

3.3 Schrodinger's wave equation : Meaning, Boundary conditions, and Applications

Group 4 & 5

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3.3 Schrodinger's wave equation: Meaning, Boundary conditions, and Applications

Abstract

In this section, we will discuss the Schrodinger equation, from which one branch of quantum mechanics - wave mechanics - has developed. We will start with the basics of quantum mechanics and then we move to the Schrodinger equation. We will discuss various quantities in the Schrodinger equation. Time-dependent and time-independent both forms will be discussed. The concept of potential well and boundary conditions for the solution of the Schrodinger equation will be discussed. We will also understand the significance of wavefunction and its role in the probability density function of subatomic particle.

I. Introduction

Through the work of Planck and Einstein, we were forced to accept that energy is quantized and that light exhibits wave-particle duality. Then, de Broglie extended this duality to include matter as well, meaning that all matter has a wavelength, from a tiny electron to our whole human body, to a massive star. However, an object's wavelength is inversely proportional to its mass, so objects bigger than a molecule has a wavelength that is so tiny that it is completely negligible. But an electron is incredibly small, so small that its wavelength is indeed relevant, being around the size of an atom, so we must view electrons as both particles and waves from now on [1]. Therefore, we must discuss the wave nature of the electron. So what kind of wave might this be? We can regard an electron in an atom as a standing wave, just like the kind we learned about in classical physics, except that rather than something like a plucked guitar string, an electron is a circular standing wave surrounding the nucleus. If we understand this, it becomes immediately apparent why quantization of energy applies to the electron, because any circular standing waves must have an integer number of wavelengths in order to exist. Given that an increasing number of wavelengths means more energy carried by the wave. Due to this wave characteristics of an electron, we will have uncertainty about its position. If we see it as a wave then electron could be anywhere within that wave. This kind of behaviour we will define in terms of probability and wave function. The wave function for any electron or subatomic particle is not as important as the square magnitude of the wave function because it depicts the probability of having an electron or subatomic particle at that place. we will also discuss it in detail later in this chapter.

We can see the Bohr model for the hydrogen atom begin to emerge as we imagine a standing wave with one wavelength, and then two, and then three and so forth. This is the reason that an electron in an atom can only inhabit a discrete set of energy levels, the circular standing wave that represents the electron can only have an integer number of wavelengths. When an electron is struck by a photon of a particular energy, this energy is absorbed, promoting the electron to a higher energy state and increasing the number of wavelengths contained within the standing wave (see Fig. 3.3.1). This is why the electron goes to inhabit a higher energy level, and this is what is fundamentally

occurring during electron excitation. Furthermore, it is the constructive interference of these standing waves that explains how orbital overlap results in covalent bonding, so we can enjoy a little more clarity in our understanding of chemistry because of modern physics. Once it was realized that electrons exhibit wave behavior, the physics community set out to find a mathematical model that could describe this behavior.

Erwin Schrodinger achieved this goal in 1925 when he developed his Schrodinger equation, which incorporated the de Broglie relation [1]. This version of quantum mechanics was based on waves. Schrodinger equation is also useful to understand the structure of the atom, especially the hydrogen atom. We can understand energy quantization and possible energy levels for the hydrogen atom. A hydrogen atom has only a single electron moving around a single proton. For multi-electron atoms, this equation requires certain assumptions and estimations which is difficult, but for the hydrogen atom, Schrodinger equation can accurately define its characteristics. So in this section, we will see what is Schrodinger equation and its significance, what are the implications and meanings of the equations, what is its solution and what it represents, etc.

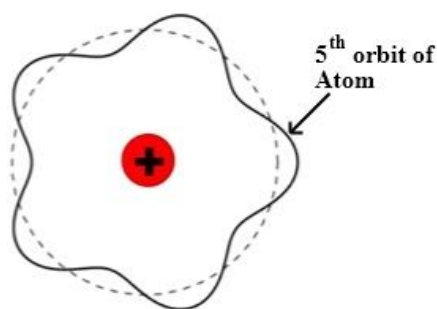


Fig. 3.3.1: Orbit of an atom [2].

II. Heisenberg Uncertainty

A. Wave-Particle Duality

Young's Double-slit test shows the wave-like characteristics of light. The experiment comprises of a light beam shining a tiny distance d apart through two adjacent slits and hitting a screen a relatively big distance away from L .

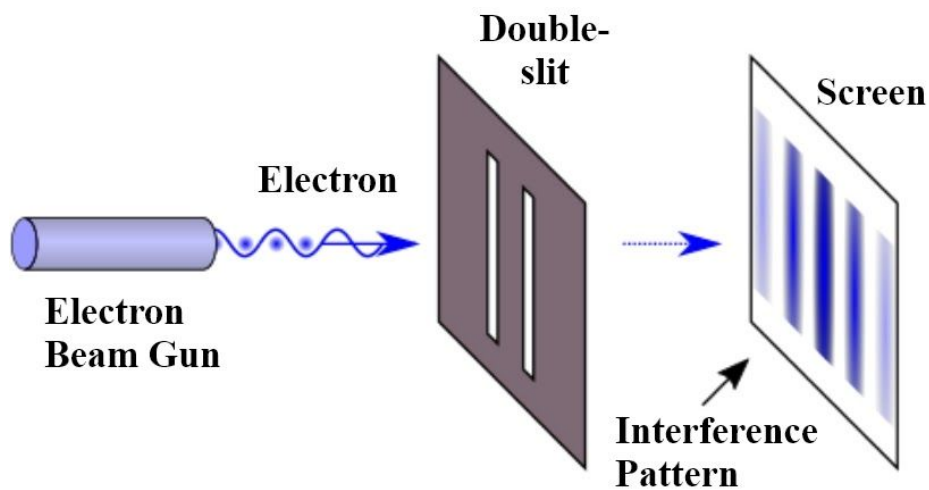


Fig. 3.3.2 Wave-Particle Double-slit experiment [3].

Experimental proof indicates that a pattern of interference was generated by the two light beams, with a maximum at range $= m\pi$ and a minimum at range $=(m-1/2)\pi$.

B. De Broglie Principle

Einstein conducted an experiment contesting the claim that light is a wave. Having discovered that light (commonly thought of as a wave) exhibited particle-like characteristics, De Broglie produced the audacious hypothesis that electrons (classically thought of as particles) might behave as waves.

$$p = mv$$

Where,

$$m = \frac{E}{c^2} \text{ and } v = c \text{ (velocity of light)}$$

So,

$$p = \frac{E}{c} \text{ Where } E = hf \text{ and } c = \frac{c}{f}$$

$$p = h$$

$$= \frac{h}{p} = \frac{h}{mv}$$

C. Probability Distribution in the BOX

In quantum physics, a vector in a cube system (also recognized as an endless prospective well or an endless rectangular well) defines a free electron to travel in a tiny room encircled by impenetrable obstacles. For instance, in conventional schemes, a particle caught inside a big container can migrate within the cabinet at any velocity and is no more probable to be discovered in one place than another [7]. Similarly, it can never have zero energy, so the particle can never "standstill." Moreover, based on its energy level, it is more probable to be discovered at certain locations than at others. At certain locations, recognized as temporal centers, the atom can never be identified.

D. The Heisenberg Uncertainty Principle

This principle states that the position and momentum of an object can never be known to 100% accuracy.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

where Δx depicts uncertainty of position, Δp depicts the uncertainty of momentum, and \hbar is $h/2\pi$ here h is called Planck's constant. In short, the Heisenberg Uncertainty Principle states that when we have more information about the position (of an object), the less information we have for the momentum (or velocity as they are directly related by mass) of that object and vice versa. waves are very spread out and particles are very localized. If an electron were somewhere in the vicinity of the wave, this does not really help us to find the position of the electron as the wave is infinite. However $p = \frac{h}{\lambda}$, so as there is only one wavelength present, we are certain about the momentum of the electron.

III. Schrodinger's Equation :

A. Schrodinger's Time-Dependent Equation :

From the theory of waves, we can say that any wave that propagates in space with time can be modeled as the below equation.

$$F(x, t) = Ae^{i(kx - \omega t)} \quad \dots\dots\dots (1)$$

The wave in equation (1) show forward propagating wave with amplitude A and angular frequency ω . Now here we are considering the wave nature of particles so we can model its wave function as per the below equation [6].

$$\psi(x, t) = Ae^{i(kx - \omega t)} \quad \dots\dots\dots (2)$$

Here we are adopting that the wave function above as suitable wave function for a free particle of momentum $p = \hbar k$ and energy $E = \hbar \omega$. from these things we can have below equation.

$$\frac{\partial^2}{\partial x^2} = -k^2 \quad \dots\dots\dots (3)$$

which can be written, using $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = \frac{p^2}{2m} \quad \dots\dots\dots (4)$$

Similarly,

$$\frac{\partial}{\partial t} = -i\omega \quad \dots\dots\dots (5)$$

Using the equation of energy,

$$i\hbar \frac{\partial}{\partial t} = \hbar\omega = E \quad \dots\dots\dots (6)$$

So now we have kinetic energy and potential energy so we can write the total energy of particle by just sum up both the energies and we have the equation as below.

$$E = \frac{p^2}{2m} + V(x) \quad \dots\dots\dots (7)$$

Now we assume that equation (4) and (6) can be applied here so the final equation, in that case, will be,

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) = i\hbar \frac{\partial}{\partial t} \quad \dots\dots\dots (8)$$

This equation (8) is what is known as time-dependent Schrodinger's equation. By analyzing and solving this equation we can understand the basics of quantum mechanics. In general, the solution of the time-dependent equation will describe the dynamic behavior of particle which is similar to Newton's classical physics where we use $F=ma$. Through Newton's formula, we can evaluate the

location of the object as a function of time, but Schrodinger's equation solution shows us how the probability of having a particle in a particular space differs as a function of time.

Time-dependent Schrodinger equation depends on space as well as time, but in most cases, time is not very important for our concern. It is also difficult to solve for quantum systems. So we have another version of the Schrodinger equation which is only depended on space. It is a time-independent Schrodinger equation and we will discuss it in the next section.

B. Time independent Schrodinger's equation :

We know how the wave function of a free particle of energy E looks like mathematically. The time dependency entered into the wave function by a complex exponential factor $\exp[-iEt/\hbar]$. This shows that to remove this time dependence, we have to take a wave-function to the Schrodinger wave equation of the form given below.

$$\psi(x, t) = \psi(x) e^{-\frac{iEt}{\hbar}} \quad \text{..... (9)}$$

where the time and space dependence of whole wave functions are kept under separate factors. Now we have to verify that this way leads us to derive an equation for $\psi(x)$, which is the space part of this wave function. If we replace this new(temporary) wave-function into the Schrodinger wave equation and use partial derivatives, we get:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} e^{-\frac{iEt}{\hbar}} + V(x) \psi(x) e^{-\frac{iEt}{\hbar}} = i\hbar \frac{\partial}{\partial t} \psi(x) e^{-\frac{iEt}{\hbar}} = E \psi(x) e^{-\frac{iEt}{\hbar}} \quad \text{..... (10)}$$

Now exponential factors will be nullified out from each side and we will get the equation,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \quad \text{..... (11)}$$

This above equation is a time-independent form of Schrodinger equation, Here E is a depiction of the total energy of a particle. It is also independent. There is no such constraints or limitations on possible values of E. Because of that if we want to calculate wave function for any particular value of E and for particular existing potential V(x), then we just have to put values of E and V(x), and calculate the wave function from equation. We will have different wave functions for different values of E. For a particular value of E, this wave function can be depicted as $\psi(x)$.

These wave functions which we found for particular values of E may not be valid. For a wave function to be valid, it has to follow two conditions, the first condition is that wave function has to be normalized which is called normalization condition. Wave function and its derivative must be continuous too. This is known as a continuous condition. Generally, these are called boundary conditions [8]. Which is described in detail in the next section. Here another point to notice is that wave function has to be finite and single-valued since it functions so it has to follow the definition of a function.

IV. Boundary Conditions :

A. Normalization Condition :

Normalization condition is required in order to converge the wave function. Basically there is no such significance of wave function as such. Mainly we use it in order to understand the probability distribution of particle over the space at a particular time instant. The wave function is the imaginary quantity and if we multiply it with its complex conjugate then we will have a square magnitude of the wave function. This gives us the probability distribution of particle over the space at that particular time instant. So this sum of all probabilities over the space has to be 1 [8]. So the integration of the probability density function of the particle over the space has to be 1. These are our normalization conditions of particle and this can be mathematically stated as below.

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad \dots\dots\dots (12)$$

Now we put the value from equation (9) then normalization condition must hold gives us the below equation.

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} |E(x)|^2 dx = 1 \quad \dots\dots\dots (13)$$

The above equation depicts that as x tends to infinity, $\Psi E(x)$ has to tend to zero then and then normalization condition holds true. It also implies the convergence of the wave function and probabilistic interpretation of the wave function.

B. Continuous Condition :

There is one additional boundary condition, which involves mathematics and it is called continuous condition. If the potential is discontinuous in some way, then it is valid for the Schrodinger equation to have findings that they are discontinuous. But discontinuous values have no probability in the real world (this would hint infinite valued force), and as we know that we always find continuous-wave functions for continuous potentials, we then put the additional conditions that spatial derivative of the wave function and wave function itself must be continuous [8]. So if we simply state the continuous condition then it says that spatial derivative, partial derivatives w.r.t. space coordinated, and wave function itself has to be continuous. Mathematically it can be stated as per below.

$$\Psi_1(p) = \Psi_2(p) \quad \dots\dots\dots (14)$$

$$\frac{\Psi_1(p)}{x} = \frac{\Psi_2(p)}{x} \quad \dots\dots\dots (15)$$

To illustrate how in the real world TISE and some properties of TISE's solutions can be derived, Here, we are going to contemplate the infinitely deep potential well theory here.

V. The solution of Schrodinger's Equation and Potential well

Let's say we have one particle having mass m within a region between space from 0 to L , which means for $0 < x < L$ potential energy is zero. This region is bounded by very high potential walls. For infinite potential wall, this wall potential is infinitely high and for a finite potential wall, this wall potential is some finite value. Here we are considering infinite potential well. To understand this consider the following example. Electron in block or piece of metal or gas on some container describes such systems very precisely. In these examples, the potential on the electron as it goes to the edge of a block of metal is infinite [7]. This doesn't allow an electron to leave the surface of the block. As can be considered for gas-container example and out infinite potential well theory too. This shows that if a particle has energy less than the height of the potential walls. An infinite potential well can be described by the following equation [4].

$$V(x) = 0 \quad 0 < x < L$$

$$= \infty \quad x \geq L; \quad x \leq 0$$

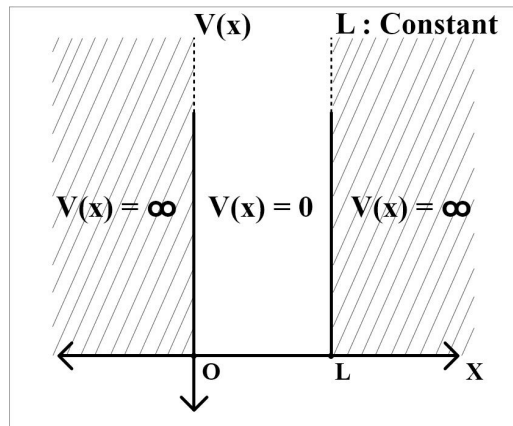


Fig. 3.3.3 Infinite Potential Well

Now we are considering finite potential well. Here the height of the wall is finite as we have seen. Any particle having energy more than this wall height can leave the system. This leads the system to state called scattering state which is not part of our discussion. So finite potential well can be mathematically modeled as:

$$V(x) = 0 \quad 0 < x < L$$

$$= v \quad x \geq L \quad x \leq 0$$

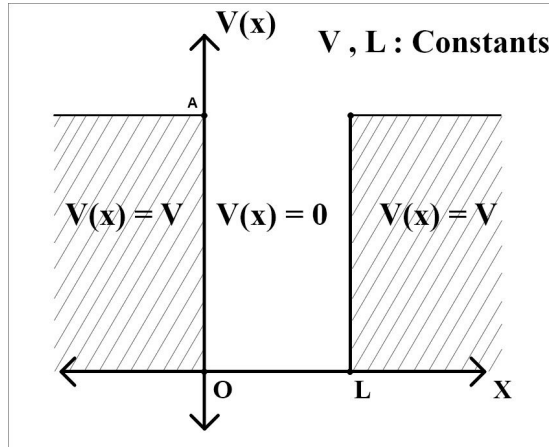


Fig. 3.3.4 Finite Potential Well

Now we will see the findings of the Schrodinger equation by taking infinite potential well into consideration.

In the area where potential is very high (infinite), at this places wave function will be zero, there will be no probability of the presence of particle at these places. So we must put this restriction i.e. boundary conditions [8].

$$\psi(0) = \psi(L) = 0 \quad \dots\dots\dots (16)$$

In the meantime, area [$0 < x < L$] the potential will be null, so the TISE will now be converted to:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \dots\dots\dots (17)$$

To get answers, we replace k by

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots\dots\dots (18)$$

So equation (17) can be written as,

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad \dots\dots\dots (19)$$

Whose general solution is as per below :

$$\psi(x) = A\sin(kx) + B\cos(kx) \quad \dots\dots\dots (20)$$

Now we will impose boundary conditions and consider $x = 0$,

$$\psi(0) = B = 0 \quad \dots\dots\dots (21)$$

So that the solution is now,

$$\psi(x) = A\sin(kx) \quad \dots\dots\dots (22)$$

Now second boundary condition at $x = L$ will give us,

$$\psi(L) = A\sin(kL) = 0 \quad \dots\dots\dots (23)$$

That indicated to us that either $A = 0$, that is $\psi(x) = 0$, which is a trivial solution (not a useful solution, it says that there is no particle in the well at all !) or $\sin(kL) = 0$, which gives a solution for k :

$$kL = n\pi, \quad n = 0, \pm 1, \pm 2, \dots \quad \dots\dots\dots (24)$$

Here we were excluded $n = 0$ situation as that would give again $\psi(x) = 0$, and of course we are going to discard negative values of n since this will again result in the same solution set (apart from opposite sign) as we got in positive values. So we now have

$$k_n = \frac{n\pi}{L}, \quad n = 1, 2, \dots \quad \dots\dots\dots (25)$$

This will give, on using Eq. (18),

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}, \quad n = 1, 2, \dots \quad \dots\dots\dots (26)$$

After considering this boundary condition and the normalization boundary condition we will have a final solution as per below [8] :

$$\begin{aligned} \psi_n(x) &= \sqrt{\frac{2}{L}} \sin(n\pi x/L) & 0 < x < L \\ &= 0 & x < 0, \quad x > L \end{aligned} \quad \dots\dots\dots (27)$$

Equation (27) shows a wave function that is a solution of the Schrodinger equation by infinite potential well model. Equation (26) shows the quantization of energy where n is standing for quantization. Now we have a wave function of particle which is sinusoidal. It means sinusoidal wave behavior between two endpoints [7]. If we put those two endpoints two together then we have a structure like an Fig. 3.3.1. For now, we can visualize the particle which shows various wave functions for various energy levels and only those who follow the conditions for valid wave function

will give us quantization of energy.

VI. Interpretation of wave function in terms of probability density function :

We have a solution of the Schrodinger's equation which is our wave function. This wave function has no such significance because it is an imaginary quantity in general cases. What is important is its magnitude square which is multiplication of wave function with its complex conjugate [5]. This gives us a probability density function of the particle over the space at that time instance. So now if we want to find the probability of having particle within some specific range (e.g. A to B) then we just have to integrate the probability density function of a particle at that time from A to B which will give us the probability of having particle between A and B.

$$P(A \leq x \leq B) = \int_A^B |\psi(x)|^2 dx \quad \dots\dots\dots (28)$$

Another important concept is energy quantization. Energy quantization shows that there are only certain levels of energy are possible within which the particle can stay [5]. From the quantized energy equation, we can also find the wavelength of that particle for that particular energy level. The integer multiple of this wavelength has to be fit within the perimeter of the orbit corresponds to that particular energy level [2]. This also gives insights to particle-wave duality nature. So this is how the Schrödinger equation explains the various quantum phenomena under the umbrella of quantum physics.

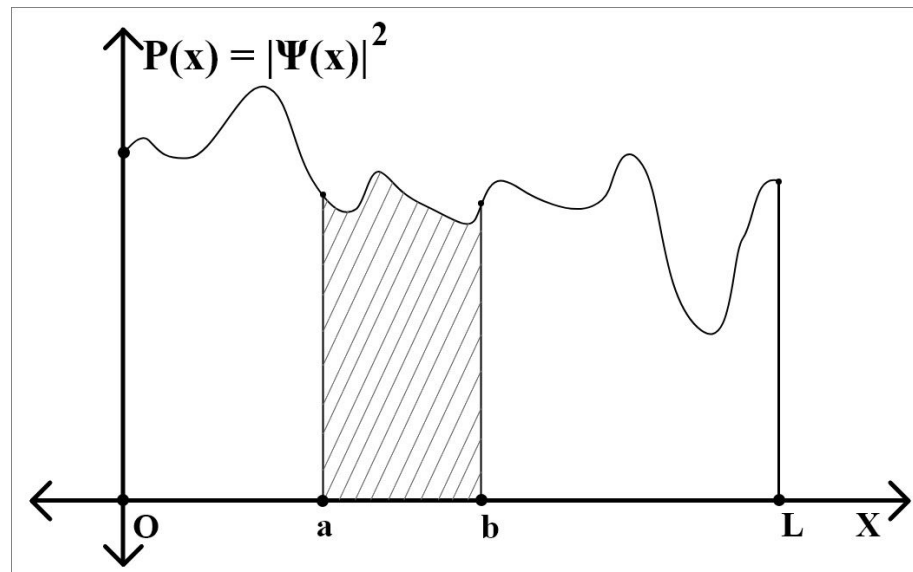


Fig. 3.3.5 Probability of having subatomic particle between a to b.

Wavefunction is not as important as its squared magnitude is. As we have seen in earlier sections that square magnitude gives us the probability density function. In figure 3.3.6 shows wave

functions and corresponding probability density functions for different values of n . Probability density function shows how electrons can be found at some places with high probability and at some places its probability is zero. This is a phenomenon we can not be explained using classical physics and that's why we need quantum physics to understand such behaviour.

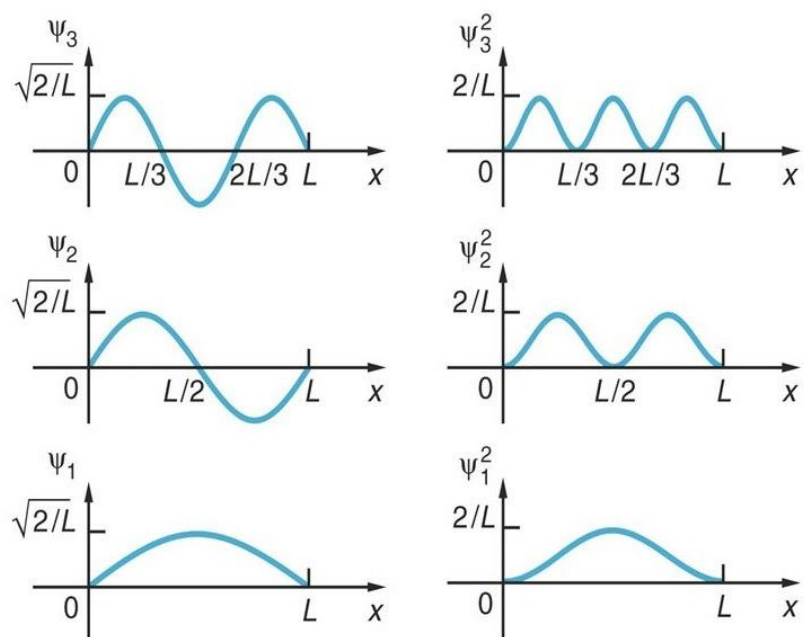


Fig. 3.3.6 Wavefunctions and PDFs for various n values [10].

VIII. Application of Schrodinger Equation in Atomic structure :

In the previous section, we have seen the solution and interpretation of wave function. Solution of schrodinger equation gives us set of wave functions and energy levels for those wave functions. This quantized energy concept leads us to study of the structure of the atom. Possible values of quantized energy is what we called “Orbits” of an atom. Electron in any atom can only stay in specific orbits only. These orbits also contains “Orbitals”. Orbital is description of spatial density of electron within an orbit. These Orbitals are described by a set of quantum numbers. This quantum number shows the position and state of electrons within an atom. It is analogous to cartesian coordinate system of mathematics. Probability of having electrons in orbitals is very high compared to forbidden spaces within atom. Various types of quantum numbers are used in order to characterize the position and state of an electron. Now we will see the significance of each quantum number and how it characterises an electron.

Orbitals in an atom are represented by numerals and letters. The main quantum number which is depiction of possible quantized energy levels is called “Principal quantum number” [9]. It is shown

by symbol 'n'. This is depiction of energy levels on which orbitals can reside. Second quantum number is called "Azimuth quantum number". It is description of angular momentum of an electron. Symbolic representation of it is 'l'. For particular value of n, possible values of l are 1 to n-1. l=0 is for s orbital, l=1 is for p orbital, l=2 is for d orbital and l=3 is for f orbital. These various values of l gives orbitals with various shapes. These shapes are shapes of probability density function. Third quantum number is known as "Magnetic quantum number" [9]. It gives the orientation of orbitals with respect to the magnetic field. This orientation is 3 dimensional orientation of orbitals. Notation of magnetic quantum number is m_l . Possible values of m_l are integer values from -l to +l where l is angular momentum quantum number. Fourth quantum is known as "Spin quantum number". Two electrons live in same orbit has not same energy because they do not have the same spin. This quantum number describes the magnetic field of an electron which affects its energy. Spin quantum number can have only two possible values , $\frac{1}{2}$ or $-\frac{1}{2}$ [9]. These quantum numbers are briefly explained in table 3.3.1.

Name	Symbol	Values	Property
Principal	n	Positive integers(1,2,3,..., n)	Energy levels
Angular Momentum	l	Positive integers (1,2,..., n-1)	Orbital shape (Probability distribution)
magnetic	m_l	Integers from -l to +l	Orbital orientation
spin	m_s	$+\frac{1}{2}$ or $-\frac{1}{2}$	Direction of electron spin

Table 3.3.1

Structure of atom is useful to understand the chemical bonding between atoms. As we have seen that quantized energy is inversely proportional to the square of distance from the nucleus. So electrons which are far from the nucleus are less attracted and electrons which are near to the nucleus is strongly attracted. So electrons in outermost orbit are mainly responsible for the chemical bonding. By electron sharing or pairing, atoms make bonds between them. Depending upon the exchange of electrons, it results in nature of bond.

Now we will understand this using structure of hydrogen atom. Hydrogen is the simplest atom. Hydrogen atom has one proton and one electron. Proton is placed at the nucleus and electrons rotate around the nucleus. Coulomb attractive force between them is given by equation (29). To understand the structure of a hydrogen atom we will solve the schrodinger equation for hydrogen atom.

$$V(r) = \frac{1}{4\pi\epsilon} \frac{e^2}{r} \dots\dots\dots(29)$$

Here, r is the distance between the proton and electron. If we consider cartesian coordinate system to solve the schrodinger equation, then it will be very difficult. So we will use spherical coordinate system to solve the schrodinger equation. Here we will not focus on mathematical solution

of schrodinger equation for hydrogen atom. We will only look into the interpretation and understanding of structure by the solution. Values of r , θ and Φ will be map to quantum numbers for hydrogen atoms. Value of r is depiction of quantum number n , value of θ is depiction of azimuthal quantum number and Φ is depiction of magnetic quantum number. Hydrogen atom has only one electron which will stay in orbit with $n=1$. So energy of that electron will -13.6eV from the quantized energy formula. Here eV stands for unit of energy which is equal to 1.602×10^{-19} joule. If this electron gats energy more than 13.6 eV then it will leave the hydrogen atom. This is also called binding energy for that electron. Values of azimuthal quantum number $l=0$ shows spherical shapes orbital or s-orbital. Value of magnetic quantum number will also be 0 since $l=0$. This magnetic quantum number is projection of azimuthal quantum number on z axis.

In this chapter we have seen the formulation of Schrodinger equation, concept of potential well, solution of Schrodinger's equation, characteristic of wave function, interpretation and significance of wave function and application of Schrodinger's equation in structure of an atom.

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