangle = \frac{\int_{-\infty}^{\infty} dx \ \psi^*(x)\hat{O}(x, \partial/\partial x)\psi(x)}{\int_{-\infty}^{\infty} dx \ \psi^*(x)\psi(x)}, \tag{2.14}$$

where the integration limits span the physically allowed region in space. Unless otherwise mentioned we consider operators which involve x and/or its derivatives. The last assumption is a little involved- the result of observation of $\hat{O}$ is always one of its eigenvalues. Repeated observations will produce a statistical distribution of these eigenvalues and according to the assumption (3), we know its average value. In particular if $\psi(x) = u_n(x)$ then $\langle a_\psi \rangle = a_n$ consistent with the assumption (1).

But how does on choose the mathematical form of the operator corresponding to an observation? In order to develop a sound mathematical formalism for representing the observables, we add the following *Correspondence Principle* to the above assumptions. The principle simply states that *quantum mechanics must reduce to classical mechanics in the limit where systems become "large" and the "disturbances" during observations become small and therefore negligible.* To ensure this we require that the essentially definitive relations between physical variables in classical mechanics are also satisfied by the corresponding operators. For example the angular momentum in classical mechanics is given by the corresponding operator relations in quantum mechanics:

$$\begin{array}{rlcl} & l_x = yp_z - zp_y & \Longrightarrow & \hat{l_x} = \hat{y}\hat{p_z} - \hat{z}\hat{p_y}, \\ CM: & l_y = zp_x - xp_z & \Longrightarrow & \hat{l_x} = \hat{z}\hat{p_x} - \hat{x}\hat{p_z}, \quad : QM \\ & l_z = xp_y - yp_x & \Longrightarrow & \hat{l_x} = \hat{x}\hat{p_y} - \hat{y}\hat{p_x}. \end{array} \tag{2.15}$$

and the classical Hamiltonian in one dimension is given by

$$CM: \quad H = \frac{p^2}{2m} + V(x) \Longrightarrow \hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}), \quad QM \tag{2.16}$$

where $V(x)$ is some one dimensional potential. This can be generalised to any dimension and degrees of freedom. The example chosen above for the Hamiltonian is a special case of a non-relativistic particle which may be generalised.

To this we add the notion of *Complementarity*. Two observables are said to be complementary (or conjugate) if a measurement of one leads to a disturbance in the corresponding conjugate quantity. For example, measurement of position of a particle leads to a disturbance which affects the corresponding momentum in that direction. The two observations therefore do not commute. We may therefore write

$$[\hat{x}, \hat{p}] = \alpha\hbar \tag{2.17}$$

where $\hbar$ is planck's constant which dimensionally accounts for the left-hand side and α is a dimensionless constant to be determined and the square brackets represent the commutator.

In order to evaluate α we need have a representation for these operators. The simplest, not the only one, representation for $\hat{x}$ is x itself- position variable. It is easy to see that if we choose

$$\hat{p} = -\alpha\hbar\frac{\partial}{\partial x} \tag{2.18}$$

the above commutation relation is easily satisfied. Furthermore, if $u_p(x)$ is an eigenstate of $\hat{p}$, then the eigenvalue equation gives

$$\hat{p}u_p(x) = [-\alpha\hbar\frac{\partial}{\partial x}]u_p(x) = pu_p(x)\ , \tag{2.19}$$

where p is the classical momentum of the particle. It easy to see that the form of the eigenstate should be

$$u_p(x) = e^{-px/\alpha\hbar}. \tag{2.20}$$

We now take the next big-step towards setting up Quantum Mechanics. If we now identify $\alpha = i$, then $u_p(x) = e^{ipx/\hbar}$ is simply the space part of the de-Broglie wave for a particle with momentum p. This is precisely the connection we need:

$$\begin{array}{l} \hat{x} \to x \\ \hat{p} \to -i\hbar\dfrac{\partial}{\partial x} \end{array} \implies [\hat{x}, \hat{p}] = i\hbar. \tag{2.21}$$

The $\hat{x}$ and $\hat{p}$ are said to be complimentary to each other. In classical mechanics we refer to these as canonically conjugate variables.

We note that in classical mechanics translation symmetry implies momentum conservation using Noether's theorem. The generators of translation are differential operators which are now identified with momentum itself in the operator representation.

By the requirement of special theory of relativity, if the quantum theory is ever to fit the requirement of the special theory of relativity, the quantum rule $p_i = -i(\hbar\partial/\partial x_i)$ should also extend to energy which is the zeroth component of the four vector (t, x_i). Representing $E = i\hbar(\partial/\partial t)$ completes the picture.

Alternatively, we may use the wave function for one-dimensional motion given by

$$\psi(x,t) = e^{-i(wt-kx)} = e^{-i(Et-px)/\hbar} \tag{2.22}$$

where we have made use of de-Broglie hypothesis. The wave function satisfies the eigenvalue equations

$$\begin{aligned} -i\hbar\frac{\partial\psi}{\partial x} &= p\psi \\ i\hbar\frac{\partial\psi}{\partial t} &= E\psi \end{aligned} \tag{2.23}$$

for momentum and energy.

2.4 Schroedinger equation

We now put together the complementarity principle and the assumption that the possible value of an observable is given by an eigenvalue equation. The energy operator is the Hamiltonian and in the Schroedinger representation we have

$$H(\hat{x}, \hat{p}) = H(x, -i\hbar\partial/\partial x) \tag{2.24}$$

and

$$H(x, -i\hbar\partial/\partial x)\psi(x) = E\psi(x), \tag{2.25}$$

where E is the energy eigenvalue and $\psi(x)$ is an energy eigenstate.

More generally we may write the Schroedinger equation as

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}, \tag{2.26}$$

which reduces to the eigenvalue equation for energy when $\Psi(x,t) = e^{-iEt/\hbar}\psi(x)$, that is when the Hamiltonian is not explicitly dependent on time. In general $\Psi(x,t)$ is a complex valued function which specifies the state of the system. The Schroedinger equation in the above form is the quantum evolution equation and its solution $\Psi(x,t)$ is assumed to provide the complete description of the system described by the Hamiltonian. Its form, no matter how complicated the system, remains the same for any quantum system. The real test of the formalism resides in its agreement with experiments in particular cases. The validity and usefulness is demonstrated through such tests alone.

The Hamiltonian is a repository of all the information about the system under consideration, as in classical mechanics. It has the same form as in classical mechanics, with the observables replaced by the corresponding operators operating on the wave function or the state function. The solution for the state function is obtained by specifying the appropriate boundary conditions corresponding to the physical situation. The Schroedinger equation is therefore regarded as the equation of quantum dynamics just as Newtons second law of motion, or its equivalent formulations, is the evolution equation for the classical dynamics. The meaning of $\Psi(x,t)$ as state function will become clear soon.

The Schroedinger equation is strictly linear in the wave function. As we shall see the experimental data are consistent with this form. Unlike the equations of motion in classical mechanics (or even in Electro-dynamics), which may be non-linear, in quantum mechanics the evolution equation is strictly linear. Therefore independent of the details of the system (degrees of freedom, relativistic, non-relativistic, etc) the following fact remains true: If Ψ_1 and Ψ_2 are any two solutions of the equation, then

$$\Psi = c_1\Psi_1 + c_2\Psi_2 \tag{2.27}$$

is also a solution of the Schroedinger equation. This statement is called the *Superposition Principle* and is a fundamental to the nature of quantum mechanics. It is also at the root of some of the features that seem perplexing from every day experience.

As an example, consider a non-relativistic particle moving in one dimension under the action of a potential. The classical Hamiltonian is given by

$$H = \frac{p^2}{2m} + V(x), \tag{2.28}$$

where the first term is the kinetic energy and the second term corresponds to the potential energy. The corresponding equation in quantum dynamics is

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi_E(x) = E\psi_E(x), \tag{2.29}$$

where $\psi_E(x)$ is the eigenfunction corresponding to an energy eigenvalue E. We may generalise this to three-dimensions (or any other dimensions) by simply writing

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_E(\vec{r}) = E\psi_E(\vec{r}), \tag{2.30}$$

the actual solution depends on the boundary conditions on ψ.

2.5 Particle in box

In order clarify many conceptual issues, let us consider a simple example– the quantum dynamics of a particle confined to move in a one dimensional infinite box.

$$\begin{aligned} V(x) &= 0, \quad |x| \leq a \\ V(x) &= \infty \quad |x| > a \end{aligned} \tag{2.31}$$

Classically the particle can execute back and forth motion between $a \leq x \leq -a$. Quantum mechanically we have

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x) = E\psi(x), \tag{2.32}$$

which is satisfied every where $-\infty < x < \infty$.

Outside the box, $|x| > a$, $V(x) \to \infty$, while all other terms are finite. Therefore for the equation to be valid, we have

$$\psi(x) = 0; \quad |x| \geq 0 \tag{2.33}$$

Inside the box the equation is then

$$\left[\frac{\partial^2}{\partial x^2} + k^2\right]\psi(x) = 0, \quad k^2 = \frac{2mE}{\hbar^2}. \tag{2.34}$$

which has two solutions $\sin(kx), \sin(kx)$. Matching the solutions at the boundary we have two possible solutions:

$$\begin{aligned}\psi_{2n}(x) &= A\sin(kx); \Longrightarrow k_{2n} = 2n\frac{\pi}{2a}; \quad n = 1,2,3,\cdots \\ \psi_{2n+1}(x) &= B\cos(kx); \Longrightarrow k_{2n+1} = (2n+1)\frac{\pi}{2a}; \quad n = 0,1,2,\cdots \end{aligned} \tag{2.35}$$

Combining the two solutions we may write, for any n,

$$\begin{aligned}k_n &= n\,\frac{\pi}{2a}, \quad n = 1,2,3,\cdots \\ E_n &= \frac{\hbar^2}{2m}\frac{\pi^2}{4a^2}\,n^2\end{aligned} \tag{2.36}$$

which has the essential feature of a quantum spectrum- discrete energy spectrum- appearing naturally.

2.6 The State function

From the example of one dimensional box, it is clear that the eigenvalues– the quantum spectrum– do not depend on the overall normalisation of the eigenfunction. The constants A, B may be set arbitrarily. Let us remove this arbitrariness by the normalisation condition

$$\int \psi^*(x)\psi(x)\; dx = 1 \tag{2.37}$$

where the integration is over all allowed values of x. For such normalised state functions, the expectation or average value of any repeated observations of an operator $\hat{A}$ takes a simpler form

$$\langle a_\psi\rangle = \int \psi^*(x)\hat{A}\psi(x)\; dx. \tag{2.38}$$

For example

$$\langle x_\psi\rangle = \int \psi^*(x)\hat{x}\psi(x)\; dx = \int dx\; x|\psi(x)|^2. \tag{2.39}$$

and

$$p_\psi = \int \psi^*(x)\hat{p}\psi(x)\; dx. \tag{2.40}$$

The equation for x_ψ has far reaching implications. Defining

$$P_\psi = |\psi(x)|^2. \tag{2.41}$$

as the weighting factor for calculating the average value of x, we have an interpretation of $\psi(x)$ as the probability density of particle space. This means that the $P_\psi(x)dx$ is the probability of finding a particle in a distance interval dx about x, when a large number of measurements are made on independent particles each of which is described by the function $\psi(x)$. The normalisation condition ensures that the probability of finding the particle some where in the whole region is equal to unity. This should be so provided the normalising constant is independent of time. Furthermore the normalisation integral converges which puts a condition on the type of functions that may be interpreted as state functions. This is the interpretation that was first given by Born.

Given this interpretation, we may now ask what is the probability that an observation $\hat{A}$ on the system whose state function is $\psi(x)$ produces a result a_n? The plausible answer is to consider the eigenstate of the operator $\hat{A}$ such that

$$\hat{A}\ u_n(x) = a_n\ u_n(x) \tag{2.42}$$

where $u_n(x)$ is an eigenstate of the operator. If $\psi(x)$ coincides with $u_n(x)$ then every measurement yields the result a_n. Otherwise, the result is quantitatively given by the overlap integral

$$\int u_n^*(x)\psi(x)\ dx \tag{2.43}$$

and the probability that the result of measurement is a_n is given by

$$P_\psi(a_n) = \left|\int u_n^*(x)\psi(x)\ dx\right|^2 \tag{2.44}$$

which is the modulus square of the overlap integral.

This may be seen more directly by expanding the state function $\psi(x)$.

$$\psi(x) = \sum_n \alpha_n u_n(x) \tag{2.45}$$

where $u_n(x)$ are eigenstates (ortho-normal) of the operator $\hat{A}$ which form a complete set. Hence any function of x may be expanded in-terms of these complete set of functions. Therefore

$$\hat{A}\psi(x) = \sum_n \alpha_n a_n\ u_n(x) \tag{2.46}$$

Multiplying on the left by the conjugate of $\psi(x)$ and integrating we have

$$\int\ dx\ \psi^*(x)\hat{A}\psi(x) = \sum_n a_n\ \alpha_n\alpha_m^*\ \int\ dx\ u_m^*(x)u_n(x) = \sum_n a_n\alpha_n\alpha_m^*\ \delta_{nm} \tag{2.47}$$

The expectation value

$$\langle a_\psi\rangle = \sum_n a_n\ |\alpha_n|^2 = \sum_n a_n\ P_\psi, \tag{2.48}$$

where P is the overlap integral given above. Note that this result is independent of the phase factor, that is $\psi(x)$ and $e^{i\theta}\psi(x)$ yield identical results.

2.7 Box normalisation

In general the state functions may be either well localised and those that remain finite at large distances. In the former case the associated eigenvalues tend to be discrete while in the later case the eigenvalues tend to possess a continuous range of eigenvalues. We will encounter both these cases as we go along. As we noticed in the case of infinite box, the eigenvalues are in general discrete, but as the box dimension becomes larger they tend to become almost continuous.

As an explicit example, consider the momentum eigenstates. The momentum eigenfunctions are solutions of the eigenvalue equation

$$-i\hbar\frac{\partial u_p}{\partial x} = pu_p. \tag{2.49}$$

The eigenfunctions have the form

$$u_p(x) = N\ e^{ipx/\hbar} = N\ e^{ikx} : \quad k = p/\hbar, \tag{2.50}$$

where N is normalisation which should be independent of time.

In general the eigenvalues of an operator corresponding to a physical observable are real. Furthermore the eigenvectors belonging to different eigenvalues of an observable are orthogonal (have zero overlap). For discrete eigenvalues, this means the corresponding eigenvectors obey

$$\int dx\ u^*_{n'}(x)u_n(x) = \delta_{nn'} \tag{2.51}$$

For continuous eigenvalues like p above, however, we need a generalisation of the Kronecker δ-function. Dirac δ function is a generalisation that is used when we have continuous eigenvalues. For particles with definite momenta in an infinite volume we write

$$N^2\int\ dx\ u^*_p(x)u_{p'}(x) = N^2\int_{-\infty}^{\infty} dxe^{-i(p-p')x/\hbar} = \delta(p-p'). \tag{2.52}$$

In its simplest representation the Dirac δ function is defined as

$$\delta(y) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\ dx\ e^{-iyx} \tag{2.53}$$

Comparing the two equations above, we fix the normalisation factor to be

$$N^2 = \frac{1}{2\pi\hbar} \tag{2.54}$$

It should however be noted that whether we normalise in a finite length box or over infinite length using the delta function, the final results typically do not change.

Here are some properties of the delta function that may be proved easily:

1. $$\delta(x) = \delta(-x)$$

2.
$$\delta'(x) = -\delta'(-x)$$

3.
$$x\delta(x) = 0$$

4.
$$x\delta'(x) = -\delta(x)$$

5.
$$x\delta(ax) = \delta(x)/a$$

6.
$$\int dx\ f(x)\delta(x-a) = f(a)$$

7.
$$\int dx\ \delta(a-x)\delta(x-b) = \delta(a-b)$$

Using the many identities involving the delta function above, we may make a few statements about the state of the system. We already know that the state of the system can not be characterised by both momentum and position since they are not simultaneously specified precisely. However, since momentum is an observable there is an operator corresponding to it and as we have done before we can find the eigenstates- de Broglie wave function.

What about position? The position is of course observable too. Therefore there must be an operator whose eigenvalue is position. That is

$$\hat{x}\psi(x) = x\psi(x) = x_0\psi(x) \tag{2.55}$$

and therefore

$$(x - x_0)\psi(x) = 0 \tag{2.56}$$

a rather strange equation since x is a variable. The function $\psi(x)$ is therefore zero everywhere except at $x = x_0$. For ordinary functions this is a confusing statement- that it is zero everywhere except at one point in space. But that is precisely the property of the delta function $\psi(x) = \delta(x - x_0)$ and it represents eigenfunction of position located at the point $x = x_0$. Thus we may interpret the delta function as the probability density in position space. Since the integral is unity this interpretation is consistent.

2.8 Expectation values

The position probability density as

$$P(x,t) = |\Psi(x,t)|^2 \tag{2.57}$$

makes it possible to calculate what is called as the *expectation value* of the position of the particle. We can do this in any dimension, but for now let us stick to one dimensional motion. The probability is defined in such a way its integral over all space is unity. The normalisation constant therefore is independent of time.

The expectation value is the average of the result of a large number of measurements on independent systems described by the same state function. We may write this as

$$\langle x\rangle = \int dx\ xP(x,t) = \int dx\ x\Psi^*(x,t)\Psi(x,t), \tag{2.58}$$

where the integration is taken over the allowed region of space. We may now ask what is the expectation value for the momentum p. As discussed before through fundamental assumptions, we may simply write

$$\langle p\rangle = -i\hbar \int dx \Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t), \tag{2.59}$$

where the operator acts on the right. Similarly for energy we may write

$$\langle E\rangle = i\hbar \int dx \Psi^*(x,t)\frac{\partial}{\partial t}\Psi(x,t). \tag{2.60}$$

Consider a particle moving in one dimension whose classical Hamiltonian is given by

$$H(x,p,t) = \frac{p^2}{2m} + V(x,t) \tag{2.61}$$

The instantaneous change in position expectation value is given by

$$\frac{d\langle x\rangle}{dt} = \int dx\ x\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t} + \frac{\partial\Psi^*(x,t)}{\partial t}\Psi(x,t)\right]. \tag{2.62}$$

We may simplify this using the Schroedinger equation for Ψ, Ψ^*,

$$\begin{aligned} i\hbar\frac{\partial\Psi}{\partial t} &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \\ -i\hbar\frac{\partial\Psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + V\Psi^*. \end{aligned} \tag{2.63}$$

Substituting

$$\begin{aligned} \frac{d\langle x\rangle}{dt} &= \frac{i}{\hbar}\int dx\ \left[\Psi^* x[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi] - [-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + V\Psi^*]x\Psi\right] \\ &= \frac{i\hbar}{2m}\int dx\ \left[\Psi^* x\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}(x\Psi)\right] \end{aligned} \tag{2.64}$$

The second part of the equation may be simplified by partial integration to get

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int dx\ \left[\Psi^*\frac{\partial^2(x\Psi)}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}(x\Psi)\right] - \frac{i\hbar}{m}\int\ dx\ \Psi^*\frac{\partial}{\partial x}\Psi \tag{2.65}$$

The first term can be integrated to give a boundary term

$$\left[\Psi^*\frac{\partial(x\Psi)}{\partial x}-\frac{\partial\Psi^*}{\partial x}(x\Psi)\right]$$

which should vanish at the physical boundary of space in which the particle exists. Therefore we have

$$\frac{d\langle x\rangle}{dt}=-\frac{i\hbar}{m}\int dx\ \Psi^*\frac{\partial}{\partial x}\Psi=\frac{\langle p\rangle}{m}, \tag{2.66}$$

which is the non-relativistic expression for classical momentum. Furthermore, by taking the time derivative of momentum, and using the quantum equation of motion we have

$$\begin{aligned}\frac{d\langle p\rangle}{dt} &= -i\hbar\frac{d}{dt}\int dx\ \Psi^*\frac{\partial}{\partial x}\Psi \\ &= -i\hbar\left[\int dx\ \frac{\partial\Psi^*}{\partial t}\frac{\partial}{\partial x}\Psi+\int dx\ \Psi^*\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial t}\right]. \\ &= -\left[\int dx\ \Psi^*\frac{\partial(V\Psi)}{\partial x}-\int dx\ \Psi^*V\frac{\partial\Psi}{\partial x}\right] \\ &= -\int dx\ \Psi^*\frac{\partial V}{\partial x}\Psi=\langle-\frac{\partial V}{\partial x}\rangle, \end{aligned} \tag{2.67}$$

using the wave equation. This is the analogous equation to the classical equation of motion

$$\frac{dp}{dt}=-\frac{dV}{dx}=F \tag{2.68}$$

Thus we have the correspondence that the expectation values obey the classical evolution equation. This is the content of the Ehrenfest Theorem. Note that in the above, we follow the convention that is commonly used in quantum mechanics that the complex conjugate is written always to the left and the operators act to the left. This acquires meaning when internal degrees of freedom is included and the wave functions are not merely complex valued functions but column vectors.

2.9 Uncertainty Principle

The statement that $[\hat{x},\hat{p}]\neq 0$ is a statement asserting the mutual disturbance between two types of observation. They could be any two non-commuting operators, in general. To make this so-called disturbance more quantitative, let us consider a normalised state function of the form

$$\psi(x)=N\ e^{-x^2/2\Delta_x^2} \tag{2.69}$$

which is a Gaussian with a normalisation factor N which can be easily determined and Δ_x is the half width of the distribution. The corresponding probability distribution is

$$P_\psi(x)=N^2\ e^{-x^2/\Delta_x^2} \tag{2.70}$$

Suppose a measurement of momentum is made, the probability amplitude that the result has a value p is found is given by the overlap integral

$$\phi(p) = \int_{-\infty}^{\infty} u_p^*(x)\psi(x)\ dx, \tag{2.71}$$

where $u_p(x) = e^{ipx/\hbar}$ are the momentum eigenstates. Therefore

$$\phi(p) = \int_{-\infty}^{\infty} e^{-ipx/\hbar}\psi(x)\ dx = Ce^{-p^2\Delta_x^2/2\hbar^2} = Ce^{-p^2/2\Delta_p^2}, \tag{2.72}$$

where $\Delta_p = \hbar/\Delta_x$ and C is a constant. Therefore, we have

$$\Delta_p\Delta_x \ = \ \hbar \tag{2.73}$$

The precise equality is due to the fact that we assumed a Gaussian state function. In general, however, the relation takes the form

$$\Delta_p\Delta_x \ \geq \ \hbar \tag{2.74}$$

This is a precise statement of the magnitude of mutual disturbance between two complementary variables and is a statement of the *Uncertainty Principle* in quantum mechanics.

Similar relationship holds in general for two non-commuting operators and can be proved rigorously. It is important to note that this is a fundamental property of all quantum systems and not an effect related to observation like accuracy. It is in the nature of things described by quantum mechanics.

Chapter 3

Bound systems and discrete eigenvalues

We have already seen an example of the bound system, namely particle in a box of finite extension where the potential infinite outside the box. The eigenvalues are discrete. Here we consider examples of systems where the particle is confined by external forces, classically allowed to move in a finite space. There are not many such problems which may be solved analytically. However, such problems are important since they may be used to approximate more complicated problems.

One such problem which is ubiquitous is the linear harmonic oscillator. We first consider this problem in one dimension and extend it to higher dimensions later.

3.1 One dimensional harmonic oscillator

Consider a point particle of mass m attracted to a fixed centre at the origin by a force proportional to the displacement from the center. We assume the motion is non-relativistic. It is a fundamental problem in classical mechanics as well as in quantum mechanics and appears every where even as an approximate description of more complicated physical systems. The problem may also be solved using different methods.

The classical Hamiltonian of the system is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \tag{3.1}$$

where k is the force constant with $F = -kx$ as the force. The classical frequency of oscillation is given by $\omega = \sqrt{k/m}$. The energy of the oscillator is by definition always positive and classically can take continuous values. At each energy the classical motion is confined between two turning points given by

$$-\sqrt{\frac{2E}{m\omega}} \leq x \leq \sqrt{\frac{2E}{m\omega}}$$

The equation of motion is easily solved to give a solution in the form

$$x(t) = A\cos(\omega t + \phi).$$

The quantum evolution of the system is described by the Schroedinger equation given by

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}m\omega^2 x^2\right]\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}. \tag{3.2}$$

Since the Hamiltonian is independent of time, at an energy E, we may write

$$\Psi(x,t)=e^{-iEt/\hbar}u(x). \tag{3.3}$$

Substituting in the Schroedinger equation, we have

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2}+\frac{1}{2}m\omega^2x^2u=Eu. \tag{3.4}$$

Note that $-\infty < x < \infty$. Note that the energy is always positive. This is now an eigenvalue equation with eigenvalue energy E and $u(x)$ are eigenfunction to be determined for each allowed eigenvalue. To make life easier we can write the above equation by transforming to dimensionless variables. To this end let us define a length

$$l_\omega=\sqrt{\frac{\hbar}{m\omega}}, \tag{3.5}$$

usually called the oscillator length (has dimensions of length any way) and depends only on the constant parameters of the Hamiltonian. We can scale

$$y=\frac{x}{l_\omega}; \quad -\infty<y<\infty,$$

where y is now dimensionless. In these units we have

$$\frac{d^2u}{dy^2}+[\lambda-y^2]u=0; \quad \lambda=\frac{2E}{\hbar\omega} \tag{3.6}$$

where λ can only take positive values. Thus we have now a simple looking linear second order differential equation for u whose eigenvalues are given in terms of λ.

Let us first look at the asymptotic behaviour of the solutions as $y\to\pm\infty$. The potential given by y^2 blows up in this limit and for finite energy solutions we need to cancel this term. We must find solutions that remain finite as $y\to\pm\infty$. It appears therefore that$e^{\pm y^2/2}$ should be a factor in $u(y)$. However the solution with the positive sign in the exponent will not work as a probability amplitude. So we choose the one with negative sign and let

$$u(y)=y^ne^{-y^2/2}.$$

Substituting this asymptotic form in the equation we get

$$\begin{aligned}[y^2-(2n+1)+n(n-1)y^{-2}+(\lambda-y^2)]y^ne^{-y^2/2} &= 0\\ \left[(\lambda-(2n+1))+\frac{n(n-1)}{y^2}\right]y^ne^{-y^2/2} &= 0. \end{aligned} \tag{3.7}$$

Several things have happened here- the y^2 divergence of the potential for large y is cancelled by the derivative acting on the Gaussian. Again for large values of y the first term in the second equation dominates. The asymptotic solution for large y may be obtained by setting

$$\lambda = 2n + 1,$$

In particular the asymptotic solution is also an exact solution for $n = 0, 1$ since $n(n-1)$ vanishes for these values of n yielding the first two exact solutions to the problem:

$$u_0(y) = N_0 e^{-y^2/2}; \quad \lambda_0 = 1 \Longrightarrow E = \frac{1}{2}\hbar\omega, \tag{3.8}$$

and

$$u_1(y) = N_1 y e^{-y^2/2}; \quad \lambda_1 = 3 \Longrightarrow E = \frac{3}{2}\hbar\omega, \tag{3.9}$$

These are in fact the two lowest energy eigenstates of the quantum harmonic oscillator.

The general solution may be obtained by assuming a solution of the form

$$u(y) = H(y) e^{-y^2/2}, \tag{3.10}$$

where $H(y)$ is a polynomial in y of degree less than $(\lambda - 1)/2$. This will ensure finite solutions both at $y = 0$ and at $y = \infty$ as demanded by the interpretation of the solutions of the Schroedinger equation (normalisable). Substituting the above form in the equation yields a differential equation for $H(y)$

$$H'' - 2yH' + (\lambda - 1)H = 0 \tag{3.11}$$

where primes denote differentiation w.r.t y. This is a well known differential equation called the Hermite equation which may be solved by the standard series method and the solutions are well known. Let

$$H(y) = \sum_{k-0}^{\infty} a_k y^k. \tag{3.12}$$

Substituting this in the Hermite equation and rearranging the terms we get

$$\sum_{k=0}^{\infty} [a_{k+2}(k+2)(k+1) - a_k(2k+1-\lambda)] y^k = 0. \tag{3.13}$$

This can be satisfied if every coefficient is zero for arbitrary value of y. Therefore we have

$$a_{k+2} = \frac{2k+1-\lambda}{(k+2)(k+1)} a_k. \tag{3.14}$$

For large k this approximates to

$$a_{k+2} = \frac{2a_k}{k}. \tag{3.15}$$

Note that they have the same sign and furthermore, the sum diverges as $y \to \infty$. This is not acceptable as a physically meaningful wave function. Therefore the series must terminate for some value of $k = n$. We have already seen this from the asymptotic analysis and therefore we have

$$\lambda = 2n + 1 \tag{3.16}$$

Without going through further details we shall write the exact eigenstates and eigenenergies of the quantum oscillator here:

$$\begin{aligned} \lambda = (2n+1) \implies E_n &= \hbar\omega(n + \frac{1}{2}) \\ u_n(y) &= C_n H_n(y) e^{-y^2/2}, \end{aligned} \tag{3.17}$$

where C_n is normalisation constant given by

$$C_n = \frac{1}{\sqrt{2^n n! \pi^{1/2}}}. \tag{3.18}$$

Let us note some important facts here:

- The infinite sequence of levels are equally spaced- an idea used first by Planck in his derivation of the blackbody distribution formula.
- The lowest energy state is not zero, but $\hbar\omega/2$ which is called the zero point energy. This is a characteristic of all quantum systems and is related to the uncertainty principle- that there is always a finite spread in momentum and position.

Eigenfunctions corresponding to two distinct eigenvalues are orthogonal, can be checked explicitly, that is

$$\int_{-\infty}^{\infty} dy \; u_n(y) u_{n'}(y) = C_n^2 \int_{-\infty}^{\infty} dy \; H_n(y) H_{n'}(y) e^{-y^2} = \delta_{nn'} \tag{3.19}$$

which is the ortho-normality condition for eigenfunctions. Notice that there is no complex conjugation since the eigenfunctions are real. We give some Hermite polynomials here explicitly:

$$H_0(y) = 1; \quad H_1(y) = y; \quad H_2(y) = 4y^2 - 2; \quad H_3(y) = 8y^3 - 12y; \quad \cdots \tag{3.20}$$

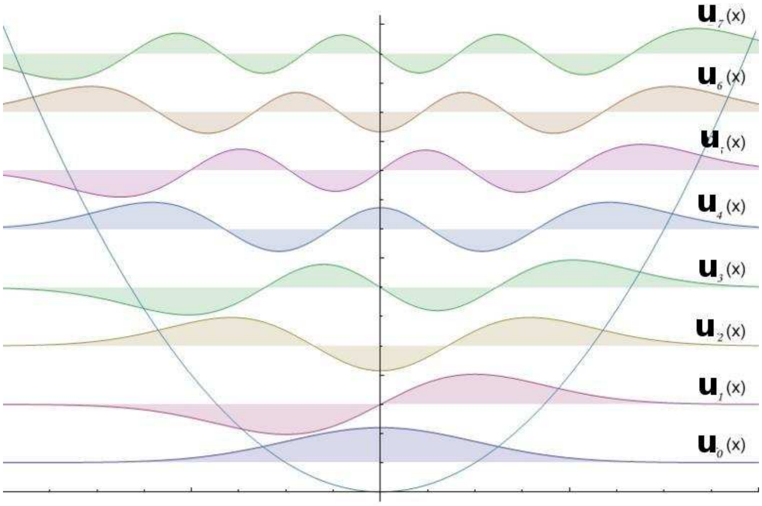


Figure 3.1: Examples of harmonic oscillator eigenfunctions. (Source: Wikipedia)

The oscillator Hamiltonian is symmetric under parity transformation, namely $x \to -x$. This parity symmetry is reflected in the eigenfunctions which are eigenstates of the parity operator:

$$\begin{aligned} u_n(-x) &= u_n(x); \quad n\ even \\ u_n(-x) &= -u_n(x); \quad n\ odd \end{aligned} \tag{3.21}$$

The expectation value of the potential is easily calculated using the eigenfunctions of energy

$$\langle V_n \rangle = \int_{\infty}^{infty} dx u_n^*(x) V(x) u_n^*(x) = \frac{1}{2}(n+\frac{1}{2})\hbar\omega = \frac{E_n}{2}. \tag{3.22}$$

As a consequence, we have the expectation of kinetic energy given by

$$\langle T \rangle = \langle \frac{p^2}{2m} \rangle = \frac{1}{2}(n+\frac{1}{2})\hbar\omega = \frac{E_n}{2}. \tag{3.23}$$

Thus we have the virial theorem in the case of harmonic oscillator that the kinetic and potential energies are equal and equal to half the energy of the state.

Furthermore, by definition we have

$$\langle x \rangle = 0, \quad \langle p \rangle = 0.$$

As a result the standard deviation

$$(\Delta x)^2 = \langle x^2 \rangle - (\langle x \rangle)^2 = \langle x^2 \rangle,$$

$$(\Delta p)^2 = \langle p^2 \rangle - (\langle p \rangle)^2 = \langle p^2 \rangle.$$

It follows therefore

$$(\Delta x)(\Delta p) = (n+\frac{1}{2})\hbar \geq \hbar/2.$$

The minimum uncertainty is obtained in the ground state.

We may now go back to the general solution of the time dependent Schroedinger equation for the harmonic oscillator. The full solution $\Psi(x,t)$ can be expanded, in general, in terms of the stationary solutions (superposition principle) as

$$\Psi(x,t) = \sum_{n=0}^{\infty} A_n u_n(x) e^{-iE_n t/\hbar} = e^{-i\omega/2} \sum_{n=0}^{\infty} A_n u_n(x) e^{-in\omega t}, \tag{3.24}$$

where A_n are arbitrary constants. Interestingly apart from the over all phase factor, which is entirely quantum in origin, the solution is a periodic function with the period of the classical oscillator. It suggests that it may be possible to form a wave packet out of these solutions whose centre oscillates with the period of the classical motion.

An important point to be noticed here is that the approach to solutions, namely eigenvalues and eigenfunctions, is determined by the physical conditions. Mathematically, the differential equations allow many different solutions. However, the solutions that we have determined are based on physical requirement- they should be finite and allow probabilistic interpretation of the square of the wave function (square intergrability). Ortho-normality ensures this, and further yields unique solutions at each energy value.

Since the differential equations are local in nature, asymptotic analysis can be used to glean quite a lot of information about eigenvalues even if eigenfunctions remain approximate in these limits.

Using the above example, we can outline a recipe to solve the quantum evolution of a system using the Schroedinger approach:

- Choose the Hamiltonian of the system that you are interested in solving.

- We need to know how the system is prepared (by an “apparatus or machine”), that is the knowledge of Ψ at some time $t = t_0$. This provides the boundary conditions necessary.

- Find the eigenstates and eigenvalues by solving the time independent or stationary equation
$$\hat{H} u_n(x) = E_n u_n(x).$$

- Using the fact that $\Psi(x, t_0) = \sum A_n u_n(x)$, where A_n depend on how the system is prepared, we may write in general
$$\Psi(x,t) = \sum_{n=0}^{\infty} A_n e^{-iE_n t/\hbar} u_n(x) \tag{3.25}$$
which is valid for all times t.

- Now we use this to predict probability amplitude for an observation using the overlap integral between the eigenstate of the operator corresponding to the observation with the time dependent state of the system given above.

3.2 Harmonic oscillator in higher dimensions

We may easily extend the results of one dimensional harmonic oscillator to higher dimensions as long as there is no coupling between them. In principle in d dimensions the Hamiltonian is simply sum of one dimensional oscillators:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \cdots + \hat{H}_d \tag{3.26}$$

where

$$\hat{H}_k = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_k^2} + \frac{1}{2}m\omega^2 x_k^2\right] \tag{3.27}$$

for some $1 \leq k \leq d$. For a planar oscillator we have $d = 2$ and x_1, x_2 are the relevant coordinates and $d = 3$ for an oscillator in three dimensions. We have assumed the mass and the oscillator frequency to be the same, this may be relaxed if necessary but the system will have reduced symmetry.

The equation of motion for the full $d-$dimensional oscillator is then given by

$$\sum_{k=1}^{d}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_k^2} + \frac{1}{2}m\omega^2 x_k^2\right] U_N = E_N U_N \tag{3.28}$$

Since this is a separable Hamiltonian the solution is easily found and is given by

$$U_N(x_1, \cdots, x_d) = u_{n_1}(x_1)u_{n_2}(x_2)u_{n_3}(x_3)\cdots u_{n_d}(x_d), \tag{3.29}$$

where each u is the solution of a one dimensional oscillator

$$\hat{H}_k u_{n_k}(x_k) = e_{n_k} u_{n_k}(x_k). \tag{3.30}$$

The energy eigenvalues are given by

$$E_N = (N + d/2)\hbar\omega = (n_1 + n_2 + \cdots + n_d + d/2)\hbar\omega; \quad N = \sum_{k=1}^{d} n_k, \tag{3.31}$$

where N is the total quantum number which is the sum of individual quantum numbers in each direction.

Once again the energy levels are equally spaced corresponding to the values of the total quantum number $N = 0, 1, 2, \cdots$. However except the ground state, excited states are non degenerate. The ground state is non-degenerate in any dimension. We given some examples below explicitly in $d = 2, 3$.

N	E (d=2)	degeneracy (d=2)	E (d=3)	degeneracy (d=3)
0	1	1	3/2	1
1	2	2	5/2	3
2	3	3	7/2	6
3	4	4	9/2	10
⋮	⋮	⋮	⋮	⋮
N	N+1	N+1	(N+3/2)	(N+1)(N+2)/2

The degeneracy of the state for a given N is simply the number of ways in which N can be partitioned into d positive integers. As a simple practical application, these degeneracies may be used to understand the magic numbers or stable states in the simple oscillator shell model of quantum dots (in two-dimensions) and light nuclei (in three-dimensions).

For an isotropic oscillator considered here, it also reflects the rotational symmetry of the Hamiltonian. This is best seen in polar coordinates. We will discuss this next.

3.3 Quantum theory of Angular Momentum

As a preliminary to the discussion of problems in three dimensions with rotational symmetry, not just harmonic oscillator, let us now discuss the quantum theory of angular momentum. To do this, it is better to change to spherical coordinates from Cartesian coordinates that we have used earlier. The two systems are related by

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta, \end{aligned} \tag{3.32}$$

where $r \geq 0,\ 0 \leq \theta \leq \pi,\ \ -\pi \leq \phi \leq \pi$, with the inverse relations given by

$$\begin{aligned} r &= \sqrt{x^2+y^2+z^2} \\ \cos\theta &= z/r \\ \tan\phi &= y/x. \end{aligned} \tag{3.33}$$

The derivatives may be transformed using the following relations-

$$\begin{gathered} \frac{\partial r}{\partial x} = \sin\theta\cos\phi;\ \frac{\partial r}{\partial y} = \sin\theta\sin\phi;\ \frac{\partial r}{\partial z} = \cos\theta \\ \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r};\ \frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r};\ \frac{\partial\theta}{\partial z} = -\frac{\sin\theta}{r} \\ \frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta};\ \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta};\ \frac{\partial\phi}{\partial z} = 0 \end{gathered}$$

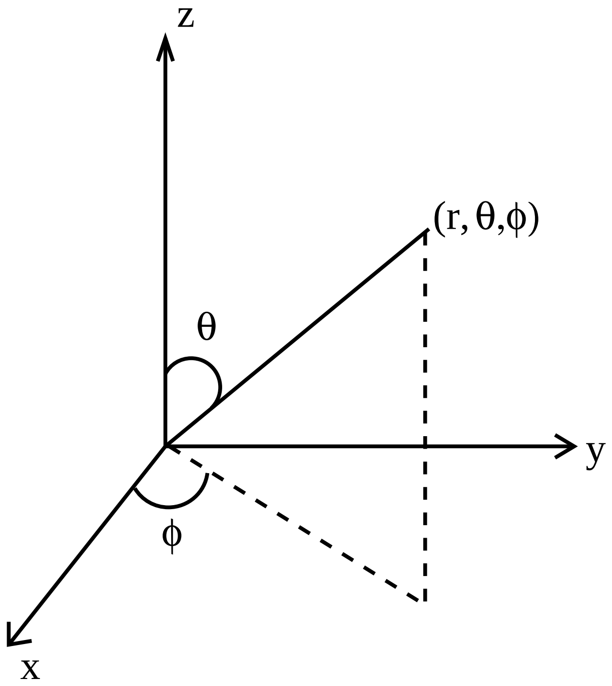
The angular momentum operators, about the origin, are constructed using the correspondence principle

$$\begin{aligned} \hat{l}_x &= -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right] = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right] \\ \hat{l}_y &= -i\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] = i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right] \\ \hat{l}_z &= -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] = -i\hbar\frac{\partial}{\partial\phi} \end{aligned} \tag{3.34}$$

It is easy to check that these operators do not commute. For example,

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z \tag{3.35}$$

We may choose one of these operators to define a set of eigenstates and eigenvalues.



3.3.1 The z-component

The form of $\hat{l}_z$ immediately shows that

$$[\hat{\phi}, \hat{l}_z] = i\hbar; \quad \hat{\phi} = \phi \tag{3.36}$$

As in the case of momentum $\hat{p}$, here again we may determine the eigenstates and eigenvalues of the $z-$ component of the angular momentum using

$$-i\hbar \frac{\partial}{\partial \phi} u_m = \ \hbar \ m \ u_m \ \Longrightarrow \ u_m(\phi) = e^{im\phi}. \tag{3.37}$$

Since ϕ is an angle variable, the same state is denoted by

$$u_m(\phi) = e^{im\phi} = e^{im(\phi+2\pi)} \ \Longrightarrow \ e^{2im\pi} = 1. \tag{3.38}$$

Therefore m is an integer given by $m = 0, \pm 1, \pm 2, \cdots$. The eigenvalues of the angular momentum operator $\hat{l}_z$ are thus quantised.

3.3.2 The total angular momentum

It is easy to check that the angular momentum operators do not commute, that is

$$[\hat{l}_i, \hat{l}_j] \neq 0. \tag{3.39}$$

Therefore it not possible to have the precise knowledge of more than one component in any measurement. However, we may construct the total angular momentum operator, given by

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \tag{3.40}$$

substituting for the operators on the r.h.s,

$$\hat{l}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{3.41}$$

Immediately it follows that

$$[\hat{l}^2, \hat{l}_z] = 0 \tag{3.42}$$

since $\hat{l}^2$ does not have explicit dependence on angle ϕ. Thus it is possible to find eigenvalues of $\hat{l}^2$ and $\hat{l}_z$ simultaneously since they commute. There exist simultaneous eigenfunctions of these two operators. Let us denote these by

$$\begin{aligned} \hat{l}_z Y_{\beta m} &= \hbar m Y_{\beta m} \\ \hat{l}^2 Y_{\beta m} &= \hbar^2 \beta Y_{\beta m}, \end{aligned} \tag{3.43}$$

where we have multiplied by $\hbar$ to keep the same dimension on both sides. Since the first of these equations is already solved, we may write

$$Y_{\beta m}(\theta, \phi) = P_{\beta m}(\theta) e^{im\phi} \tag{3.44}$$

which satisfies the eigenvalue equation for $\hat{l}_z$. Let us look at the equation for $\hat{l}^2$.

$$\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] P_{\beta m} = \beta P_{\beta m}. \tag{3.45}$$

We may simplify the equation by making a change in notation with

$$w = \cos\theta : \quad -1 \leq \ w \ \leq +1$$

so that

$$\partial/\partial w = -(1/\sin\theta)\partial/\partial\theta.$$

Substituting the above form in the equation for $\hat{l}^2$ we get

$$\begin{aligned} \frac{d}{dw} \left((1-w^2) \frac{dP}{dw} \right) + \left(\beta - \frac{m^2}{1-w^2} \right) P &= 0 \\ \frac{d^2P}{dw^2} - \frac{2w}{1-w^2} \frac{dP}{dw} + \left(\frac{\beta}{1-w^2} - \frac{m^2}{(1-w^2)^2} \right) P &= 0, \end{aligned} \tag{3.46}$$

where we have dropped the subscripts on the function P for now.

Let us look at the asymptotic solutions. The last term is the most singular at $w = \pm 1$. Therefore the solution should be of the form

$$P(w) = (1-w^2)^{|m|/2} f(w) \tag{3.47}$$

which will get rid of the most divergent term at the boundary of w and we get

$$(1-w^2) \frac{d^2 f}{dw^2} - 2(|m|+1) w \frac{df}{dw} + (\beta - |m|(|m|+1)) f = 0. \tag{3.48}$$

Now we can try the series solution of the form

$$f(w) = \sum_{k=0}^{\infty} a_k w^z, \tag{3.49}$$

and equate the coefficients of powers of w to zero to obtain

$$(k+2)(k+1)a_{k+2} = [(k+|m|)(k+|m|+1) - \beta]a_k \tag{3.50}$$

which is a recurrence relation that determines the coefficients of the series for f. Note that for very large k, for a fixed m, we have

$$a_{k+2} \approx a_k, \tag{3.51}$$

if the series does not terminate. This means that for very large values of k

$$f(w) \approx \frac{1}{(1-w^2)} \tag{3.52}$$

which diverges at $w = \pm 1$ and therefore P for some values of m. So for finite solutions, it is necessary that the series terminate at some value of k. That is $f(w)$ must be a polynomial and therefore

$$\beta = (k+|m|)(k+|m|+1) = l(l+1); \quad k = l - |m| \tag{3.53}$$

If k is even the polynomial will have only even powers (provided a_1=0) and if k is odd the polynomial will have odd powers (provided $a_0 = 0$). These are in fact well known polynomials and are called as the Associated Legendre Polynomials.

Going back to the eigenvalue equation for $\hat{l}^2$, therefore, we may write the eigenvalues as

$$\hbar^2\beta = \hbar^2 l(l+1); \quad l = 0, 1, 2, \cdots \tag{3.54}$$

and since $k \geq 0$ we have $l \geq |m|$. Thus for any given value of l we have

$$l_z = \hbar m; \quad m = \pm 0, \pm 1, \pm 2, \cdots, \pm l. \tag{3.55}$$

This may be interpreted as saying that the angular momentum vector $\vec{l}$ is allowed to have only certain orientations corresponding to discrete values of its projection m along the z-axis. This was referred to as space quantisation in old quantum theory. However this interpretation can not be precise due to the presence of uncertainty relations.

The simultaneous eigenfunction of the corresponding operators are

$$\begin{aligned} Y_{lm}(\theta,\phi) &= P_{lm}(\cos\theta)\; e^{im\phi}, \\ \hat{l}_z\; Y_{lm}(\theta,\phi) &= \hbar m\; Y_{lm}(\theta,\phi) \\ \hat{l}^2\; Y_{lm}(\theta,\phi) &= \hbar^2 l(l+1)\; Y_{lm}(\theta,\phi) \end{aligned} \tag{3.56}$$

where $P_{lm}(\cos\theta)$ are usually known as Associated Legendre Polynomials and Y_{lm} are known as Spherical Harmonics and appear in many applications where the potential is spherical symmetric. It is important to note that the eigenstates of $\hat{l}^2$ have all the same eigenvalue $l(l+1)$ and hence $(2l+1)$ degenerate.

For any given l there are $(2l+1)$ solutions corresponding to $m = -l, \cdots, 0, \cdots, +l$ with the same eigenvalue $l(l+1)$ with respect to total angular momentum operator. Some examples for small values of l are given below:

$$\begin{aligned} Y_{00}(\theta,\phi) &= \frac{1}{\sqrt{4\pi}} \\ Y_{1\pm1}(\theta,\phi) &= -(\pm)\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \\ Y_{10}(\theta,\phi) &= \sqrt{\frac{3}{4\pi}}\cos\theta \end{aligned} \tag{3.57}$$

The spherical harmonics may be normalised so that the total probability of finding angular momentum in any orientation is unity,

$$Y_{lm}(\theta,\phi) = i^{m+|m|}\sqrt{\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]}P_{lm}(\cos\theta)e^{im\phi} \tag{3.58}$$

The spherical harmonics are orthonormal with this definition

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \; Y^*_{l'm'}(\theta,\phi)\; Y_{lm}(\theta,\phi) = \delta_{ll'}\delta_{mm'} \tag{3.59}$$

With the above definitions and normalisation, it is possible to show that the spherical harmonics have definite parity. In three dimensions, the parity transformation is given by

$$(x,y,z) \longrightarrow (-x,-y,-z).$$

The corresponding transformations in spherical polar coordinates are given by

$$r' = r,\;\; \theta' = \pi - \theta,\;\; \phi' = \pi + \phi.$$

These transformations on the spherical harmonics yields

$$Y_{lm}(\theta',\phi') = (-1)^l\; Y_{lm}(\theta,\phi). \tag{3.60}$$

Thus the eigenvalue of the parity operator on spherical harmonic is simply $(-1)^l$ and is not dependent on m.

3.4 Motion in a spherical symmetric potential

A particle moving in a three dimensional space under the action of a potential $V(r,\theta,\phi) = V(r)$ is said to be moving in a central potential. The potential $V(r)$ is independent of the orientation or spherically symmetric. Examples of such potentials are the harmonic oscillator potential

$$V(r) = \frac{1}{2}m\omega^2(x^2+y^2+z^2) = \frac{1}{2}m\omega^2\; r^2 \tag{3.61}$$

and Coulomb potential $V(r) = e^2/r$. They constitute one of the simplest but useful application of Schroedinger equation.

Let us consider the non-relativistic motion of a particle moving in such a potential. The Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r). \tag{3.62}$$

There is no explicit time dependent term, and the energy eigenvalue equation is given by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right] u_E = E\ u_E. \tag{3.63}$$

Since the potential is spherical symmetric or central, it is useful to write this explicitly in spherical polar coordinates (r, θ, ϕ),

$$-\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] u_E + V(r)u_E = E\ u_E. \tag{3.64}$$

By inspection, we see that the terms involving angular derivatives are familiar, in fact it is simply the operator $\hat{l}^2$. Therefore

$$-\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{l}^2\right] u_E + V(r)u_E = E\ u_E. \tag{3.65}$$

It is easy to check that

$$[\hat{H}, \hat{l}^2] = 0, \quad [\hat{H}, \hat{l}_z] = 0 \tag{3.66}$$

It is therefore possible to specify energy, angular momentum and its projection, simultaneously for a particle moving in a central potential. Since we already know the eigenstate of operator $\hat{l}^2$, without loss of generality we may write the general form of the solution as

$$u_{nlm}(r, \theta, \phi) = f_{nl}(r)\ Y_{lm}(\theta, \phi), \tag{3.67}$$

where n is an additional quantum number we introduce to account for radial excitations. The meaning of this will become clear soon. Consequently it is only the radial equation that needs to be solved

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2}\right] f_{nl} + V(r)f_{nl} = E_{nl}f_{nl}, \tag{3.68}$$

where E_{nl} is now independent of the azimuthal quantum number m. We may use this equation to solve for a whole class of central potentials in principle.

3.4.1 Revisit Harmonic Oscillator

Let us rewind to the isotropic harmonic oscillator problem in three dimensions. The potential is spherical symmetric since

$$V(r) = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) = \frac{1}{2}m\omega^2 r^2 \tag{3.69}$$

As before we introduce the dimensionless variable using the oscillator length

$$q = \sqrt{\frac{m\omega}{\hbar}}r = \frac{r}{l_\omega}. \tag{3.70}$$

The radial equation in terms of $q \geq 0$ may be written as

$$\frac{\hbar\omega}{2}\left[-\frac{1}{q^2}\frac{\partial}{\partial q}\left(q^2\frac{\partial}{\partial q}\right) + \frac{l(l+1)}{q^2} + q^2\right] f_{nl} = E_{nl}f_{nl}. \tag{3.71}$$

We have already discussed the solution using the Cartesian decomposition in terms of three independent oscillators in x, y, z. The solutions may also be obtained in terms of polar coordinates. Here is a brief summary: We rewrite the basic equation as

$$\left[\frac{d^2}{dq^2} + \frac{2}{q}\frac{d}{dq} - \frac{l(l+1)}{q^2} + \lambda_{nl} - q^2\right] f_{nl} = 0; \quad \lambda_{nl} = \frac{2E_{nl}}{\hbar\omega} \tag{3.72}$$

Let us look at the asymptotic properties of this equation. In the limit $q \to \infty$, we have

$$\left[\frac{d^2}{dq^2} - q^2\right] f_{nl} \approx 0. \tag{3.73}$$

Therefore we demand

$$f(q) \approx e^{\pm q^2/2}. \tag{3.74}$$

The solution with positive sign diverges in the asymptotic limit and is not normalisable, so we keep the solution with the negative sign- this should be a feature for all solutions,

$$f(q) \approx e^{-q^2/2}. \tag{3.75}$$

Unlike in the one dimensional problem, we have a problem of divergence as $q \to 0$ also since in this limit the equation is of the form

$$\left[\frac{d^2}{dq^2} + \frac{2}{q}\frac{d}{dq} - \frac{l(l+1)}{q^2}\right] f_{nl} \approx 0 \tag{3.76}$$

Let us then try a solution of the form q^s, in this limit. Substituting in the equation we obtain

$$s(s-1) + 2s - l(l+1) = s(s+1) - l(l+1) = 0 \implies s = l, \ \textit{or} \ s = -(l+1). \tag{3.77}$$

Again the normalisability condition implies that we choose $s = l$. Thus the most general solution that satisfies the asymptotic conditions has to have the form

$$f_{nl}(q) = q^l L_{nl}(q)e^{-q^2/2}, \tag{3.78}$$

where $L_{nl}(q)$ is a series in q which must terminate since we have already taken care of asymptotic behaviour. Substituting this form in the full radial equation gives

$$\frac{d^2L_{nl}}{dq^2} + 2\left(\frac{l+1}{q} - q\right)\frac{dL_{nl}}{dq} + (\lambda_{nl} - 2l - 3)L_{nl} = 0. \tag{3.79}$$

Once again this may be reduced to a standard equation whose solutions are called Associated Laguarre Polynomials. We will deal with these functions later, but for now it suffices to say that this equation meaningful solutions when

$$\lambda_{nl} - 2l - 3 = n \tag{3.80}$$

where n is an integer. This immediately yields the energy eigenvalues for the three dimensional oscillator in the form

$$E_{nl} = \hbar\omega(n + l + \frac{3}{2}) = \hbar\omega(N + \frac{3}{2}), \tag{3.81}$$

where n is called the radial quantum number which has appeared throughout this analysis but now acquires a definite meaning and N is the principle quantum number. The levels are equally spaced and states corresponding to each l are $(2l{+}1)$ degenerate. One can enumerate the states with their energies as follows:

N	n	l	E (d=3)	degeneracy (d=3)
0	0	0	3/2	1
1	0	1	5/2	3
2	2	0	7/2	1
2	0	2	7/2	5

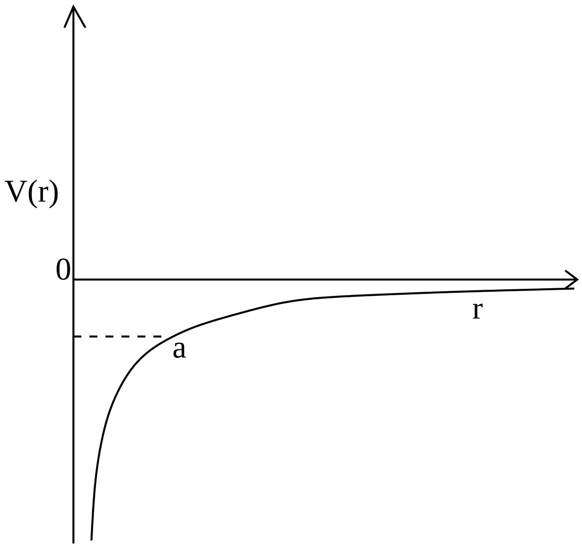
It is easy to check that the energies and degeneracies match with the ones calculated in Cartesian basis. This way, one may understand the degeneracies as associated with the symmetry of the problem, namely, rotational invariance. In fact this is an example of the intimate connection between symmetries and degenerate states in quantum mechanics. The states are now labelled by quantum numbers n, l, m instead of n_x, n_y, n_z. The energy for a given N is independent of the m quantum number.

3.5 Motion in a Coulomb Potential

We now consider the crucial problem of the Hydrogen atom which ensured the applicability of Schroedinger equation in the beginning and allowed for detailed comparison with the observed spectrum of the Hydrogen atom. In general this is a two-body problem of electron moving around the nucleus. For simplicity let us assume that the nucleus is infinitely heavy. This reduces this to a one body problem- that of an electron moving under the action of a potential- Coulomb potential. We take this potential to be

$$V(r) = -\frac{Ze^2}{r}; \quad r = \sqrt{x^2 + y^2 + z^2} \tag{3.82}$$

where $Z = 1$ for hydrogen atom and the sign ensures that the potential is attractive. Classically this is very similar to the well-known Kepler problem-there are two distinct regions, for negative energies the electron is bound and is unbound for positive energies. Classically at a given energy the electron is confined to a finite region, say $0 \leq r \leq a$.



The potential is spherically symmetric, hence the eigenstates are simultaneous eigenfunctions of energy, $\hat{l}^2$ and $\hat{l}_z$. We focus on the negative energy region where the states are bound. The radial equation of motion given by

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{Ze^2}{r}+\frac{\hbar^2 l(l+1)}{2mr^2}\right]u_{nl}=E\ u_{nl}, \tag{3.83}$$

where l is as before the angular momentum eigenvalue and the equation is independent of the value of its projection m.

As in the case of the oscillator problem, we may transform the equation in terms of dimensionless variables using the following scaling transformations: Let

$$\epsilon=-E, \quad \alpha^2=\frac{8m\epsilon}{\hbar^2}, \quad q=\alpha r, \quad \lambda=\frac{Ze^2}{\hbar}\sqrt{\frac{m}{2\epsilon}} \tag{3.84}$$

The radial equation in terms of $q \geq 0$ may be written as

$$\left[\frac{1}{q^2}\frac{\partial}{\partial q}\left(q^2\frac{\partial}{\partial q}\right)+\frac{\lambda}{q}-\frac{1}{4}-\frac{l(l+1)}{q^2}\right]u_{nl}=0. \tag{3.85}$$

We expand the basic equation as

$$\left[\frac{d^2}{dq^2}+\frac{2}{q}\frac{d}{dq}-\frac{l(l+1)}{q^2}+\frac{\lambda}{q}-\frac{1}{4}\right]u_{nl}=0. \tag{3.86}$$

Let us look at the asymptotic properties of this equation. In the limit $q\to\infty$, we have

$$\left[\frac{d^2}{dq^2}-\frac{1}{4}\right]u_{nl}\approx 0. \tag{3.87}$$

Therefore we demand

$$u(q)\approx e^{\pm q/2}. \tag{3.88}$$

The solution with positive sign diverges in the asymptotic limit and is not normalisable, so we keep the solution with the negative sign- this should be a feature for all solutions,

$$u(q) \approx e^{-q/2}. \tag{3.89}$$

We also need to look as the asymptotic region as $q \to 0$ also since in this limit the equation is of the form

$$\left[\frac{d^2}{dq^2} + \frac{2}{q}\frac{d}{dq} - \frac{l(l+1)}{q^2}\right] f_{nl} \approx 0 \tag{3.90}$$

Let us then try a solution of the form q^s, in this limit. Substituting in the equation we obtain

$$s(s-1) + 2s - l(l+1) = s(s+1) - l(l+1) = 0 \implies s = l,\ or\ s = -(l+1). \tag{3.91}$$

Again the normalisability condition implies that we choose $s = l$. Thus the most general solution that satisfies the asymptotic conditions has to have the form

$$u_{nl}(q) = q^l L_{nl}(q) e^{-q/2}, \tag{3.92}$$

where $L_{nl}(q)$ is a series in q which must terminate (we will show this below) since we have already taken care of asymptotic behaviour at $q \to 0$ and at $q \to \infty$. Substituting this form in the full radial equation gives

$$q\frac{d^2 L_{nl}}{dq^2} + (2(l+1) - q)\frac{dL_{nl}}{dq} + (\lambda - l - 1)L_{nl} = 0. \tag{3.93}$$

Now consider a series solution of the form

$$L_{nl}(q) = \sum_{k=0}^{\infty} a_k q^k. \tag{3.94}$$

Substituting this in the differential equation and equating coefficient of q^k, we get

$$(k+1)[k + 2(l+1)]a_{k+1} = [k + (l + 1 - \lambda)]a_k \tag{3.95}$$

It turns for large k, we have

$$a_{k+1} \approx \frac{a_k}{k} \tag{3.96}$$

so the $L(q) \approx e^q$ which is unacceptable as it diverges for large q. Therefore the series must terminate to satisfy the boundary conditions. The series termination may be ensured if $\lambda = n(> l)$, where n is an integer. Choice of n dictates the energy eigenvalue and the corresponding eigenfunction in terms of the Associated Laguarre Polynomials.

The energy eigenvalues are given by

$$E_n = -\frac{mZ^2e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{Z^2e^2}{2a_0}\frac{1}{n^2}; \quad a_0 = \frac{\hbar^2}{me^2}, \tag{3.97}$$

where a_0 is the Bohr radius. The energy levels of hydrogen are recovered for $Z = 1$ which is essentially the Bohr formula. The energy levels are completely specified by a single quantum number n which is the *principal quantum number* which is positive and non-zero integer

$$n = 1, 2, 3, \cdots \tag{3.98}$$

For a given value of n we have $l = 0, 1, \cdots, (n-1)$ as allowed values. The eigenvalues of the square of the angular momentum is $\hbar^2 l(l+1)$ and for each l we have the azimuthal quantum number $m = \pm 0, \pm 1, \cdots, \pm l$ corresponding to $(2l+1)$ values. Thus corresponding to a given principle quantum number n with energy E_n, we have the degeneracy of the n-th level given by

$$D_n = \sum_{l=0}^{n-1} (2l+1) = n^2. \tag{3.99}$$

Some low lying states are given in the table below:

n	l	m	-E	degeneracy
1	0	0	1	1
2	0,1	0,1,0,-1	1/4	4
3	0,1,2	0,1,0,-1,2,1,0,-1,-2	1/9	9

Notice that the degeneracies are different from those of the three dimensional oscillator. The eigenfunctions corresponding to each of these states labelled by quantum numbers $n, l.m$ are given by

$$u_{nlm}(r, \theta, \phi) = N_{nlm} u_{nl}(r) Y_{lm}(\theta, \phi), \tag{3.100}$$

where

$$u_{nl}(r) = r^l \; L_{nl}(r) \; e^{-Zr/a_0 n} \tag{3.101}$$

The normalised ground state and first excited are given by

$$u_{100} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \tag{3.102}$$

$$u_{200} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \tag{3.103}$$

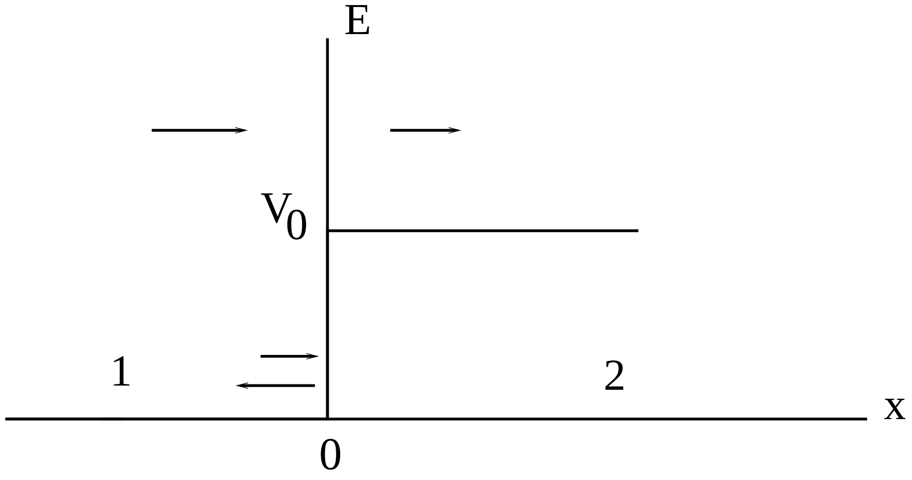
where the first excited is degenerate and only $l = 0, m = 0$ state is shown. These states are orthogonal as they are eigenstates.

Chapter 4

The Quantum Step

In the previous chapter we discussed the problem of bound states in quantum mechanics. in this chapter we will briefly discuss the motion of a particle when there is a potential step, also called the barrier penetration problem, in one dimension.

Let us start with a single potential step as shown here with an idealised step $V = 0(x < x_0, region1), V = V_0(x > x_0, region2)$:



Classically the energy of the particle is given by the sum of kinetic and potential energies

$$E = T + V. \tag{4.1}$$

When $E_0 > V_0$ particle coming from left approaches the potential barrier with kinetic energy E_0. The particle is slowed by the barrier since in region 1 the energy is $E_0 = T$ and in region 2 the energy $E_0 = T_1 + V$ such that $T_1 < T$. But since the energy $E_0 > V$ there is total transmission always.

When $E_0 < V_0$ particle coming from left approaches the potential barrier with kinetic energy E_0 but it reverses its motion at the step.– that is total reflection. Classically we have these two situations–total transmission and total reflection.

For a quantum mechanical description, consider the time independent Schroedinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2 u_E}{\partial x^2} + V(x)u_E = Eu_E, \tag{4.2}$$

where m is the mass of the particle and

$$V(x) = 0, \quad x < 0; \quad V(x) = V_0 \quad x > 0$$

Since u_E is finite every, we have the boundary condition u_E and u'_E are continuous at $x = 0$ so that $u''(0)$ is finite where the primes denote derivatives.

We have to distinguish two cases $E > V_0$ and $E < V_0$.

Case I: $E > V_0$ Define

$$k_1^2 = \frac{2mE}{\hbar^2}; \quad k_2^2 = \frac{2m(E - V_0)}{\hbar^2} \tag{4.3}$$

Substituting this in the Schroedinger equation we have

$$x < 0 : \quad \frac{\partial^2 u_1}{\partial x^2} + k_1^2 u_1 = 0 \tag{4.4}$$

$$x > 0 : \quad \frac{\partial^2 u_2}{\partial x^2} + k_2^2 u_2 = 0 \tag{4.5}$$

Let us assume the particle is moving from the left to right along the positive direction initially. They may be either transmitted or reflected at $x = 0$. The solutions are simply de Broglie waves given by

$$\begin{aligned} u_1(x) = Ae^{ik_1x} + Be^{-ik_1x}&, \\ u_2(x) = Ce^{ik_2x}&, \end{aligned} \tag{4.6}$$

where u_1 has both incident and reflected components. Matching the boundary conditions at $x = 0$, continuity of the function and its derivative, we have

$$A + B = C; \quad k_1(A - B) = k_2C.$$

Solving these we have

$$B = \frac{k_1 - k_2}{k_1 + k_2}; \quad C = \frac{2k_1}{k_1 + k_2}$$

The interesting thing about these coefficients is that B is not zero- that is there is a reflection coefficient at the boundary $x = 0$ even though the energy is greater than the barrier energy. We can quantify this by defining a reflection coefficient given by

$$R = \frac{|B|^2}{|A|^2} = \left|\frac{k_1 - k_2}{k_1 + k_2}\right|^2. \tag{4.7}$$

This of course contradicts the classical result where the particle simply goes through with reduced momentum. The classical limit is approached when the energy of the particle is much higher than the barrier energy. This limit is obtained if we put $k_1 \approx k_2$ so that $R \approx 0$ that is no reflection. The relative probability of finding the particle at some point $x < 0$ is given by

$$P_u(x) = |u_1(x)|^2 = \left| e^{ik_1 x} + \frac{B}{A} e^{-ik_1 x} \right|^2 = 1 + R + 2\frac{B}{A}\cos(2k_1 x) \tag{4.8}$$

where the first term is the incident particle beam while the second one corresponds to the reflected beam along with an oscillating term which averages to 1/2 over length scales larger than $2\pi/k_1$.

Now consider the second case:

Case I: $E < V_0$ Define as before

$$k_1^2 = \frac{2mE}{\hbar^2}; \quad k^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{4.9}$$

Substituting this in the Schroedinger equation we have

$$x < 0: \quad \frac{\partial^2 u_1}{\partial x^2} + k_1^2 u_1 = 0 \tag{4.10}$$

$$x > 0: \quad \frac{\partial^2 u_2}{\partial x^2} - k^2 u_2 = 0 \tag{4.11}$$

Correspondingly the solutions in the two regions are given by

$$\begin{aligned} u_1(x) &= Ae^{ik_1 x} + Be^{-ik_1 x}, \\ u_2(x) &= Ce^{-kx} + De^{kx}. \end{aligned} \tag{4.12}$$

Since u_2 should be normalisable, we set $D = 0$. Notice that the solution in region 2 is qualitatively different from the one in region 1. The continuity conditions at $x = 0$ then imply

$$A + B = C; \quad ik_1(A - B) = -Ck. \tag{4.13}$$

Therefore

$$B = \frac{k_1 - ik}{k_1 + ik}A; \quad C = \frac{2k_1}{k_1 + ik}A. \tag{4.14}$$

The most surprising aspect of this result is that $C \neq 0$, the probability of finding the particle in classically forbidden region, $x > 0$, is non-zero.

The reflection coefficient given by

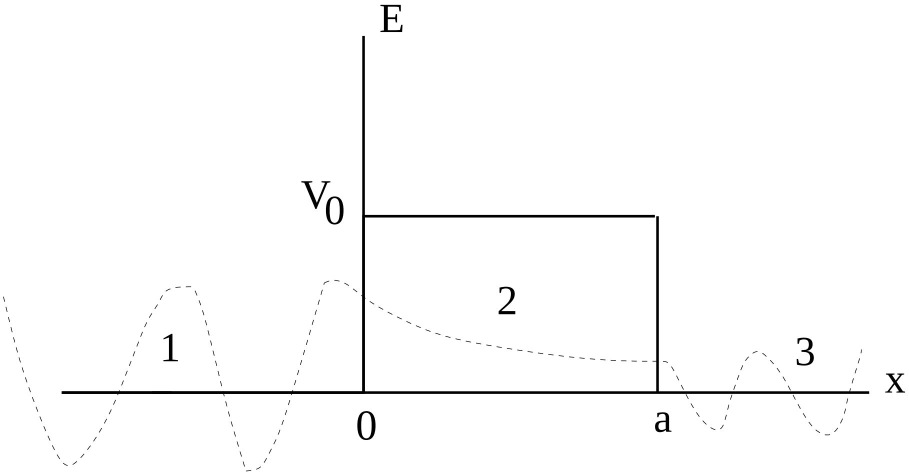
$$R = \frac{|B|^2}{|A|^2} = \left| \frac{k_1 - ik}{k_1 + ik} \right|^2 = 1. \tag{4.15}$$

Therefore for any energy in this region, there is total reflection even though there exists a finite probability of finding the particle in the classical forbidden region given by

$$|u_2(x)|^2 = \frac{4k_1^2}{k_1^2 + k^2} e^{-2kx}. \tag{4.16}$$

In either of the two cases we have no restriction on energy.

An important consequence of the above result in case 2, is the phenomenon of tunnelling when instead of a step we have a potential barrier as shown below.



Now we have three distinct regions. The fact that the particle can penetrate a potential barrier even when its energy is less than the potential barrier has interesting consequences. When the energy $E > V_0$, the system is similar to the earlier case except that it slows down in the region of potential $0 < x < a$ at a given energy. However, when $E < V_0$, there are now three regions which are described by the Schroedinger equations

$$\begin{aligned} x<0: \quad \frac{\partial^2 u_1}{\partial x^2} + k_1^2 u_1 &= 0 \\ 0<x<a: \quad \frac{\partial^2 u_2}{\partial x^2} - k^2 u_2 &= 0 \\ x>a: \quad \frac{\partial^2 u_1}{\partial x^2} + k_1^2 u_1 &= 0 \end{aligned} \tag{4.17}$$

The solutions in three regions may be written as

$$\begin{aligned} u_1(x) &= Ae^{ik_1x} + Be^{-ik_1x}, \\ u_2(x) &= Ce^{kx} + De^{-kx}, \\ u_3(x) &= Fe^{ik_1x} + Ge^{-ik_1x}. \end{aligned} \tag{4.18}$$

Note that the region 2 admits both solutions since the normalisation of the state is between $0 < x < a$. We may set $G = 0$ since there is only transmitted wave in region 3 since the particle is moving from left to right. The functions and their derivatives must be continuous at $x = 0$ and $x = a$. Therefore we have, when $E < V_0$

$$\begin{aligned} A + B &= C + D, \\ ik_1(A - B) &= k(C - D), \\ Ce^{ka} + De^{-ka} &= Fe^{ik_1a}, \\ k[Ce^{ka} - De^{-ka}] &= F(ik_1)e^{ik_1a}. \end{aligned} \tag{4.19}$$

The probability of tunnelling or transmission through the barrier to region 3 is given by the coefficient $|F|^2$. It can be obtained by solving the set of equations above keeping A arbitrary and defined through over all normalisation of the solution in region 1. We simply give the result here

$$T = \left|\frac{F}{A}\right|^2 = \frac{1}{\cosh^2 ka + \frac{1}{4}(\frac{k}{k_1} - \frac{k_1}{k})\sinh^2 ka} \tag{4.20}$$

which may be checked by solving for the coefficients.