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**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF PHYSICS**

## **UNIT – I – Introduction to Quantum Mechanics – SPH1314**

## I. Introduction

Quantum mechanics is the branch of physics that deals with extremely small particles and other objects on similar scales such as atoms. The term “quantum” comes from “quantus,” which means “how great,” but in context, it refers to the fact that energy and other quantities like angular momentum take on discrete, quantized values at the scales of quantum mechanics

### Postulates of Quantum Mechanics

Postulate 1. The state of a quantum mechanical system is completely specified by a

function  $\Psi(\mathbf{r}, t)$  that depends on the coordinates of the particle(s) and on time. This function, called the wave function or state function, has the important property

that  $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau$  is the probability that the particle lies in the volume element  $d\tau$  located at  $\mathbf{r}$  at time  $t$ .

The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the probability of finding it *somewhere* is 1, so that we have the normalization condition

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau = 1$$

It is customary to also normalize many-particle wavefunctions to 1. The wavefunction must also be single-valued, continuous, and finite.

Postulate 2. To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

If we require that the expectation value of an operator  $\hat{A}$  is real, then  $\hat{A}$  must be a Hermitian operator. Some common operators occurring in quantum mechanics are collected in Table 1.

Table 1: Physical observables and their corresponding quantum operators (single particle)

Observable	Observable	Operator	Operator
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Name	Symbol	Symbol	Operation
Position	$\underline{\mathbf{r}}$	$\hat{\mathbf{r}}$	Multiply by $\underline{\mathbf{r}}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar \left( \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right)$
Kinetic energy	$T$	$\hat{T}$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	$E$	$\hat{H}$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r})$
Angular momentum	$l_x$	$\hat{l}_x$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$l_y$	$\hat{l}_y$	$-i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$l_z$	$\hat{l}_z$	$-i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

Postulate 3. In any measurement of the observable associated with operator  $\hat{A}$ , the only values that will ever be observed are the eigenvalues  $\underline{a}$ , which satisfy the eigenvalue equation

$$\hat{A}\Psi = a\Psi$$

This postulate captures the central point of quantum mechanics--the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states). If the system is in an eigenstate of  $\hat{A}$  with eigenvalue  $a$ , then any measurement of the quantity  $A$  will yield  $a$ .

Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of  $\hat{A}$  *initially*. An arbitrary state can be expanded in the complete set of eigenvectors

of  $\hat{A}$  ( $\hat{A}\Psi_i = a_i\Psi_i$ ) as

$$\Psi = \sum_i^n c_i \Psi_i$$

where  $n$  may go to infinity. In this case we only know that the measurement of  $A$  will

yield *one* of the values  $a_i$ , but we don't know which one. However, we do know

the *probability* that eigenvalue  $a_i$  will occur--it is the absolute value squared of the

coefficient,  $|c_i|^2$ , leading to the fourth postulate below.

An important second half of the third postulate is that, after measurement of  $\Psi$  yields some

eigenvalue  $a_i$ , the wavefunction immediately "collapses" into the corresponding

eigenstate  $\Psi_i$  (in the case that  $a_i$  is degenerate, then  $\Psi$  becomes the projection of  $\Psi$  onto the degenerate subspace). Thus, measurement affects the state of the system. This fact is used in many elaborate experimental tests of quantum mechanics.

Postulate 4. If a system is in a state described by a normalized wave function  $\Psi$ , then the average value of the observable corresponding to  $\hat{A}$  is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau$$

Postulate 5. The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}$$

Postulate 6. The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates.

The Pauli exclusion principle is a direct result of this *antisymmetry principle*. We will later see that Slater determinants provide a convenient means of enforcing this property on electronic wavefunctions.

## The Wave Function

Wave-particle duality is one of the key concepts in quantum physics, and that's why each particle is represented by a wave function. This is usually given the Greek letter  $\Psi$  (psi) and is a function of position (x) and time (t), and it contains all of the information that can be known about the particle.

Think about that point again – despite the probabilistic nature of matter at the quantum scale, the wave function allows for a complete description of the particle, or at least as complete a description as is possible. The output may be a probability distribution, but it still manages to be complete in its description.

The modulus (i.e. absolute value) of this function squared tells you the probability you'll find the particle being described at position  $x$  (or within a small range  $dx$ , to be precise) at time  $t$ . Wave functions have to be normalized (set so that the probability is 1 that it will be found somewhere) for this to be the case, but this is almost always done, and if it isn't, you can normalize the wave function yourself by summing the modulus squared over all values of  $x$ , setting it to equal 1 and defining a normalization constant accordingly.

You can use the wave function to calculate the expectation value for the position of a particle at time  $t$ , which is essentially the average value you would obtain for the position over many measurements.

You calculate the expectation value by surrounding the “operator” for the observable (e.g. for position, this is just  $x$ ) with the wave function and its complex conjugate (like a sandwich) and then integrating over all of space. You can use this same approach with different operators to calculate expectation values for energy, momentum and other observables.

## The Schrodinger Equation

The Schrodinger equation is the most important equation in quantum mechanics, and it describes the evolution of wave function with time, and allows you to determine the value of it. It's closely related to the conservation of energy and is ultimately derived from it, but it plays a role similar to that played by Newton's laws in classical mechanics. The simplest way to write the equation is:

This acts on the wave function to describe its evolution in space and time, and in the time-independent version of the Schrodinger equation, it can be considered the energy operator for the quantum system. Quantum mechanical wave functions are solutions to the Schrodinger equation.

### Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle is one of the most famous principles of quantum mechanics, and states that the position  $x$  and momentum  $p$  of a particle cannot both be known with certainty, or more specifically, to an arbitrary degree of precision.

There is a fundamental limit to the level of accuracy with which you can measure both of these quantities simultaneously. The result comes from the particle wave duality of quantum mechanical objects, and specifically the way they are described as a wave packet of multiple component waves.

While the position and momentum uncertainty principle is the most well-known, there is also the energy-time uncertainty principle (which says the same thing about energy and time) but also the generalized uncertainty principle.

In short, this states that two quantities which do not “commute” with each other (where  $AB - BA \neq 0$ ) can’t be known simultaneously to arbitrary precision. There are many other quantities which do not commute with each other, and so many pairs of observables that can’t be precisely determined at the same time – precision in one measurement means a huge amount of uncertainty in the other.

This is one of the main things about quantum mechanics that’s hard to understand from our macroscopic perspective. Objects you encounter on a day-to-day basis all have clearly defined values for things like their position and their momentum at all times, and measuring the corresponding values in classical physics is only limited by the precision of your measuring equipment.

In quantum mechanics, though, nature itself sets a limit to the precision you can measure two non-commuting observables to. It's tempting to think this is simply a practical problem and you'll be able to achieve it one day, but that simply isn't the case: It's impossible.

## Interpretations of Quantum Mechanics

The weirdness implied by the mathematical formalism of quantum mechanics gave physicists a lot to think about: What was the physical interpretation of the wave function, for example? Was an electron really a particle or a wave, or could it really be both? The Copenhagen interpretation is the most well-known attempt to answer questions like this and still the most widely-accepted one.

The interpretation essentially says that the wave function and the Schrodinger equation are a complete description of the wave or particle, and any information that cannot be derived from them simply doesn't exist.

For example, the wave function spreads across space, and this means that the particle itself doesn't have a fixed location until you measure it, at which point the wave function "collapses," and you obtain a definite value. In this view, the wave-particle duality of quantum mechanics doesn't mean that a particle is both a wave and a particle; it simply means that a particle like an electron will behave as a wave in some circumstances and as a particle in others.

Niels Bohr, the biggest proponent of the Copenhagen interpretation, would reportedly criticize questions like, "Is the electron actually a particle, or is it a wave?"

He said they were meaningless, because in order to find out you have to conduct a measurement, and the form of the measurement (i.e. what they were designed to detect) would determine the result you obtained. In addition, all measurements are fundamentally probabilistic, and this probability is built into nature rather than being due to a lack of knowledge or precision on the part of the scientists.



## Other Interpretations of Quantum Mechanics

There is still a lot of disagreement about the interpretation of quantum mechanics, though, and there are alternative interpretations that are worth learning about too, in particular the many worlds interpretation and the de Broglie-Bohm interpretation.

The many worlds interpretation was proposed by Hugh Everett III, and essentially removes the need for the collapse of the wave function entirely, but in doing so proposes multiple parallel “worlds” (which has a slippery definition in the theory) coexisting with your own.

In essence, it says that when you make a measurement of a quantum system, the result you obtain doesn’t involve the wave function collapsing onto one particular value for the observable, but multiple worlds untangling and you finding yourself in one and not the others. In your world, for example, the particle is at position A rather than B or C, but in another world it will be at B, and in yet another it will be at C.

This is in essence a deterministic (rather than a probabilistic theory), but it’s your uncertainty about which world you inhabit that creates the apparently probabilistic nature of quantum mechanics. The probability really relates to whether you’re in world A, B or C, not where the particle is within your world. However, the “splitting” of worlds arguably raises as many questions as it answers, and so the idea is still quite a controversial one.

The de Broglie-Bohm interpretation is sometimes called pilot wave mechanics, and it follows from the Copenhagen interpretation in that particles are described by wave functions and the Schrodinger equation.

However, it states that every particle has a definite position even when it isn’t being observed, but it is guided by a “pilot wave,” for which there is another equation you use to calculate the evolution of the system. This describes the wave-particle duality by essentially saying that a particle “surfs” at a definite position on a wave, with the wave guiding it’s motion, but it still exists even when not observed.

Compton's formula established that an electromagnetic wave can behave like a particle of light when interacting with matter. In 1924, Louis de Broglie proposed a new speculative hypothesis that electrons and other particles of matter can behave like waves. Today, this idea is known as de Broglie's hypothesis of matter waves. In 1926, De Broglie's hypothesis, together with Bohr's early quantum theory, led to the development of a new theory of wave quantum mechanics to describe the physics of atoms and subatomic particles. Quantum mechanics has paved the way for new engineering inventions and technologies, such as the laser and magnetic resonance imaging (MRI). These new technologies drive discoveries in other sciences such as biology and chemistry.

According to de Broglie's hypothesis, massless photons as well as massive particles must satisfy one common set of relations that connect the energy  $E$  with the frequency  $f$ , and the linear momentum  $p$  with the wavelength

$$E = hf$$

$$\lambda = \frac{h}{p}.$$

Here,  $E$  and  $p$  are, respectively, the relativistic energy and the momentum of a particle. De Broglie's relations are usually expressed in terms of the wave vector  $\vec{k}$ ,  $k = 2\pi / \lambda$ , and the wave frequency  $\omega = 2\pi f$ , as we usually do for waves:

$$E = \hbar\omega$$

$$\vec{p} = \hbar \vec{k}.$$

Wave theory tells us that a wave carries its energy with the group velocity. For matter waves, this group velocity is the velocity  $u$  of the particle. Identifying the energy  $E$  and momentum  $p$  of a particle with its relativistic energy  $mc^2$  and its relativistic momentum  $mu$ , respectively, it follows from de Broglie relations that matter waves satisfy the following relation:

$$\lambda f = \frac{\omega}{k} = \frac{E/\hbar}{p/\hbar} = \frac{E}{p} = \frac{mc^2}{mu} = \frac{c^2}{u} = \frac{c}{\beta}$$

Using the concept of the electron matter wave, de Broglie provided a rationale for the quantization of the electron's angular momentum in the hydrogen atom, which was postulated in Bohr's quantum theory. The physical explanation for the first Bohr quantization condition comes naturally when we assume that an electron in a hydrogen atom behaves not like a particle but like a wave. To see it clearly, imagine a stretched guitar string that is clamped at both ends and vibrates in one of its normal modes. If the length of the string is  $l$  ((Figure)), the wavelengths of these vibrations cannot be arbitrary but must be such that an integer  $k$  number of half-wavelengths  $\lambda/2$  fit exactly on the distance  $l$  between the ends. This is the condition  $l = k\lambda/2$  for a standing wave on a string. Now suppose that instead of having the string clamped at the walls, we bend its length into a circle and fasten its ends to each other. This produces a circular string that vibrates in normal modes, satisfying the same standing-wave condition, but the number of half-wavelengths must now be an even number  $k$ ,  $k = 2n$ , and the length  $l$  is now connected to the radius  $r_n$  of the circle. This means that the radii are not arbitrary but must satisfy the following standing-wave condition:

$$2\pi r_n = 2n\frac{\lambda}{2}.$$

Phase velocity

The **phase velocity** of a wave is the rate at which the phase of the wave propagates in space. This is the velocity at which the phase of any one frequency component of the wave travels. For such a component, any given phase of the wave (for example, the crest) will appear to travel at the phase velocity. The phase velocity is given in terms of the wavelength  $\lambda$  (lambda) and time period  $T$ .

Group velocity

The **group velocity** of a wave is the velocity with which the overall envelope shape of the wave's amplitudes.

The **phase velocity** is the ratio of the angular frequency to the wave number. The **group velocity** is the derivative of the angular frequency with respect to the wave number.

### **Davisson and Germer Experiment**

The experimental setup for the Davisson and Germer experiment is enclosed within a vacuum chamber. Thus the deflection and scattering of electrons by the medium are prevented. The main parts of the experimental setup are as follows:

- Electron gun: An electron gun is a Tungsten filament that emits electrons via thermionic emission i.e. it emits electrons when heated to a particular temperature.
- Electrostatic particle accelerator: Two opposite charged plates (positive and negative plate) are used to accelerate the electrons at a known potential.
- Collimator: The accelerator is enclosed within a cylinder that has a narrow passage for the electrons along its axis. Its function is to render a narrow and straight (collimated) beam of electrons ready for acceleration.
- Target: The target is a Nickel crystal. The electron beam is fired normally on the Nickel crystal. The crystal is placed such that it can be rotated about a fixed axis.
- Detector: A detector is used to capture the scattered electrons from the Ni crystal. The detector can be moved in a semicircular arc as shown in the diagram above.

### **Browse more Topics under Dual Nature of Radiation and Matter**

- Electron Emission
- Experimental Study of Photoelectric Effect
- Wave Nature of Matter
- Einstein's Photoelectric Equation: Energy Quantum of

### **Radiation The Thought Behind the Experimental Setup**

The basic thought behind the Davisson and Germer experiment was that the waves reflected from two different atomic layers of a Ni crystal will have a fixed phase difference. After reflection, these waves will interfere either constructively or destructively. Hence producing a diffraction pattern. In the Davisson and Germer experiment waves were used in place of electrons. These electrons formed a diffraction pattern. The dual nature of matter was thus verified. We can relate the de Broglie equation and the Bragg's law as shown below:

From the de Broglie equation, we have:

$$\begin{aligned}
 \lambda &= h/p \\
 &= h/\sqrt{2mE} \\
 &= h/\sqrt{2meV} \quad \dots (1)
 \end{aligned}$$

where,  $m$  is the mass of an electron,  $e$  is the charge on an electron and  $h$  is the Plank's constant.

Therefore for a given  $V$ , an electron will have a wavelength given by equation (1).

The following equation gives Bragg's Law:

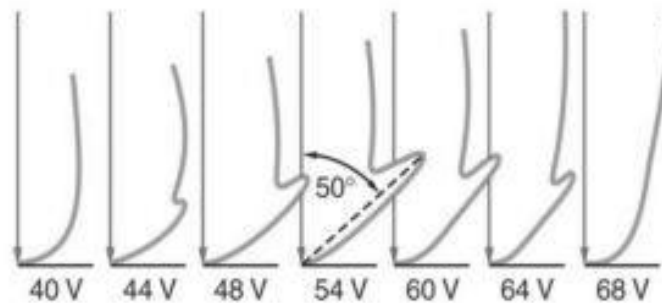
$$n\lambda = 2d \sin(\theta) \quad \dots(2)$$

Since the value of  $d$  was already known from the X-ray diffraction experiments. Hence for various values of  $\theta$ , we can find the wavelength of the waves producing a diffraction pattern from equation (2).

### Observations of the Davisson and Germer Experiment

The detector used here can only detect the presence of an electron in the form of a particle. As a result, the detector receives the electrons in the form of an electronic current. The intensity (strength) of this electronic current received by the detector and the scattering angle is studied. We call this current as the electron intensity.

The intensity of the scattered electrons is not continuous. It shows a maximum and a minimum value corresponding to the maxima and the minima of a diffraction pattern produced by X-rays. It is studied from various angles of scattering and potential difference. For a particular voltage (54V, say) the maximum scattering happens at a fixed angle only as shown below:



*Plots between  $I$  – the intensity of scattering (X-axis) and the angle of scattering  $\theta$  for given values of Potential difference.*

### Results of the Davisson and Germer Experiment

From the Davisson and Germer experiment, we get a value for the scattering angle  $\theta$  and a corresponding value of the potential difference  $V$  at which the scattering of electrons is

maximum. Thus these two values from the data collected by Davisson and Germer, when used in equation (1) and (2) give the same values for  $\lambda$ . Therefore, this establishes the de Broglie's wave-particle duality and verifies his equation as shown below:

From (1), we have:

$$\lambda = h / \sqrt{2meV}$$

For  $V = 54 \text{ V}$ , we have

$$\lambda = 12.27 / \sqrt{54} = 0.167 \text{ nm} \dots (3)$$

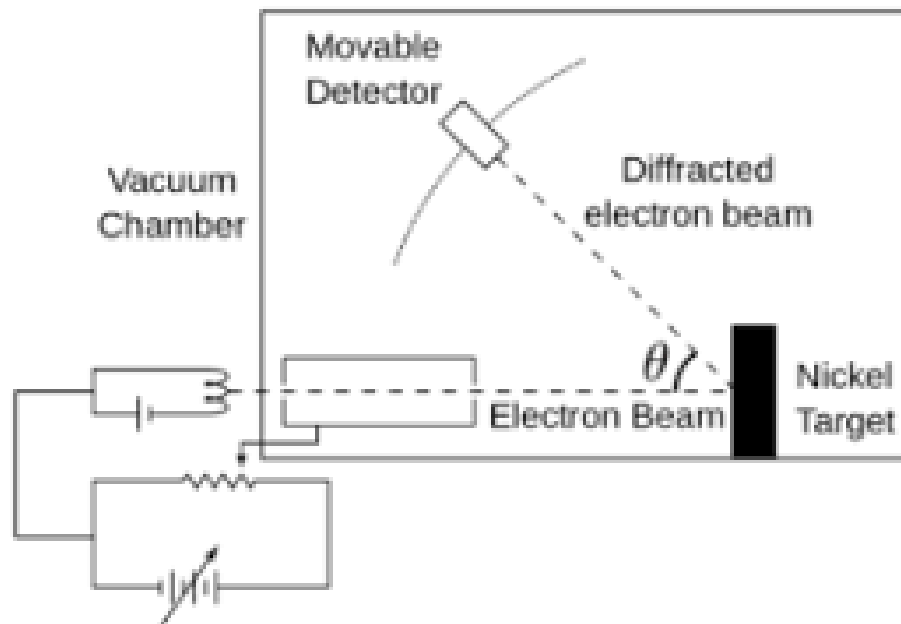
Now the value of 'd' from X-ray scattering is  $0.092 \text{ nm}$ . Therefore for  $V = 54 \text{ V}$ , the angle of scattering is  $(50^\circ)$ , using this in equation (2), we have:

$$n\lambda = 2 (0.092 \text{ nm}) \sin((90^\circ - 50^\circ)/2)$$

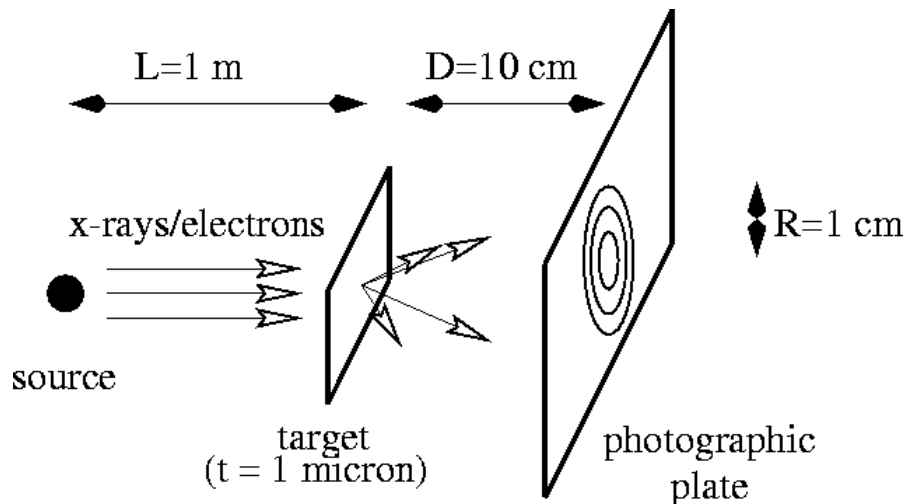
For  $n = 1$ , we have:

$$\lambda = 0.165 \text{ nm} \dots (4)$$

Therefore the experimental results are in a close agreement with the theoretical values got from the de Broglie equation. The equations (3) and (4) verify the de Broglie equation.



## **G P Thomson Experiment**



Electrons from an electron source were accelerated towards a positive electrode into which a small hole was drilled. The resulting narrow beam of electrons was directed towards a thin, rolled foil of gold. After passing through the hole in the gold foil, the electron beam was received on a photographic plate placed perpendicular to the direction of the beam. The diffraction pattern was in the form of continuous, alternate black and white rings as diffraction was due to the crystalline grains which were randomly oriented at all possible angles in the gold foil.

Electrons were scattered at different angles from the atoms of crystallites and produced interference pattern with maxima corresponding to those angles satisfying the Bragg condition. In terms of the probabilistic interpretation of matter waves, the probability of finding an electron scattered at an angle is exactly equal to computed intensity pattern of interfering waves associated with electron beam.

The diffraction pattern due to poly crystalline material was similar to the powder diffraction pattern of X-rays having wavelength equal to the de Broglie wavelength of electrons. The wavelength of electrons was varied by changing the incident energy of the electrons, then diameters of the diffraction rings changed proportionately according to the Bragg's equation.

**Uncertainty principle**, also called **Heisenberg uncertainty principle** or **indeterminacy principle**, statement, articulated (1927) by the German physicist Werner Heisenberg, that the position and the velocity of an object cannot both be measured exactly, at the same time, even in theory.

The uncertainty principle is alternatively expressed in terms of a particle's momentum and position. The momentum of a particle is equal to the product of its mass times its velocity. Thus, the product of the uncertainties in the momentum and the position of a particle equals  $h/(4\pi)$  or more. The principle applies to other related (conjugate) pairs of observables, such as energy and time: the product of the uncertainty in an energy measurement and the uncertainty in the time interval during which the measurement is made also equals  $h/(4\pi)$  or more. The same relation holds, for an unstable atom or nucleus, between the uncertainty in the quantity of energy radiated and the uncertainty in the lifetime of the unstable system as it makes a transition to a more stable state.



## Normalization of $\psi(x,t)$ :

$|\Psi(x, t)|^2$ : is the probability density for finding the particle at point  $x$ , at time  $t$ .

Because the particle must be found somewhere between  $x=-\infty$  and  $x=+\infty$  the wave function must obey the normalization condition

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

Without this, the statistical interpretation would be meaningless. Thus, there is a multiplication factor. However, the wave function is a solution of the Schrodinger eq:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi.$$

Therefore, one can't impose an arbitrary condition on  $\psi$  without checking that the two are consistent.

Interestingly, if  $\psi(x, t)$  is a solution,  $A\psi(x, t)$  is also a solution where  $A$  is any (complex) constant.

Therefore, one must pick a undetermined multiplicative factor in such a way that the Schrodinger Equation is satisfied. This process is called **normalizing** the wave function.

If  $P_{ab}(t)$  be the probability of finding the particle in the range  $(a < x < b)$ , at time  $t$ , then

$$\frac{dP_{ab}}{dt} = J(a, t) - J(b, t) \quad \text{where} \quad J(x, t) \equiv \frac{i\hbar}{2m} \left( \Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right).$$

$$P_{ab}(t) = \int_a^b |\Psi(x, t)|^2 dx, \quad \text{so} \quad \frac{dP_{ab}}{dt} = \int_a^b \frac{\partial}{\partial t} |\Psi|^2 dx.$$

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[ \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]$$

$$\therefore \frac{dP_{ab}}{dt} = - \int_a^b \frac{\partial}{\partial x} J(x, t) dx = - [J(x, t)]_a^b = J(a, t) - J(b, t).$$

Probability is dimensionless, so  $J$  has the dimensions 1/time, and units  $\text{second}^{-1}$

For some solutions to the Schrodinger equation, the integral is infinite; in that case no multiplicative factor is going to make it 1. The same goes for the trivial solution  $\psi = 0$ . Such non-normalizable solutions cannot represent particles, and must be rejected.

Physically realizable states correspond to the "square-integrable" solutions to Schrodinger's equation.

What all you need is that 
$$\int_{-\infty}^{\infty} dx |\psi(x, 0)|^2 < \infty$$

that is, the initial state wave functions must be square integrable.

Since we may need to deal with integrals of the type

$$\int_{-\infty}^{\infty} dx \psi^*(x, t) x^n \psi(x, t)$$

you will require that the wave functions  $\psi(x, 0)$  go to zero rapidly as  $x \rightarrow \pm\infty$  often faster than any power of  $x$ .

We shall also require that the wave functions  $\psi(x, t)$  be continuous in  $x$ .

The emphasis on  $|\psi(x, t)|^2$  as the physically relevant quantity might lead to the impression that the *phase* of the wave function is of no importance. If we write  $\psi = R e^{i\theta}$ , then indeed  $|\psi|^2 = R^2$  independent of  $\theta$ . However, the linearity of the equation allows us to add solutions, as in our discussion of the electron interference pattern with two slits. We see that

$$|R_1 e^{i\theta_1} + R_2 e^{i\theta_2}|^2 = R_1^2 + R_2^2 + 2R_1 R_2 \cos(\theta_1 - \theta_2)$$

depends on the relative phase. An overall phase in the total wave function can be ignored, or chosen arbitrarily for convenience.

Suppose we have normalized the wave function at time  $t = 0$ . How do we know that it will *stay* normalized, as time goes on and  $\Psi(x, t)$  evolves?

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx. \quad \text{[Note that the integral is a function only of } t, \text{ but the integrand is a function of } x \text{ as well as } t.]$$

By the product rule,  $\frac{\partial}{\partial t} |\Psi|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi$

The Schrodinger equation and its complex conjugate are

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi, \quad \text{and} \quad \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*$$

$$\text{So,} \quad \frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[ \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]$$

$$\text{Then,} \quad \frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \frac{i\hbar}{2m} \left( \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{+\infty} = 0$$

$$J(x, t) \equiv \frac{i\hbar}{2m} \left( \Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right)$$

Is the probability current.

Since  $\Psi(x, t)$  must go to zero as  $x$  goes to  $(\pm)$  infinity—otherwise the wave function would not be normalizable. Thus, if the wave function is normalized at  $t = 0$ , it stays normalized for all future time.

The Schrodinger equation has the property that it automatically preserves the normalization of the wave function—without this crucial feature the Schrodinger equation would be incompatible with the statistical interpretation.

## Review Questions

### Part A

1. Physically interpreting a wave function, Analyse.
2. Summarise the commutators of quantum mechanics.
3. Analyse the condition for normalisation.
4. State any two postulates of quantum mechanics.
5. Illustrate the uncertainty principle.
6. Discuss properties of wave function
7. Point the physical significance of wave function
8. Analyse the condition for orthogonality
9. Discuss the linearity principle
10. Discuss the superposition principle
11. Derive the operators for kinetic energy and potential energy.
12. Compose the most important limitations on the wave function.
13. Differentiate group velocity and phase velocity
14. Calculate the de Broglie wavelength of an electron which has kinetic energy equal to 15 eV.
15. An electron has a speed of  $1.05 \times 10^4$  m/s within the accuracy of 0.01%. Calculate the uncertainty in the position of electron.

### Part B

1. Deduce the radius of the Bohrs first orbit using uncertainty principle.
2. Report all the postulates of Quantum mechanics
3. Explain uncertainty principle with any one example
4. Evaluate the commutation relation between momentum and Hamiltonian
5. Assess the condition for physical significance and physical interpretation of wave function.

## **UNIT – II- Schrodinger Wave Equation – SPH1314**

## Derivation of the Schrödinger Wave Equation

The Schrödinger equation has two ‘forms’, one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is often referred to as the time dependent Schrödinger wave equation. The other is the equation in which the time dependence has been ‘removed’ and hence is known as the time independent Schrödinger equation and is found to describe, amongst other things, what the allowed energies are of the particle. These are not two separate, independent equations – the time independent equation can be derived readily from the time dependent equation (except if the potential is time dependent, a development we will not be discussing here). In the following we will describe how the first, time dependent equation can be ‘derived’, and in then how the second follows from the first.

In the discussion of the particle in an infinite potential well, it was observed that the wave function of a particle of fixed energy  $E$  could most naturally be written as a linear combination of wave functions of the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

representing a wave travelling in the positive  $x$  direction, and a corresponding wave travelling in the opposite direction, so giving rise to a standing wave, this being necessary in order to satisfy the boundary conditions. This corresponds intuitively to our classical notion of a particle bouncing back and forth between the walls of the potential well, which suggests that we adopt the wave function above as being the appropriate wave function

for a *free* particle of momentum  $p = \hbar k$  and energy  $E = \hbar\omega$ . With this in mind, then note that

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi$$

which can be written, using  $E = p^2/2m = \hbar^2 k^2/2m$ :

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi.$$

Similarly

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi$$

which can be written, using  $E = \hbar\omega$ :

$$i\hbar \frac{\partial \Psi}{\partial t} = \hbar\omega \Psi = E\Psi.$$

We now generalize this to the situation in which there is both a kinetic energy potential energy present, then  $E = p^2/2m + V(x)$  so that

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

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

which is the famous time dependent Schrödinger wave equation. It is setting up and solving this equation, then analyzing the physical contents of its solutions that form the basis of that branch of quantum mechanics known as wave mechanics.

Even though this equation does not look like the familiar wave equation that describes, for instance, waves on a stretched string, it is nevertheless referred to as a ‘wave equation’ as it can have solutions that represent waves propagating through space. We have seen an example of this: the harmonic wave function for a free particle of energy  $E$  and momentum  $p$  is

$$\Psi(x, t) = Ae^{-i(px-Et)/\hbar}$$



is a solution of this equation with, as appropriate for a free particle,  $V(x) = 0$ . But this equation can have distinctly non-wave like solutions whose form depends, amongst other things, on the nature of the potential  $V(x)$  experienced by the particle.

In general, the solutions to the time dependent Schrödinger equation will describe the *dynamical* behaviour of the particle, in some sense similar to the way that Newton's equation  $F = ma$  describes the dynamics of a particle in classical physics. However, there is an important difference. By solving Newton's equation we can determine the position of a particle as a function of time, whereas by solving Schrödinger's equation, what we get is a wave function  $\Psi(x, t)$  which tells us (after we square the wave function) how the *probability* of finding the particle in some region in space varies as a function of time.

It is possible to proceed from here look at ways and means of solving the full, time dependent Schrödinger equation in all its glory, and look for the physical meaning of the solutions that are found. However this route, in a sense, bypasses much important physics contained in the Schrödinger equation which we can get at by asking much simpler questions. Perhaps the most important 'simpler question' to ask is this: what is the wave

function for a particle of a given energy  $E$ ? Curiously enough, to answer this question requires 'extracting' the time dependence from the time dependent Schrödinger equation. To see how this is done, and its consequences, we will turn our attention to the closely related time independent version of this equation.

## The Time Independent Schrödinger Equation

We have seen what the wave function looks like for a free particle of energy  $E$  – one or the other of the harmonic wave functions – and we have seen what it looks like for the particle in an infinitely deep potential well – see Section 5.3 – though we did not obtain that result by solving the Schrödinger equation. But in both cases, the time dependence entered into the wave function via a complex exponential factor  $\exp[-iEt/\hbar]$ . This suggests that to 'extract' this time dependence we guess a solution to the Schrödinger wave equation of the form

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

i.e. where the space and the time dependence of the complete wave function are contained in separate factors<sup>1</sup>. The idea now is to see if this guess enables us to derive an equation for  $\psi(x)$ , the spatial part of the wave function.

If we substitute this trial solution into the Schrödinger wave equation, and make use of the meaning of partial derivatives, we get:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} e^{-iEt/\hbar} + V(x)\psi(x)e^{-iEt/\hbar} = i\hbar \frac{\partial}{\partial t} \psi(x)e^{-iEt/\hbar} = E\psi(x)e^{-iEt/\hbar}. \quad (6.10)$$

We now see that the factor  $\exp[-iEt/\hbar]$  cancels from both sides of the equation, giving

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

If we rearrange the terms, we end up with

$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + (E - V(x))\psi(x) = 0$$

which is the time independent Schrödinger equation. We note here that the quantity  $E$ , which we have identified as the energy of the particle, is a free parameter in this equation. In other words, at no stage has any restriction been placed on the possible values for  $E$ . Thus, if we want to determine the wave function for a particle with some specific value of  $E$  that is moving in the presence of a potential  $V(x)$ , all we have to do is to insert this value of  $E$  into the equation with the appropriate  $V(x)$ , and solve for the corresponding wave function. In doing so, we find, perhaps not surprisingly, that for different choices of  $E$  we get different solutions for  $\psi(x)$ . We can emphasize this fact by writing  $\psi_E(x)$  as the solution associated with a particular value of  $E$ . But it turns out that it is not all quite as simple as this. To be physically acceptable, the wave function  $\psi_E(x)$  must satisfy two conditions, one of which we have seen before namely that the wave function must be normalizable (see Eq. (5.3)), and a second, that the wave function and its derivative must be continuous. Together, these two requirements, the first founded in the probability interpretation of the wave function, the second in more esoteric mathematical necessities which we will not go into here and usually only encountered in somewhat artificial problems, lead to a rather remarkable property of physical systems described by this equation that has enormous physical significance: the quantization of energy.

### The Quantization of Energy

At first thought it might seem to be perfectly acceptable to insert any value of  $E$  into the time independent Schrödinger equation and solve it for  $\psi_E(x)$ . But in doing so we must remain aware of one further requirement of a wave function which comes from its probability interpretation: to be physically acceptable a wave function must satisfy the normalization condition, Eq. (5.3)

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

for all time  $t$ . For the particular trial solution introduced above,

$$\Psi(x, t) = \psi_E(x)e^{-iEt/\hbar}$$

the requirement that the normalization condition must hold gives, on substituting  $\Psi(x, t)$ , the result<sup>2</sup>

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

Since this integral must be finite, (unity in fact), we *must* have  $\psi_E(x) \rightarrow 0$  as  $x \rightarrow \pm\infty$  in order for the integral to have any hope of converging to a finite value. The importance of this with regard to solving the time dependent Schrödinger equation is that we must check whether or not a solution  $\psi_E(x)$  obtained for some chosen value of  $E$  satisfies the normalization condition. If it does, then this is a physically acceptable solution, if it does not, then that solution *and the corresponding value of the energy* are not physically acceptable. The particular case of considerable physical significance is if the potential  $V(x)$  is attractive, such as would be found with an electron caught by the attractive Coulomb force of an atomic nucleus, or a particle bound by a simple harmonic potential (a mass on a spring), or, as we have seen in Section 5.3, a particle trapped in an infinite potential well. In all such cases, we find that except for certain discrete values of the energy, the wave function  $\psi_E(x)$  does not vanish, or even worse, diverges, as  $x \rightarrow \pm\infty$ . In other words, it is only for these discrete values of the energy  $E$  that we get physically acceptable wave functions  $\psi_E(x)$ , or to put it more bluntly, the particle can never be observed to have any energy other than these particular values, for which reason these energies are often referred to as the ‘allowed’ energies of the particle. This pairing off of allowed energy and normalizable wave function is referred to mathematically as  $\psi_E(x)$  being an eigenfunction of the Schrödinger equation, and  $E$  the associated energy eigenvalue, a terminology that acquires more meaning when quantum mechanics is looked at from a more advanced standpoint.

So we have the amazing result that the probability interpretation of the wave function forces us to conclude that the allowed energies of a particle moving in a potential  $V(x)$  are restricted to certain discrete values, these values determined by the nature of the potential. This is the phenomenon known as the quantization of energy, a result of quantum mechanics which has enormous significance for determining the structure of atoms, or, to go even further, the properties of matter overall. We have already seen an example of this quantization of energy in our earlier discussion of a particle in an infinitely deep potential well, though we did not derive the results by solving the Schrödinger equation itself. We will consider how this is done shortly.

The requirement that  $\psi(x) \rightarrow 0$  as  $x \rightarrow \pm\infty$  is an example of a *boundary condition*. Energy quantization is, mathematically speaking, the result of a combined effort: that  $\psi(x)$  be a solution to the time independent Schrödinger equation, and that the solution satisfy these boundary conditions. But both the boundary condition and the Schrödinger equation are derived from, and hence rooted in, the nature of the physical world: we have here an example of the unexpected relevance of purely mathematical ideas in formulating a physical theory.



**Continuity Conditions** There is one additional proviso, which was already mentioned briefly above, that has to be applied in some cases. If the potential should be discontinuous in some way, e.g. becoming infinite, as we have seen in the infinite potential well example, or having a finite discontinuity as we will see later in the case of the finite potential well, it is possible for the Schrödinger equation to have solutions that themselves are discontinuous. But discontinuous potentials do not occur in nature (this would imply an infinite force), and as we know that for continuous potentials we always get continuous wave functions, we then place the extra conditions that the wave function *and* its spatial derivative also must be continuous<sup>3</sup>. We shall see how this extra condition is implemented when we look at the finite potential well later.

**Bound States and Scattering States** But what about wave functions such as the harmonic wave function  $\Psi(x, t) = A \exp[i(kx - \omega t)]$ ? These wave functions represent a particle having a definite energy  $E = \hbar\omega$  and so would seem to be legitimate and necessary wave functions within the quantum theory. But the problem here, as has been pointed out before in Chapter 5, is that  $\Psi(x, t)$  does *not* vanish as  $x \rightarrow \pm\infty$ , so the normalization condition, Eq. (6.14) cannot be satisfied. So what is going on here? The answer lies in the fact that there are two kinds of wave functions, those that apply for particles trapped by an attractive potential into what is known as a bound state, and those that apply for particles that are free to travel to infinity (and beyond), otherwise known as scattering states. A particle trapped in an infinitely deep potential well is an example of the former: the particle is confined to move within a restricted region of space. An electron trapped by the attractive potential due to a positively charged atomic nucleus is also an example – the electron rarely moves a distance more than  $\sim 10$  nm from the nucleus. A nucleon trapped within a nucleus by attractive nuclear forces is yet another. In all these cases, the probability of finding the particle at infinity is zero. In other words, the wave function for the particle satisfies the boundary condition that it vanish at infinity. So we see that it is when a particle is trapped, or confined to a limited region of space by an attractive potential  $V(x)$  (or  $V(\mathbf{r})$  in three dimensions), we obtain wave functions that satisfy the above boundary condition, and hand in hand with this, we find that their energies are quantized. But if it should be the case that the particle is free to move as far as it likes in space, in other words, if it is not bound by any attractive potential, (or even repelled by a repulsive potential) then we find that the wave function need not vanish at infinity, and nor is its energy quantized. The problem of how to reconcile this with the normalization condition, and the probability interpretation of the wave function, is a delicate mathematical issue which we cannot hope to address here, but it can be done. Suffice to say that provided the wave function does not diverge at infinity (in other words it remains finite, though not zero) we can give a physical meaning of such states as being an idealized mathematical limiting case which, while it does not satisfy the normalization condition, can still be dealt with in, provided some care is taken with the physical interpretation, in much the same way as the bound state wave functions.

In order to illustrate how the time independent Schrödinger equation can be solved in practice, and some of the characteristics of its solutions, we will here briefly reconsider the infinitely deep potential well problem, already solved by making use of general properties of the wave function, in Section 5.3. We will then move on to looking at other simple applications.

## Solving the Time Independent Schrödinger Equation

Suppose we have a single particle of mass  $m$  confined to within a region  $0 < x < L$  with potential energy  $V = 0$  bounded by infinitely high potential barriers, i.e.  $V = \infty$  for  $x < 0$  and  $x > L$ . The potential experienced by the particle is then:

$$\begin{aligned} V(x) &= 0 & 0 < x < L \\ &= \infty & x \geq L; \quad x \leq 0 \end{aligned}$$

In the regions for which the potential is infinite, the wave function will be zero, for exactly the same reasons that it was set to zero in Section 5.3, that is, there is zero probability of the particle being found in these regions. Thus, we must impose the boundary conditions

$$\psi(0) = \psi(L) = 0.$$

Meanwhile, in the region  $0 < x < L$ , the potential vanishes, Schrödinger equation becomes:

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

To solve this, we define a quantity  $k$  by

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

so that Eq. (6.18) can be written

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

whose general solution is

$$\psi(x) = A \sin(kx) + B \cos(kx).$$

$$\psi(0) = B = 0$$

so that the solution is now

$$\psi(x) = A \sin(kx).$$

Next, applying the boundary condition at  $x = L$  gives

$$\psi(L) = A \sin(kL) = 0$$

which tells us that either  $A = 0$ , in which case  $\psi(x) = 0$ , which is not a useful (it says that there is no particle in the well at all!) or else  $\sin(kL) = 0$ , which equation for  $k$ :

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

We exclude the  $n = 0$  possibility as that would give us, once again  $\psi(x) = 0$ , exclude the negative values of  $n$  as they will merely reproduce the same set of (except with opposite sign<sup>4</sup>) as the positive values. Thus we have

$$k_n = n\pi/L, \quad n = 1, 2, \dots$$

where we have introduced a subscript  $n$ . This leads to, on using Eq.

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

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

## The Finite Potential Well

The infinite potential well is a valuable model since, with the minimum amount of fuss, it shows immediately the way that energy quantization as potentials do not occur in nature. However, for electrons trapped in a block of metal, or gas molecules contained in a bottle, this model serves to describe very accurately the quantum character of such systems. In such cases the potential experienced by an electron as it approaches the edges of a block of metal, or as experienced by a gas molecule as it approaches the walls of its container are effectively infinite as far as these particles are concerned, at least if the particles have sufficiently low kinetic energy compared to the height of these potential barriers.

But, of course, any potential well is of finite depth, and if a particle in such a well has an energy comparable to the height of the potential barriers that define the well, there is the prospect of the particle escaping from the well. This is true both classically and quantum mechanically, though, as you might expect, the behaviour in the quantum mechanical case is not necessarily consistent with our classical physics based expectations. Thus we now proceed to look at the quantum properties of a particle in a finite potential well.

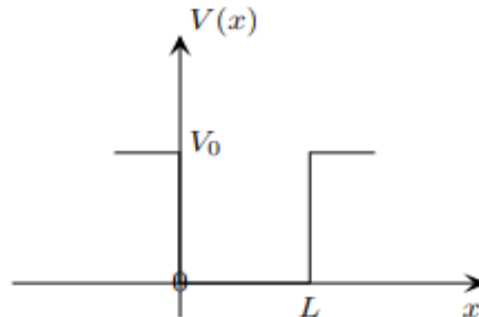


Figure 6.1: Finite potential well.

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

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

i.e. we have ‘lowered’ the infinite barriers to a finite value  $V$ . We now want to solve the time independent Schrödinger equation for this potential.

To do this, we recognize that the problem can be split up into three parts:  $x \leq 0$  where the potential is  $V$ ,  $0 < x < L$  where the potential is zero and  $x \geq L$  where the potential is once again  $V$ . Therefore, to find the wave function for a particle of energy  $E$ , we have to solve three equations, one for each of the regions:

$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + (E - V)\psi(x) = 0 \quad x \leq 0$$

$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0 \quad 0 < x < L$$

$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + (E - V)\psi(x) = 0 \quad x \geq L.$$

The solutions to these equations take different forms depending on whether  $E < V$  or  $E > V$ . We shall consider the two cases separately.



$$E < V$$

First define

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \alpha = \sqrt{\frac{2m(V-E)}{\hbar^2}}.$$

Note that, as  $V > E$ ,  $\alpha$  will be a real number, as it is square root of a positive number. We can now write these equations as

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) &= 0 & x \leq 0 \\ \frac{d^2\psi(x)}{dx^2} + k^2\psi(x) &= 0 & 0 < x < L \\ \frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) &= 0 & x \geq L. \end{aligned}$$

Now consider the first of these equations, which will have as its solution

$$\psi(x) = Ae^{-\alpha x} + Be^{+\alpha x}$$

where  $A$  and  $B$  are unknown constants. It is at this point that we can make use of the boundary condition, namely that  $\psi(x) \rightarrow 0$  as  $x \rightarrow \pm\infty$ . In particular, since the solution we are currently looking at applies for  $x < 0$ , we should look at what this solution does for  $x \rightarrow -\infty$ . What it does is diverge, because of the term  $A \exp(-\alpha x)$ . So, in order to guarantee that our solution has the correct boundary condition for  $x \rightarrow -\infty$ , we have  $A = 0$ . Thus, we conclude that

$$\psi(x) = Be^{\alpha x} \quad x \leq 0.$$

We can apply the same kind of argument when solving Eq. (6.37) for  $x \geq L$ . In that case the solution is

$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x}$$

but now we want to make certain that this solution goes to zero as  $x \rightarrow \infty$ . To guarantee this, we must have  $D = 0$ , so we conclude that

$$\psi(x) = Ce^{-\alpha x} \quad x \geq L.$$

Finally, at least for this part of the argument, we look at the region  $0 < x < L$ . The solution of Eq. (6.36) for this region will be

$$\psi(x) = P \cos(kx) + Q \sin(kx) \quad 0 < x < L$$

but now we have no diverging exponentials, so we have to use other means to determine the unknown coefficients  $P$  and  $Q$ .

At this point we note that we still have four unknown constants  $B$ ,  $P$ ,  $Q$ , and  $C$ . To determine these we note that the three contributions to  $\psi(x)$  do not necessarily join together smoothly at  $x = 0$  and  $x = L$ . This awkward state of affairs has its origin in the fact that the potential is discontinuous at  $x = 0$  and  $x = L$  which meant that we had to solve three separate equations for the three different regions. But these three separate solutions cannot be independent of one another, i.e. there must be a relationship between the unknown constants, so there must be other conditions that enable us to specify the constants. The extra conditions that we impose, as discussed in Section 6.1.2, are that the wave function has to be a continuous function, i.e. the three solutions:

$$\begin{aligned} \psi(x) &= Be^{\alpha x} & x \leq 0 \\ &= P \cos(kx) + Q \sin(kx) & 0 < x < L \\ &= Ce^{-\alpha x} & x \geq L. \end{aligned}$$

## Expectation Value of Momentum

We can make use of Schrödinger's equation to obtain an alternative expression for the expectation value of momentum given earlier in Eq. (5.13). This expression is

$$\langle p \rangle = m \langle v(t) \rangle = m \int_{-\infty}^{+\infty} x \left[ \frac{\partial \Psi^*(x, t)}{\partial t} \Psi(x, t) + \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial t} \right] dx.$$

We note that the appearance of time derivatives in this expression. If we multiply both sides by  $i\hbar$  and make use of Schrödinger's equation, we can substitute for these time derivatives to give

$$\begin{aligned} i\hbar \langle p \rangle &= m \int_{-\infty}^{+\infty} x \left[ \left\{ \frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*(x, t)}{\partial x^2} - V(x) \Psi^*(x, t) \right\} \Psi(x, t) \right. \\ &\quad \left. + \Psi^*(x, t) \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) \right\} \right] dx. \end{aligned}$$



The terms involving the potential cancel. The common factor  $\hbar^2/2m$  can be moved out of the integral, while both sides of the equation can be divided through by  $i\hbar$ , yielding a slightly less complicated expression for  $\langle p \rangle$ :

$$\langle p \rangle = -\frac{1}{2}i\hbar \int_{-\infty}^{+\infty} x \left[ \frac{\partial^2 \Psi^*(x, t)}{\partial x^2} \Psi(x, t) - \Psi^*(x, t) \frac{\partial^2 \Psi(x, t)}{\partial x^2} \right] dx.$$

Integrating both terms in the integrand by parts then gives

$$\begin{aligned} \langle p \rangle = & \frac{1}{2}i\hbar \int_{-\infty}^{+\infty} \left[ \frac{\partial \Psi^*(x, t)}{\partial x} \frac{\partial \Psi(x, t)}{\partial x} - \frac{\partial x \Psi^*(x, t)}{\partial x} \frac{\partial \Psi(x, t)}{\partial x} \right] dx \\ & + \frac{1}{2}i\hbar \left[ \frac{\partial \Psi^*(x, t)}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} \right]_{-\infty}^{+\infty} \end{aligned}$$

As the wave function vanishes for  $x \rightarrow \pm\infty$ , the final term here will vanish. Carrying out the derivatives in the integrand then gives

$$\langle p \rangle = \frac{1}{2}i\hbar \int_{-\infty}^{+\infty} \left[ \frac{\partial \Psi^*(x, t)}{\partial x} \Psi(x, t) - \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} \right] dx$$

Integrating the first term only by parts once again then gives

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} dx + \frac{1}{2}i\hbar \Psi^*(x, t) \Psi(x, t) \Big|_{-\infty}^{+\infty}.$$

Once again, the last term here will vanish as the wave function itself vanishes for  $x \rightarrow \pm\infty$  and we are left with

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} dx.$$

This is a particularly significant result as it shows that the expectation value of momentum can be determined directly from the wave function – i.e. information on the momentum of the particle is contained within the wave function, along with information on the position of the particle. This calculation suggests making the identification

$$p \rightarrow -i\hbar \frac{\partial}{\partial x}$$

which further suggests that we can make the replacement

$$p^n \rightarrow \left( -i\hbar \frac{\partial}{\partial x} \right)^n$$

so that, for instance

$$\langle p^2 \rangle = -\hbar^2 \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial^2 \Psi(x, t)}{\partial x^2} dx$$

and hence the expectation value of the kinetic energy of the particle is

$$\langle K \rangle = \frac{\langle p^2 \rangle}{2m} = -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial^2 \Psi(x, t)}{\partial x^2} dx.$$

We can check this idea by turning to the classical formula for the total energy of a

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

#### Part A

1. Discuss the significance of Schrodinger wave equation
2. Write notes on stationary waves and energy packets
3. Explain the terms node and excited energy states with example
4. Define the terms Eigen values and Eigen functions
5. Explain probability current density
6. Discuss time dependent Schrodinger wave equation
7. What do you mean by Hamiltonian operator?
8. Deduce the commutation relation between energy and momentum operator.
9. Explain the operator formalism in quantum mechanics
10. Show that the Eigen values are discrete using Schrodinger wave equation
11. Differentiate real and complex wave functions
12. Appraise on the utility of normalisation of wave function

#### Part B

1. Deduce time independent Schrodinger wave equation
2. Deduce the expression for time dependent Schrodinger wave equation
3. Deduce the Eigen values, energy states and Hamiltonian of time dependent Schrodinger wave equation
4. Explain the concept of probability current density
5. Discuss the commutation rules for the components of quantum mechanics

## **UNIT – III- General Discussion on boundary states – SPH1314**

### Physical interpretation of the expansion coefficients:

Let's consider an observable  $A$  with eigenstates  $\psi_n$  and eigenvalues  $a_n$

$$A |\psi_n\rangle = a_n |\psi_n\rangle .$$

If a system is in an eigenstate of this observable the expectation value equal to the corresponding eigenvalue

$$\langle A \rangle = \langle \psi_n | A | \psi_n \rangle = a_n \langle \psi_n | \psi_n \rangle = a_n .$$

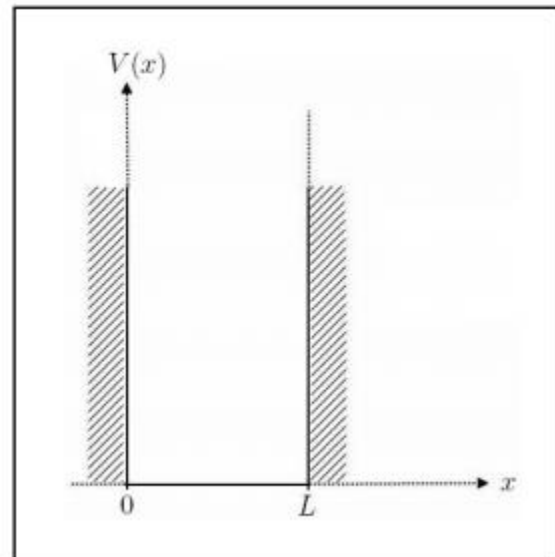
$$|\psi_n\rangle \xrightarrow{A} |\psi_n\rangle .$$

If the system, however, is in a general state  $|\psi\rangle$ , which is a superposition of the eigenstates, the expectation value is given by the sum of all eigenvalues, weighted with squared of the expansion coefficients

$$\begin{aligned} \langle A \rangle &= \langle \psi | A | \psi \rangle = \sum_n \sum_m \langle c_m \psi_m | A | c_n \psi_n \rangle \\ &= \sum_n \sum_m c_m^* c_n a_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} = \sum_n |c_n|^2 a_n . \end{aligned}$$

## Infinite Potential Well

$$V(x) = \begin{cases} 0 & \text{for } x \in [0, L] \\ \infty & \text{else} \end{cases}$$



This means that the quantum object is limited to a certain region between  $x = 0$  and  $x = L$  where it moves freely but cannot ever leave. Thus mathematically we have

$$\psi(x) = 0 \quad \text{for} \quad x \notin [0, L] .$$

Furthermore, for the wave function to be continuous we have to require that it is continuous at the boundaries

$$\psi(0) = \psi(L) = 0 .$$

The only region where particles are allowed is inside the well, where they behave like free particles, i.e. they are not exposed to a potential. Therefore we need to solve (time-independent) Schrödinger equation with the boundary conditions from Eq. (1.10)

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

With the abbreviation

$$k^2 = \frac{2mE}{\hbar^2} , \quad k = \frac{\sqrt{2mE}}{\hbar}$$

the free Schrödinger equation takes the following form

$$\frac{d^2}{dx^2} \psi(x) = -k^2 \psi(x) ,$$

where the general solution is well known, and given by

$$\psi(x) = a \sin(kx) + b \cos(kx) .$$

Here  $a$  and  $b$  are some constants that are yet to be determined by the boundary conditions. Starting with  $\psi(0) = 0$

$$0 = \psi(0) = a \underbrace{\sin(0)}_0 + b \cos(0) \quad \Rightarrow \quad b = 0 .$$

Exploiting the second boundary condition  $\psi(L) = 0$ , leads to discrete values of  $k$

$$0 = \psi(L) = a \sin(kL) \quad \Rightarrow \quad kL = n\pi \quad \Rightarrow \quad k = \frac{n\pi}{L},$$

where  $n = 1, 2, 3, \dots$  can be any natural number. Inserting our result into Eq. and solving it with respect to  $E$  we see that the *energy is quantized*. Labeling the energy levels by  $n$  we find

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

Finally, the value of the constant  $a$  follows from the normalization of the wave fu

$$\int_0^L dx |\psi|^2 = 1 \quad \Rightarrow \quad |a|^2 \int_0^L dx \sin^2\left(\frac{n\pi}{L}x\right) = 1 \quad \Rightarrow \quad |a|^2 = \frac{2}{L}.$$

Thus the bound states of the infinite potential well, which form a CONS, are given by

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

For  $n = 1$  we get the ground state energy and wave function  $E_1, \psi_1$  of the infinite potential well, the higher states with  $n > 1$  are called *excited states*.

The time-independent Schrödinger equation is again our starting point where we insert the following potential  $V(x)$  into our Hamiltonian

$$V(x) = \begin{cases} -V_0 & \text{for } |x| \leq L \\ 0 & \text{for } |x| > L \end{cases}$$

For the possible energy range  $E > -V_0$  we consider separately the two energy ranges:  $-V_0 < E < 0$  for the *bound states* and  $E > 0$  for the *scattered states*. We also split the whole  $x$ -range into the three regions I, II, and III, where we solve the equations sep

## Bound States

**Region I:**  $x < -L$ ,  $V(x) = 0$

Here we have again the free Schrödinger equation

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

which we rewrite by substituting  $\kappa = \frac{1}{\hbar} \sqrt{-2mE}$ , where  $\kappa > 0$  because  $E < 0$ ,

$$\frac{d^2}{dx^2} \psi(x) = \kappa^2 \psi(x).$$

We already know that the general solution of Eq. (4.42) is given by

$$\psi(x) = A e^{-\kappa x} + B e^{\kappa x},$$

where  $A$  and  $B$  are constants, yet to be determined. Since we are in the region  $x < -L < 0$  the exponent of the first term would ever increase for  $x \rightarrow -\infty$ . In order to keep the wave function normalizable we must demand that the constant  $A$  be identically zero, and we get as solution for region I

$$\psi(x) = B e^{\kappa x}.$$

**Region II:**  $-L \leq x \leq L$ ,  $V(x) = -V_0$

In this region acts the potential and we have

$$\text{Schrödinger equation:} \quad \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - V_0 \right) \psi(x) = E \psi(x),$$

which, by introducing a new constant  $q$ , becomes the equation

$$\frac{d^2}{dx^2} \psi(x) = -q^2 \psi(x) \quad q = \frac{1}{\hbar} \sqrt{2m(E + V_0)} > 0,$$

with the general solution

$$\psi(x) = \bar{C} e^{-iqx} + \bar{D} e^{iqx} = C \sin(qx) + D \cos(qx).$$

Again,  $C = i(\bar{D} - \bar{C})$  and  $D = \bar{C} + \bar{D}$  are some constants.

**Region III:**  $x > L, \quad V(x) = 0$

Here we have the same case as in region I with the Schrödinger equation (4.41) and solution

$$\psi(x) = F e^{-\kappa x} + G e^{\kappa x}.$$

But now, in order to keep the wave function normalizable we have to set  $G = 0$  or the corresponding exponent would ever increase for increasing  $x$ . We thus get as solution of region III

$$\psi(x) = F e^{-\kappa x}.$$

**Summary:** Let's summarize the solutions for the energy range  $-V_0 < E < 0$ . We

$$\psi(x) = \begin{cases} B e^{\kappa x} & \text{in region I} \\ C \sin(qx) + D \cos(qx) & \text{in region II} \\ F e^{-\kappa x} & \text{in region III} \end{cases}$$



**Remark:** The motion of a classical particle with energy  $E < 0$  is strictly confined to region II. A quantum mechanical particle, however, can penetrate into the classically forbidden regions I and III, i.e. the probability density is non-vanishing,  $|\psi(x)|^2 \neq 0$ . How far the particle can penetrate depends on the respective energy, it can reach a depth about

$$\Delta x \propto \frac{1}{\kappa} = \frac{\hbar}{\sqrt{-2mE}} \longrightarrow 0 \text{ for } |E| \longrightarrow \infty,$$

which vanishes for large energies in deep potentials. Accordingly, there exists a momentum uncertainty which a classical particle would need to overcome the potential barrier

$$\Delta p \propto \frac{\hbar}{\Delta x} = \sqrt{-2mE}.$$

If we now remember Theorem 4.2 we can conclude that for the symmetric potential defined in Eq. (4.40) there is a family of even and odd solutions, which we will call  $\psi^{(+)}(x)$  and  $\psi^{(-)}(x)$ , sketched in Fig. 4.2

$$\psi^{(+)}(x) = \begin{cases} B e^{\kappa x} & \text{I} \\ D \cos(qx) & \text{II} \\ B e^{-\kappa x} & \text{III} \end{cases} \quad \psi^{(-)}(x) = \begin{cases} -B e^{\kappa x} & \text{I} \\ C \sin(qx) & \text{II} \\ B e^{-\kappa x} & \text{III} \end{cases}$$

At the boundaries of the potential well the functions that are solutions in their respective areas need to merge smoothly into each other. Mathematically this means, the total wave function needs to be smooth, i.e. the values as well as the first derivative of the respective partly solutions must match at  $\pm L$ .

We can summarize these two requirements into the statement, that the *logarithmic derivative* of the wave function must be continuous

$$\text{logarithmic derivative: } \frac{d}{dx} \ln(\psi(x)) = \frac{\psi'(x)}{\psi(x)} \text{ continuous.}$$

For the even solutions<sup>1</sup> this translates to

$$\left. \frac{\psi^{(+)\prime}(x)}{\psi^{(+)}(x)} \right|_{x \rightarrow L} \Rightarrow \frac{-D q \sin(q L)}{D \cos(q L)} = \frac{-B \kappa e^{-\kappa L}}{B e^{-\kappa L}}.$$

Eq. (4.55) can then easily be rewritten as

$$q \tan(q L) = \kappa.$$

Since  $\kappa$  and  $q$  depend on the energy  $E$  via

$$\kappa = \frac{1}{\hbar} \sqrt{-2mE} \quad , \quad q = \frac{1}{\hbar} \sqrt{2m(E - V_0)}$$

Eq. (4.56) becomes a formula for the permitted energies, a *quantization condition*

The analogous calculation as in Eq. (4.55) can be done for the odd solutions, then gives the corresponding condition for the odd states

$$q \cot(qL) = -\kappa.$$

$$z := qL \quad , \quad z_0 := \frac{L}{\hbar} \sqrt{2mV_0}.$$

To relate our old variables  $\kappa$  and  $q$  to the new ones, we first look at

$$\kappa^2 + q^2 = \frac{-2mE}{\hbar^2} + \frac{2m(E + V_0)}{\hbar^2} = \frac{2mV_0}{\hbar^2},$$

which we multiply with  $L^2$  to get

$$\begin{aligned} \Rightarrow \kappa^2 L^2 + \underbrace{q^2 L^2}_{z^2} &= z_0^2 \quad \Rightarrow \quad \frac{\kappa^2 L^2}{q^2 L^2} = \frac{z_0^2 - z^2}{z^2} = \left(\frac{z_0}{z}\right)^2 - 1 \\ \Rightarrow \frac{\kappa}{q} &= \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \quad \Rightarrow \quad \text{insert in Eq. (4.56)} \end{aligned}$$

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}.$$

Let us now return again to the even and odd wavefunctions, Eq. (4.53), where we have to determine the constants  $B$ ,  $C$  and  $D$ . We first use the continuity at  $x = L$  the equations

$$\psi^{(+)} : D \cos(q_n L) = B e^{-\kappa_n L} \quad , \quad \psi^{(-)} : C \sin(q_n L) = B e^{-\kappa_n L},$$

providing us with

$$D = B \frac{e^{-\kappa_n L}}{\cos(q_n L)} \quad , \quad C = B \frac{e^{-\kappa_n L}}{\sin(q_n L)}.$$

Finally we obtain the constant  $B$  from the normalization

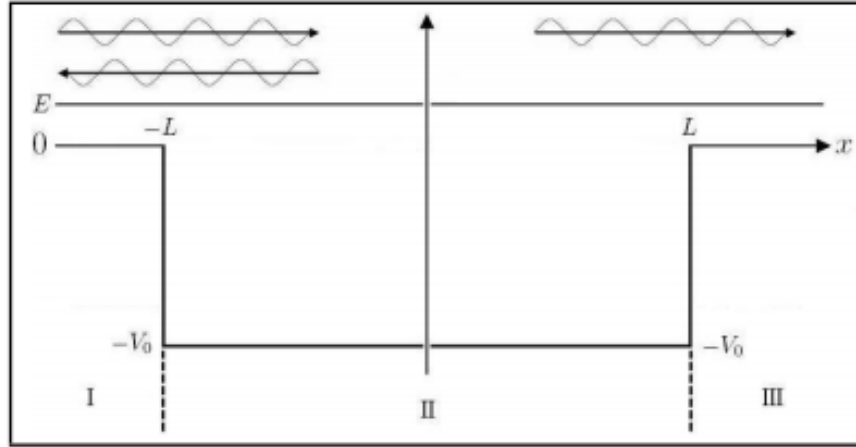
$$B_n = \frac{\cos(q_n L)}{\sqrt{1 + \kappa_n L}} e^{-\kappa_n L} \quad \Rightarrow \quad C_n = D_n = \frac{1}{\sqrt{1 + \kappa_n L}}.$$

We will now investigate the Schrödinger equation, including the potential from Eq. (4.40) for positive energies  $E > 0$ . We will assume that an initial plane wave travels from  $x = -\infty$  to our potential and study the possible states that are not bound but scattered, i.e. transmitted or reflected by the potential, see Fig. 4.7. As before we will analyze our problem for the regions I, II and III separately before combining our results.

**Region I:**  $x < -L$ ,  $V(x) = 0$

In this region we have to solve the free Schrödinger equation

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \quad \text{where} \quad k^2 = \frac{2mE}{\hbar^2}.$$



Like in Eq. (4.46) we can write down the general solution to this equation as

$$\psi(x) = \underbrace{A e^{ikx}}_{\text{incoming}} + \underbrace{B e^{-ikx}}_{\text{reflected}} \quad \text{with} \quad k = \frac{1}{\hbar} \sqrt{2mE} > 0.$$

**Region II:**  $-L \leq x \leq L$ ,  $V(x) = -V_0$

In total analogy to the case for bound states, Eq. (4.45), we get in region II

$$\psi(x) = C \sin(qx) + D \cos(qx) \quad q = \frac{1}{\hbar} \sqrt{2m(E + V_0)} > 0.$$

**Region III:**  $x > L$ ,  $V(x) = 0$

Here we have exactly the situation as in region I, and can thus easily write the solution as in Eq. (4.75) with new constants  $F$  and  $G$ , but we set  $G \equiv 0$  since we have no reflection at infinity (the associated solution would represent a wave travelling right to left).

$$\psi(x) = \underbrace{F e^{ikx}}_{\text{transmitted}}.$$

Summarizing our solutions we have

$$\psi(x) = \begin{cases} A e^{ikx} + B e^{-ikx} & \text{I} \\ C \sin(qx) + D \cos(qx) & \text{II} \\ F e^{ikx} & \text{III} \end{cases}$$

where the constants  $A$ ,  $B$  and  $F$  now characterize the incoming, reflected and transmitted parts of our solution respectively. We then regard the boundary conditions, i

continuity of the wave function and its first derivative at the edges of the potential

$$\psi(x) \xrightarrow{x \rightarrow -L} A e^{-ikL} + B e^{ikL} = -C \sin(qL) + D \cos(qL)$$

$$\psi'(x) \xrightarrow{x \rightarrow -L} ik (A e^{-ikL} - B e^{ikL}) = q (C \cos(qL) + D \sin(qL))$$

$$\psi(x) \xrightarrow{x \rightarrow +L} C \sin(qL) + D \cos(qL) = F e^{ikL}$$

$$\psi'(x) \xrightarrow{x \rightarrow +L} q (C \cos(qL) - D \sin(qL)) = ik F e^{ikL}.$$

Together with the normalization condition we thus have 5 equations for our 5 variables  $A$ ,  $B$ ,  $C$ ,  $D$  and  $F$ . To solve this system of equations we start by calculating

$$\text{Eq. (4.81)} \cdot \sin(qL) + \text{Eq. (4.82)} \cdot \frac{1}{q} \cos(qL) \Rightarrow$$

$$\underbrace{(\sin^2(qL) + \cos^2(qL))}_1 C = C = \left( \sin(qL) + i \frac{k}{q} \cos(qL) \right) F e^{ikL}$$

$$\text{Eq. (4.81)} \cdot \cos(qL) + \text{Eq. (4.82)} \cdot \frac{1}{q} \sin(qL) \Rightarrow$$

$$\underbrace{(\cos^2(qL) + \sin^2(qL))}_1 D = D = \left( \cos(qL) - i \frac{k}{q} \sin(qL) \right) F e^{ikL}.$$

Then we insert the results for  $C$  and  $D$  into Eq. (4.79) and Eq. (4.80) to get  $A$  and dependence of  $F$

$$\begin{aligned} A e^{-ikL} + B e^{ikL} &= -\text{Eq. (4.83)} \cdot \sin(qL) + \text{Eq. (4.84)} \cdot \cos(qL) \\ &= \left( -\sin^2(qL) - 2i \frac{k}{q} \sin(qL) \cos(qL) + \cos^2(qL) \right) F e^{ikL} \end{aligned}$$

Using the following identities we can then rewrite Eq. (4.85)

$$\cos^2 x - \sin^2 x = \cos(2x) \quad , \quad 2 \sin x \cos x = \sin(2x)$$

$$\Rightarrow A e^{-2ikL} + B = \left( \cos(2qL) - i \frac{k}{q} \sin(2qL) \right) F ,$$

and applying the same procedure for Eq. (4.80) gives

$$\begin{aligned} ik (A e^{-ikL} - B e^{ikL}) &= q (\text{Eq. (4.83)} \cdot \cos(qL) + \text{Eq. (4.84)} \cdot \sin(qL)) \\ &= \left( i \frac{k}{q} \cos^2(qL) + 2 \sin(qL) \cos(qL) - i \frac{k}{q} \sin^2(qL) \right) F e^{ikL} \end{aligned}$$

$$\stackrel{\text{Eq. (4.86)}}{\Rightarrow} A e^{-2ikL} - B = -i \frac{q}{k} \left( \sin(2qL) + i \frac{k}{q} \cos(2qL) \right) F .$$

At last we subtract Eq. (4.88) from Eq. (4.87) to get the coefficient  $B$ , which characterizes the reflection from the potential well

$$\begin{aligned} \text{Eq. (4.87)} - \text{Eq. (4.88)} &= 2B = i \left( \frac{q}{k} - \frac{k}{q} \right) \sin(2qL) F \\ \Rightarrow \frac{B}{F} &= i \frac{q^2 - k^2}{2kq} \sin(2qL) \quad \text{reflexion/transmission amplitude} . \end{aligned}$$

This can be understood as a balance between the reflected and the transmitted parts of the wave function. To get the probability for the reflection or transmission we have to normalize each part by the amplitude of the incoming wave and to take the modulus squared of each expression. We also want to express the quantities  $q$  and  $k$  by the familiar constants  $m$ ,  $\hbar$  and  $V_0$ , using Eq. (4.75) and Eq. (4.76)

$$\begin{aligned} (q^2 - k^2)^2 &= \frac{1}{\hbar^4} (2m(E + V_0) - 2mE)^2 = \frac{(2m)^2 V_0^2}{\hbar^4} \\ 4q^2 k^2 &= 4 \frac{1}{\hbar^4} (2m)^2 E(E + V_0) . \end{aligned}$$

Thus we find for the **reflection coefficient**  $R(E)$  describing the probability of reflection

$$R(E) = \frac{|B|^2}{|A|^2} = \frac{V_0^2}{4E(E + V_0)} \sin^2(2qL) \frac{|F|^2}{|A|^2} \neq 0.$$

We conclude that there is a nonzero possibility for a reflection of the wave at the potential well, a purely quantum mechanical effect that is not possible classically.

The reflection, of course, is related to the transmission of the wave. Focussing on the transmission, we can calculate the *transmission coefficient*  $T(A) = \frac{|F|^2}{|A|^2}$  which rates the transmitted against the incoming intensity. We first calculate the sum of Eq. (4.87) and Eq. (4.88) to get the *transmission amplitude*

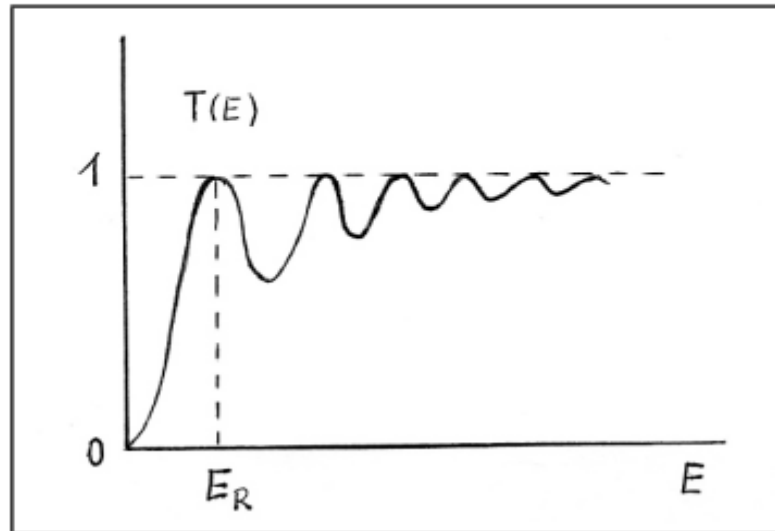
$$\text{Eq. (4.87) + Eq. (4.88)} = A e^{-2ikL} = 2 \left( \cos(2qL) - i \sin(2qL) \frac{1}{2} \left( \frac{q}{k} + \frac{k}{q} \right) \right) F$$

$$\Rightarrow \frac{F}{A} = e^{-2ikL} \left( \cos(2qL) - i \frac{q^2 + k^2}{2kq} \sin(2qL) \right)^{-1},$$

and by taking the modulus squared and inserting the expressions for  $q$  and  $k$  and Eq. (4.76)) we obtain the **transmission coefficient**  $T(E)$

Of course, both coefficients are related by

$$R(E) + T(E) = 1.$$



## Review Questions

### Part A

1. Write notes on bound states
2. Explain the continuity of wave function
3. Appraise on discrete energy levels
4. What do you mean by zero point energy?
5. Explain reflection coefficient
6. Discuss transmission coefficient
7. Predict the energy equation of particle in a box
8. Analyse, why particle trapped in a box cannot be at rest?
9. Find the lowest energy of an electron confined to move in a 1 dimensional box of length  $1 \text{ \AA}$
10. Calculate the energy Eigen value for the motion of a particle in One dimensional box
10. Calculate the energy Eigen value for the motion of a particle in One dimensional box
11. A beam of electrons incident on the square barrier potential, from left. Find the fraction of electrons reflected & transmitted if the energy of the incident electrons is  $\frac{V_0}{2}$  &  $2a \frac{\sqrt{mV_0}}{\hbar} = \frac{3}{2}$

### Part B

1. Write notes on Bound states, Continuity of wave function, Eigen values and Eigen functions.
2. Deduce Schrodinger equation for a particle in Square well potential and obtain energy Eigen functions
3. Write down Schrodinger equation for a particle in a box. Solve it to obtain Eigen functions and show that the Eigen values are discrete.
4. Deduce Schrodinger equation for a linear harmonic oscillator and solve it to obtain the Eigen values and Eigen functions.
5. Infer the reflection coefficient for a rectangular barrier of width 'a' and height  $V_0$  for the case  $E < V_0$

## **UNIT – IV- Quantum theory of Hydrogen like atom – SPH1314**



## THE SCHRODINGER EQUATION IN SPHERICAL COORDINATES

Depending on the symmetry of the problem it is sometimes more convenient to work with a coordinate system that best simplifies the problem. For example, the hydrogen atom can be most conveniently described by using spherical coordinates since the potential energy  $U(r)$  and force  $F(r)$  both depend on the radial distance ' $r$ ' of the electron from the nucleus (proton).

$$U(r) = -\frac{Zke^2}{r}, \quad (Z=1)$$

$$F(r) = -\frac{dU(r)}{dr} = \frac{Zke^2}{r^2}$$

Since the force is a conservative force, then the energy (kinetic + potential) remains constant and we will show that it is quantized. Since the energy is quantized, it leads to stationary states where,

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$$

where  $E = \hbar\omega$  is the particle energy

Where  $\psi(\mathbf{r})$  is the solution to the Time Independent Schrodinger Equation in spherical coordinates:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Where,

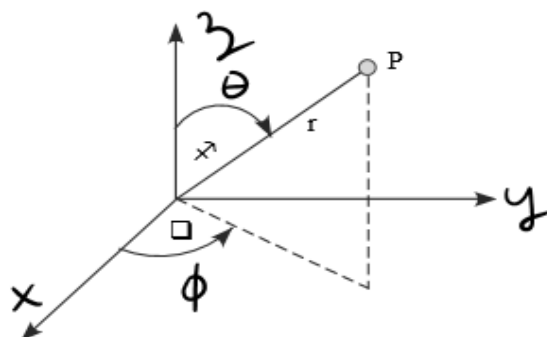
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

is the Laplacian Operator in spherical coordinates. Recall that in spherical coordinates:

$$r: 0 \rightarrow \infty$$

$$\theta: 0 \rightarrow \pi$$

$$\phi: 0 \rightarrow 2\pi$$



Thus, In spherical coordinates  $\psi(r) = \psi(r, \theta, \phi)$ . Substituting the Laplacian Operator in the TISE we get:

$$\boxed{-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) + U(r)\psi = E\psi}$$

We will show that the solution to this equation will demonstrate the quantization of ENERGY and ANGULAR MOMENTUM! The solution will also show the origin and physical meaning of the quantum numbers:

- $n$  = principal quantum number (describes the size and energy of an orbital)
- $\ell$  = orbital quantum number (describes the shape of the orbital)
- $m_\ell$  = magnetic quantum number (describes the orientation of orbital in space)

Using separation of variable,

$$\boxed{\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi)} \text{ substitute into the TISE:}$$

$$-\frac{\hbar^2}{2m} \left( \frac{fg}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{Rg}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{Rf}{r^2 \sin^2 \theta} \frac{\partial^2 g}{\partial \phi^2} \right) = (E - U)Rfg$$

$$\frac{\hbar^2}{2m} \left( fg \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{Rg}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{Rf}{\sin^2 \theta} \frac{\partial^2 g}{\partial \phi^2} \right) = -\frac{2m}{\hbar^2} (E - U)r^2 Rfg$$

Divide both sides by Rfg:

$$\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{f \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{g \sin^2 \theta} \frac{\partial^2 g}{\partial \phi^2} = -\frac{2m}{\hbar^2} (E - U)r^2$$

Rearranging:

$$\boxed{\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{2mr^2}{\hbar^2} (E - U) = - \left[ \frac{1}{f(\theta) \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{df(\theta)}{d\theta} \right) + \frac{1}{g(\phi) \sin^2 \theta} \frac{d^2 g(\phi)}{d\phi^2} \right]}$$

Note that the LHS is a function of  $r$  only and the RHS is a function of  $\theta$  and  $\phi$  only. Since the variables are independent, changes in  $r$  cannot effect the RHS and changes in  $\theta$  and  $\phi$  cannot effect the LHS. Thus, the two sides must be equal to the same constant, which we will call  $\ell(\ell+1)$

## SOLUTION TO THE ANGULAR DEPENDENCE

$$\left[ \frac{1}{f(\theta) \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{df(\theta)}{d\theta} \right) + \frac{1}{g(\phi) \sin^2 \theta} \frac{d^2 g(\phi)}{d\phi^2} \right] = -\ell(\ell+1)$$

$$\frac{1}{g(\phi)} \frac{d^2 g(\phi)}{d\phi^2} = -\ell(\ell+1) \sin^2 \theta - \frac{\sin \theta}{f(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{df(\theta)}{d\theta} \right)$$

Setting both sides equal to the constant  $-m^2$ :

### LHS

$$\frac{1}{g(\phi)} \frac{d^2 g(\phi)}{d\phi^2} = -m^2$$

$$\frac{d^2 g(\phi)}{d\phi^2} + m^2 g(\phi) = 0$$

$$g(\phi) = e^{im\phi}$$

Since  $\psi(r, \theta, \phi)$  must be single-valued, then:

$$g(\phi) = g(\phi + 2\pi)$$

$$e^{im\phi} = e^{im(\phi+2\pi)}$$

$$e^{im\phi} = e^{im\phi} e^{i2\pi m}$$

$$e^{i2\pi m} = 1$$

$$e^{i2\pi m} = \cos(2\pi m) + i \sin(2\pi m)$$

$$m = 0, \pm 1, \pm 2, \dots \text{ magnetic quantum number}$$

### RHS

$$-\ell(\ell+1)\sin^2\theta - \frac{\sin\theta}{f(\theta)} \frac{d}{d\theta} \left( \sin\theta \frac{df(\theta)}{d\theta} \right) = -m^2$$

*Solution:*

$$f_\ell^m(\theta) = \frac{(\sin\theta)^{|m|}}{2^\ell \ell!} \left[ \frac{d}{d(\cos\theta)} \right]^{\ell+1} (\cos^2\theta - 1)^\ell \quad (\text{Associated Legendre Functions})$$

$$\ell = 0, 1, 2, 3, \dots$$

$$m = 0, \pm 1, \pm 2, \dots, \pm \ell$$

$\ell$  = angular momentum quantum number

$$f_0^0 = 1$$

$$f_1^0 = 2 \cos\theta$$

$$f_1^1 = \sin\theta$$

$$f_2^0 = 4(3 \cos^2\theta - 1)$$

Some Associated Legendre Functions

The product of the angular dependence are called the Spherical Harmonics:

$$Y_\ell^m(\theta, \phi) = f_\ell^m(\theta) g_m(\phi) \text{ Spherical Harmonics}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \frac{1}{2} \sqrt{\frac{3 \cos\theta}{\pi}}$$

$$Y_1^{\pm 1} = \pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin\theta e^{\pm i\phi}$$

Some Spherical Harmonics

## SOLUTION TO THE RADIAL DEPENDENCE

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} (E - U) = \ell(\ell + 1)$$

multiply by :  $-\frac{\hbar^2}{2mr^2}$

$$-\frac{\hbar^2}{2mr^2} \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + (U - E) = -\frac{\hbar^2}{2mr^2} \ell(\ell + 1)$$

For the hydrogen atom  $U(r) = -\frac{Zke^2}{r}$  where  $(Z = 1)$

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left( -\frac{Zke^2}{r} + \frac{\hbar^2}{2mr^2} \ell(\ell + 1) \right) R = ER$$

The solution to this equation is:

$$R_{n\ell} = \frac{a_0^n e^{-\left(\frac{r}{a_0}\right)}}{r} L_{n\ell}(r/a_0)$$

where  $L_{n\ell}(r/a_0) = \text{Laguerre Polynomials}$

The result for the energy of the Hydrogen atom is as expected, same as the Bohr Theory!!!

$$\boxed{E_n = -\frac{ke^2}{2a_0} \left( \frac{Z}{n} \right)^2} \quad \text{Energy of Hydrogen Atom}$$

Where  $n=1,2,3,\dots$  and  $n > \ell$ .  $\ell = 0, 1, 2, 3, \dots, (n-1)$

## THE COMPLETE WAVEFUNCTION FOR THE HYDROGEN ATOM

$$\psi_{n\ell m}(r, \theta, \phi) = C_{n\ell m} R_{n\ell}(r) Y_{\ell}^m(\theta, \phi)$$

Where  $C_{n\ell m}$  is a constant determined by the normalization conditions.

## THE HYDROGEN ATOM; ATOMIC ORBITALS

### Atomic Spectra

When gaseous hydrogen in a glass tube is excited by a 5000-volt electrical discharge, four lines are observed in the visible part of the emission spectrum: red at 656.3 nm, blue-green at 486.1 nm, blue violet at 434.1 nm and violet at 410.2 nm:



Figure 1. Visible spectrum of atomic hydrogen.

Other series of lines have been observed in the ultraviolet and infrared regions. Rydberg (1890) found that all the lines of the atomic hydrogen spectrum could be fitted to a single formula

$$\frac{1}{\lambda} = \mathcal{R} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_1 = 1, 2, 3, \dots, \quad n_2 > n_1 \quad (1)$$

where  $\mathcal{R}$ , known as the Rydberg constant, has the value  $109,677 \text{ cm}^{-1}$  for hydrogen. The reciprocal of wavelength, in units of  $\text{cm}^{-1}$ , is in general use by spectroscopists. This unit is also designated *wavenumbers*, since it represents the number of wavelengths per cm. The Balmer series of spectral lines in the visible region, shown in Fig. 1, correspond to the values  $n_1 = 2$ ,  $n_2 = 3, 4, 5$  and 6. The lines with  $n_1 = 1$  in the ultraviolet make up the Lyman series. The line with  $n_2 = 2$ , designated the Lyman alpha, has the longest wavelength (lowest wavenumber) in this series, with  $1/\lambda = 82.258 \text{ cm}^{-1}$  or  $\lambda = 121.57 \text{ nm}$ .

Other atomic species have line spectra, which can be used as a “fingerprint” to identify the element. However, no atom other than hydrogen has a simple relation analogous to (1) for its spectral frequencies. Bohr in 1913 proposed that all atomic spectral lines arise from transitions between discrete energy levels, giving a photon such that

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad (2)$$

This is called the *Bohr frequency condition*. We now understand that the atomic transition energy  $\Delta E$  is equal to the energy of a photon, as proposed earlier by Planck and Einstein.

## The Bohr Atom

The nuclear model proposed by Rutherford in 1911 pictures the atom as a heavy, positively-charged nucleus, around which much lighter, negatively-charged electrons circulate, much like planets in the Solar system. This model is however completely untenable from the standpoint of classical electromagnetic theory, for an accelerating electron (circular motion represents an acceleration) should radiate away its energy. In fact, a hydrogen atom should exist for no longer than  $5 \times 10^{-11}$  sec, time enough for the electron's death spiral into the nucleus. This is one of the worst quantitative predictions in the history of physics. It has been called the Hindenberg disaster on an atomic level. (Recall that the Hindenberg, a hydrogen-filled dirigible, crashed and burned in a famous disaster in 1937.)

Bohr sought to avoid an atomic catastrophe by proposing that certain orbits of the electron around the nucleus could be exempted from classical electrodynamics and remain stable. The Bohr model was quantitatively successful for the hydrogen atom, as we shall now show.

We recall that the attraction between two opposite charges, such as the electron and proton, is given by Coulomb's law

$$F = \begin{cases} -\frac{e^2}{r^2} & \text{(gaussian units)} \\ -\frac{e^2}{4\pi\epsilon_0 r^2} & \text{(SI units)} \end{cases} \quad (3)$$

We prefer to use the gaussian system in applications to atomic phenomena. Since the Coulomb attraction is a central force (dependent only on  $r$ ), the potential energy is related by

$$F = -\frac{dV(r)}{dr} \quad (4)$$

We find therefore, for the mutual potential energy of a proton and electron,

$$V(r) = -\frac{e^2}{r} \quad (5)$$



Bohr considered an electron in a circular orbit of radius  $r$  around the proton. To remain in this orbit, the electron must be experiencing a centripetal acceleration

$$a = -\frac{v^2}{r} \quad (6)$$

where  $v$  is the speed of the electron.

Using (4) and (6) in Newton's second law, we find

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \quad (7)$$

where  $m$  is the mass of the electron. For simplicity, we assume that the proton mass is infinite (actually  $m_p \approx 1836m_e$ ) so that the proton's position remains fixed. We will later correct for this approximation by introducing reduced mass. The energy of the hydrogen atom is the sum of the kinetic and potential energies:

$$E = T + V = \frac{1}{2}mv^2 - \frac{e^2}{r} \quad (8)$$

Using Eq (7), we see that

$$T = -\frac{1}{2}V \quad \text{and} \quad E = \frac{1}{2}V = -T \quad (9)$$

This is the form of the virial theorem for a force law varying as  $r^{-2}$ . Note that the energy of a bound atom is *negative*, since it is lower than the energy of the separated electron and proton, which is taken to be zero.

For further progress, we need some restriction on the possible values of  $r$  or  $v$ . This is where we can introduce the quantization of angular momentum  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . Since  $\mathbf{p}$  is perpendicular to  $\mathbf{r}$ , we can write simply

$$L = rp = mvr \quad (10)$$

Using (9), we find also that

$$r = \frac{L^2}{me^2} \quad (11)$$

We introduce angular momentum quantization, writing

$$L = n\hbar, \quad n = 1, 2, \dots \quad (12)$$

excluding  $n = 0$ , since the electron would then not be in a circular orbit. The allowed orbital radii are then given by

$$r_n = n^2 a_0 \quad (13)$$

where

$$a_0 \equiv \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{m} = 0.529 \text{\AA} \quad (14)$$

which is known as the *Bohr radius*. The corresponding energy is

$$E_n = -\frac{e^2}{2a_0 n^2} = -\frac{me^4}{2\hbar^2 n^2}, \quad n = 1, 2, \dots \quad (15)$$

Rydberg's formula (1) can now be deduced from the Bohr model. We have

$$\frac{hc}{\lambda} = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4}{h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (16)$$

and the Rydberg constant can be identified as

$$\mathcal{R} = \frac{2\pi^2 me^4}{h^3 c} \approx 109,737 \text{ cm}^{-1} \quad (17)$$

The slight discrepancy with the experimental value for hydrogen (109,677) is due to the finite proton mass. This will be corrected later.

The Bohr model can be readily extended to hydrogenlike ions, systems in which a single electron orbits a nucleus of arbitrary atomic number  $Z$ . Thus  $Z = 1$  for hydrogen,  $Z = 2$  for  $\text{He}^+$ ,  $Z = 3$  for  $\text{Li}^{++}$ , and so on. The Coulomb potential (5) generalizes to

$$V(r) = -\frac{Ze^2}{r}, \quad (18)$$

the radius of the orbit (13) becomes

$$r_n = \frac{n^2 a_0}{Z} \quad (19)$$

and the energy (15) becomes

$$E_n = -\frac{Z^2 e^2}{2a_0 n^2} \quad (20)$$

De Broglie's proposal that electrons can have wavelike properties was actually inspired by the Bohr atomic model. Since

$$L = rp = n\hbar = \frac{nh}{2\pi} \quad (21)$$

we find

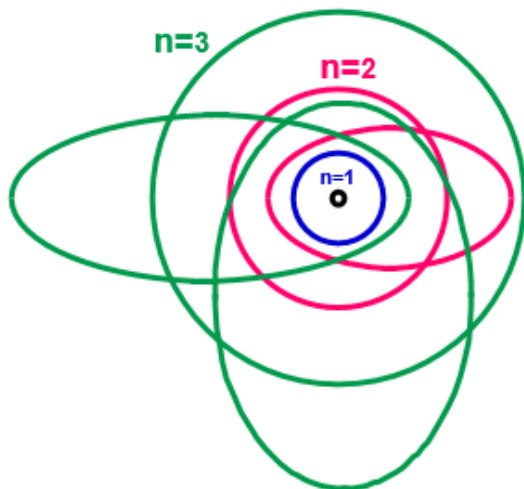
$$2\pi r = \frac{nh}{p} = n\lambda \quad (22)$$

Therefore, each allowed orbit traces out an integral number of de Broglie wavelengths.

Wilson (1915) and Sommerfeld (1916) generalized Bohr's formula for the allowed orbits to

$$\oint p \, dr = nh, \quad n = 1, 2, \dots \quad (23)$$

The Sommerfeld-Wilson quantum conditions (23) reduce to Bohr's results for circular orbits, but allow, in addition, elliptical orbits along which the momentum  $p$  is variable. According to Kepler's first law of planetary motion, the orbits of planets are ellipses with the Sun at one focus. Fig. 2 shows the generalization of the Bohr theory for hydrogen, including the elliptical orbits. The lowest energy state  $n = 1$  is still a circular orbit. But  $n = 2$  allows an elliptical orbit in addition to the circular one;  $n = 3$  has three possible orbits, and so on. The energy still depends on  $n$  alone, so that the elliptical orbits represent degenerate states. Atomic spectroscopy shows in fact that energy levels with  $n > 1$  consist of multiple states, as implied by the splitting of atomic lines by an electric field (Stark effect) or a magnetic field (Zeeman effect). Some of these generalized orbits are drawn schematically in Fig. 2.



**Figure 2.** Bohr-Sommerfeld orbits for  $n = 1, 2, 3$  (not to scale).

The Bohr model was an important first step in the historical development of quantum mechanics. It introduced the quantization of atomic energy levels and gave quantitative agreement with the atomic hydrogen spectrum. With the Sommerfeld-Wilson generalization, it accounted as well for the degeneracy of hydrogen energy levels. Although the Bohr model was able to sidestep the atomic “Hindenberg disaster,” it cannot avoid what we might call the “Heisenberg disaster.” By this we mean that the assumption of well-defined electronic orbits around a nucleus is completely contrary to the basic premises of quantum mechanics. Another flaw in the Bohr picture is that the angular momenta are all too large by one unit, for example, the ground state actually has zero orbital angular momentum (rather than  $\hbar$ ).

### Quantum Mechanics of Hydrogenlike Atoms

In contrast to the particle in a box and the harmonic oscillator, the hydrogen atom is a real physical system that can be treated exactly by quantum mechanics. In addition to their inherent significance, these solutions suggest prototypes for atomic orbitals used in approximate treatments of complex atoms and molecules.

For an electron in the field of a nucleus of charge  $+Ze$ , the Schrödinger equation can be written

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right\} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (24)$$

It is convenient to introduce *atomic units* in which length is measured in

bohrs:

$$a_0 = \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} \equiv 1 \text{ bohr}$$

and energy in hartrees:

$$\frac{e^2}{a_0} = 4.358 \times 10^{-18} \text{ J} = 27.211 \text{ eV} \equiv 1 \text{ hartree}$$

Electron volts (eV) are a convenient unit for atomic energies. One eV is defined as the energy an electron gains when accelerated across a potential difference of 1 volt. The ground state of the hydrogen atom has an energy of  $-1/2$  hartree or  $-13.6$  eV. Conversion to atomic units is equivalent to setting

$$\hbar = e = m = 1$$

in all formulas containing these constants. Rewriting the Schrödinger equation in atomic units, we have

$$\left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right\} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (25)$$

Since the potential energy is spherically symmetrical (a function of  $r$  alone), it is obviously advantageous to treat this problem in spherical polar coordinates  $r, \theta, \phi$ . Expressing the Laplacian operator in these coordinates [cf. Eq (6-20)],

$$\begin{aligned} -\frac{1}{2} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \\ \times \psi(r, \theta, \phi) - \frac{Z}{r} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \end{aligned} \quad (26)$$

Substituting (27) into (26) and using the angular momentum eigenvalue equation (6-34), we obtain an ordinary differential equation for the radial function  $R(r)$ :

$$\left\{ -\frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\ell(\ell+1)}{2r^2} - \frac{Z}{r} \right\} R(r) = E R(r) \quad (28)$$

Note that in the domain of the variable  $r$ , the angular momentum contribution  $\ell(\ell+1)/2r^2$  acts as an effective addition to the potential energy. It can be identified with *centrifugal force*, which pulls the electron outward, in opposition to the Coulomb attraction. Carrying out the successive differentiations in (29) and simplifying, we obtain

$$\frac{1}{2} R''(r) + \frac{1}{r} R'(r) + \left[ \frac{Z}{r} - \frac{\ell(\ell+1)}{2r^2} + E \right] R(r) = 0 \quad (29)$$

another second-order linear differential equation with non-constant coefficients. It is again useful to explore the asymptotic solutions to (29), as  $r \rightarrow \infty$ . In the asymptotic approximation,

$$R''(r) - 2|E|R(r) \approx 0 \quad (30)$$

having noted that the energy  $E$  is negative for bound states. Solutions to (30) are

$$R(r) \approx \text{const } e^{\pm \sqrt{2|E|} r} \quad (31)$$

We reject the positive exponential on physical grounds, since  $R(r) \rightarrow \infty$  as  $r \rightarrow \infty$ , in violation of the requirement that the wavefunction must be finite everywhere. Choosing the negative exponential and setting  $E = -Z^2/2$ , the ground state energy in the Bohr theory (in atomic units), we obtain

$$R(r) \approx \text{const } e^{-Zr} \quad (32)$$

It turns out, very fortunately, that this asymptotic approximation is also an *exact* solution of the Schrödinger equation (29) with  $\ell = 0$ , just what happened for the harmonic-oscillator problem in Chap. 5. The solutions to Eq (29), designated  $R_{n\ell}(r)$ , are labelled by  $n$ , known as the *principal*

*quantum number*, as well as by the angular momentum  $\ell$ , which is a parameter in the radial equation. The solution (32) corresponds to  $R_{10}(r)$ . This should be normalized according to the condition

$$\int_0^\infty [R_{10}(r)]^2 r^2 dr = 1 \quad (33)$$

A useful definite integral is

$$\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}} \quad (34)$$

The normalized radial function is thereby given by

$$R_{10}(r) = 2Z^{3/2} e^{-Zr} \quad (35)$$

Since this function is nodeless, we identify it with the ground state of the hydrogenlike atom. Multiplying (35) by the spherical harmonic  $Y_{00} = 1/\sqrt{4\pi}$ , we obtain the total wavefunction (27)

$$\psi_{100}(r) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr} \quad (36)$$

This is conventionally designated as the  $1s$  function  $\psi_{1s}(r)$ .

Integrals in spherical-polar coordinates over a spherically-symmetrical integrand can be significantly simplified. We can do the reduction

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f(r) r^2 \sin \theta dr d\theta d\phi = \int_0^\infty f(r) 4\pi r^2 dr \quad (37)$$

since integration over  $\theta$  and  $\phi$  gives  $4\pi$ , the total solid angle of a sphere. The normalization of the  $1s$  wavefunction can thus be written as

$$\int_0^\infty [\psi_{1s}(r)]^2 4\pi r^2 dr = 1 \quad (38)$$



## Review Questions

### Part A

1. Discuss spherical symmetry
2. Time independent Schrodinger equation in spherical polar coordinates, illustrate
3. Discuss the steps of solution of radial wave equation
4. Explain the shapes of probability density for ground state and first excited state
5. Define and explain angular momentum operator
6. What do you mean by Quantum numbers
7. Demonstrate the solution of radial wave function

### Part B

1. Write the time independent Schrodinger wave equation for the hydrogen atom in spherical polar coordinates.
2. Solve angular-dependent Portion of the Schrodinger Equation in spherical polar coordinates.
3. Write notes on Shapes of hydrogen atom wave functions: s orbitals
4. Discuss radial probability distribution.



## **UNIT – V- Atoms in Electric and Magnetic fields – SPH1314**

Angular momentum plays a central role in both classical and quantum mechanics. In classical mechanics, all isolated systems conserve angular momentum (as well as energy and linear momentum); this fact reduces considerably the amount of work required in calculating trajectories of planets, rotation of rigid bodies, and many more.

Similarly, in quantum mechanics, angular momentum plays a central role in understanding the structure of atoms, as well as other quantum problems that involve rotational symmetry.

Like other observable quantities, angular momentum is described in QM by an operator. This is in fact a vector operator, similar to momentum operator. However, as we will shortly see, contrary to the linear momentum operator, the three components of the angular momentum operator do not commute.

In QM, there are several angular momentum operators: the total angular momentum (usually denoted by  $\vec{J}$ ), the orbital angular momentum (usually denoted by  $\vec{L}$ ) and the intrinsic, or **spin** angular momentum (denoted by  $\vec{S}$ ). This last one (spin) has no classical analogue. Confusingly, the term “angular momentum” can refer to either the total angular momentum, or to the orbital angular momentum.

The classical definition of the orbital angular momentum,  $\vec{L} = \vec{r} \times \vec{p}$  can be carried directly to QM by reinterpreting  $\vec{r}$  and  $\vec{p}$  as the operators associated with the position and the linear momentum.

The spin operator,  $\mathbf{S}$ , represents another type of angular momentum, associated with “intrinsic rotation” of a particle around an axis; Spin is an intrinsic property of a particle (nearly all elementary particles have spin), that is unrelated to its spatial motion. The existence of spin angular momentum is inferred from experiments, such as the Stern-Gerlach experiment, in which particles are observed to possess angular momentum that cannot be accounted for by orbital angular momentum alone.

The total angular momentum,  $\mathbf{J}$ , combines both the spin and orbital angular momentum of a particle (or a system), namely  $\vec{J} = \vec{L} + \vec{S}$ .

## 2. Orbital angular momentum

Consider a particle of mass  $m$ , momentum  $\vec{p}$  and position vector  $\vec{r}$  (with respect to a fixed origin,  $\vec{r} = 0$ ). In classical mechanics, the particle's orbital angular momentum is given by a vector  $\vec{L}$ , defined by

$$\vec{L} = \vec{r} \times \vec{p}. \quad (1)$$

This vector points in a direction that is perpendicular to the plane containing  $\vec{r}$  and  $\vec{p}$ , and has a magnitude  $L = rp \sin \alpha$ , where  $\alpha$  is the angle between  $\vec{r}$  and  $\vec{p}$ . In Cartesian coordinates, the components of  $\vec{L}$  are

$$\begin{aligned} L_x &= yp_z - zp_y; \\ L_y &= zp_x - xp_z; \\ L_z &= xp_y - yp_x. \end{aligned} \quad (2)$$

The corresponding QM operators representing  $L_x$ ,  $L_y$  and  $L_z$  are obtained by replacing  $x$ ,  $y$ ,  $z$  and  $p_x$ ,  $p_y$  and  $p_z$  with the corresponding QM operators, giving

$$\begin{aligned} L_x &= -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \\ L_y &= -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \\ L_z &= -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \end{aligned} \quad (3)$$

In a more compact form, this can be written as a **vector operator**,

$$\vec{L} = -i\hbar(\vec{r} \times \vec{\nabla}). \quad (4)$$

It is easy to verify that  $\vec{L}$  is Hermitian.

Using the commutation relations derived for  $\vec{x}$  and  $\vec{p}$ , the commutation relations between the different components of  $\vec{L}$  are readily derived. For example:

$$[L_x, L_y] = [(yp_z - zp_y), (zp_x - xp_z)] = [yp_z, zp_x] + [zp_y, xp_z] - [yp_z, xp_z] - [zp_y, zp_x] \quad (5)$$

Since  $y$  and  $p_x$  commute with each other and with  $z$  and  $p_z$ , the first term reads

$$[yp_z, zp_x] = yp_z zp_x - zp_x yp_z = yp_x [p_z, z] = -i\hbar yp_x \quad (6)$$

Similarly, the second commutator gives

$$[zp_y, xp_z] = zp_y xp_z - xp_z zp_y = xp_y [z, p_z] = i\hbar xp_y \quad (7)$$

The third and forth commutators vanish; we thus find that

$$[L_x, L_y] = i\hbar(xp_y - yp_x) = i\hbar L_z. \quad (8)$$

In a similar way, it is straightforward to show that

$$[L_y, L_z] = i\hbar L_x \quad (9)$$

and

$$[L_z, L_x] = i\hbar L_y \quad (10)$$

The three equations are equivalent to the vectorial commutation relation:

$$\vec{L} \times \vec{L} = i\hbar \vec{L}. \quad (11)$$

Note that this can only be true for operators; since, for regular vectors, clearly  $\vec{L} \times \vec{L} = 0$ .

The fact that the operators representing the different components of the angular momentum do not commute, implies that it is impossible to obtain definite values for all component of the angular momentum when measured simultaneously. This means that if the system is in eigenstate of one component of the angular momentum, it will in general not be an eigenstate of either of the other two components.

We define the operator representing the square of the magnitude of the orbital angular momentum by

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2. \quad (12)$$

It is easy to show that  $\vec{L}^2$  does commute with each of the three components:  $L_x$ ,  $L_y$  or  $L_z$ . For example (using  $[L_x^2, L_x] = 0$ ):

$$\begin{aligned} [\vec{L}^2, L_x] &= [L_y^2 + L_z^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= -i\hbar(L_y L_z + L_z L_y) + i\hbar(L_z L_y + L_y L_z) = 0. \end{aligned} \quad (13)$$

Similarly,

$$[\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0, \quad (14)$$

which can be summarized as

$$[\vec{L}^2, \vec{L}] = 0. \quad (15)$$

Physically, this means that one can find simultaneous eigenfunctions of  $\vec{L}^2$  and one of the components of  $\vec{L}$ , implying that both the magnitude of the angular momentum and one of its components can be precisely determined. Once these are known, they fully specify the angular momentum.

In order to obtain the eigenvalues of  $\vec{L}^2$  and one of the components of  $\vec{L}$  (typically,  $L_z$ ), it is convenient to express the angular momentum operators in spherical polar coordinates:  $r, \theta, \phi$ , rather than the Cartesian coordinates  $x, y, z$ . The spherical coordinates are related to the Cartesian ones via

$$\begin{aligned} x &= r \sin \theta \cos \phi; \\ y &= r \sin \theta \sin \phi; \\ z &= r \cos \theta. \end{aligned} \quad (16)$$

After some algebra, one gets:

$$\begin{aligned} L_x &= -i\hbar \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ L_y &= -i\hbar \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ L_z &= -i\hbar \frac{\partial}{\partial \phi}; \\ \vec{L}^2 &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \end{aligned} \quad (17)$$

We thus find that the operators  $L_x, L_y, L_z$  and  $\vec{L}^2$  depend on  $\theta$  and  $\phi$  only, that is they are independent on the radial coordinate  $r$ . All these operators therefore commute with any function of  $r$ ,

$$[L_x, f(r)] = [L_y, f(r)] = [L_z, f(r)] = [\vec{L}^2, f(r)] = 0. \quad (18)$$

Also, obviously, if a wavefunction depends *only* on  $r$  (but not on  $\theta, \phi$ ) it can be simultaneously an eigenfunction of  $L_x, L_y, L_z$  and  $\vec{L}^2$ . In all cases, the corresponding eigenvalue will be 0. (This is the only exception to the rule that eigenvalues of one component (e.g.,  $L_x$ ) cannot be simultaneously eigenfunctions of the two other components of  $\vec{L}$ ).

### 3. Eigenvalues and eigenfunctions of $\vec{L}^2$ and $L_z$

Let us find now the common eigenfunctions to  $\vec{L}^2$  and  $L_z$ , for a single particle. The choice of  $L_z$  (rather than, e.g.,  $L_x$ ) is motivated by the simpler expression (see Equation 17).

### 3.1. Eigenvalues of $L_z$

Since, in spherical coordinates  $L_z$  depends only on  $\phi$ , we can denote its eigenvalue by  $m\hbar$  and the corresponding eigenfunctions by  $\Phi_m(\phi)$ . We thus have:

$$L_z \Phi_m(\phi) = m\hbar \Phi_m(\phi), \quad (19)$$

namely

$$-i\frac{\partial}{\partial\phi}\Phi_m(\phi) = m\Phi_m(\phi). \quad (20)$$

The solutions to this equation are

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \quad (21)$$

This is satisfied for any value of  $m$ ; however, physically we require the wave function to be *single valued* (alternatively: *continuous*), namely  $\Phi_m(2\pi) = \Phi_m(0)$ , from which we find

$$e^{i2\pi m} = 1. \quad (22)$$

This equation is satisfied for  $m = 0, \pm 1, \pm 2, \pm 3, \dots$ . The eigenvalues of the operator  $L_z$  are thus  $m\hbar$ , with  $m$  being integer (positive or negative) or zero. The number  $m$  is called the **magnetic quantum number**, due to the role it plays in the motion of charged particles in magnetic fields.

This means, that when measuring the  $z$ -component of an orbital angular momentum, one can only obtain  $0, \pm\hbar, \pm 2\hbar, \dots$ . Since the choice of the  $z$  direction was arbitrary, we see that the component of the orbital angular momentum about **any** axis is quantized.

The wavefunctions  $\Phi_m(\phi)$  are orthonormal, namely

$$\int_0^{2\pi} \Phi_n^*(\phi) \Phi_m(\phi) d\phi = \delta_{nm}. \quad (23)$$

Furthermore, they form a complete set, namely every function  $f(\phi)$  can be written as

$$f(\phi) = \sum_{m=-\infty}^{+\infty} a_m \Phi_m(\phi), \quad (24)$$

where the coefficients  $a_m$  are C-numbers.



### 3.2. Simultaneous eigenvalues of $L^2$ and $L_z$

Let us denote simultaneous eigenfunctions of the operator  $L^2$  and  $L_z$  as  $Y_{lm}(\theta, \phi)$ . We will write the eigenvalues of  $L^2$  as  $l(l+1)\hbar^2$  (from reason which will become clear shortly). We then have:

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (25)$$

and

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \quad (26)$$

Comparing equation 26 and equation 19, we see that we can separate  $Y_{lm}(\theta, \phi)$ ,

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta) \Phi_m(\phi) \quad (27)$$

where the functions  $\Phi_m(\phi)$  are given by Equation 21,  $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ .

Using the expression for  $L^2$  in spherical coordinates (Equation 17), we write Equation 25 as

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y_{lm}(\theta, \phi) = -l(l+1) Y_{lm}(\theta, \phi). \quad (28)$$

Using the variable separation, as well as equation 21 for  $\Phi_m(\phi)$ , Equation 28 becomes

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) + \left\{ l(l+1) - \frac{m^2}{\sin^2 \theta} \right\} \right] \Theta_{lm}(\theta) = 0 \quad (29)$$

This equation is not easy to solve. In order to proceed, we change variable, writing  $w = \cos \theta$  and  $F_{lm}(w) = \Theta_{lm}(\theta)$ . Equation 29 becomes

$$\left[ (1-w^2) \frac{d^2}{dw^2} - 2w \frac{d}{dw} + l(l+1) - \frac{m^2}{1-w^2} \right] F_{lm}(w) = 0 \quad (30)$$

This equation is known in mathematics as the **Legendre's associated differential equation** (the  $m = 0$  case is simply called **Legendre's differential equation**), honoring the French mathematician [Adrien-Marie Legendre](#).

The solutions to this equation are given by the **associated Legendre's functions**,  $P_l^m(w)$ , which are defined by

$$P_l^m(w) = (1-w^2)^{|m|/2} \left( \frac{d}{dw} \right)^{|m|} P_l(w), \quad (31)$$

where  $P_l(w)$  is known as the  **$l$ th Legendre polynomial**, which is defined by the **Rodrigues formula**,

$$P_l(w) = \frac{1}{2^l l!} \left( \frac{d}{dw} \right)^l (w^2 - 1)^l \quad (32)$$

In order for Rodrigues formula to make sense,  $l$  **must be non-negative integer**. Moreover, if  $|m| > l$ , then Equation 31 implies  $P_l^m = 0$ . Thus, the physically accepted values of  $l$  and  $m$  are

$$\begin{aligned} l &= 0, 1, 2, \dots \\ m &= -l, -l+1, \dots, -2, -1, 0, 1, 2, \dots, l-1, l. \end{aligned} \quad (33)$$

This result can be understood physically as follows: Since  $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ , the expectation value of  $\mathbf{L}^2$  in a given state  $\Psi$  is  $\langle \mathbf{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$ . Since  $L_x$  and  $L_y$  are Hermitian,  $\langle L_x^2 \rangle \geq 0$  and  $\langle L_y^2 \rangle \geq 0$ , and therefore

$$\langle \mathbf{L}^2 \rangle \geq \langle L_z^2 \rangle \quad (34)$$

For a state  $\Psi$  such that its angular part is an eigenfunction of both  $\mathbf{L}^2$  and  $L_z$ , we thus have from Equations 25, 26 and 34

$$l(l+1) \geq m^2, \quad (35)$$

from which the result in Equation 33, namely that  $m$  is restricted to  $|m| \leq l$  follows. The quantum number  $l$ , whose allowed values are given in Equation 33, is called the **orbital angular momentum quantum number**.

By using Rodrigues formula (Equation 32), one can immediately find the first few Legendre Polynomials:

$$\begin{aligned} P_0(w) &= 1; \\ P_1(w) &= \frac{1}{2} \frac{d}{dw}(w^2 - 1) = w; \\ P_2(w) &= \frac{1}{2}(3w^2 - 1); \\ P_3(w) &= \frac{1}{2}(5w^3 - 3w); \\ P_4(w) &= \frac{1}{8}(35w^4 - 30w^2 + 3); \\ P_5(w) &= \frac{1}{8}(63w^5 - 70w^3 + 15w); \end{aligned} \quad (36)$$

and so on.

Using Equation 31, one can determine the associated Legendre's functions,  $P_l^m$ . The first few are (inserting again  $w = \cos \theta$ ):

$$\begin{aligned} P_0^0 &= 1; \\ P_1^0 &= \cos \theta; & P_1^1 &= \sin \theta; \\ P_2^0 &= \frac{1}{2}(3 \cos^2 \theta - 1); & P_2^1 &= 3 \sin \theta \cos \theta; & P_2^2 &= 3 \sin^2 \theta; \\ P_3^0 &= \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta); & P_3^1 &= \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1); & P_3^2 &= 15 \sin^2 \theta \cos \theta; & P_3^3 &= 15 \sin^3 \theta; \end{aligned} \quad (37)$$

etc.

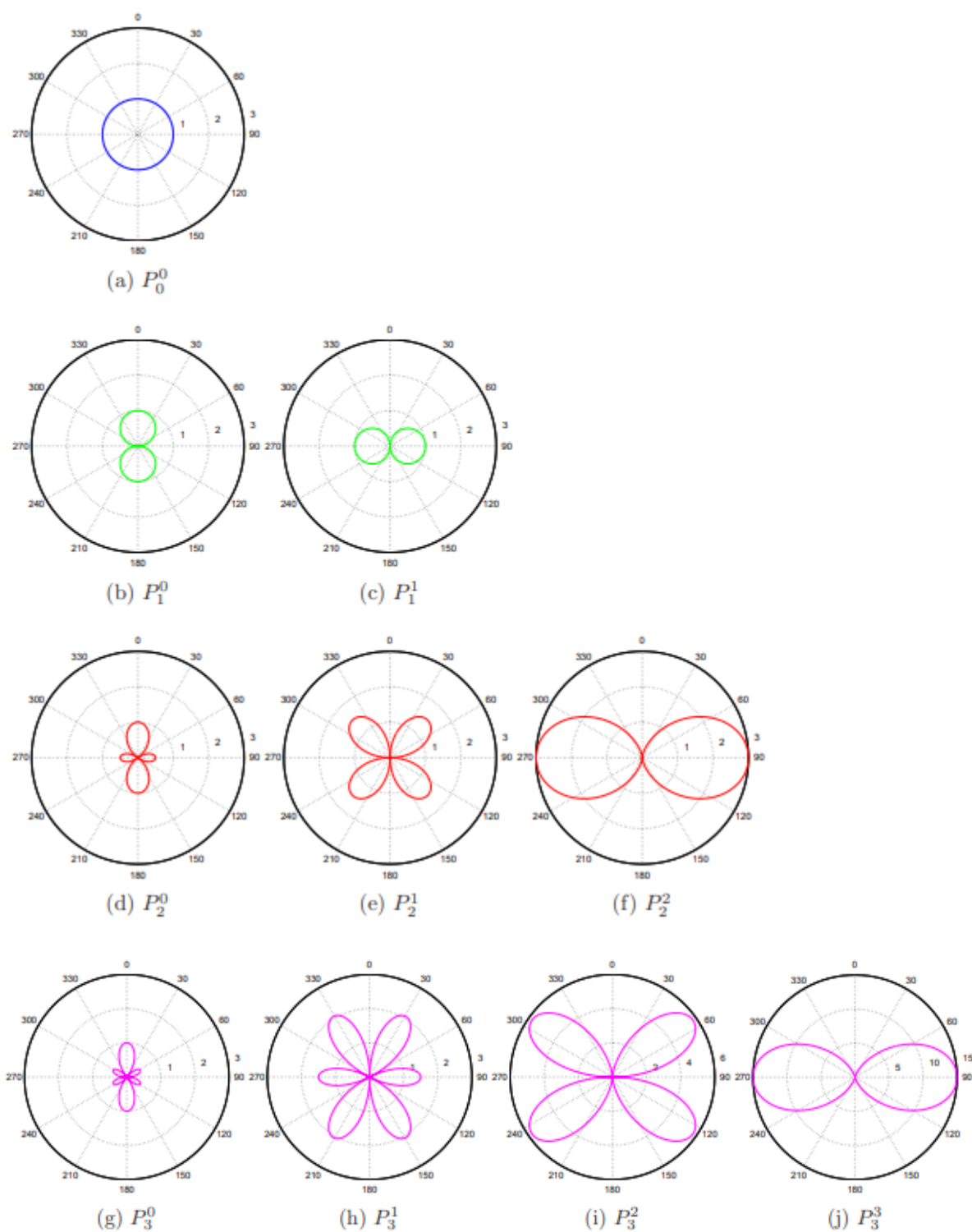


Fig. 1.— Polar plots of  $r = \text{abs}[P_l^m(\theta)]$  as a function of  $\theta$ .

Plots of the first few associated Legendre functions,  $P_l^m(\theta)$  are shown in Figure 1.

Using Rodrigues formula and integrating by parts, one can show that the associated Legendre's functions,  $P_l^m$  are *orthogonal* to each other, but *are not normalized* to unity, namely:

$$\int_{-1}^{+1} dw P_l^{|m|}(w) P_{l'}^{|m|}(w) = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ll'} \quad (38)$$

However, with the use of Equation 38, one can multiply  $P_l^m(w)$  with the appropriate normalization factor, and obtain a normalized solution  $F_{lm}(w)$  to Equation 30 - up to an uncertain phase factor of modulus 1.

The corresponding physical solutions to equation 29  $\Theta_{lm}(\theta)$  are given by

$$\Theta_{lm}(\theta) = \begin{cases} (-1)^m \left[ \frac{(2l+1)}{2} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta), & m \geq 0 \\ (-1)^m \Theta_{l|m|}(\theta) & m < 0. \end{cases} \quad (39)$$

These functions are normalized, namely

$$\int_0^\pi \Theta_{l'm}^*(\theta) \Theta_{lm}(\theta) \sin(\theta) d\theta = \delta_{ll'}. \quad (40)$$

We can now (finally) write the simultaneous eigenfunctions  $Y_{lm}(\theta, \phi)$  common to the operators  $\mathbf{L}^2$  and  $L_z$  (see equations 25 and 26) as

$$Y_{lm}(\theta, \phi) = \begin{cases} (-1)^m \left[ \frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}, & m \geq 0 \\ (-1)^m Y_{l,-m}^*(\theta, \phi) & m < 0. \end{cases} \quad (41)$$

(where we have adopted the commonly use convention for the phase). These functions are known as **spherical harmonics**.

The spherical harmonics are normalized to unity on a unit sphere, and are orthogonal:

$$\int Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) d\Omega \equiv \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) = \delta_{ll'} \delta_{mm'} \quad (42)$$

They further form a **complete set**, namely, every (arbitrary) function  $f = f(\theta, \phi)$  can be expanded as

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta, \phi) \quad (43)$$

The lowest order spherical harmonics are summarized in table 1.

$l$	$m$	$Y_{lm}(\theta, \phi)$
0	0	$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
1	0	$Y_{1,0} = \left(\frac{3}{8\pi}\right)^{1/2} \cos \theta$
	$\pm 1$	$Y_{1,1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$
2	0	$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$
	$\pm 1$	$Y_{2,\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$
	$\pm 2$	$Y_{2,\pm 2} = \mp \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$Y_{3,0} = \left(\frac{7}{16\pi}\right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$
	$\pm 1$	$Y_{3,\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
	$\pm 2$	$Y_{3,\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
	$\pm 3$	$Y_{3,\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$

Table 1: The first few spherical harmonics,  $Y_{lm}$ .



The discovery of the Zeeman effect (1896) and its theoretical interpretation demonstrated that atoms have magnetic dipole moments. However, no constraint was placed on the orientation of the moments by the "classical" explanation of the *normal* Zeeman effect, in which the spectral lines of some elements in a magnetic field are split into three components. Bohr's theory (1913) of the hydrogen atom assumed circular orbits and required the quantization of angular momentum and, by implication, quantization of the associated magnetic moment. Sommerfeld (1916) generalized the Bohr theory to allow elliptical orbits described by three quantum numbers:  $n$ ,  $k$ , and  $m$ . The number  $n = 1, 2, 3, \dots$ , called the principal quantum number, corresponded to the quantum number of the Bohr theory. The number  $k = 1, 2, 3, \dots, n$  defined the shape of the orbit which was circular for  $k = n$ . The number  $m = -k, -k + 1, \dots, k - 1, +k, m \neq 0$ , determined the projection of the vector angular momentum on any prescribed axis, a consequence of the theory that was called space quantization. Sommerfeld showed that his theory could account for the fine structure of the hydrogen atom (now explained in terms of spin-orbit coupling) when relativistic effects on the motion in the elliptical orbits were considered. The Sommerfeld theory also provided an alternative explanation of the normal Zeeman effect. Nevertheless, the question remained as to whether space quantization really occurs, e. g., whether the projections of the angular momentum and its associated magnetic moment on an axis defined by the direction of an imposed magnetic field are quantized.

Otto Stern proposed (1921) a definitive experiment to decide the issue. It would consist of passing a beam of neutral silver atoms through an inhomogeneous magnetic field and observing how the beam was deflected by the force exerted by the field on the magnetic dipole moments of the atoms. The detector would be a glass plate on which the silver atoms in the deflected beam would be deposited. Since the silver atom has one valence electron, it was assumed that  $k = n = 1$  and  $m = \pm 1$  in the ground state. If the magnetic moments were randomly oriented, then the distribution of deflections would decrease monotonically on either side of zero deflection, reflecting a random distribution of the dipole orientations. If space quantization was a reality, then the beam should be split into two distinct beams corresponding to the parallel and anti-parallel alignments of the magnetic moments with respect to the direction of the inhomogeneous magnetic field. Stern was clumsy with his hands and never touched the apparatus of his experiments. He enlisted Walther Gerlach, a skilled experimentalist, to collaborate in the experiment.

Stern predicted that the effect would be just barely observable. They had difficulty in raising support in the midst of the post war financial turmoil in Germany. The apparatus, which required extremely precise alignment and a high vacuum, kept breaking down. Finally, after a year of struggle, they obtained an exposure of sufficient length to give promise of an observable silver deposit. At first, when they examined the glass plate they saw nothing. Then, gradually, the deposit became visible, showing a beam separation of 0.2 millimeters!

Apparently, Stern could only afford cheap cigars with a high sulfur content. As he breathed on the glass plate, sulfur fumes converted the invisible silver deposit into visible black silver sulfide, and the splitting of the beam was discovered.

The new quantum mechanics of Heisenberg, Schrödinger, and Dirac (1926-1928) showed that the orbital angular momentum of the silver atom in the ground state is actually zero. Its magnetic moment is associated with the intrinsic spin angular momentum of the single valence electron the projection of which has values of  $\pm\frac{\hbar}{2}$ , consistent with the fact that the silver beam is split in two. If Stern had chosen an atom with  $L = 1, S = 0$ , then the beam would have split into three, and the gap between the  $m=+1$  and  $m=-1$  beams would have been filled in, and no split would have been visible! Vol. II, chapters 34 and 35, and Vol. III, chapters 5 and 6 of the Feynman Lectures gives a lucid explanation of the quantum theory of the Stern-Gerlach experiment. Platt (1992) has given a complete analysis of the experiment using modern quantum mechanical techniques. Here we present an outline of the essential ideas.

## **Review Questions**

### **Part A**

1. Define electron angular momentum
2. Express Eigen functions and Eigen values of angular momentum
3. What do you mean by space quantization
4. Appraise on the terms electron spin and spin angular momentum
5. State Larmors theorem
6. Differentiate spin magnetic moment and electron magnetic moment
7. Demonstrate the principle of Stern Gerlach experiment
8. Describe Zeeman effect
9. What do you mean by Electron Magnetic energy
10. Write about Gyromagnetic ratio and Bohr magneton

### **Part B**

1. Deduce Eigen functions and Eigen values of angular momentum in spherical polar coordinates
2. Explain in detail Stern Gerlach experiment with schematic diagram
3. Discuss electron spin and spin angular momentum
4. Summarise about Larmors theorem in Quantum mechanics