Book 1

Introductory Atomic Physics and Quantum Mechanics

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Chapter 1

Introductory Atomic Physics

I.1.1 Introduction

An understanding of modern solid state theory is possible only after the fundamentals of quantum mechanical principles and the application of these principles to atomic systems are clearly understood. With this in mind, we will proceed to develop the concepts of quantum mechanics and their application to physical systems in Part I of the book. In Chapter I, we will trace the inability of concepts of classical physics to explain some of the experimental observed phenomena, In particular, classical physics proved to be unsuccessful in the following areas:

(1) Inability to provide a satisfactory theory of the atom
(2) Inability to explain the characteristic spectral lines of the various elements
(3) Failure to provide a theory for the observe characteristics of thermal radiation
(4) inadequacy to explain the photoelectric phenomenon

Planck (thermal radiation), Einstein (Photoelectric effect) and Bohr (atomic model) made some bold assumptions to remove the failures of classical physics. Each made hypothetical assumptions to suit his particular model. There was no justification for these assumptions other than the fact that the model explained the experimental results.

In the following paragraphs we will discuss the above failures of classical physics and the models of Planck, Einstein and Bohr.

I.1.2 Early Atomic Theories

As in other fields, the early Greeks contributed to the modern atomic theory. Democritus (460-370 BC) postulated that “the universe consists of empty space and an almost infinite number of indivisible and invisible particles” which differ in form, position and arrangement. These elementary particles were called atoms. The developments in the field of chemistry in the 19^{th} century led to the

distinction between atoms and molecules. A collection of atoms of one type which cannot be decomposed into simpler units by any chemical transformation is called an element. The elements can be combined in many ways to form compounds. The smallest particle preserving the characteristics of the compound is called the molecule and the smallest particle similarly preserving the characteristics of the element is called the atom. The size of the atom or the molecule is so small that only indirect evidence for their existence can obtained.

The interest in atomic structure was renewed with the discovery of electrons in low pressure gas discharge experiments towards the end of the 19^{th} century. Since electrons came from atoms it was surmised that any model for the structure of atoms should have electrons in it. Since electrons are negative in charge and atoms are neutral, it was concluded that the atoms also continued positive charge to neutral, it was concluded that the atoms also contained positive charge to neutralize the electronic charge. Then two questions arose-how many electrons are there in an atom, and how are these electrons and positive charges arranged within an atom? Rutherford, based on his alpha-particle experiment, proposed a new model for an atom in which he said that the positive charge and most of the atomic mass are concentrated in a very small central region which came to be called later, the nucleus, about which the electrons are grouped in some sort of configuration, Rutherford's model suffered from many disadvantages because it did not say anything about the location or movement of the electrons or the nucleus. It gave no explanation on how these electrons could remain in equilibrium about the nucleus. If, as in planetary motion, electrons were assumed to be moving in an orbit, then classical theory would lead to loss of energy through radiation which would cause the electron to spiral towards the nucleus and finally fall into the nucleus. Another defect of the Rutherford model was that it did not explain the observed spectroscopic effect.

I.1.3 Early Spectroscopy

In 1666 Isaac Newton discovered that white light could be split up into component colors by means of a prism. By the beginning of the 19^{th} century, wave theory of light was generally accepted. According to this theory, light is a wave phenomenon and the colors of light are due to waves of different

wavelengths or frequencies. When light given off by an ionized vapor of an element was examined with a prism or a grating which had better resolution than a prism, the spectrum that was obtained consisted not of just a continuous spectrum, but a series of lines in the spectrum. Such spectra were different from element to element but it was always the same for a particular element. In 1885, Balmer discovered that the wavelength of the nine then known lines in the spectrum of hydrogen can be expressed very closely by the formula

$$\lambda = b\ \frac{n^2}{n^2-4} \quad \text{where } n = \text{integer greater than 2} \qquad \text{(I.1.1)}$$

If λ, the wavelength is expressed in Angstrom units ($10^{-10}\ meter$), then b turned out to be 3645.6. n is a variable integer which takes on successive integral values greater than 2; namely, $3,4,5$, etc. In announcing this discovery Balmer raised the question as to whether or not his formula might be a special case of a more general formula applicable to other series of lines in other elements. Rydberg carried experimental work further and found that a universal formula for line wavelengths of all spectra exists in the form

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} - \frac{R}{n^2} \qquad \text{(I.1.2)}$$

where λ_1 is equal to the short wavelength limit of the series and n is an integer with a particular lower limit for each series. R is equal to a universal constant called the Rydberg constant and is numerically equal to $1.0974\ \times 10^{-7}\ m^{-1}$.

With such obvious order in the spectral of hydrogen and other elements it appeared that any model of atomic structure should be capable of explaining the spectral series and give quantitative agreement to the wavelengths of the observed spectral series. But, as pointed out earlier, Rutherford's model could not explain the spectral series that was observe by Balmer or Rydberg. It was not until Bohr used some bold assumptions in proposing a new atom model that the spectral series was explained.

I.1.4 Thermal Radiation

When a body is heated it emits energy in the form of radiation and the quantity and quality of the radiation depends on the temperature of the body.

When an incandescent lamp filament is heated the amount of energy radiated by the filament in unit time increases rapidly with increase in the temperature of the filament. The spectral characteristic of the emitted energy also changes as the temperature increases. It is also known that when thermal or light energy falls on a body, the body absorbs some of the energy and scatters the rest of the energy. At thermal equilibrium the amount of energy emitted by a body is the same as the amount of energy absorbed by the body. An ideal black surface is defined as that one which has the property that it absorbs completely all the radiation that is incident on that surface, none of the radiation being reflected. Since in thermal equilibrium the amount of energy emitted is the same as the amount of energy absorbed, black surface is also an ideal radiator. α , the absorption coefficient, is equal to $1 - r$ where r is the reflection coefficient.

It was shown by Hertz that visible and electromagnetic radiation were the same phenomena. The electromagnetic spectrum starts from a very low frequency radio wave through ultrahigh frequency radio wave. If the frequency is raised still farther we go to heat waves after which comes the visible spectrum and then the x-rays. The visible spectrum which is sandwiched between the infrared heat waves and the ultraviolet waves is just a small part of the entire spectrum. Therefore, thermal radiation, radio waves, light waves, are all one and the same. The energy that is emitted by a black body at a particular temperature is not uniformly distributed over the entire spectrum. There is a particular wavelength for a given temperature at which maximum radiation of energy takes place. This was stated as a law by Wien and Wien's displacement law states that as the temperature of a black body is raised, the wavelength at which maximum emission occurs, move in the direction of shorter wavelength such that the product $\lambda_{max}T$ is a constant. It was found experimentally by Lummer and Pringsheim that $\lambda_{max}T = 0.2896\ cm$ degrees.

The total radiation of energy (irrespective of the spectral distribution) was found to be varying as the fourth power of the absolute temperature. This is called Stefan's Law which was empirically derived according to which

$$I_T = \sigma T^4 \qquad \text{(I.1.3)}$$

Where $I_T =$ total energy emitted (over the entire wavelength spectrum) per unit time by unit area of a black body at temperature T. σ is called Stefan's constant

and is equal to 5.67 Joules/ $meter^2 degree^4 sec$. If the body was not an ideal black body but was characterized by an emissive power $\epsilon \neq 1, then\ I_T$ was given by

$$I_T = \epsilon \sigma T^4 \tag{I.1.4}$$

Two notable theories were advanced to explain the spectral variation of thermal radiation by a hot body. The first is called Wien's Displacement Law and the second is called Rayleigh-Jean Theory. Either of the two theories was not satisfactory in that, the first one did not give the functional form of the dependence of spectral distribution on λT and the latter theory agreed with experimental results only a long wavelengths, i.e., much longer than λ_{max}.

The spectral distribution of energy radiated by a black body was correctly determined by Planck. He assumed the existence of one dimensional harmonic oscillators which interacted with the radiation field. He hypothesize that

(i) Each oscillator absorbs energy from the radiation field continuously according to the laws of electrodynamics.

(ii) An oscillator can radiate energy only when its total energy is an exact integral multiple of a certain unit of energy for that oscillator. When it radiates it radiates all of its energy.

(iii) The probability of non-emission to emission of energy is proportional to the intensity of the radiation that excites the oscillator.

Planck assumed that the oscillator would radiate energy when its energy is equal to $nh\upsilon$

where $\upsilon =$ frequency of the oscillator

$n =$ Integer

$h =$ a constant called Planck's constant

In other words, Planck quantize the energy of the oscillator to be an integral multiple of a unit of energy equal to $h\upsilon$. Using these hypotheses, he arrived at the following expression for the actual energy distribution:

$$I(\lambda, T)d\lambda = \frac{2\pi c^2 h}{\lambda^5\left(e^{\frac{ch}{\lambda kT}} - 1\right)} d\lambda \tag{I.1.5}$$

The numerical value of Planck's constant h is equal to $6.62562 \times 10^{-34} Joule - sec$.

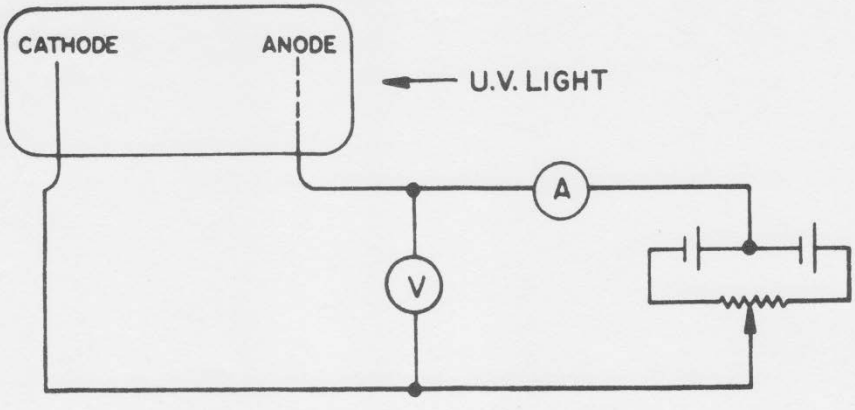
where $I(\lambda, T)d\lambda$ is the energy radiated by the unit area of the black body in unit time at temperature T, between wavelengths $\boldsymbol{\lambda}$ and $\boldsymbol{\lambda}$ + d$\boldsymbol{\lambda}$.

I.1.5 Einstein's Photoelectric Equation

Planck's hypothesis quantized only the energy of the oscillator and not the energy of the electromagnetic field.

It was Einstein who proposed that the radiation field itself should be quantized and he put forward the famous photoelectric equation to explain the observed facts of photoelectric phenomenon. The experimental verification of Einstein's photoelectric equation put Planck's quantum hypothesis on a sound basis.

The photoelectric effect was first discovered by Hertz on 1887. His apparatus is shown in Figure I.1.1. A polished metal electrode called the cathode and perforated metal plate called the anode are contained in an evacuated glass chamber. When a positive potential is applied to the anode with respect to the cathode and ultraviolet light falls on the cathode, electrons are emitted by the cathode and collected by the anode and a current flows through the ammeter in the external circuit. This phenomenon is called the photoelectric phenomenon.

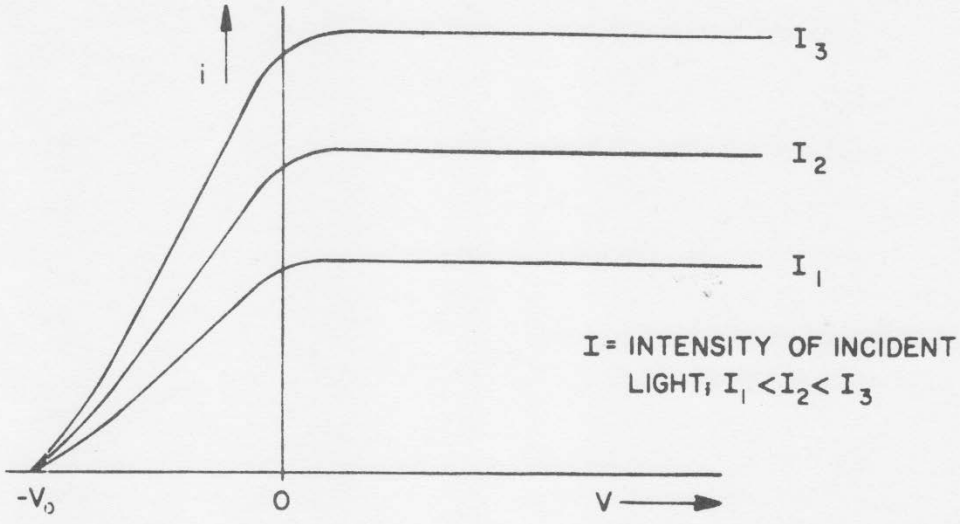


PHOTOELECTRIC CELL

FIGURE I. 1. 1

Referring to the apparatus shown in Figure (I.1.1) if the voltage on the anode is reduced to zero and then made negative, some of the photoelectrons will be repelled. At some value of negative voltage, $-V_0$, even the most energetic electron will be repelled and this value of voltage, $-V_0$, is known as the cut-off voltage. A plot of the photoelectric current I versus the anode voltage V, obtained typically in an experiment for various values of incident intensity of monochromatic beam of light is shown in Figure (I.1.2).

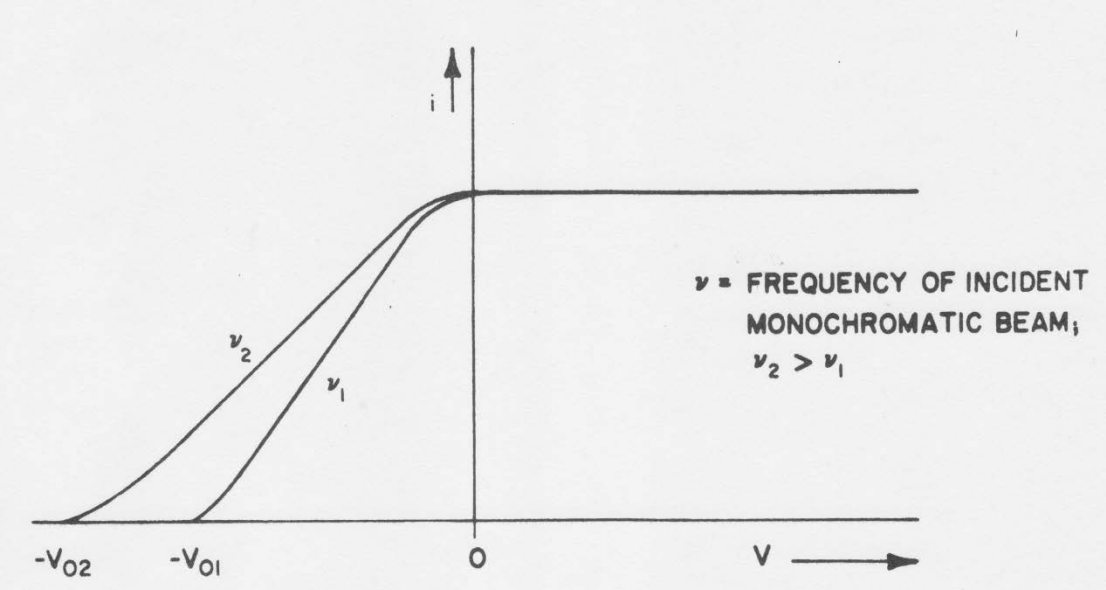
The maximum energy of the electron ejected from the cathode is equal to $-V_0$ where $-V_0$ is the cut-off voltage. As we increase the intensity of light falling on the cathode (measured in joules per second). We will expect classically the added energy to increase the kinetic energy of the emitted electrons and therefore the cut-off voltage $-V_0$ should vary with the intensity of light, a higher intensity giving rise to a more negative cut-off voltage. But experiment does not agree with this prediction, as shown in Figure (I.1.2), where the cut-off voltage remains a constant independent of the intensity.



PLOT OF i-v CHARACTERISTIC OF A PHOTOELECTRIC CELL AT VARIOUS INCIDENT INTENSITIES

FIGURE I. 1. 2

On the other hand, if the frequency of the incident monochromatic beam of light is varied keeping the intensity constant, the experimental i-v curves shown in Figure (I.1.3) are obtained. These curves show that the cut-off voltage varies with the frequency of the incident light, higher frequency corresponding to a more negative cut-off voltage. This showed that the maximum energy of the ejected electrons increased with the frequency of the incident light beam. This result could not be explained classically.



EFFECT OF FREQUENCY OF LIGHT ON THE PHOTOELECTRIC CHARACTERISTIC

FIGURE I. 1. 3

Einstein gave a successful explanation of the photoelectric phenomenon by proposing that the radiation field itself be quantized. According to Einstein's photoelectric theory, energy is discrete and not indefinitely divisible. The smallest unit of energy which can be absorbed or emitted in a single process is called a quantum. A quantum of radiation energy (electromagnetic waves) is called a photon. The energy E of a photon is proportional to the frequency υ, of the electromagnetic wave and the constant of proportionality is Planck's constant h.

i.e., $E = h\,\upsilon$

The light falling on the metal can act only as photons of energy hitting the surface of the metal. If a photon is absorbed, it means that some electron has

increased its energy by an amount equal to the photon energy. Normally the electrons are bound to the surface of the metal by a potential barrier called the surface barrier, i.e., it takes a certain amount of energy to pull an electron out from the metallic surface. The electrons have some energy inside the metal but this is not sufficient for them to overcome the surface barrier. The energy of the electrons inside the metal follows some distribution law. The difference between the height of the surface barrier and the energy of the most energetic electrons, called the work function of the metallic surface, (Figure I.1.4) represents the minimum amount that the electrons should increase their energy by, so that at least some electrons will be freed from the metallic surface. The electrons leaving the metallic surface have some initial velocity and a negative voltage on the anode tends to repel theses ejected electrons. At any given negative voltage $-V$, on the anode with respect to the cathode, only those electrons whose initial velocity v satisfies the relation

$$\frac{1}{2}\, m\, v^2 \geq e\, V$$

where $e =$ electronic charge

$m =$ mass of the electron

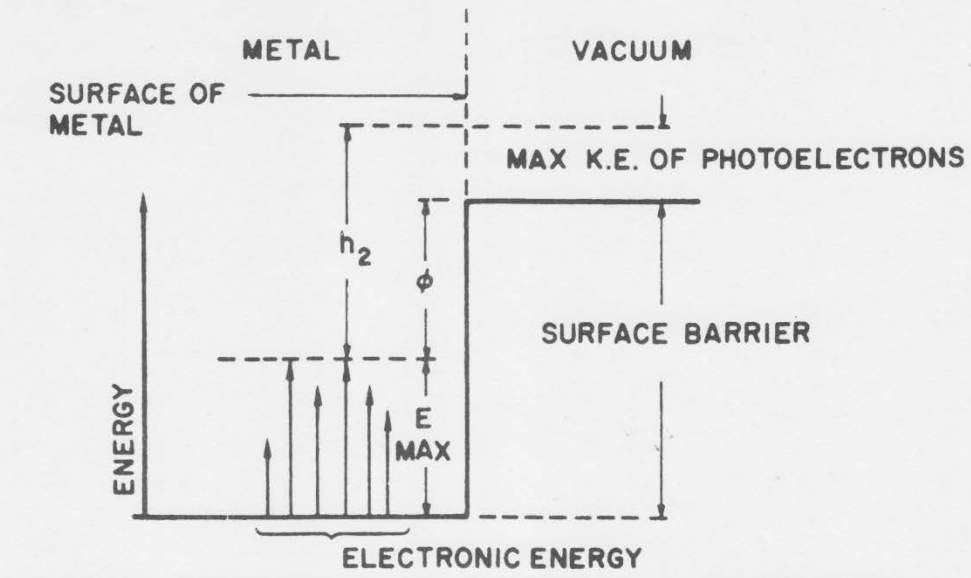
will be able to reach the anode. At the cut-off voltage $-V_0$, even the most energetic electrons are just turned away from reaching the anode. This means that the energy of the photon is just equal to the sum of the work function $\emptyset$, and the energy barrier eV_0 due to the retarding voltage on the anode, i.e.,

$$h\,\upsilon = \emptyset + eV_0$$

or

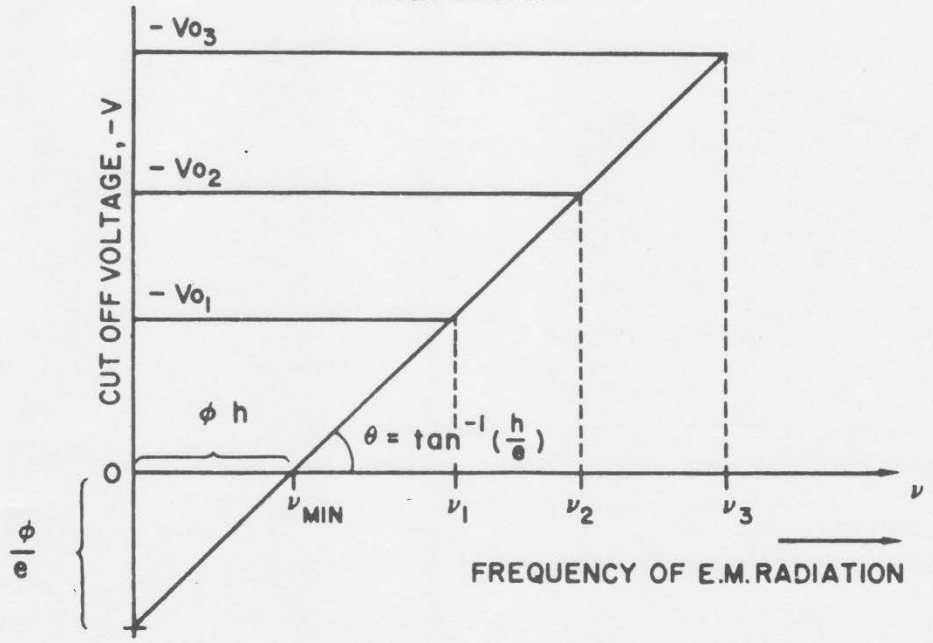
$$V_0 = \frac{h\,\upsilon}{e} - \frac{\emptyset}{e} \qquad \text{(I.1.7)}$$

This equation is known as Einstein's photoelectric equation. This predicts a linear relationship between the cut-off voltage and the frequency of the electromagnetic radiation, and is experimentally verified as shown by the straight line graph in Figure (I.1.5). Thus Einstein's photoelectric equation confirmed Planck's quantum hypothesis. However, the most striking confirmation was given by Bohr in his model of the hydrogen atom.



PICTORIAL REPRESENTATION OF ENERGY CONSIDERATIONS IN A PHOTOELECTRIC PROCESS

FIGURE I. 1. 4



EXPERIMENTAL VERIFICATION OF EINSTEIN'S PHOTOELECTRIC EQUATION

FIGURE I. 1. 5

I.1.6 Bohr Atom

Rutherford's nuclear model of the atom could not satisfy the stability criterion based on classical theory of electromagnetism. The electrostatic attractive force between the nucleus and the electron can be balanced by the centrifugal force if the electron is assumed to be rotating around the nucleus. On the other hand, an accelerating electron has to radiate energy according to classical theory and, therefore, would eventually collapse on the nucleus. This apparent conflict was resolved in 1913 by Niels Bohr who gave a successful model of the hydrogen atom Bohr postulated that:

(1) The hydrogen atom consists of heavy nucleus with a positive charge and an electron (negative charge) moving in a circular orbit as in a planetary motion, under the action of the electrostatic attraction between the nucleus and the electron.

(2) Instead of moving in any circular orbit with a radius anywhere from 0 to infinity, it is possible for the electron to move only in orbits for which the angular momentum is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant.

(3) An electron moving in an allowed orbit of energy though under constant acceleration, does not radiate energy and therefore has constant energy.

(4) If an electron, initially in an orbit of energy E_i, jumps to an orbit of energy E_f ($E_i > E_f$), electromagnetic radiation is emitted with a frequency υ

$$\upsilon = \frac{E_i - E_f}{h}$$

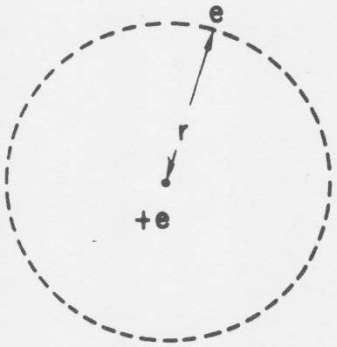
These postulates laid down by Bohr, combine classical and non-classical physics. The first postulate accepts the idea of a nucleus and an electron remaining in equilibrium according to the laws of classical electrostatics and classical mechanics. The second postulate quantizes the orbital angular momentum, and, therefore, the energy. Bohr's quantization of the orbital angular momentum is a particular case of a more general quantization rule laid down later by Sommerfeld according to which the phase integral of any variable over a complete cycle of its motion must be equal to an integral number of h:

$$\oint p_i dq_i = n_i h$$

In this formula, p_i is the generalized momentum conjugate to be generalized coordinate q_i and $\oint$ means an integral over a complete cycle of its motion. Thus if q_i is an angle, p_i is the corresponding angular momentum. If q_i is the position coordinate then p_i is the component of the linear momentum corresponding to q_i.

The third postulate again violates classical physics according to which accelerated electrons should radiate energy. The fourth postulates is called Einstein's frequency condition.

We can now proceed to determine the energy states of the hydrogen atom. Consider the heavy nucleus of charge $+e$ to be fixed in space and the elctron (of charge $-e$) which is very light in comparison to the heavy nucleus, to be rotating in a circular orbit around the nucleus, as shown in (Figure I.1.6)



AN ELECTRON IN A CIRCULAR ORBIT AROUND THE NUCLEUS ACCORDING TO BOHR'S MODEL OF THE HYDROGEN ATOM

FIGURE I. 1. 6

The electrostatic attractive force between the nucleus and the electron is given by Coulomb's law to be:

$$F = \frac{e^2}{4\,\pi\,\epsilon_0\,r^2}$$

where ϵ_0 = permittivity of free space.

The centrifugal force balances the electrostatic attractive force and therefore:

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2} \tag{I.1.8}$$

where $m =$ mass of the electron

$v =$ velocity of the electron in its orbit

$r =$ radius of the orbit

According to Bohr's second postulate, the angular momentum is quantized, i.e.,

$$m\,v\,r\ = n\ \frac{h}{2\pi} = n\hbar \tag{I.1.9}$$

From Equation (I.1.8), we have

$$mv^2 = \frac{e^2}{4\,\pi\,\epsilon_0\,r^2} \tag{I.1.10}$$

Squaring (I.1.9) and substituting (I.1.10) we have

$$m \cdot \frac{e^2}{4\,\pi\,\epsilon_0\,r} \cdot\ r^2 =\ n^2\hbar^2$$

i.e.,

$$r =\ \frac{4\,\pi\,\epsilon_0\,n^2h^2}{m\ e^2} \tag{I.1.11}$$

We will now calculate the total energy of the hydrogen atom with an electron in one of the allowed orbits. The potential energy is defined to be zero when the electron is at infinite distance from the nucleus. Then the potential energy V, at a distance r is obtained by integrating the work done in bringing the elctron from infinity to r:

$$V = \int_{\infty}^{r} \frac{e^2}{4\,\pi\,\epsilon_0\,r^2}\,dr = \frac{-\,e^2}{4\,\pi\,\epsilon_0\,r}$$

The kinetic energy, T, is equal to $\frac{1}{2}mv^2$ and from (I.1.10) is equal to

$$T = \frac{1}{2}mv^2 = \frac{1}{2}mv^2 = \frac{1}{2}\,\frac{e^2}{4\,\pi\,\epsilon_0\,r}$$

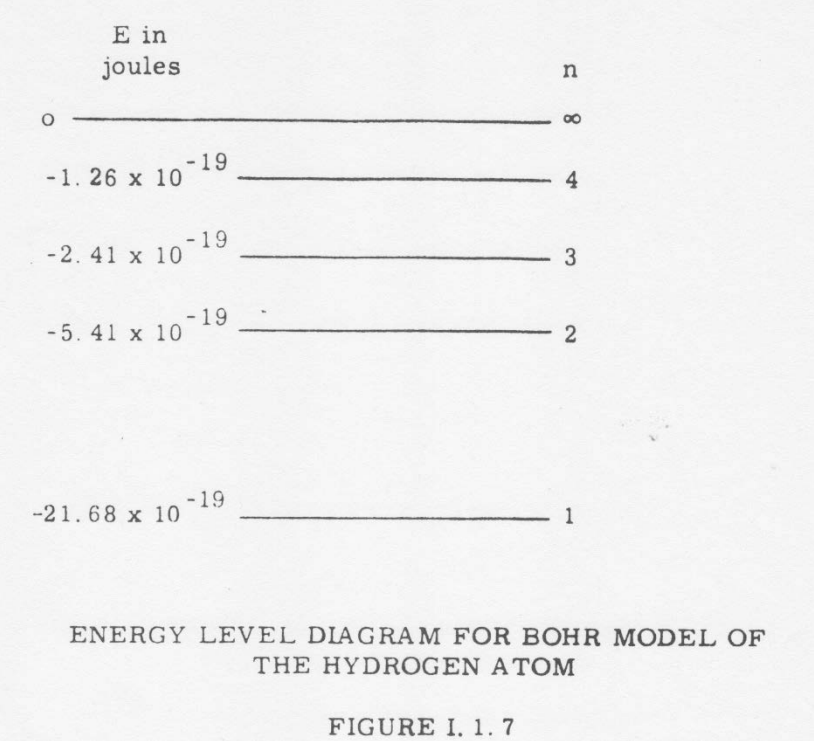
The total energy E is equal to

$$E = T + V = -\frac{1}{2}\,\frac{e^2}{4\,\pi\,\epsilon_0\,r} \qquad \text{(I.1.12)}$$

Substituting for r from (I.1.11) in (I.1.2) we have

$$E = -\frac{-m\,e^4}{32\,\pi^2\,{\epsilon_0}^2\hbar^2}\;\frac{1}{n^2} \qquad \text{(I.1.13)}$$

We see that the energy depends upon the integral number 'n' which was used to quantize the orbital angular momentum. Since there is a negative sign before the expression for energy in (I.1.13), the energy increases with increasing values of n. The lowest energy occurs when n is a minimum, i.e., $n = 1$ ($n = 0$ is not permissible since this will correspond to a radius equal to zero). Therefore, the smallest of these orbits corresponding to $n = 1$ is the one that the electron will occupy when the atom is in the "ground" state or when the atom is unexcited.



ENERGY LEVEL DIAGRAM FOR BOHR MODEL OF THE HYDROGEN ATOM

FIGURE I. 1. 7

The energy of each orbit as evaluated from Equation (I.1.13) is shown in Figure I.1.7. Hereafter, we will refer to the quantitation number n as quantum number. We will next set up the expression for the frequency of the electromagnetic radiation emitted when an electron jumps from an orbit of higher energy to one of lower energy. Let the electron be initially in an orbit characterized by the quantum number n_i and energy E_i and let it jump to another

orbit with quantum number n_f and energy E_f. Then the frequency of electdomagnetic radiation according to Einstein's frequency condition is

$$\upsilon = \frac{E_i - E_f}{h} = \frac{-1}{h} \times \frac{m\, e^4}{32\, \pi^2\, {\epsilon_0}^2 \hbar^2} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$
$$= \frac{m\, e^4}{8\ {\epsilon_0}^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

In terms of the wave number $\bar{v}$, this becomes

$$\bar{v} = \frac{m\, e^4}{8\ {\epsilon_0}^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad \text{(I.1.15A)}$$

$$\bar{v} = R\ \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad \text{(I.1.15A)}$$

Where

$R = \frac{m\, e^4}{8\ {\epsilon_0}^2 h^3}$ called the Ryberg constant

The quantitative predictions of Bohr's theory ae contained in Equations (I.1.11), (I.1.13), (I.1.14) and (I.1.15). Normally the hydrogen atom is in the lowest state or ground state $(n = 1)$. It receives energy either from collisions as in electric discharge or by absorption of electromagnetic radiation of suitable frequency and gets excited, i.e., it jumps to higher energy state $(n > 1)$. Since all physical systems are stable only in their lowest energy state, the atom will emit the excess energy and return to the ground state. The frequency of the emitted photon will be governed by Equation (I.1.14).

Earlier we had said that any satisfactory model of the atom should explain the spectroscopic series of lines obtained experimentally. Now, we see that Equation (I.1.15B) is in such a form that Balmer's empirical formula can be obtained by putting $n_f = 2$.

For,

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} = \frac{1}{R\left(\frac{1}{4} - \frac{1}{n_i^2}\right)}$$

$$= \frac{4}{R} n_i^2 \frac{1}{n_i^2 - 4} = b \frac{n_i^2}{n_i^2 - 4} \qquad \text{where} \quad b = \frac{4}{R}$$

It can be also be verified that Rydberg's universal formula can be derived. Other series of lines in the spectrum of hydrogen corresponding to other final states, i.e., other values of n_f were later found. The Laman series which is in the ultraviolet region corresponds to $n_f = 1$ as shown in Figure I.1.8. Paschen series which lies in the infrared region ends up in the terminal state $n_f = 3$ and similarly Brackett series lying in the far infrared region corresponds to $n_f = 4$. The Bohr theory thus gave an expression not only explaining the various spectral series but also quantitatively predicting the value for the coefficient R (Rydberg's constant) which was previously obtained experimentally.

It must be pointed out that the formula developed fort the hydrogen atom can also be applied with suitable but minor modifications to any atom or ion having one electron circling around the nucleus. For example, an ion with a nuclear charge $+Ze$ and an electron circling around it would have the additional factor Z^2 in the expression for its energy.

$$E_n = -\frac{\boldsymbol{Z^2 R\, c\, h}}{\boldsymbol{n^2}}$$

Or

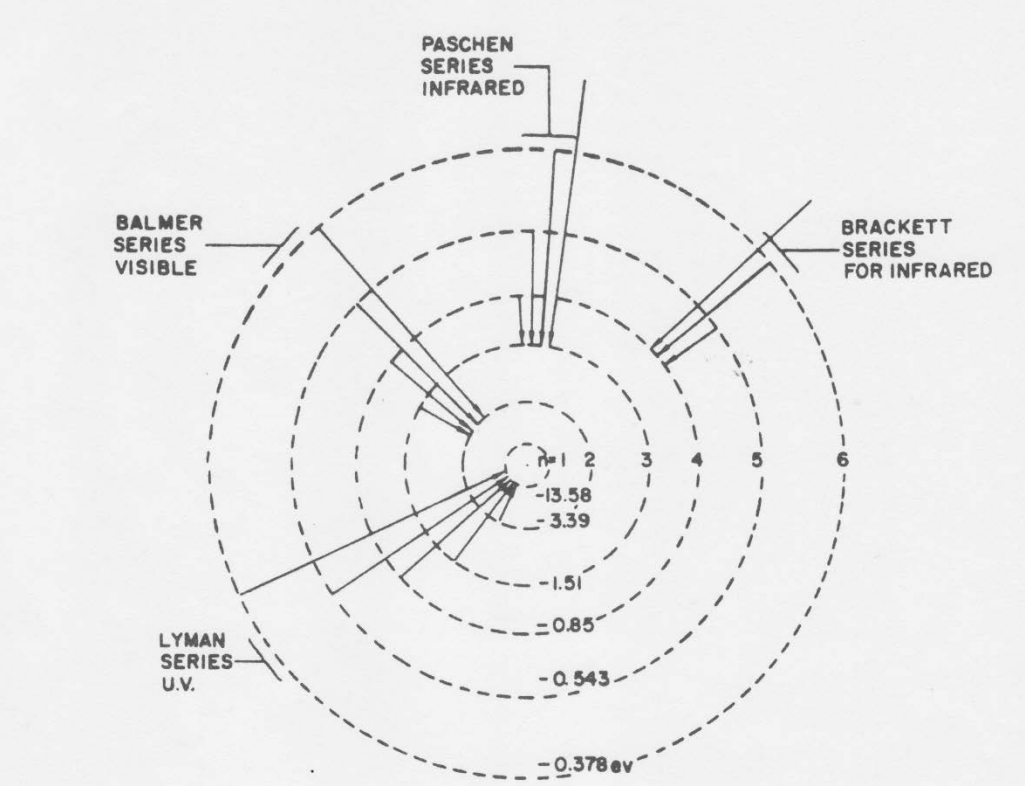
$$\bar{\nu} = Z^2 R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

In the case of singly ionized helium whose atomic number $Z = 2$, we will have

$$\bar{\nu} = 4\, R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

From refinements were added to Bohr's theory when the effect of the finite mass of the nucleus and therefore the motion of nucleus (in Bohr's model, the nucleus was assumed fixed) were taken into account. Again, as instrument became more precise; it was found that there were more spectroscopic lines than

what a single quantum number n could account for. Bohr's circular orbit model was extended to include elliptical orbits using an additional quantum number k. Thje energy or the orbit was still determine only by the first quantum number n. The quantum number k specifies the angular momentum to be $k\ \hbar$ (instead of $n\hbar$ in Bohr's model). The ratio $\frac{k}{n}$ also determines the ratio of the minor to major axis of the ellipse. k can take integral values 1 to n.



VARIOUS SPECTRAL SERIES OF THE HYDROGEN ATOM
(Radii of the orbits not drawn to scale.)
FIGURE I. 1.8

In spite of all these refinements and modifications, Bohr theory was not able to explain the spectra of complex elements. Bohr's theory was fairly successful in explaining the spectra of hydrogenic ions and atoms, i.e., atoms with a single planetary electron around a central charge. But it failed to explain the spectra of even simple elements like helium. Bohr theory had a logical inconsistency as explained earlier, in that it combined the concepts of orbits derived on the basis of classical mechanics with non-classical concepts of quantum transitions. It was necessary to have a new point of view and this was provided by quantum mechanics.

I.1.7 Digression on Units of Energy

In addition to using Joule as a unit of energy it is sometimes more practical to use other units of energy. One electron-volt is a widely used unit of energy in electronics and is equal to the energy of an electron which has been accelerated through a potential of q volt. The kinetic energy acquired by an electron falling through a potential of V volt is equal of eV joules where $e = 1.602 \times 10^{-19}$ coulombs. Therefore, 1 electron-volt $= 1.602 \times 10^{-19}$ joules.

The energy E of a photon of electromagnetic radiation is given by $E = hv$ where v =frequency of the electromagnetic radiation. The frequency of alternately the wave number can therefore be used as a measure of energy. Wave numbers are usually expressed in units of reciprocal centimeter

$$\bar{v} = \frac{1}{\lambda_{vac}} \qquad \text{where } \lambda_{vac} \text{ is in cm}$$

$$= \frac{v}{c} \text{ where c is the velocity of light in cm/second}$$

$$E = h\, c\, \bar{v}$$

Since $h = 6.62 \times 10^{-34}$ Joules sec

And $c = 3 \times 10^{10}\ \frac{cm}{sec}$

One $cm^{-1} = 1.9858\ \times 10^{-23}$ Joules

$= 1.2395 \times 10^{-4}$ eV

Conversion from one unit to another is given in Table 1.

Table 1

Conversion Factors of Energy Units

unit	Joule	Electron-Volt (eV)	cm^{-1}
Joule	1	6.2×10^{18}	5.03×10^{22}
Electron-Volt eV	1.602×10^{-19}	1	8.067.5
cm^{-1}	1.9858×10^{-23}	1.2395×10^{-4}	1

Problem: Chapter I.1

1. Given $I_\lambda d_\lambda$, the energy emitted by unit area of a blackbody surface in unit time between the wavelength $\boldsymbol{\lambda}$ and $\boldsymbol{\lambda}$+dλ, to be given by equation I.1.5 of the text, find out an expression for $I_\upsilon d\upsilon$, the energy emitted by unit area of a blackbody surface in unit time between frequency υ and $\upsilon + d\upsilon$.
2. If Planck's constant, h, had been much smaller than it is, quantum effects would have been harder to discover as separate from the classical picture. What would the Planck formula, above, become in the classical limit for $\mathrm{h} \to 0$
3. What is the energy in electron volts of a photon with wavelength (a) $\boldsymbol{\lambda}$ =10,000 Å, (b) $\boldsymbol{\lambda}$ =3,000 Å (c) =100 Å?
4. The work function of tungsten is 4.52 eV, and that of barium is 2.5 eV. What is the maximum wavelength of light that will give photoemission of electrons from tungsten? From barium? Would either of these metals be useful in a photocell for use with visible light?
5. The work function of tantalum is 4.19 eV. If light of wavelength 2536 Å is incident on a tantalum emitter in a phototube, what value of V_0 will be measured (the collector is also of tantalum)? What value of V_0 do you compute for $\boldsymbol{\lambda}$=3650 Å and what is the physical interpretation of this value?
6. Substituting the appropriate values of constants evaluate Rydberg's constant for hydrogen atom.
7. Show by direct substitution that the ionization energy of a hydrogen atom is 13.6 eV.
8. Calculate the values in electron-volts and plot on the same energy scale, the energies of the various emission lines from Hydrogen for the
   i. Lyman Series
   ii. Balmer Series
   iii. Paschen Series
9. Plot the wavelength of the Lyman Series of emission lines on a scale calibrated in angstroms ($10^{-8} cm$)

Chapter 2

Quantum Mechanical Principles

I.2.1 Introduction

All the earlier theories including Planck's and Bohr's theories used classical mechanics and classical electromagnetic theory in part of the problem but found it necessary to impose certain quantum conditions in certain other aspects of the problem. This is not a satisfactory procedure since no definite rule was laid down as to where classical principles are valid and where they are not. It was necessary to develop a completely revolutionary and self-contained set of laws within which both classical and quantum principles are embodied and which will be applicable to all physical problems.

Such a formulation of new principles of mechanics was put forward simultaneously by Schrödinger, who extended the idea of De Broglie on the wave aspect of matter, and by Heisenberg. Schrödinger's formulation makes use of partial differential equations while Heisenberg's treatment is built around matrix algebra. However, both the formulations are equivalent and predict the same results. Heisenberg's formulations is known as quantum mechanics while Schrödinger's formulation is known as wave mechanics. The wave function ψ appears explicitly in Schrödinger's theory. The terms quantum mechanics and wave mechanics have gradually become synonymous and we shall use only the name "quantum mechanics" although in this course we will be using mainly Schrödinger's formulation.

I.2.2 Wave Aspect of Matter

Louis De Broglie suggested in 1924, based on purely theoretical grounds, that electrons might have wave properties. Radiant energy in the form of light exhibits dual behavior – wave and corpuscular. The wave property is prominent in such phenomena as diffraction and interference. The corpuscular or particle-like behavior is prominent in photoelectric phenomena where the concept of photon is used. Two great entities in the world are energy and matter. De Broglie proposed that matter, like energy, should exhibit dual aspect. Matter and energy are both conserved. The theory of Relativity shows them to be equivalent. Close

analogies are known to exist between certain laws of optics and mechanics. Therefore, they should be alike in their dual properties also. De Broglie proposed that an electron in motion should exhibit properties of a packet of energy with wave properties.

De Broglie postulated that an electron with a momentum p had the wavelength λ given by

$$\lambda = \frac{h}{p} \qquad \text{(I.2.1)}$$

Where h is Planck's constant. This wavelength is referred to as De Broglie wavelength. De Broglie showed that the Bohr orbits of hydrogen can be defined by the condition that the circumference of an orbit contain an integral number of De Broglie wavelengths.

The experimental verification of De Broglie's hypothesis came in 1928 when Davission and Germer determined experimentally that a beam of low energy electrons incident on the face of a nickel crystal is reflected in such a manner that can easily be interpreted as a diffraction of plane waves by the lattice of the crystal. In other worlds, the electrons behaved like plane waves. More experiments on electron diffraction were performed by G.P. Thomson and others, and they all confirmed De Broglie's hypothesis.

Let us now determine the De Broglie wavelength for an electron that has been accelerated by an electrostatic potential V volts. If we assume that the electron is initially at rest, then all its kinetic energy arises only due to the electron falling though the potential V volts. The kinetic energy is therefore equal to

$$\frac{1}{2}mv^2 = eV$$

where $v =$ final velocity

$m =$ Mass of the electron

$e =$ Charge of the electron

The momentum p is equal to $p = mv = (2m\,eV)^{\frac{1}{2}}$. Therefore, the De Broglie wavelength is equal to

$$\lambda = \frac{h}{p} = \frac{h}{(2m\,eV)^{\frac{1}{2}}} = \frac{12.26}{\sqrt{V}}\ \text{Å} \qquad \text{where } V \text{ is in volts}$$

It was soon established that other particles also exhibited wave properties. By the same token, it was possible to speak of the momentum of the photons using De Broglie relationship.

In order to consider an electron as a wave packet, let us take some time to understand what we mean by a wave packet. Consider the superposition of two waves of different frequencies and different propagation constants. Each wave is represented by the equation $y = a\,cos\,(kx - \omega t)$, where $\omega = 2\pi$ times the frequency and k, the propagation constant, is equal to 2 π times the reciprocal of the wavelength. Superposing two waves of nearly the same frequency $\frac{\omega_1}{2\pi}$ and $\frac{\omega_2}{2\pi}$, and nearly the same propagation constants k_1 and k_2, we have the resultant as equal to:

$$y_1 + y_1 = a\,[\cos(k_1 x - \omega_1 t) + \cos(k_2 x - \omega_2 t)]$$

$$= 2a\left[\cos\left(\frac{k_1 - k_2}{2}x - \frac{\omega_1 - \omega_2}{2}t\right) + \cos\left(\frac{k_1 + k_2}{2}x - \frac{\omega_1 + \omega_2}{2}t\right)\right]$$

$$= 2a[\cos(\Delta\, k\, x - \Delta\, \omega\, t)\cos(\, k_0\, x - \, \omega_0\, t)]$$

Where k_0 = the average value, $\frac{k_1 + k_2}{2}$ and $\Delta\, k = \frac{k_1 - k_2}{2}$

And ω_0 = the average value, $\frac{\omega_1 + \omega_2}{2}$ and $\Delta\, \omega = \frac{\omega_1 - \omega_2}{2}$

It will be noticed that the above expression for the resultant contains two sinusoidally varying terms, one at the average frequency and the other at half the difference frequency. Furthermore, the propagation characteristics are also in the same relationship. The first term, i.e., the slowly varying term, modulates the amplitude of the second term. The propagation characteristic of the envelope of the sinusoidal wave is determined by the first term (Figure I.2.1). The velocity with which the individual wave travels is called the phase velocity while the velocity of the envelope is called the group velocity. The phase velocity is equal to $\frac{\omega_0}{k_0}$ while the group velocity is equal to $\frac{\Delta\, \omega}{\Delta\, k} = \frac{d\, \omega}{d\, k}$. Extending De Broglie's idea, one may interpret the superposition of the two waves as a wave packet. Actually, a stricter definition of the wave packet should be as follows. A wave function that

is made up of a great many waves of nearly equal momenta, i.e., propagation constants, superimposed in such a way as to yield a function which is zero every where except in a restricted region, is called a wave packet. A wave packet can be taken to represent a particle whose position and momentum are known approximately. We can, therefore, say that the group velocity of the wave packet is equal to the velocity of the particle.

Therefore,

$$v_g = \frac{d\omega}{dk} = \frac{d(2\pi\upsilon)}{d\left(\frac{2\pi}{\lambda}\right)} = -\lambda^2 \frac{d\upsilon}{dk}$$

$$\frac{d\upsilon}{dk} = -\frac{v_g}{\lambda^2} = -\frac{v}{\lambda^2}$$

$$E = h\upsilon = \frac{1}{2}mv^2 + V$$

$$\frac{d\upsilon}{dk} = \frac{1}{h}\, m\, v\, \frac{dv}{dk} = -\frac{v}{\lambda^2}$$

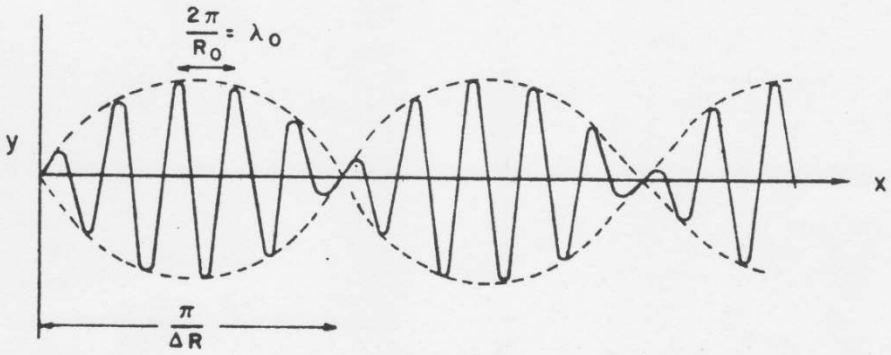
i.e., $m\, dv = -\frac{h\, d\lambda}{\lambda^2}$

$$\int_0^v m\, dv = -\int \frac{h\, d\lambda}{\lambda^2}$$

$$m\, v = \frac{h}{\lambda}$$

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

Thus, we can arrive at De Broglie relationship, starting with the representation of the particle as a wave packet.



Addition of Two Sinusoidal Waves of Slightly Differing Frequency and Propagation Constants.

FIGURE I.2.1

I.2.3 Heisenberg's Uncertainty Principle

Any correct system of mechanics should take into account a second fundamental principle that follows directly from the wave theory of matter. This refers to the uncertainty in the results of a measurement introduced by the measurement process itself. Classically, a mechanical system can be measured to any degree of precision without disturbing the motion of the mechanical system. The assumption is reasonable when one is considering the kinetics of objects of macroscopic size. On the other hand, when motion of very small particles is being observed, one should take into account the wave property, (i.e., the quantum nature) of the object and the error introduced by the measuring technique itself. As an illustration, take the case of measuring the position of an electron. We shall consider here the accuracy with which the x component of position and the x component of momentum can be determined simultaneously by observing the electron through a microscope by means of scattered light.

From principles of wave optics, one can determine the accuracy of the position measurement to be $\Delta x = \frac{\lambda}{\sin \epsilon}$ where λ is the wavelength of the radiation that enters the lens L and ϵ is half the angle subtended by the lens at the particle as shown in Figure (I.2.2). On the other hand, in order to minimize the

disturbance on the electron as much as possible, one ought to use only as low an intensity of light as a photon. The act of measuring the position of the electron has led to a scattering of a photon by the electron onto the screen S. The precise direction in which the photon is scattered into the lens in not known because of the finite size of the aperture of the lens. According to De Broglie relationship, the momentum of the photon after it is scattered is equal to $\frac{h}{\lambda}$. The uncertainty in the x component in the momentum of the photon is approximately $\left(\frac{h}{\lambda}\right)\sin\epsilon$. There is no reason why the total momentum of the system should have changed during the experiment. Also, the x components of the momenta of the electron and the photon can be accurately known before the scattering takes place. Therefore, the uncertainly in the x component of the momentum, Δp_x, of the electron after the scattering is equal to the corresponding uncertainty of the photon. Therefore, $\Delta p_x \approx \left(\frac{h}{\lambda}\right)\sin\epsilon$. We see that the combined uncertainties in the position and the momentum give

$$\Delta x\, \Delta p_x \approx h \qquad \text{(I.2.2)}$$

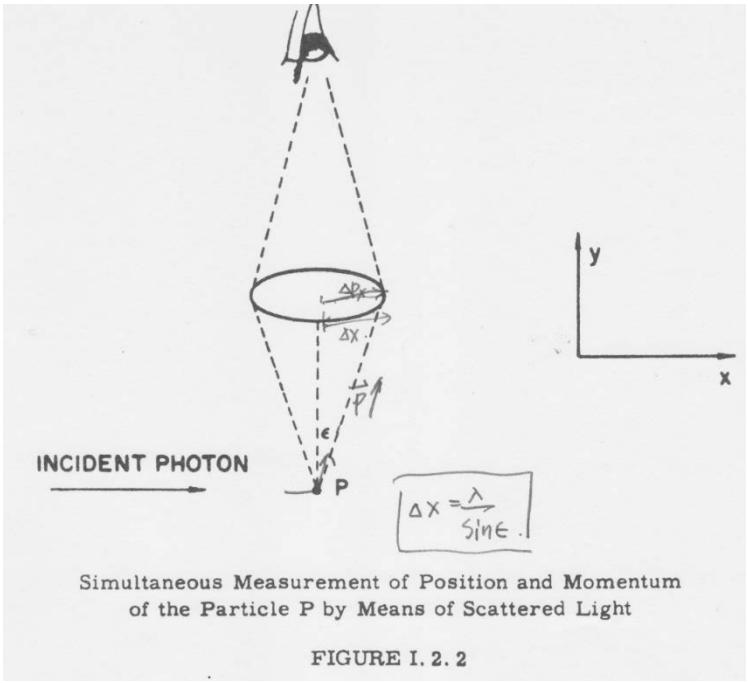
Equation (I.2.2) gives the famous "Uncertainty Principle" developed by Heisenberg in 1927. According to this principle, it is not possible to specify precisely and simultaneously the values of both the position and the momentum of the particle. The minimum, uncertainty in the simultaneous determination of two canonically conjugate variables is expressible in the general form

$$\Delta P \cdot \Delta Q \approx h \qquad \text{(I.2.3)}$$

Thus, if Q is a rectangular coordinate, P is the corresponding component of momentum; if Q is an angular coordinate, P is the corresponding angular momentum: if Q is the energy, P is the time.

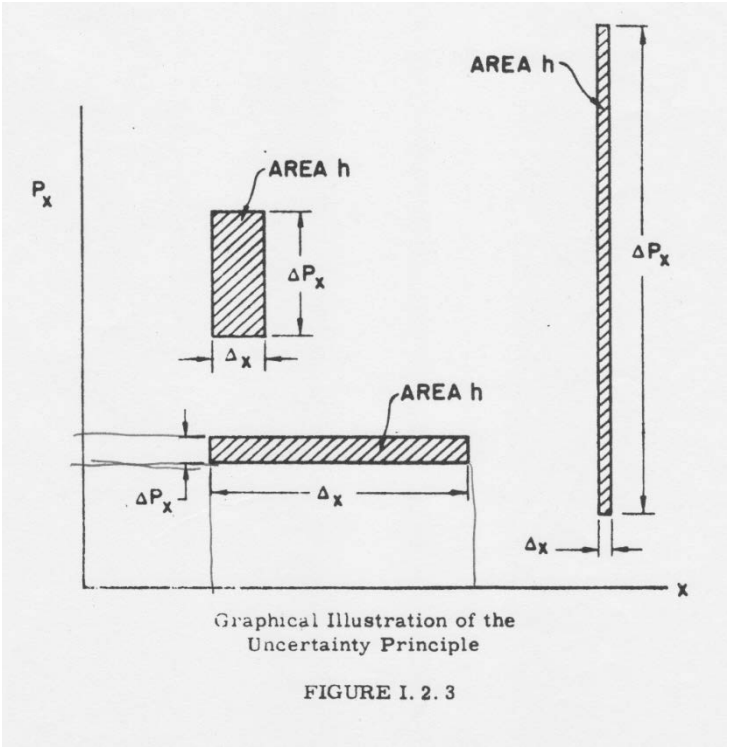
The uncertainty principle is illustrated in Figure (I.2.3). The abscissa gives the x component of position of the particle while the ordinate gives the x component of the momentum. Three rectangular boxes, each with an area equal to h, the Planck's constant, are shown. The sides of the rectangular boxes depict the uncertainties in the position and momentum. Narrowing the uncertainty, i.e., the error, in one dimension spreads the uncertainty in the other. The uncertainty

principle becomes significant only when atomistic particles are considered because of the smallness of the value of Planck's constant.



Simultaneous Measurement of Position and Momentum of the Particle P by Means of Scattered Light

FIGURE I. 2. 2



Graphical Illustration of the Uncertainty Principle

FIGURE I. 2. 3

I.2.4 Wave Packets in Space and Time

We already discussed briefly the wave packet as a concentrated bunch of waves to describe localized particles of matter as well as photons, i.e., we described the particles by a wave function that depends on the space coordinates x, y, z and time t. This quantity ψ is assumed to have three basic properties. First, it can interfere with itself. Second, it is large in magnitude where the particle is likely to be, and very small everywhere else. Third, it depicts the behavior of a single particle and not the statistical distribution of a number of particles.

A typical wave packet is shown in Figure (I.2.4a) where $\psi(x,t)$ is plotted as a function of x for a given value of t. The average wavelength λ_0 and the spread Δx of the packet are shown in the figure. The constituent waves out of which the wave packet is built can be obtained by a Fourier integral analysis of $\psi(x,t)$. The Fourier transform of $\psi\ (x,t)$ is shown in Figure (I.2.4b) where it is plotted as a function of the propagation constant $k = \frac{2\pi}{\lambda}$.

It can be shown by standard mathematical techniques

$$\Delta k\ \geq \frac{1}{\Delta x}$$

Where $\Delta k =$ approximate spread in propagation constant.

If we use De Broglie relation $p = \hbar\ k$, we obtain

$$\Delta p\ \Delta x \geq \hbar$$

This agrees with the uncertainty relation. Therefore, the uncertainty relation can be seen to follow from the description of a particle by a wave packet.

In a similar way, by considering a time packet, i.e., a wave packet as a function of time t for a given value of x, we get the relation

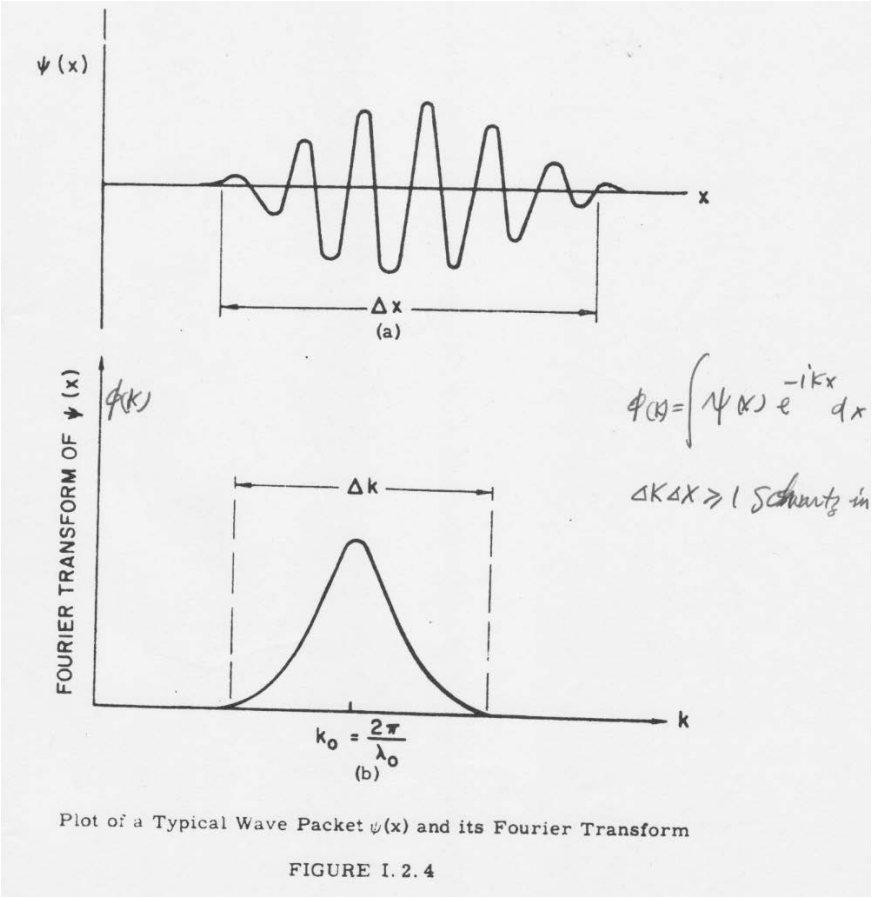
$$\Delta t\ \Delta \upsilon\ \geq \frac{1}{2\pi}$$

Therefore,

$$\Delta t\ \Delta E \geq \hbar$$

I.2.5 Quantum Mechanical Postulates

It should be possible, now, to set up a quantitative formulism based on the wave function description of the particle. We also require that this formulism should be such that the result of any calculation should reduce to the result of the corresponding classical calculation in the appropriate limit. In classical mechanics one deals with distance x, momentum p, total energy E. These quantities are called dynamic variables. These are also called observables because they can be measured in a physical experiment.



Plot of a Typical Wave Packet $\psi(x)$ and its Fourier Transform

FIGURE I. 2. 4

In quantum mechanics the dynamical variables play a completely new role. They are transformed into operators by a set of rules that are laid down as postulates. These operators operate on the wave function. An example of an operator is $\frac{d}{dx}$. When placed in front of a function $f(x)$, this symbol refers to a certain operation carried on the function, viz., differentiation with respect to x. $f(x)$ is called the operand while $\frac{d}{dx}$ is called the operator.

Our first task is to develop in a quantitative fashion the properties of the wave function. The waves which represent the particle are not electromagnetic or acoustic waves. We will give the physical interpretation of the wave function once we have developed a method for obtaining it.

Let us now study the postulates of quantum mechanics. These postulates cannot be proved or derived. The only justification for these postulates is that they are logically self-consistent and that they lead to results which agree with experiments. In a statement of these postulates, we shall consider only one space coordinate x and time t, for the sake of simplicity and ease of understanding. It is easy to extend the description to three dimensional space once the basic ideas are understood.

Postulate I:

To each physical system there can be ascribed one wave function, $\psi(x,t)$.

Postulate II:

The wave function $\psi(x,t)$ and its space derivative $\frac{\partial\psi(x,t)}{\partial x}$ must be continuous, single valued and finite for all values of x (i.e., -∞ to $+\infty$)

Postulate III:

The wave function should be normalized, i.e.,

$$\int_{-\infty}^{+\infty} \psi^{*}\psi \, dx = \int_{-\infty}^{+\infty} \psi^{2}\psi \, dx = 1 \qquad \text{(I.2.4)}$$

Postulate IV:

The dynamic variables are converted into operators that operate on the wave function by the following rules

Dynamical Variable	Operator
Position:	
x	x
Function of position:	
$f(x)$	$f(x)$
x-component of momentum: P_x	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Energy:	
E	$i\hbar\frac{\partial}{\partial t}$
Function of position and momentum:	
$f(x, P_x)$	$f\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)$

Postulate V:

The average value or the expectation value, $< \alpha >$, or any dynamical variable α, is calculated from the wavefunction ψ from the formula

$$< \alpha > = \int_{-\infty}^{+\infty} \psi^* \alpha \, \psi \, dx$$

I.2.6 Comments on the Postulates

We will now make some comments on these postulates before using them in the solution of some physical problem. According to the first postulate, the information about a system of particles is contained in a function of space coordinate and time, called the wavefunction. The wavefunction should conform to certain restrictions and these are contained in Postulate II. These restrictions are called the rules for the proper behavior of the function. A function f(x) is said

to be continuous when the function has the same value at x, no matter which direction we approach x from, i.e,. $f_-(x) = f_+(x)$ for all values of x where f_- refers to approaching x from $-\infty$ direction and f_+ refers to approaching x from $+\infty$ direction. It is in this sense that ψ and $\frac{\partial \psi}{\partial x}$ are said to be continuous.

The need for single-valuedness and postulate III will be appreciated once we try to give some physical interpretation for the wave function. We assume that all the information about the behavior of the physical system is given by the wave function. The only association we made so far, between the wave function and the particle which it represents, is that the wave function be larger where the particle is likely to be, and small elsewhere. This is not sufficient for s to extract the maximum amount of information about the behavior of the particle, out of the wave function. Therefore, we make an assumption, due to Max Born, that the wave function $\psi(x,t)$ be regarded as a measure of the probability of finding a particle at a particular position x at time t. Since probability must be real and non-negative, while ψ is generally complex, we assume that the position probability density is the product of ψ and its complex conjugate ψ^*.

$$P(x,t) = \psi^*(x,t)\psi(x,t) = |\psi(x,t)|^2$$

This means $\psi^*\psi$ dx is the probability of finding the particle in an interval dx, centered aropund the point x, at the time t, when a large number of precise position measurements are made on independent particles, each represented by one-particle wave function $\psi(x,t)$. This justification for this physical interpretation of ψ is the same as for the postulates, viz, logical consistency and agreement with experimental results. The need for restricting ψ to be single-valued is evident with this interpretation of ψ.

The probability of finding the particle somewhere in the universe ($-\infty < x < +\infty$) should be unity and therefore

$$\int_{-\infty}^{+\infty} P(x,t)\, dx = \int_{-\infty}^{+\infty} \psi^*\, \psi\, dx = 1$$

This is precisely what postulate III states (Equation (I.2.4). When ψ obeys Equation (I.2.4), it is said to be normalized. This condition also implies that

$$\psi(x,t) \to 0 \; when \; |x| \to \infty$$

Postulate IV gives us the working formula for translating the description of physical phenomena, as we know it classically, to quantum mechanical language. It is through the formula in postulate V, that one can calculate the value of observable quantities which can be compared to experiment. The expectation value is related to the idea of probability. The expectation value is not the result of one observation. The expectation value is the value predicted mathematically (in the sense of probability theory) for the result of a single measurement or it is the average of the results of measurements on a large number of independent systems each of which is represented by an identical wave function ψ.

I.2.7 Schrödinger Wave Equation

Using the rules of transformation of dynamical variables to operators, we will now set up an equation known as "Schrödinger Wave Equation", whose solutions are the wave functions that we are seeking.

The total energy E of a particle constrained to move along the x axis is

$$E(x, v_x) = \frac{1}{2} m {v_x}^2 + V(x) \qquad \text{(I.2.5)}$$

Where v_x= velocity in the x direction

m = mass of the particle

$V(x)$= potential energy of the particle arising due to electric, gravitational or any other potential field

The right hand side of Equation (I.2.5), which is a function of x and v_x, can be converted into a function x and p_x through the relation $p_x = m\, v_x$,

Since $p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$ we have,

$$\frac{1}{2} m {v_x}^2 + V(x) = \frac{{p_x}^2}{2\,m} + V(x) \rightarrow \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]$$

But we also know from postulate IV that energy E transforms into an operator $\left[i\hbar\frac{\partial}{\partial t}\right]$. Both the operators, $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]$and $\left[i\hbar\frac{\partial}{\partial t}\right]$ are therefore energy

operators, and when they operate on the wave function, should give the same resultant. Therefore,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x,t) + V(x)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \qquad \text{(I.2.6)}$$

This is the famous Schrödinger's time dependent wave Equation. The wave function $\psi(x,t)$ can therefore be obtained, by solving the Schrödinger equation once we know the potential energy $V(x)$. It is possible that in some cases V is a function of time also, i.e., $V = V(x,t)$.

In the next chapter we will solve the wave equation for some simple physical systems, thereby illustrating the use of the wave equation to get information about the physical system.

I.2.8 Digression on Probability

The probability of an occurrence is define as a number P between 0 and 1 such that in a large number of trials performed under identical conditions, the fraction of the trials in which this occurrence takes place is equal to P. If we toss a coin 100,000 times we will get 50,000 times heads and an equal number of times tails, since the probability of getting heads (or tails) is half. The probability of 1 means that the occurrence is a certainty, i.e., the occurrence will take place whatever be the number of times the trials are made. On the other hand, the probability of 0 means that the occurrence will never take place whatever be the number of times the trials are made. If $P(x)dx$ is the probability that the position would occur between x and $x + dx$, then $P(x)$ is called the position probability density. It is also called the probability distribution for position. The probability that the position would be somewhere between $-\infty$ and $+\infty$ is unity and therefore

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

Under such condition, the probability distribution is said to be normalize.

Let us now illustrate the method of calculating a mean or average value when the distribution function is known. Let us assume that we are calculating

the average age of men in a group. The average age of men is simply the sum of ages of all the men in the group divided by the number of men in the group. Instead of doing this, we can also compute the number of men whose age lies in the interval Y and $Y + dY$ years for each value of Y such that the entire range of age is covered. Let $dN(Y)$ be the number of men with ages between Y and $Y + dY$. Each value of age Y is multiplied by the number of men $dN(Y)$, whose age is between Y and $Y + dY$. The sum of all such products divided by the total number of men is equal to the average age:

$$\overline{Y} = \frac{\sum Y\, dN(Y)}{\sum dN(Y)}$$

The distribution that we talked of in this example is a discrete distribution, for the probability of a man having an age between Y and $Y + dY$ is $\frac{dN(Y)}{\sum dN(Y)}$, and changes discretely with Y.

The distribution that we commonly encounter in our studies will be continuous distribution and in these cases the average has to be computed by integration rather than by summation. If $P(Y)\, dY$ is the probability that the age of men will be between Y and $Y + dY$, then

$$\overline{Y} = \sum Y\, P(Y) dY = \int Y\, P(Y) dY \qquad since \int P(Y) dY = 1$$

The limits of integration are to be so chosen that the entire range of ages is covered.

Now we can generalize this treatment to compute the average of any arbitrary function $f(x)$, if we know the position probability density, $P(x)$. The average value of $f(x)$ denoted by $\overline{f(x)}$, is equal to

$$\overline{f(x)} = \frac{\int_{-\infty}^{+\infty} f(x)P(x)\, dx}{\int_{-\infty}^{+\infty} P(x)\, dx} = \int_{-\infty}^{+\infty} f(x)P(x)\, dx$$

The expectation value of a dynamical variable, calculated according to quantum mechanical postulate V, follows exactly the discussion we had in the last few paragraphs. If $P(x) = \psi^* \psi$ is the position probability density of a particle, the average or the expectation value of any function of positon is

$$< f(x) >= \int f(x)P(x)dx = \int f(x)\,\psi^*\,\psi dx = \int \psi^*\,f(x)\,\psi\;\,dx$$

The question arises as to how differential operators (as in momentum operator) can be combined with position probability density. Therefore, we define the expectation value generally with the operator acting on the wave function ψ, and multiplied on the left by ψ^*. For example, the expectation value for energy is

$$< E >= \int \psi^*\, i\hbar \frac{\partial}{\partial t}\,\psi\;\,dx$$

Having calculated the average value of a function f(x), let us now evaluate the average value of $[f(x)]^2$ denoted by $\overrightarrow{[f(x)]^2}$, to be

$$\overrightarrow{[f(x)]^2} = \int_{-\infty}^{+\infty} \big(f(x)\big)^2 P(x)\;dx$$

The standard deviation in (x) , σ, is obtained from

$$\sigma^2 = \overrightarrow{\left[f(x) - \overrightarrow{f(x)}\right]^2} = \int_{-\infty}^{+\infty} \left[f(x) - \overrightarrow{f(x)}\right]^2 P(x)\;dx$$

$$= \textstyle\int_{-\infty}^{+\infty} [f(x)]^2\,P(x)\;dx - 2\,\overrightarrow{f(x)}\;\int_{-\infty}^{+\infty} f(x)\,P(x)dx + \left[\overrightarrow{f(x)}\right]^2 \int_{-\infty}^{+\infty}\;P(x)\;dx$$

$$= \overrightarrow{[f(x)]^2} - \left[\;\overrightarrow{f(x)}\;\right]^2$$

The above result is important because of its relation to the expectation value of an operator corresponding to any dynamical variable, σ. Given the wave function, ψ, we can calculate $\overrightarrow{\sigma}$ as well as $\overrightarrow{\sigma^2}$. If $\overrightarrow{\sigma}^2$ is equal to $\overrightarrow{\sigma^2}$, then σ^2 is equal to zero. That means the expectation value is an exact number and there is no spread in the value of the dynamical variable. All of the measurements would give the same value. This result is very important.

I.2.9 Eigenvalues

Suppose we have an operator $\tilde{o}$ which operating on a function $f(x)$ satisfies the following equation:

$$\tilde{o}f(x) = \lambda f(x)$$

where λ is a constant

Such an equation is called an eigenvalue equation, $f(x)$ is an eigenfunction of the operator $\tilde{o}$ and λ is called the eigenvalue. λ is also called a characteristic value and $f(x)$ is called "characteristic" function.

Let us now consider an observable O whose quantum mechanical operator $\widetilde{O}$ satisfies the eigenvalue equation where wavefunction $\psi(x,t)$ is the eigenfunction

$$\widetilde{O}\,\psi(x,t) = K\,\psi(x,t)$$

We now proceed to calculate the expectation value of the observable, the expectation value of the square of the observable and the expectation value of the n^{th} power of the observable.

$$< O > = \int_{-\infty}^{+\infty} \psi^*(x,t)\,\widetilde{O}\;\psi(x,t)\,dx$$

$$= K\int_{-\infty}^{+\infty} \psi^*(x,t)\;\psi(x,t)\,dx = K$$

$$< O^2 > = \int_{-\infty}^{+\infty} \psi^*(x,t)\,\widetilde{O}\left(\widetilde{O}\,\psi(x,t)\right)\,dx$$

$$= \int_{-\infty}^{+\infty} \psi^*(x,t)\,\widetilde{O}\,(\,K\,\psi(x,t))\;\,dx$$

$$= K^2\int_{-\infty}^{+\infty} \psi^*(x,t)\,\psi(x,t)\;\,dx$$

$$= K^2 =< O >^2$$

Similary,

$$< O^n > =< O >^n$$

This means therefore that the wavefunction $\psi(x,t)$ is characterized by an exact value k for the observable O. The same value K will be obtained for the

observable each time a measurement is made on the system in the state whose wavefunction is $\psi(x,t)$.

Problems: Chapter I.2

1. What is the De Broglie wavelength of a laboratory-scale particle (for example, a mass of 12 gm) moving at a laboratory-scale velocity (for example, 10 m/sec)? Is it necessary to consider the wave properties of matter in this case?
2. Consider a pendulum bob of mass 0.10 Kg moving at 3 m/sec. Suppose that the momentum p_x cannot be known more accurately than $\Delta p_x = 10^{-6}\, p_x$. What limitation does the indeterminancy principle impose on the simultaneous measurement of x?
3. The De Broglie relationship tells us that the wavelength of the electron in any direction is inversely proportional to its momentum along that direction. If an electron microscope is to resolve two atoms space 3 Å apart normal to the electron beam, and the acceleration voltage along the beam is 50,000 volts,
   a. What is the largest undesired voltage that can be allowed to act on the electron normal to the beam before it reaches the target?
   b. What distance is the beam capable of resolving normal to the beam, assuming wavelength is the only limitation?
4. The mass of a hydrogen nucleus (proton) is 1.67×10^{-27}kg. Suppose a certain excited state of a hydrogen atom is known to have a lifetime of 2.5×10^{-14} sec, what is the minimum error with which the energy of the excited state can be measured? If the center of a hydrogen atom can be located with a precision of 0.01 Å, what is the corresponding uncertainty in its velocity?
5. If ψ_1 and ψ_2 each be a solution of Schrödinger equation, show that $\psi_1 + \psi_2$ also is a solution of the Schrödinger equation. This is called the "Superposition Property".
6. According to postulate 4, we can express any function of x, $f(x)$ as a multiplication operator $f(x)$. In this sense, we know the operator for the potential energy $V(x)$. Is it possible to express the operator for $V(x)$ in any

other way? If so, write down the operator for $V(x)$. [Hint: Total energy =kinetic energy + potential energy.]

7. Are the following functions, eigen functions of momentum? If so, what is the eigen value? If not, what is the expectation value?
   a. $\psi(x) = Ae^{i4x}$
   b. $\psi(x) = A \sin kx$
   c. $\psi(x) = \sum_l A_l \, e^{ikx}$
8. The differential equation of transverse vibration of a stretched string is

$$m\frac{d^2y}{dt^2} = T\frac{d^2y}{dx^2}$$

$$where\ m\ is\ mass\ per\ unit\ length$$

   T is tension

   The string of length L is fastened at both ends so that

$$y(0) = 0$$
$$y(L) = 0$$

   Assume a solution of the form

$$y = A \cdot \sin kx \cdot e^{i\omega t}$$

   Show that this leads to the two eigenvalue equations

$$\frac{d^2y}{dt^2} = -\omega^2 y, \qquad and \ \frac{d^2y}{dx^2} = -k^2 y$$

   Solve this problem for
   a. The eigenvalues of k_n
   b. The eigen frequencies, ω_n
   c. The eigen functions, y_n, corresponding to the eigenvalues.
      [Remember that $e^{i\theta} = \cos\theta + i \sin\theta$]

9. If 0 is an observable whose quantum mechanical operator $\widetilde{O}$ satisfies the eigenvalue equation

$$\widetilde{O}\,\psi(x,t) = k\,\psi(x,t)$$

   Prove that

$$< O^3 > = < O >^3$$

Chapter 3

Solution of Schrödinger Wave Equation:

One Dimensional Problems

I.3.1 Time Independent Schrödinger Equation

In the last chapter, we saw that the wave function $\psi(x,t)$ can be obtained by solving the Schrödinger's equation. We will illustrate the solution of Schrödinger's equation for simple physical problems in this chapter.

We mentioned that it is possible for the potential energy V of a particle to be a function of time and space coordinates. Therefore, the most general form of Schrödinger's equation is,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \qquad \text{(I.3.1)}$$

Most of the problems that we will be encountering in our studies will be those in which the potential energy is not a function of time. In such cases, the Schrödinger's time dependent equation takes the form of Equation (I.2.6) and is repeated here

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x,t) + V(x)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \qquad \text{(I.3.2)}$$

This equation, which contains two variables, can now be separated into two equations, each of which contains only one of the variables x or t.

Let us assume that the solution ψ can be expressed as a product of two separate functions, $\psi(x)$ which is only a function of x and $T(t)$ which is only a function of t.

$$\psi(x,t) = \psi(x)T(t) \qquad \text{(I.3.3)}$$

On substitution of this solution in Equation (I.3.2), we get

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

Dividing this equation by $\psi(x)T(t)$ on both sides, we get

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2}{dx^2}\psi(x)+V(x)=\frac{i\hbar}{T(t)}\frac{\partial}{\partial t}T(t) \qquad \text{(I.3.4)}$$

We notice that the left hand side is a function of the variable x only and the right hand side is a function of the variable t only. But x, the position and t, the time are independent variables therefore, Equation (I.3.4) is possible only if the left hand side and the right hand side of the equation are independently equal to a constant which we will denote by E.

Then,

$$i\hbar\frac{\partial}{\partial t}T(t)=ET(t) \qquad \text{(I.3.5)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x) \qquad \text{(I.3.6)}$$

These two equations can be written in the form

$$\frac{\partial T(t)}{\partial t}=\frac{-iE}{\hbar}T(t) \qquad \text{(I.3.5a)}$$

$$\frac{d^2\psi(x)}{dx^2}=-\frac{2\,m}{\hbar^2}(E-V)\,\psi(x) \qquad \text{(I.3.6a)}$$

Equation (I.3.5a) can be integrated directly and setting the arbitrary multiplication constant equal to unity, we have

$$T(t)=\exp\left(\frac{-iEt}{\hbar}\right) \qquad \text{(I.3.7)}$$

It is clear that (x) , which is the solution to Equation (I.3.6a), is the amplitude of $\psi(x)$ and $T(t)$ is the phase factor. Equation (I.3.6a) is called Schrödinger's time independent equation.

The total wave function $\psi(x)$ is therefore equal to

$$\psi(x,t)=\psi(x)\exp\left(\frac{-iEt}{\hbar}\right) \qquad \text{(I.3.8)}$$

Let us now calculate the probability that a particle, represented by the wave function given in Equation (I.3.8), lies between x and $x+dx$. This is equal to

$$\psi^*(x,t)\,\psi(x,t)dx=\psi^*(x)\exp\left(\frac{iEt}{\hbar}\right)\psi(x)\exp\left(\frac{-iEt}{\hbar}\right) \qquad \text{(I.3.9)}$$

First, we note that the position probability density is independent of time. Second, the position probability density is determined by $\psi(x)$ which is the solution to the time-independent equation (I.3.6a). Therefore, a particle whose wave function is a solution of the time independent equation is said to be in a stationary state and the wave function is called the stationary solution.

The time-independent equation (I.3.6a) or the equation (I.3.5a), does not place any restriction on the value of E and, therefore, in principle, we can have infinite number of solutions for the wave function corresponding to infinite number of values of E. But, in practical physical problems, the requirements of proper behavior for the wave function to be one of those that correspond to certain allowed values of E. If we denote an allowed value of energy by a subscript n, then the corresponding wave function is also denoted by the same subscript n to show that ψ_n is an solution of the Schrödinger's time-independent equation when $E = E_n$ and these ψ_n's for various values of E_n are the only acceptable wave functions.

I.3.2 Significance of E

The separation constant E, that we used to separate the time-dependence equations into two equations (I.3.5) and (I.3.6), has an important physical significance. We saw that the time-dependent part $T(t)$ was only a phase factor while the space-dependent part $\psi(x)$ determined the amplitude of the total wave function $\psi(x,t)$. This means that the exponent in $T(t)$ has no dimensions. That is, $\frac{Et}{\hbar}$ has no dimensions. Since $\hbar$ has dimensions of energy-time, it means E should have dimensions of energy.

We can now show that E is actually the total energy. If we want to calculate the expectation value of the total energy, then according to postulate IV in the last chapter, we must replace the total energy by either the operator $i\hbar\frac{\partial}{\partial t}$ or the operator $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]$, in the expression for expectation value given in postulate V. Taking the operator $i\hbar\frac{\partial}{\partial t}$, the expectation value of energy is equal to

$$\int \psi^*(x,t) i\hbar \frac{\partial}{\partial t}\ \psi(x,t) dx = \int \psi^*(x)\ e^{\frac{iEt}{\hbar}} \left(i\hbar \frac{\partial}{\partial t}\right)\ \psi(x) e^{\frac{-iEt}{\hbar}} dx$$

$$= E \int \psi^*(x)\ \ \psi(x) e^{\frac{-iEt}{\hbar}} dx = E \qquad \text{(I.3.10)}$$

If we had started with the operator $\left[-\frac{\hbar^2}{2m}\ \frac{d^2}{dx^2} + V(x)\right]$, we would have arrived at the same result that the expectation value of energy is E. We have to show next, that E is the exact of the particle. Recalling our discussion on probability if in each measurement we get the same value for the result, it means that the spread in the measured values is zero and the value that we obtain is the precise value for the measured observable. If in any series of measurements of a single observable, the mean square deviation of the results of measurement is zero, then the measured value is precise. We first observe that $\psi(x,t)$ is an eigenfunction of energy with eigenvalue E.

If we start with the energy operator $i\hbar \frac{\partial}{\partial t}$, we get

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = i\hbar \frac{\partial}{\partial t} \left(\psi(x) e^{\frac{-iEt}{\hbar}}\right)$$

$$= E\psi(x) e^{\frac{iEt}{\hbar}} = E\psi(x,t) \qquad \text{(I.3.11)}$$

We would have obtained an eigenvalue if we had started with the energy operator $\left[-\frac{\hbar^2}{2m}\ \frac{d^2}{dx^2} + V(x)\right]$.

We conclude, therefore, that E is the precise value one would get for measurement of energy, no matter how many times the measurements are made.

We summarize, now, the procedures for obtaining the wave function ψ_n and the corresponding allowed energy value E_n, for a particle in a physics problem.

(1) Write down the classical expression for potential energy V, of the particle, in the given situation.

(2) If V, the potential energy, is a function of time, set up Schrödinger's time-dependent equation using the operator $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]$ for energy in the left hand side of the equation and the operator $i\hbar\frac{\partial}{\partial t}$ for energy in the right hand side.

(3) If V is independent of time, i.e., $V = V(x)$, set up Schrödinger's time independent equation.

(4) Using the boundary conditions in the given problem to solve the Schrödinger equation, find out the allowed values, E_n, of energy, and the corresponding wave function ψ_n.

We will now illustrate these procedures by using them to find out E_n and ψ_n for various physical systems and conditions.

I.3.3 Particle in a Force Free Region

Let us consider a particle of mass m which moves in a region where the potential energy is constant, i.e., $V = V_0$ for $-\infty < x < \infty$. We will assume that the particle is constrained to move only along the x direction since we are only equipped so far to consider one-dimensional problems. Since the potential energy is constant, there is no force acting on the particle since force is equal to the negative gradient of potential energy. The total energy operator is equal to $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_0\right]$. Since the potential energy is not a function of time, we use the time-independent Schrödinger equation.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x,t)+V_0=E\,\psi(x,t)$$

i.e.,

$$\frac{d^2\psi(x,t)}{dx^2}+\frac{2m(E-V_0)}{\hbar^2}\psi(x,t)=0 \qquad \text{(I.3.12)}$$

We will now distinguish two cases according to whether $E > V_0$ *or* $E < V_0$.

Case 1. $E > V_0$

Let us put $k^2 = \frac{2m(E-V_0)}{\hbar^2}$

Then a general solution of Equation (I.3.12) is

$$\psi = A'e^{ikx} + B'e^{-ikx} \qquad \text{(I.3.13)}$$

where A' and B' are constants to be evaluated from the conditions of the problem. It can be verified that Equation (I.3.13) is a solution to Equation (I.3.12) by direct substitution. Equation (I.3.12) is a second order equation and since the solution equation (I.3.13) contains two arbitrary constants A' and B', it is the general solution. If we write the expression for total wave function $\psi(x,t)$ we will get

$$\psi(x,t) = A'e^{ikx - \frac{iEt}{\hbar}} + B'e^{-ikx - \frac{iEt}{\hbar}}$$

$$= A^{'}e^{i\,(kx - \omega t)} + B^{'}e^{-\,i(kx - \omega t)} \qquad \text{(I.3.14)}$$

Where $\omega = \frac{E}{\hbar}$

The first term in the solution equation (I.3.14) represents a plane wave traveling toward the $+x$ direction and the second term represents a plane wave traveling toward the $-x$ direction, with frequency $\upsilon = \frac{\omega}{2\pi} = \frac{E}{\hbar}$ and wavelength $\lambda = \frac{2\pi}{k}$

An equally valid solution can be

$$\psi = A\,Sin\,kx\; + B\cos kx \qquad \text{(I.3.15)}$$

If we include the time dependence, we would have

$$\psi = A\sin kx\, e^{-i\omega t} + B\cos kx\, e^{-i\omega t} \qquad \text{(I.3.16)}$$

where $\omega = \frac{E}{\hbar}$

Each term in Equation (I.3.16) represents a standing wave. The choice between traveling wave solution and standing wave solution depends on the physical problem. If we want to characterize an electron moving in the $+x$ direction, then we will use the traveling plane wave solution which represents a wave advancing toward the $+x$ direction. If we want to talk of an electron in a finite enclosure, then we will find it more useful to represent it by a standing wave solution. When the particle is restricted to a certain region, the particle would bounce back and forth between the ends of the region with momentum of the same magnitude but of opposite direction. This will give rise to a standing wave description of the electron due to the superposition of positive going and negative going waves of equal amplitude.

Let us consider the traveling wave solution. If we try to calculate the position probability density $\psi^* \psi$ it is uniform all over the space from $x = -\infty \; to \; x = +\infty$. In fact this is a consequence of the uncertainty relation since the momentum ($p = \hbar k$) is very accurately known once k is known and, therefore, the uncertainty in the position is infinite. If we want to localize a particle within certain region Δx, then we must construct a wave packet made up of plane wave solutions (of Schrödinger equation) whose k values have a spread $\Delta k \cong \frac{1}{\Delta x}$.

Case 2 $E < V_0$

When the total energy is less than the potential energy, it means the kinetic energy is negative. Classically a particle can have only positive kinetic energy. Therefore, the situation $E < V_0$, is possible only quantum mechanically.

The Schrödinger equation reduces in this case to

$$\frac{d^2\psi}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\,\psi = \beta^2 \psi \qquad \text{(I.3.17)}$$

where $\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$

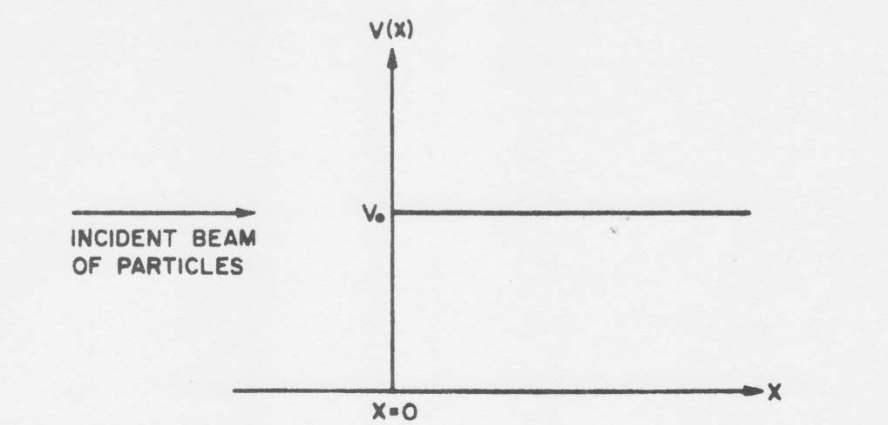
The general solution to this equation is

$$\psi = A\, e^{-\beta x} + B e^{+\beta x} \qquad \text{(I.3.18)}$$

The wave function is an exponential function. Because of the requirement that ψ should be zero. When $|x|$ goes to infinity, only exponentially decaying solutions will be allowed. We will see more about this in later problems.

I.3.4 Transmission and Reflection at a Barrier

Let us consider a beam of particles which impinges on a potential barrier of height V_0 as shown in Figure (I.3.1).



A POTENTIAL BARRIER

The particles are incident from the left. Let the discontinuity in the potential be located at $x = 0$. The Schrödinger equation in the two regions $x < 0$ and $x > 0$ are as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_l(x) = E\,\psi_l(x) \qquad for\ x < 0 \qquad \text{(I.3.19)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_r(x) = (E - V_0)\psi_r(x) \qquad for\ x > 0 \qquad \text{(I.3.20)}$$

Where the subscripts l and r on the wave functions denote wave functions in the regions $x < 0$ and $x > 0$ respectively.

The general solutions are

$$\psi_l(x) = A\,e^{k_1 x} + Be^{-k_1 x} \qquad \text{(I.3.21)}$$

$$\psi_r(x) = C\,e^{k_2 x} + De^{-k_2 x} \qquad \text{(I.3.22)}$$

where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

and

$$k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

We now distinguish two cases $E < V_0$ and $E > V_0$

Case 1. $E < V_0$

In this case k_1 is real while k_2 is imaginary in Equation (I.3.21) and (I.3.22). This gives rise to real coefficient in the exponent of the Equation (I.3.22).

The solutions are

$$\psi_l(x) = A\, e^{k_1 x} + B e^{-i\, k_1 x} \qquad \text{(I.3.23a)}$$

$$\psi_r(x) = C\, e^{-k_2' x} + D e^{+k_2' x} \qquad \text{(I.3.23b)}$$

where

$$-k_2' = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

Since we require ψ_r to be finite as $x \to \infty$, we have to set D=0. The boundary conditions are

$$\psi_l(0) = \psi_r(0)\ and\ \left.\frac{d\psi_r}{dx}\right|_{x=0}$$

This means $A + B = C$

$$ik_1(A - B) = -k_2' C$$

We may now solve for $\frac{B}{A}$ and $\frac{C}{A}$ as equal to

$$\frac{B}{A} = \frac{ik_1 + k_2'}{ik_1 - k_2'} \qquad \text{(I.3.24a)}$$

$$\frac{C}{A} = \frac{2\,ik_1}{ik_1 - k_2'} \qquad \text{(I.3.24b)}$$

What is the physical interpretation of these results? Particles with energy E are incident on the potential barrier from the left. This is represented by $A\,e^{k_1 x}$ in Equation (I.3.23a). At the potential barrier, classically the particle will be totally reflected since $E < V_0$. But quantum mechanically only partial reflection takes place, the reflected particle being represented by $Be^{-i\,k_1 x}$ in equation (I.2.23a). The particle has a finite probability of penetrating into the region $x > 0$. The wave function for the transmitted particle is exponentially decay with x as given by $C\,e^{-k_2' x}$.

Therefore, to the left of the barrier we have an incident and reflected wave while to the right of the barrier we have an exponentially decaying probability of finding the particle.

Case 2 $E > V_0$

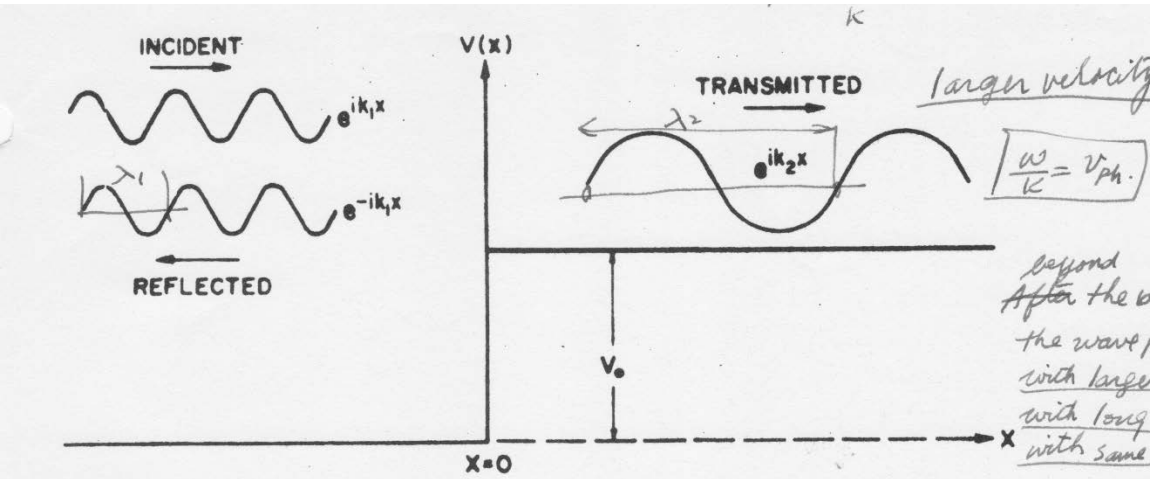
In this case both $k_1\ and\ k_2$ are real. We are considering particles that are incident on the barrier from the left. As before, the first term in Equation (I.3.21) represents one such particle. The reflected particle is represented ty the second term in Equation (I.3.21). The transmitted particle in the region $x > 0$ is represented by the first term in Equation (I.3.22). Since no particles are incident on the barrier from the right, we take $D = 0$ in Equation (I.3.22). The boundary condition at $x = 0$ gives

$$A + B = C \qquad \text{and} \qquad \text{i}k_1(A - B) = ik_2\ \text{C}$$

This leads to

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \qquad\qquad \frac{C}{A} = \frac{2\,k_1}{k_1 + k_2} \qquad \text{(I.3.25)}$$

We see, therefore, that the particle incident from the left particle incident from the left has a certain probability of getting reflected and certain probability of getting transmitted. The wavefunctions are shown in Figure (I.3.2)

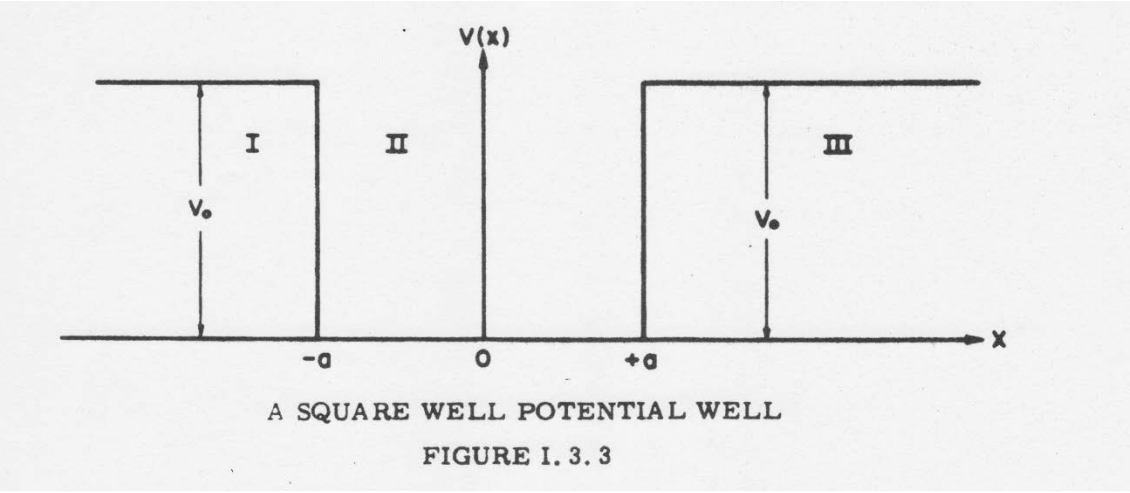


WAVEFUNCTION FOR E > V_0 FOR A PARTICLE INCIDENT ON THE POTENTIAL BARRIER

FIGURE I. 3. 2

I.3.5 Finite Potential Well;

We will now consider the problem of a particle moving under a potential well as shown in Figure (I.3.3). The potential is zero for $|x|$ less than a, and is equal to V_o for $|x| > a$. Such a potential is called rectangular or square well potential. Again we distinguish two cases $E > V_o$, $E < V_o$.



A SQUARE WELL POTENTIAL WELL

FIGURE I. 3. 3

Case 1 $E < V_o$:

Classically, the particle is trapped inside the well ($-a < x < a$) since outside the well the energy E is less than V_0. However, quantum mechanically there is a certain probability that the particle will be found outside the well. We will consider three regions as follows:

Region I $x < a$

Region II $-a < x < a$

Region III $x > a$

The Schrödinger equations in the three regions are as follows:

The Region I and III, we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V_0\psi(x) = E\,\psi(x) \qquad \text{(I.3.26)}$$

In Region II, we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\,\psi(x) \qquad \text{(I.3.27)}$$

From our previous discussions we can write the general solutions for the wavefunction in the three regions as follows:

In Region I, $\psi_I(x) = A\,e^{k_2 x} + Be^{-k_2 x}$ (I.3.28)

In Region II, $\psi_{II}(x) = C\,e^{ik_1 x} + De^{-i\,k_1 x}$ (I.3.29)

In Region III, $\psi_{III}(x) = G\,e^{ik_2 x} + Fe^{-i\,k_2 x}$ (I.3.30)

Where

$$k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

And

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

These wavefunctions $\psi_I, \psi_{II}, \psi_{III}$ should satisfy the conditions of finiteness single-valuedness and continuity.

In Region I, when $x \to -\infty$, the term $e^{-k_2 x}$ will increase to infinity and therefore we set $B = 0$. Similarly, in Region III, we set $G = 0$, in order that $\psi_{III \to 0}\ \ as\ x \to -\infty$. The wavefunctions becomes

$$\psi_I(x) = A\, e^{k_2 x} \quad \text{(I.3.31)}$$

$$\psi_{II}(x) = C\, e^{ik_1 x} + De^{-i\,k_1 x} \quad \text{(I.3.32)}$$

$$\psi_{III}(x) = Fe^{-i\,k_2 x} \quad \text{(I.3.33)}$$

The boundary conditions are

$$\psi_I(-a) = \psi_{II}(-a) \quad \text{and} \quad \left.\frac{d\psi_I}{dx}\right|_{x=-a} = \left.\frac{d\psi_{II}}{dx}\right|_{x=-a}$$

and

$$\psi_{II}(a) = \psi_{III}(a) \quad \text{and} \quad \left.\frac{d\psi_{II}}{dx}\right|_{x=a} = \left.\frac{d\psi_{III}}{dx}\right|_{x=a}$$

These boundary conditions yield

$$A\, e^{-k_2 a} = C\, e^{-ik_1 a} + De^{\,i\,k_1 a} \quad \text{(I.3.33a)}$$

$$k_2 A\, e^{-k_2 a} = ik_1 C\, e^{-ik_1 a} - i\,k_1 De^{\,i\,k_1 a} \quad \text{(I.3.33b)}$$

$$Fe^{-i\,k_2 a} = C\, e^{ik_1 a} + De^{-i\,k_1 a} \quad \text{(I.3.33c)}$$

$$-k_2 Fe^{-i\,k_2 a} = ik_1 C\, e^{ik_1 a} - i\,k_1 De^{-i\,k_1 a} \quad \text{(I.3.33d)}$$

By eliminating A between Equation (I.3.33a) and (I.3.33b) we get

$$Ck_2\, e^{-ik_1 a} + Dk_2 e^{\,i\,k_1 a} = ik_1 C\, e^{-ik_1 a} - i\,k_1 De^{\,i\,k_1 a} \quad \text{(I.3.34)}$$

i.e.,

$$C(k_2 - ik_1)e^{-ik_1 a} = -D(k_2 + i\,k_1)e^{\,i\,k_1 a}$$

Therefore,

$$\frac{C}{D} = -\left(\frac{k_2 + ik_1}{k_2 - i\,k_1}\right) e^{\,i\,2\,k_1 a} \quad \text{(I.3.35)}$$

Similarly by eliminating F between Equation (I.3.33c) and (I.3.33d), we get

$$-k_2 C\, e^{ik_1 a} - k_2 De^{-i\,k_1 a} = ik_1 C\, e^{ik_1 a} - i\,k_1 De^{-i\,k_1 a} \quad \text{(I.3.36)}$$

i.e.,

$$-C(k_2 + i\,k_1)e^{ik_1a} = D(k_2 - i\,k_1)e^{-i\,k_1a}$$

$$\frac{C}{D} = -\left(\frac{k_2 - ik_1}{k_2 + i\,k_1}\right)e^{-i\,2\,k_1a} \qquad \text{(I.3.37)}$$

Multiplying Equation (I.3.35) and (I.3.37), we get

$$\frac{C^2}{D^2} = 1 \qquad \text{i.e.,} \qquad \frac{C}{D} = \pm 1 \qquad \text{(I.3.38)}$$

Let $C = D$. Then comparing Equation (I.3.33a) and (I.3.33c), we see $A = F$. On the other hand, if $C = -D$, we will get $A = -F$. By putting $C = D$ in Equation (I.3.34) we get

$$e^{ik_1a} + e^{-k_1a} = \frac{i\,k_1}{k_2}\left(e^{-ik_1a} - e^{ik_1a}\right)$$

$$= \frac{k_1}{i\,k_2}\left(e^{ik_1a} - e^{-ik_1a}\right)$$

i.e.,

$$\cos k_1a = \frac{k_1}{k_2}\sin k_1a \text{ or } \tan(k_1a) = \frac{k_2}{k_1} \qquad \text{(I.3.39)}$$

Similarly by putting $C = -D$, we get

$$\cos k_1a = -\frac{k_1}{k_2}\cos k_1a$$

$$\tan(k_1a) = -\frac{k_1}{k_2} \qquad \text{(I.3.40)}$$

We recall that

$$k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

and

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

Solution to Equation (I.3.39) and (I.3.40) can be found graphically. For this purpose we write Equation (I.3.40) as

$$\cos\, k_1 a = -\frac{k_1}{k_2} \tag{I.3.41}$$

Given the value of a and V_0 , we must solve Equation (I.3.39) and (I.3.41).

We can transform Equations (I.3.39) and (I.3.41) to be

$$\epsilon \tan\epsilon = \sqrt{\frac{2mV_0\, a^2}{\hbar^2} - \epsilon^2} \tag{I.3.42}$$

and

$$-\epsilon \cot\epsilon = \sqrt{\frac{2mV_0\, a^2}{\hbar^2} - \epsilon^2} \tag{I.3.43}$$

where

$$\epsilon = k_1 a = \sqrt{\frac{2mE\, a^2}{\hbar^2}} \tag{I.3.44}$$

If we plot the function $p(\epsilon) = \epsilon \tan\epsilon$ as a function of ϵ and plot the function $q(\epsilon) = \sqrt{\frac{2m\, V_0\, a^2}{\hbar^2} - \epsilon^2}$ on the same graph sheet., the points of intersection give the solutions to Equation (I.3.42). In Figure (I.3.4) the function $p(\epsilon)$ has zeros at $\epsilon = 0, \pi, 2\pi,\ \ etc\ \ldots and\ asymptotes\ at\ \epsilon = \frac{\pi}{2}, \frac{3\,\pi}{2},$ etc.. The function $q(\epsilon)$ is a quarter cycle with radius $\sqrt{\frac{2mV_0\, a^2}{\hbar^2}}$. It is clear from this figure that only discrete solutions are possible corresponding to the points of intersection for $E < V_0$. The number of such solutions depends on V_0, which determines the value of the radius of the quarter cycle. Larger value of V_0 corresponds to a larger number of points of intersection.

Equation (I.3.43) can be solved similarly by plotting a function $p'(\epsilon) = -\epsilon \cot\epsilon$ and $q(\epsilon) = \sqrt{\frac{2m\, V_0\, a^2}{\hbar^2} - \epsilon^2}$ on the same graph sheet. The functdion $p'(\epsilon) = -\epsilon \cot\epsilon$ has zeros at $\frac{\pi}{2}, \frac{3\,\pi}{2},$ etc.. and asymptotes at $\pi, 2\pi,\ \ etc.$

The bound state wavefunctions are shown in Figure (I.3.5)

To summarize, the energy values of a particle moving under the influence of a potential well are discrete for $E < V_0$, i.e., the energy values are quantized. The existence of such quantize energy levels is characteristic of all cases where the particle, according to classical picture, is bound to a small region of space. For this reason, the discrete energy levels are called bound states. It must be borne in mind that classical physics does not require quantization of energy levels of particles which are bound in space. If we make the width 2a, of the square well, large enough to approach laboratory scale, then the discrete levels will be so close that the energy can almost be considered continuous. Thus we see the quantum mechanical theory predicts the same results as classical theory when we consider systems of macroscopic dimensions.

Case $E > V_0$

In this case, it can be verified that the solution for the wavefunctions are as follows:

Region I, $$\psi_I(x) = A\, e^{ik_2 x} + Be^{-k_2 x} \tag{I.3.45}$$

Region II, $$\psi_{II}(x) = C\, e^{ik_1 x} + De^{-i\,k_1 x} \tag{I.3.46}$$

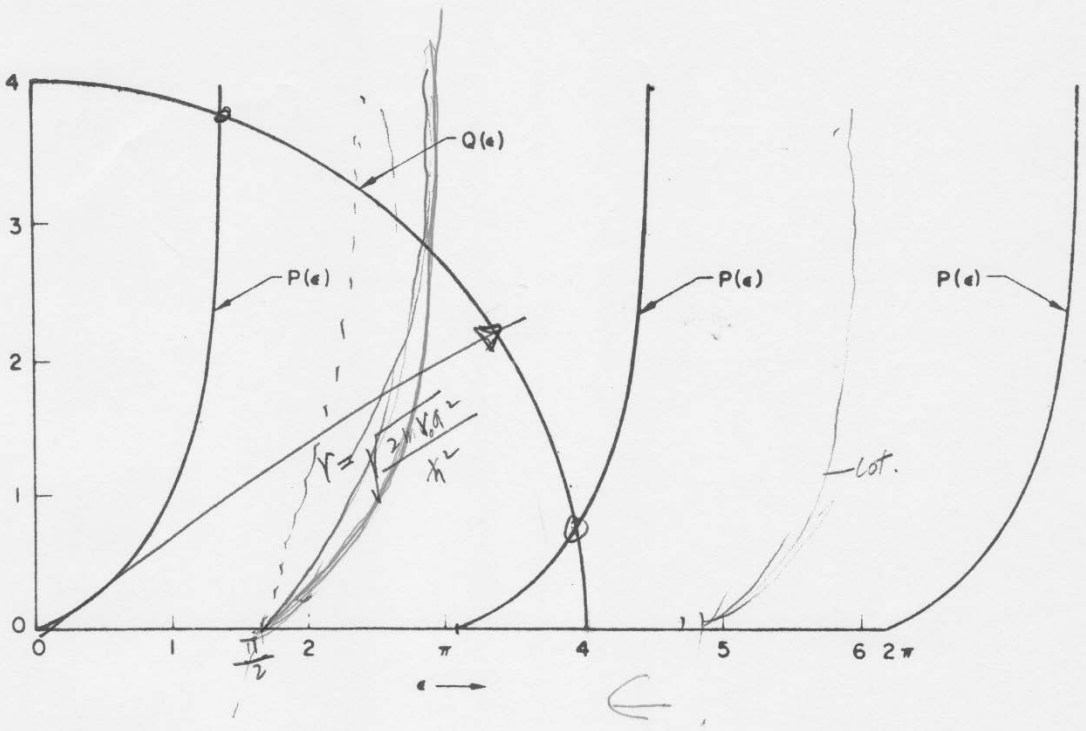
Region III, $$\psi_{III}(x) = G\, e^{ik_2 x} + Fe^{-i\,k_2 x} \tag{I.3.47}$$

where

$$k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

and

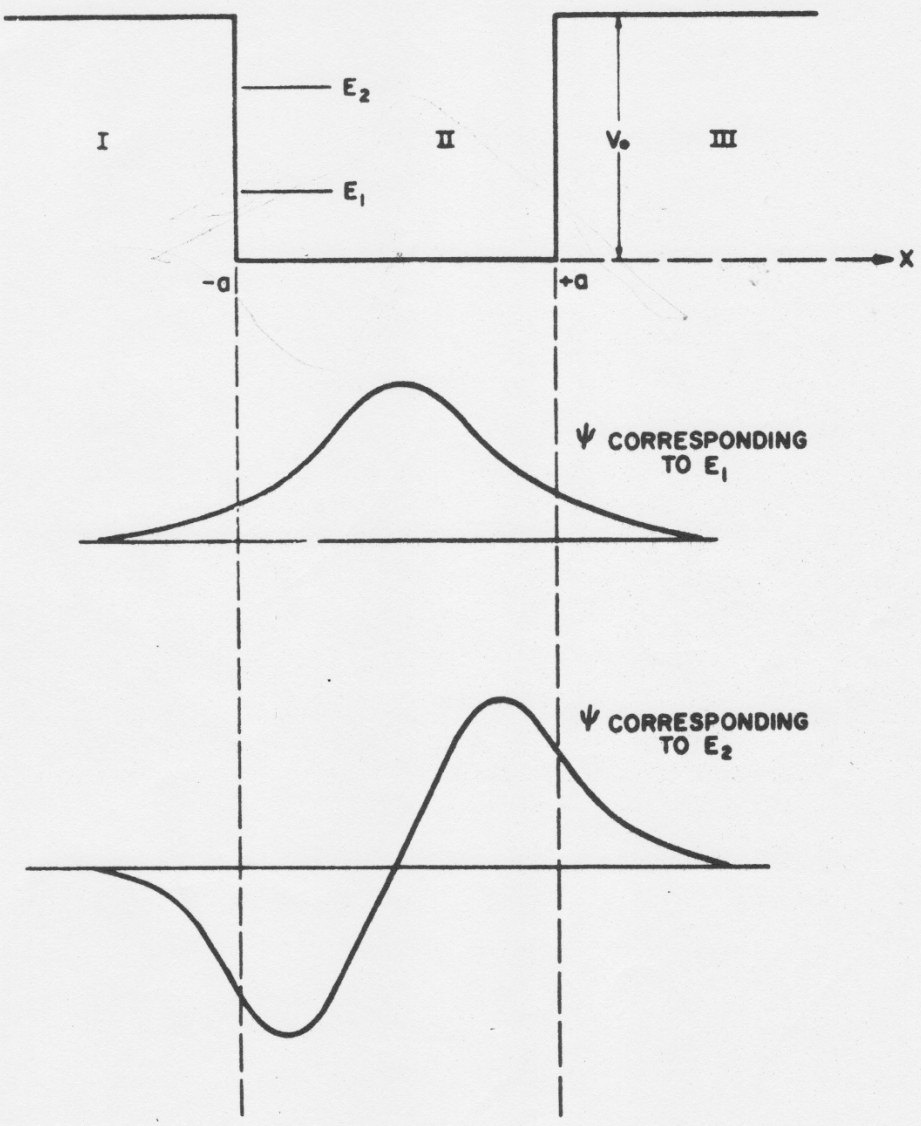
$$k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$



GRAPHICAL SOLUTION OF THE EQUATION

$$p(\epsilon) = \epsilon \tan \epsilon = \sqrt{\frac{2mV_o a^2}{\hbar^2} - \epsilon^2} = q(\epsilon)$$

FIGURE I. 3. 4



WAVEFUNCTIONS FOR THE LOWEST TWO BOUND STATES OF A PARTICLE IN A SQUARE WELL POTENTIAL

FIGURE I. 3. 5

I-3-18

The solutions in all the three regions are now sinusoidal, the only difference being that the solutions in Region and III have smaller momentum (linger wavelength) and the solution in Region II corresponds to a larger momentum (shorter wavelength). The boundary conditions are the same as before at $x = -a$ and $x = a$. On inserting these boundary conditions it will be seen that there is no restriction on the value of energy can enter this region of space. For this reason, these energy states are called free states.

I.3.6 Infinite Potential Well

We now consider the case of a particle confined to move under the influence of a square well whose walls are infinitely high. The potential energy is, $V_0 = 0$ when the particle is inside the well and is infinite everywhere else. We will choose the origin of the coordinate system differently this time. It must be pointed out that the answer to physical problems will not depend on the choice of the coordinate system or the origin. The reason for our changing to a different origin this time is just to expose the student to various methods of treating the problem. Therefore, we define the infinite potential well as follows:

$$V_0 = 0 \quad \text{when} \quad 0 < x < L$$

$$V_0 = \infty \quad \text{when} \quad x < 0 \quad and \; x > L$$

The requirement that the potential energy is infinite on the walls gives us the condition that the wavefunction ψ is 0 on the walls. The solution to the Schrödinger Wave Equation is

$$\psi = A \sin kx \; + B \cos kx \quad \text{where} \; \; k = \sqrt{\frac{2mE}{\hbar^2}}$$

Inside the well and is zero everywhere else. The boundary condition is $\psi = 0$ at $x = 0 \; and \; x = L$.

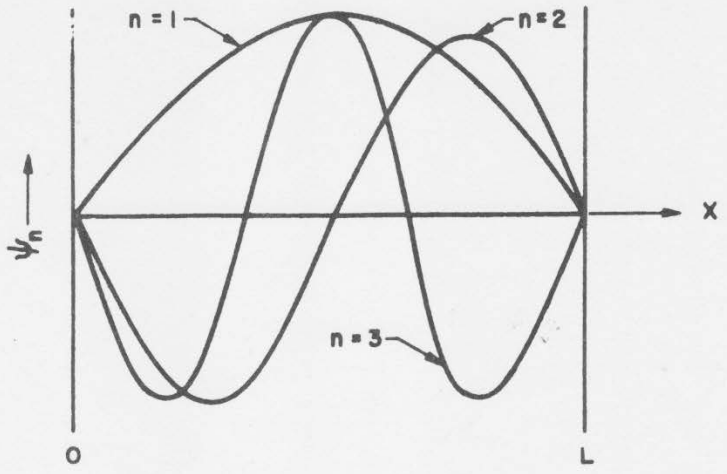
In order for ψ to be zero at the origin we must put $B = 0$. At $x = L$, again is zero. This means $sin(kL) = 0$. Therefore, $KL = n\pi$. The wavefunction becomes,

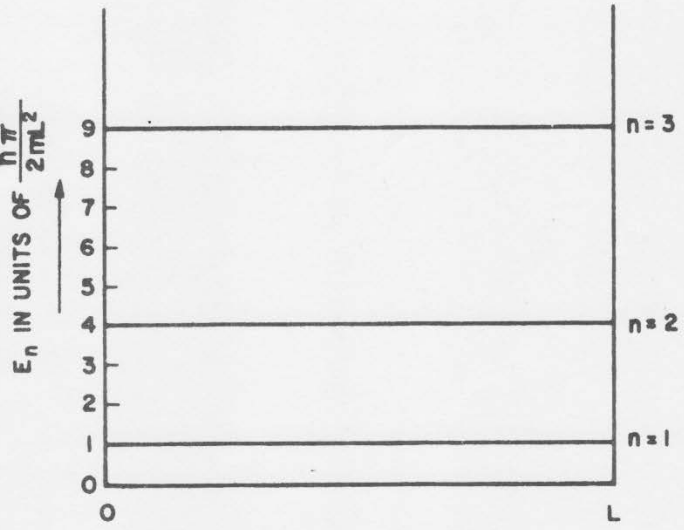
$$\psi = A \sin \frac{n\pi x}{L}$$

The normalization constant A, can be shown equal to $\sqrt{\frac{2}{L}}$. The energy of the particle is equal to

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m}\ \frac{n^2}{L^2} \qquad \text{(I.3.48)}$$

Therefore, we see that energy is quantized and the quantum number is n which specifies a particular energy level for each value of n. Thys we have arrived at the important result that the particle confined to an infinite well can take on only one or another of a set of discrete values of energy. The wavefunctions for the three lowest energy states for the square well with infinite sides are shown in Figure (I.3.6)





WAVEFUNCTIONS AND THE ENERGY LEVELS OF THE THREE LOWEST STATES FOR THE INFINITE WELL

FIGURE I. 3. 6

Problems: Chapter I.3

1. Consider a one dimensional potential well defined as follows: $V = -V_0$ between $x = 0\ and\ x =$ a . $V = 0$ is everywhere else. If particles are traveling in position x direction $(E > 0)$, find the amplitude of the wave representing the particle reflected at $x = 0$ in terms of the amplitude of the wave representing the particle incident from left to right at $x = 0$.
2. Calculate the root mean square position $\sqrt{< x^2 >}$ for the state $n = 1$ for an electron confined in a one dimensional infinite well of width 'a'. [Refer to the appropriate table of integrals.]
3. We saw that the wave function of an electron confined to the space $0 \leq x \leq L$ is given by $u(x) = A \sin \frac{n\pi x}{L}$ where n = integer. A is called the normalization constant. Show A is equal to $\sqrt{\frac{2}{L}}$.
4. If we solved the problem of the particle confined in a one dimensional infinite well of width L, by choosing the origin of the coordinate system to be in the center of the well, what solutions would you obtain? Show these solutions lead exactly to the same results as the ones obtained with the origin of the coordinate system chosen at one end of the wall.
5. Consider a potential barrier of height V_0 existing between $x = 0$ and $x = a$. Assume potential energy is zero everywhere else. Calculate the tunneling probability of an electron incident from left to right with energy $E < V_0$.
6. Find out the energy eigenstates of an electron bound in a square well potential of height of 10 eV and width 10 Å. Determine the energy of each of the eigenstates. Plot qualitatively the charge distribution in the three cases.
7. For a particle confined to the one dimensional region from – a to $+a$ on the x axis, with $V_0 = 0$ in this region and $V_0 > E$ outside:
   Considering the graphical solution to Schrödinger equation shown in Figure I.3.4 of the text
   a. How can we make the radius of the quadrant of the circle, q(ϵ), very large compared to the p(ϵ) plot shown?
   b. What does doing so represent physically?
   c. This gives us many possible solutions, with closely spaced energy levels. Find a crude approximation for a formula for the first few energy levels

in this case. [Hint: Assume the intersections of p(ϵ) and q(ϵ) occur along the almost horizontal portion of q(ϵ) approximately at the asymptotes of p(ϵ),]

d. From this formula, show how the energy level separation depends upon $h, a\ and\ m$.

e. Substitute your formula for allowed energies into the expression for k_1, and draw sketches showing how the first few wave functions (lowest energy levels) look between – $a\ and\ a$.
[Hint: The approximations called for here are the same as those for the infinite potential well.]

8. How small must a single crystal of a metal be if the spacing between electronic energy levels at low quantum numbers is to be detected in a physical experiment that can detected an energy change of 0.01 eV? Assume that the problem can be treated as a single electron free to move within the walls of a cubic box.
9. What is the potential energy if the wave function of a particle moving under this potential is $e^{9000x-1.4\times10^7 t}$ where x is measured in cm?
10. In Figure I.3.4, we considered solutions only in the first quadrant i.e. positive values for $\epsilon, p(\epsilon), and\ p'(\epsilon)$. Give arguments to justify this,

Chapter I.4

Three Dimensional Schrödinger Equation

I.4.1 Three Dimensional Systems

Until now, we have been concerning ourselves only with physical systems which are one dimensional. While the one dimensional problems illustrated the essential features of quantum mechanics, the real physical problems are three dimensional. We will now study the extension of the quantum mechanical principles to three dimensional case. The wavefunction now, will be a function of not only x and t, but also of y and z, i.e., $\psi = \psi(x, y, z, t)$. The operators corresponding to y, z, $P_y \; and \; P_z$ are exactly similar to the operators for x and P_x. In other words, the position variables y and z become multiplication operators y and z which multiply the wavefunction. The y and z components of the momentum operators $P_y and \; P_z$ become differential operators, $\frac{\hbar}{i}\frac{\partial}{\partial y}$ and $\frac{\hbar}{i}\frac{\partial}{\partial z}$, which operate on the wavefunction. The requirement on the proper behavior of the wavefunction becomes that ψ, $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y} \; and \; \frac{\partial \psi}{\partial z}$ are finite, continuous and single-values, throughout the configuration space, i.e., for all values of x, y,and z. The normalization condition or the square integrable condition becomes

$$\int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=-\infty}^{\infty} \psi^* \, \psi \; dxdydz = \int_{all \; volume} \psi^* \psi \; dr$$

where dr, the elementary volume$= dxdydz$

Similarly the domain of integration for the calculation of the expectation value is three dimensional. We have so far considered only the Cartesian coordinate variables x, y, z but it is possible to use other coordinate variables also, as will see now.

The operator corresponding to the momentum vector $\vec{P}$ can now be written by vectorially combining the operators for the components of momentum.

Therefore,

$$\vec{P}_{operator} = \frac{\hbar}{i}\left[\vec{a}_x \frac{\partial}{\partial x} + \vec{a}_y \frac{\partial}{\partial y} + \vec{a}_z \frac{\partial}{\partial z}\right]$$

This can now be shortened to $\frac{\hbar}{i}\ \vec{\nabla}$ where $\vec{\nabla}$ is the gradient operator operating on the wavefunction. Similarly, the operator for the square of the momentum can be written as - $\hbar^2\nabla^2$ where ∇^2 is the familiar Laplacian operator and is equal to the divergence of the gradient. In Appendix I we have given the gradient and divergence operator in the Cartesian, cylindrical and spherical coordinate system.

I.4.2 Particle in a Three Dimensional Box

We will now consider the case of a particle of mass m confined to a rectangular three dimensional box. Since the box is rectangular, we will choose the cartesian coordinate system. The box is bounded by $x = 0$ and $x = L_x, y = o$ and $y = L_y$ and $z = 0$ and $z = L_z$. The potential energy is taken as zero inside the box and infinite on the walls.

The Schrödinger equation for the particle is given by

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi(x,y,z) = E\,\psi(x,y,z) \qquad \text{(I.4.1)}$$

By writing ψ as a product of three functions $\psi = X\,Y\,Z$, where X is only a function of x. Y is only a function of y and Z is only a function of z, we can separate the Equation (I.4.1) into three single variable equations given below:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\,X(x) = E_x X(x) \qquad \text{(I.4.2)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}\,Y(y) = E_y Y(y) \qquad \text{(I.4.3)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\,Z(z) = E_z Z(z) \qquad \text{(I.4.4)}$$

where

$$E = E_x + E_y + E_z$$

Once we solve the three one dimensional equations and determine X, Y, Z and $E_x, E_y\ and\ E_x$, we have determined ψ and E. Let us consider Equation (I.4.2). We readily recognize this as the equation for the one dimensional infinite well which

we have already solved in the last chapter. The boundary condition for X is that $X = 0$ at $x = 0\ and\ x = L_x$. The wavefunction X is equal to

$$X = \sqrt{\frac{2}{L_x}} \sin \frac{n_x \pi x}{L_x} \tag{I.4.5}$$

Where n_x is a positive integer. Similarly the other solutions , $Y$and Z are given by

$$Y = \sqrt{\frac{2}{L_y}} \sin \frac{n_y \pi y}{L_y} \tag{I.4.6}$$

$$Z = \sqrt{\frac{2}{L_z}} \sin \frac{n_z \pi z}{L_z} \tag{I.4.7}$$

The total wavefunction ψ is therefore equal to

$$\psi = \sqrt{\frac{8}{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \tag{I.4.8}$$

The total energy E which we will characterize by the subscripts n_x, n_y, n_z to denote the quantum numbers, is equal to

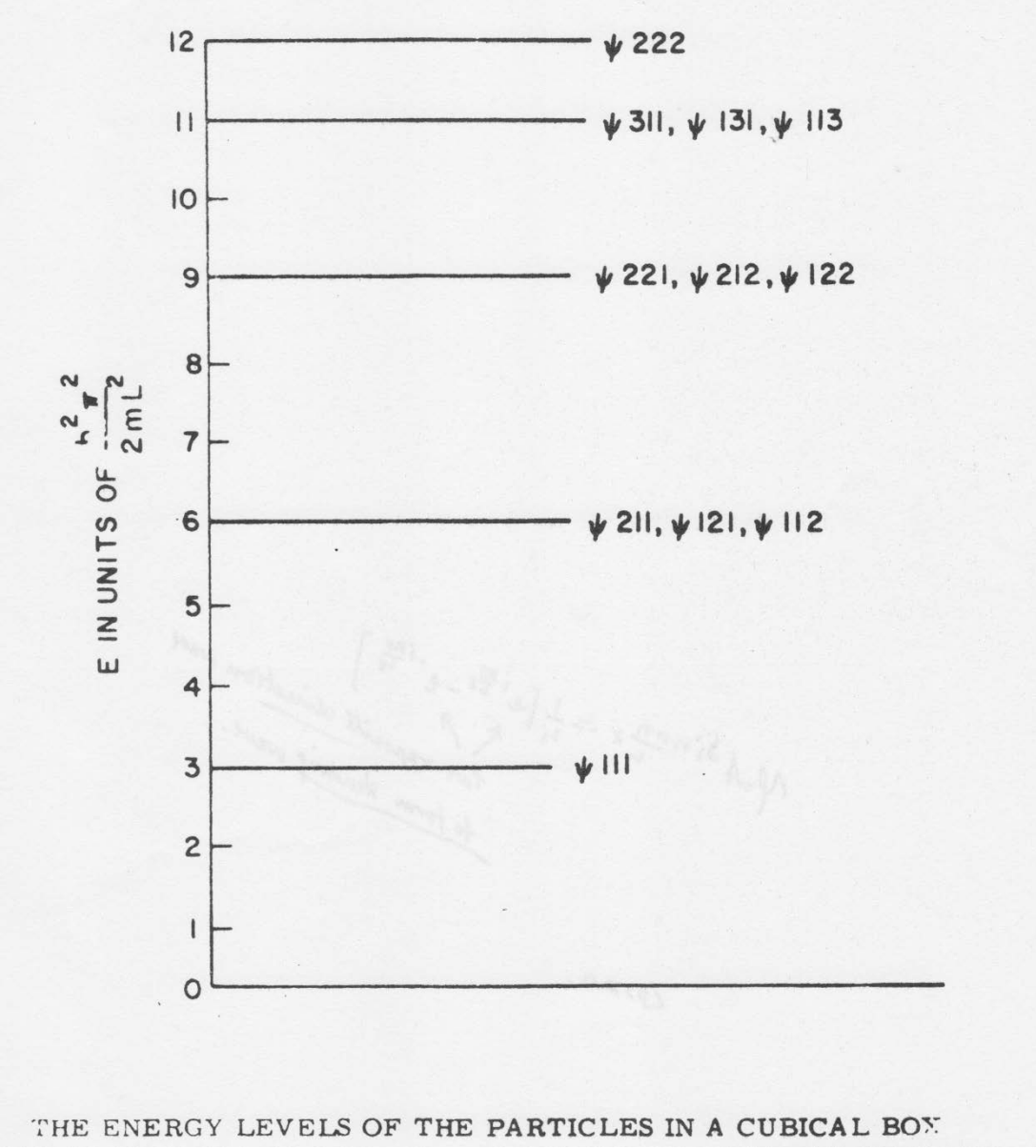
$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\frac{{n_x}^2}{{L_x}^2} + \frac{{n_y}^2}{{L_y}^2} + \frac{{n_z}^2}{{L_z}^2} \right] \tag{I.4.9}$$

Similarly each wavefunction is characterized by the quantum numbers $n_x, n_{y,} n_z$ and therefore for each set of integral numbers $n_x, n_{y,} n_z$ we have a wavefunction. We now see a new possibility which we had not seen earlier, viz., the possibility of two wavefunctions corresponding to the same energy. When this happens the two wavefunctions are said to be degenerate.

As an example let us consider a cubical box $L_x = L_y = L_z = L$. Then

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m\ L^2} \left[{n_x}^2 + {n_y}^2 + {n_z}^2 \right]$$

All the different wavefunctions which are related such that ${n_x}^2 + {n_y}^2 + {n_z}^2 = sam\ value$, are degenerate. For example, ψ_{112}, ψ_{121} and ψ_{211} are degenerate with the same energy equal to $\frac{6\ \hbar^2 \pi^2}{2m\ L^2}$. In Figure (I.4.1) we have shown the energy levels of the cubical box and the degeneracies involved.



THE ENERGY LEVELS OF THE PARTICLES IN A CUBICAL BOX

I.4.3 Hydrogen Atom

Let us now treat the hydrogen atom quantum mechanically. We shall assume as before that the nucleus is infinitely heavy in comparison with the electron and therefore we will consider the nucleus as fixed at the origin. The position of the electron is specified by the three spherical coordinate, r, θ and $\emptyset$, as shown in Figure I.4.2. The time independent Schrödinger equation is

$$\nabla^2\psi + \frac{2m}{\hbar^2}[\mathrm{E} - \mathrm{V(r)}]\,\psi = 0 \qquad \text{(I.4.10)}$$

where the potential energy is $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ (I.4.11)

In a spherical coordinates,

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\emptyset^2} \quad \text{(I.4.12)}$$

Assuming the solution ψ is a product of the three functions, R which is a function of r only, Θ which is a function of θ only, and ϕ which is a function of $\emptyset$,

$$\psi(r,\theta,\emptyset) = R(r)\ \Theta(\theta)\ \phi(\emptyset\ )$$

So, $\nabla^2\psi$ is

$$\nabla^2\psi = \frac{\Theta\phi}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R\phi}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right) + \frac{R\Theta}{r^2 sin^2\theta}\frac{\partial^2\phi}{\partial\emptyset^2}$$

By substituting this in Equation (I.4.10) and the Schrödinger equation becomes

$$\frac{\Theta\phi}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R\phi}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right) + \frac{R\Theta}{r^2 sin^2\theta}\frac{\partial^2\phi}{\partial\emptyset^2}$$

$$+\frac{2m}{\hbar^2}\big(\mathrm{E} - \mathrm{V(r)}\big)R\Theta\phi = 0 \quad \text{(I.4.13)}$$

We can rewrite this equation as

$$\frac{1}{\phi}\frac{\partial^2\phi}{\partial\emptyset^2} = -\left[\frac{sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right)\right] - \frac{2m}{\hbar^2}\big(\mathrm{E} - \mathrm{V(r)}\big)\ r^2 sin^2\theta$$

(I.14.14)

where the left hand side is a function of $\emptyset$ only , and the right hand side is only a function of r and θ. As argued before this is possible only if each side is independently equal to the same constant which we will write as $-m_l^2$ for convenience. Then

$$\frac{\partial^2\phi}{\partial\emptyset^2} = -m_l^2\phi \quad \text{(I.14.15)}$$

The solution to this equation is

$$\phi = \mathrm{A}\ e^{\pm i m_l \emptyset} \quad \text{(I.14.16)}$$

where A is a normalization constant. If we normalize each of the three solutions $R(r)\Theta(\theta)\phi(\emptyset)$, then their product equal to ψ will also be normalized. It can be shown that the normalization constant A for ϕ, is equal to $\sqrt{\frac{1}{2\pi}}$.

Therefore,

$$\phi = \sqrt{\frac{1}{2\pi}}\ e^{\,im_l \emptyset} \tag{I.4.17}$$

We also require that ϕ be single values. This means

$$\phi(\emptyset) = \phi(\emptyset + 2\pi) \qquad \text{i.e. } e^{\,im_l \emptyset} = e^{\,im_l (\emptyset + 2\pi)}$$

This is possible only if m_l is an integer positive or negative. For a given value of m_l, we can write Equation (I.4.14) as

$$\frac{sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right) + \frac{2m}{\hbar^2}[\mathrm{E} - \mathrm{V(r)}]\, r^2 sin^2\theta - m_l^2 = 0 \tag{I.4.18a}$$

This equation can be rewritten as

$$\frac{1}{sin\theta}\frac{1}{\Theta}\frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right) - \frac{m_l^2}{sin^2\theta} = -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2m}{\hbar^2}[\mathrm{E} - \mathrm{V(r)}]\, r^2 \tag{I.4.18b}$$

Where the left hand side is only a function of θ and the right hand side is only a function of r. As before, setting the separation constant as equal to $-l(l+1)$, we get

$$\frac{1}{sin\theta}\ \frac{\partial}{\partial\theta}\left(sin\theta\ \frac{\partial\Theta}{\partial\theta}\right) - \frac{m_l^2}{sin^2\theta}\Theta + l(l+1)\,\Theta = 0 \tag{I.4.19}$$

This equation is known as Associated Legendre equation. Physically meaningful solution are obtained only if l is a positive integer and when $|m_l| \leq l$. These solutions are called Associated Legendre polynomials. These solutions are denoted by Θ_{l,m_l} and the first few solutions are given below.

$$\Theta_{l,m_l} = \mathrm{N}_{l,m_l}\mathrm{P}_{l,m_l}(\theta)$$

where N_{l,m_l} is a normalization constant.

$$N_{l,m_l} = \sqrt{\frac{(2l+1)}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}}$$

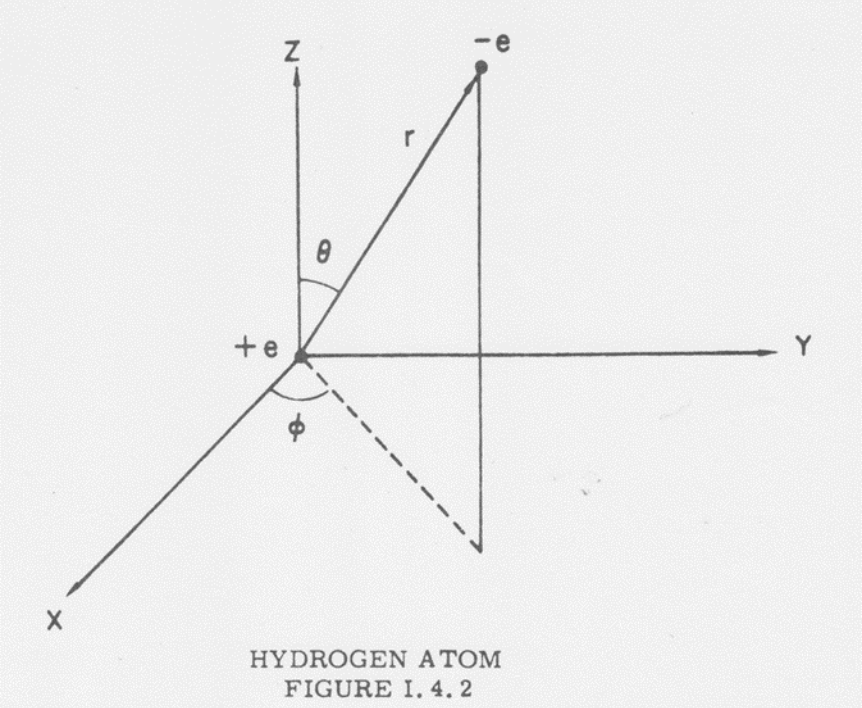
The first few $P_{l,m_l}(\theta)$ are:

$P_{0,0}(\theta) = 1$

$P_{1,0}(\theta) = \cos\theta; \quad P_{1,\pm1}(\theta) = \sin\theta$

$P_{2,0}(\theta) = (3\cos^2\theta - 1)$

$P_{2,\pm1}(\theta) = \sin\theta\cos\theta; \quad P_{2,\pm2}(\theta) = \sin^2\theta$



HYDROGEN ATOM
FIGURE I. 4. 2

The function R is called the radial function since it depends only on the radial distance r. The equation for the radial function $R(r)$ can now be written from equation (I.4.18) to be

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{l(l+1)R}{r^2} + \frac{2m}{\hbar^2}[E - V(r)]R = 0 \qquad \text{(I.4.20)}$$

We now consider those values of energy which are less than the ionization energy for the electrons; i.e., we consider negative values of energy. The solution to Equation (I.4.20) is

$$R(r) = e^{-\alpha r}\ (2\alpha r)^l L(2\alpha r) \qquad \text{(I.4.21)}$$

where

$L(2\alpha r)\ obeys\ Associated\ Laguerre\ equation$. This equation has meaningful solutions only if

$$n^2 = -\frac{m\, e^4}{8\, h^2 E \epsilon_0^2} \qquad \text{(I.4.22)}$$

where $n = 1,2,3, \ldots\ldots$ $\qquad l \leq n-1 \qquad and \qquad \alpha^2 = -\frac{2\, m\, E}{\hbar^2}$

The value of energy is therefore equal to

$$E = -\frac{m\, e^4}{8\, h^2 \epsilon_0^2\, n^2} \qquad \text{(I.4.23)}$$

Since n can take only integral values we see the energy is quantized and we indicate this by a subscript n. Therefore

$$E_n = -\frac{m\, e^4}{8\, h^2 \epsilon_0^2}\frac{1}{n^2} \qquad \text{(I.4.24)}$$

We indicate α also by a subscript n.

$$\alpha_n^2 = -\frac{2m\, E_n}{\hbar^2} = \frac{m^2\, e^4}{(4\pi)^2\, h^4 \epsilon_0^2}\frac{1}{n^2}$$

$$\alpha_n = \frac{m\, e^2}{4\pi\, \hbar^2 \epsilon_0}\frac{1}{n} = \frac{1}{a_0 n} \qquad \text{(I.4.25)}$$

where

$$a_0 = \frac{4\pi\, \hbar^2 \epsilon_0}{m\, e^2}$$

The associated Laguerre function $L(2\alpha r)$ is therefore characterized by two number n and l and is therefore denoted by $L_{n,l}(2\alpha r)$. The radial wave function $R_{n,l}(r)$ is equal to

$$R(r) = e^{-\frac{r}{a_0 n}}\ (2\alpha r)^l\ L_{n,l}(2\alpha r)$$

where we have neglected the normalization constant. The typical Associated Laguerre functions are as follows:

$L_{1,0}(2\alpha r) = 1$

$L_{2,0}(2\alpha r) = (1 - \alpha r)$; $\quad L_{2,1}(2\alpha r) = 1$

$L_{3,0}(2\alpha r) = (3 - 6\,\alpha r + 2\,\alpha^2 r^2)$; $\quad L_{3,1}(2\alpha r) = (2 - \alpha r)$; $\quad L_{3,2}(2\alpha r) = 1$

The total wave function is characterized by three quantum numbers, n, l, m_l

$$\psi_{n,l,m_l}(r, \theta, \emptyset) = R_{n,l,m_l}(r)\,\Theta_{n,l,m_l}(\theta)\,\phi_{n,l,m_l}(\emptyset)$$

where

$$\phi_{m_l}(\emptyset) = \sqrt{\frac{1}{2\pi}}\; e^{\,i m_l \emptyset} \qquad \text{(I.4.26)}$$

$$\Theta_{n,l,m_l} = \left(\frac{(2l+1)}{2}\,\frac{(l - |m_l|)\,!}{(l + |m_l|)\,!}\right)^{\frac{1}{2}} \mathrm{P}_{l,m_l}(\theta)$$

$$R_{n,l,m_l}(r) = const\; \times e^{-\frac{r}{a_0 n}}\,(2\alpha r)^l L_{n,l}(2\alpha r)$$

$$\alpha_n = \frac{1}{a_0 n}$$

$$a_0 = \frac{4\pi\,\hbar^2 \epsilon_0}{m\,e^2}$$

It will be recalled that a_0 is precisely the same expression as the radius of the smallest orbit in the Bohr model of the hydrogen atom. The numerical value of a_0 is approximately equal to 0.53 A. The Schrödinger equation can be interpreted as the energy operator operating on the wavefunction to give a number E_n times the wavefunction. Such an equation where an operator operating on a function gives a constant times the same function is called an eigenvalue equation. The function is called the eigenfunction and the constant is called the eigenvalue. The wavefunction is therefore an energy eigenfunction and E_n is an eigenvalue. If for any other operator the wavefunction which is the energy eigenfunction is an eigenfunction, then it is easy to show that the expectation value for this operator with this wavefunction is an exact value. The

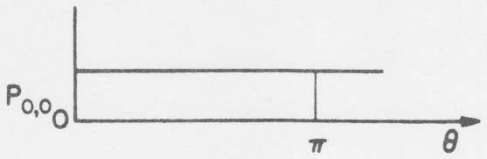
solution ψ_{n,l,m_l} is an eigenfunction of energy and we will later show that it is also an eigenfunction of other operators.

Let us now pause for a moment to consider how the electronic charge is distributed around the nucleus. With the help of Equation (I.4.17) we see that the probability density is independent of $\emptyset$. In other words, the electron is symmetrically smeared about the z axis. We can examine the θ dependence by considering Θ_{n,l,m_l}. They are illustrated in Figure I.4.3. We see that the state $n = 1$ and $l = 0$ corresponds to a spherical distribution of electronic charge. The radial functions for the first three states area shown in Figure I.4.4. To get a picture of how the electronic charge varies as a function of r we must plot $\left|R_{n,l}\right|^2 r^2$ and this is done in Figure (I.4.5). We see that a maximum occurs for $n = 1$ and $l = 0$ at approximately the same distance as the radius of the first Bohr orbit, a_0.

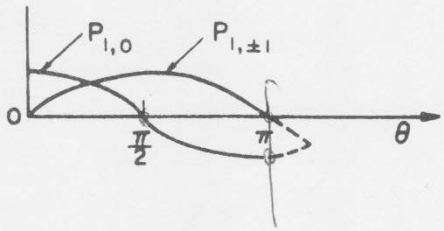
To summarize, we find in the quantum mechanical treatment that the electron cannot be thought of as being in a definite orbit at all, as being at a given location with a certain probability. The quantum number 'n' corresponds to the total quantum number 'n' in Bohr theory. The quantum numbers 'l' and 'm_l'will be shown, later on, to have some physical significance. For the present, all we know is that the energy is determined by n while the radial distribution of electronic charge density is determined by n and l and the angular distribution of electronic charge is determined by l and m_l.

The normal state of the hydrogen atom is the state in which the electron has the lowest energy. This state, also called the ground state, corresponds to $n = 0, l = 0, m_l = 0$. All states which are at a higher energy level than the ground state are called the 'excited' states. For example, the state with $n = 2, l = 1, m_l = 0$ is an excited state.

Since energy is dependent only on n, while each electronic states is characterized by n, l, m_l values, it means that we have degeneracies in each energy level. Later on, we will see that there is a fourth quantum number which is required to describe the state of the electron completely.

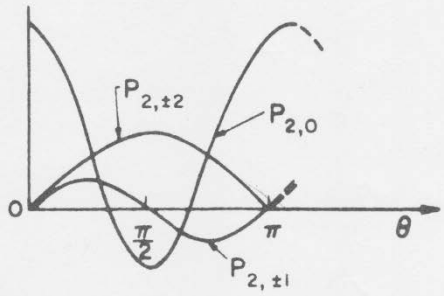


$P_{0,0} = 1$



$P_{1,\pm1} = \sin\theta$

$P_{1,0} = \cos\theta$



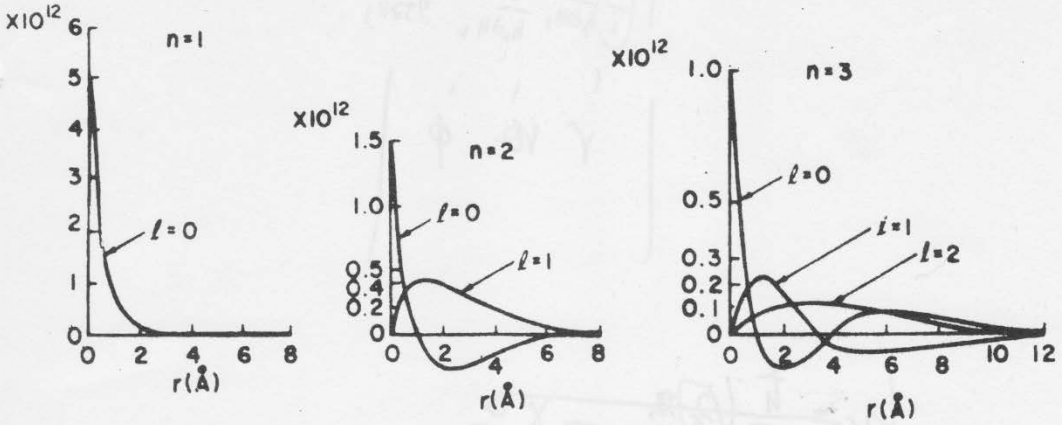
$P_{2,\pm2} = \sin^2\theta$

$P_{2,\pm1} = \sin\theta\cos\theta$

$P_{2,0} = (3\cos^2\theta - 1)$

PLOT OF θ DEPENDENT PART OF HYDROGEN WAVE FUNCTION

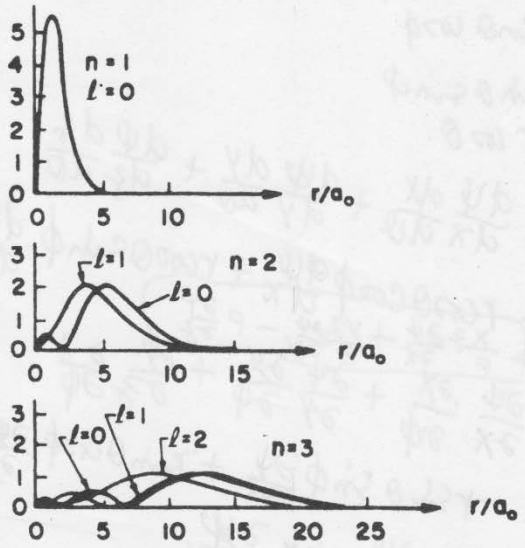
FIGURE I. 4. 3



THE RADIAL PART OF HYDROGEN WAVE FUNCTION

The distance from the nucleus is plotted along the abscissa in units of $A^{o}(10^{-10}m)$ while the ordinate gives normalized radial part.

FIGURE I.4.4



THE RADIAL PROBABILITY DENSITY AS A FUNCTION OF RADIAL DISTANCE

The abscissa gives the radial distance in units of $a_{o}(0.53A^{o})$. The ordinate gives the probability density in arbitrary units.

FIGURE I.4.5

I.4.4 One Electron Wavefunction

The previous treatment of the hydrogen atom can be carried over to describe any physical system where the electron is moving in a central field or force. By a central field or force, we mean the attractive force pulling the electron to the origin where the magnitude of the force is inversely proportional to the square of the radial distance r, of the electron from the origin.

If we assume that the nuclear charge is $+Ze$ instead of $+e$ as in the case of the hydrogen atom, and is located in the origin, while a single electron is rotating about this nucleus, we have for the energy of the electron,

$$E_n = -\frac{m\,e^4}{8\,h^2\epsilon_0^2}\frac{1}{n^2} \tag{I.4.27}$$

The expression for α_n

$$\alpha_n = \frac{Z}{a_0 n} \tag{I.4.28}$$

where

$$a_0 = \frac{4\pi\,\hbar^2\epsilon_0}{m\,e^2}$$

These equations apply to any ionized atom where we have a single electron revolving around a central charge distribution. For example, these equations will apply to singly ionized Helium atoms where $Z = 2$.

The wavefunction for an electron moving in a central field can be separated into a radial part and angular part as in the case of the hydrogen atom and the wave function will be characterized by the three quantum numbers n, l, m_l.

We will now give some physical interpretation for the quantum numbers $l\ and\ m_l$. The angular momentum L of a particle is given classically to be $r \times p$. By transforming this to corresponding operator formalism $\left(x \rightarrow x_{op};\ p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}\right)$, it can be shown that the $x, y, and\ z$ components of the angular momentum are equal to

$$L_x = \frac{\hbar}{i}\left[-\sin\emptyset\ \frac{\partial}{\partial\theta} - cot\theta\ cos\emptyset\frac{\partial}{\partial\emptyset}\right] \tag{I.4.29}$$

$$L_y = \frac{\hbar}{i}\left[\cos\emptyset\ \frac{\partial}{\partial\theta} - \cot\theta\ \ cos\emptyset\frac{\partial}{\partial\emptyset}\right] \quad \text{(I.4.30)}$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\emptyset} \quad \text{(I.4.31)}$$

The square of the magnitude of the total angular momentum is equal to

$$|L^2| = \hbar^2\left[\frac{1}{\sin\theta}\ \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\emptyset^2}\right] \quad \text{(I.4.32)}$$

We see, by operating on the wavefunction with the operator for the Z-component of the angular momentum given in Equation (I.4.31) we get $m_l\hbar$ to be the eigenvalue for the operator L_z. This gives $m_l\hbar$ to be the exact value of the Z-component of the angular momentum of the electron whose quantum numbers are n, l, m_l. In other words, the Z-component of the angular momentum is quantized. What this means is that the angular momentum vector can be only oriented in certain directions in space such that the Z-component of the angular momentum is an integral number of $\hbar$. For this reason, the angular momentum is said to be "space quantized".

Similarly if we operate on the wavefunction with the operator for the square of the angular momentum given in Equation (I.4.32) we get the eigenvalue $l(l+1)\hbar^2$ for the operator $|L^2|$. This shows that the magnitude of angular momentum is also quantized with l as the quantum number. Therefore, an electron described by a wavefunction characterized by n, l, m_l is in a state where the angular momentum magnitude is equal to $\sqrt{l(l+1)}\,\hbar$ and Z-component of the angular momentum is equal to $m_l\hbar$. In order to distinguish this angular momentum which is associated with the orbital motion of the electron from an intrinsic angular momentum that we will discuss shortly, we call this the orbital angular momentum.

I.4.5 Orbital Magnetic Moment

We saw earlier that an electron in a quantum state characterized by certain l and m_l values has an angular momentum of magnitude $\sqrt{l(l+1)}\,\hbar$ and z component of angular momentum $m_l\hbar$. By rigorous quantum mechanical analysis, it can be shown that an electron with a given angular momentum,

possesses a proportionate magnetic moment. However, for our purpose, we will use the Bohr's picture of an electron revolving around the nucleus, to derive an expression for the magnetic moment which is exactly identical to what one would obtain by more rigorous methods.

Let an electron of mass m and charge $-e$ revolve around the nucleus, in a circular orbit of radius r. The magnitude of angular momentum due to this orbital motion is equal to

$$\left|\vec{L}\right| = m\, r^2 \omega$$

This electron motion is equal to a current of $\frac{e\omega}{2\pi}$ (Figure I.4.6). According to electromagnetic theory, a circular loop of current of I amps gives rise to a magnetic moment of $\mu = A\, I$ where A is area in square meters. Therefore the electron orbital motion gives rise to a magnetic moment of magnitude

$$|\mu_l| = \pi r^2\, \frac{e\omega}{2\pi} = \frac{e\, r^2 \omega}{2} = \frac{e}{2\, m}\left|\vec{L}\right|$$

Vectorially, $\overrightarrow{\mu_l}$ and $\vec{L}$ are oppositely directed because of the negative sign of the electronic charge so that

$$\overrightarrow{\mu_l} = -\frac{e}{2\, m}\vec{L}$$

The subscript $l\ and\ \mu_l$ serves the purpose of denoting that this magnetic moment arises from orbital motion of the electron, i.e., from the orbital angular momentum.

We define a unit of magnetic moment called the Bohr magneton as equal to $\mu_B = \frac{e\hbar}{2\, m}$ which is the magnetic moment of a particle of mass same as that of the electron and charge $+e$. In terms of μ_B, $\overrightarrow{\mu_l}$ becomes

$$\overrightarrow{\mu_l} = -\frac{\mu_B}{\hbar}\vec{L} \qquad \text{(I.4.33)}$$

We will now generalize (without proof) that no matter what kind of orbital motion the electron executes, Equation (I.4.33) gives the correct relation between magnetic moment and orbital angular momentum. Therefore, we can substitute the quantum mechanical expression for $\vec{L}$ in Equation (I.4.33).

Quantum mechanically

$$|\vec{L}| = \sqrt{l(l+1)}\,\hbar$$

therefore,

$$|\vec{\mu_l}| = \mu_B\sqrt{l(l+1)} \qquad \text{(I.4.34)}$$

From Equation (I.4.33) we see that the Z components of magnetic moment and angular momentum are related by

$$\mu_{l_z} = -\frac{\mu_B L_z}{\hbar} \qquad \text{(I.4.35)}$$

Since $L_z = m_l\hbar$, this means that the magnetic moment $\vec{\mu_l}$ and therefore, $\vec{L}$ can have only certain orientations in space with respect to the Z-axis. However, any direction could have been chosen as a Z direction and as such it is meaningless to talk of space quantization. We must have an external field (electric or magnetic) then this direction can be taken as our quantization axis. In the next section we consider the effect of an external magnetic field.

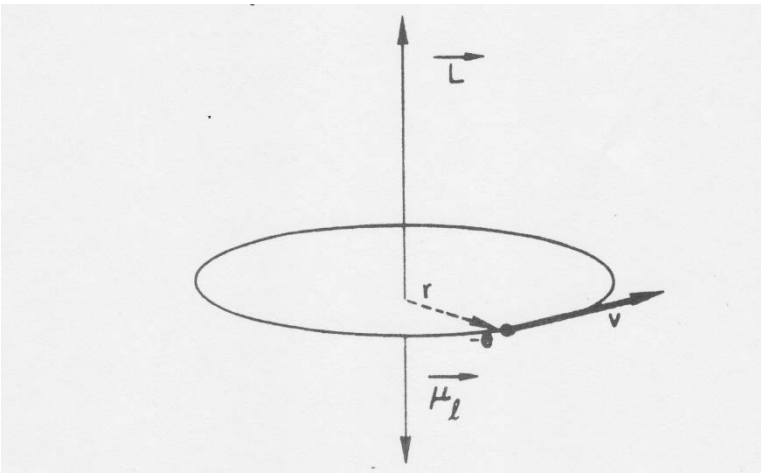


Fig. I. 4. 6 Magnetic moment of an electron in a circular orbit.

I.4.6 Effect of a magnetic field

Let the electron with a magnetic moment μ_l be placed in an uniform magnetic flux density B. From electromagnetic theory we know a torque is acting on the magnetic moment tending to orient the magnetic moment parallel to the uniform field. The magnitude and direction of this torque is equal to

$$\vec{\Gamma} = -\overrightarrow{\mu_l} \times \vec{B} \qquad (\text{I.4.36})$$

However, the potential energy due to the orientation of the magnetic moment is equal to

$$\Delta E = -\overrightarrow{\mu_l} \cdot \vec{B}$$

The potential energy is a minimum when the elementary magnet is aligned parallel to the magnetic field. In any other orientation, the potential energy is higher and the elementary magnet should be able to transfer this excess energy if it were to align itself parallel to the field. In the absence of any such dissipative mechanism the magnet has to maintain the same orientation as it had before the application of the field. The effect of the torque $\vec{\Gamma}$ is therefore to make the magnetic moment precess around the direction of the external field. We will now find an expression for the precessional angular velocity. From classical mechanics, we know the torque to be the time-rate of change of angular momentum. We know the torque to be the time rate of change of angular momentum, i.e.

$$\frac{d\vec{L}}{dt} = \vec{\Gamma}$$

But

$$\vec{\Gamma} = -\frac{\mu_B}{\hbar}\ \vec{L} \times \vec{B}$$

Therefore,

$$\frac{d\vec{L}}{dt} = -\frac{\mu_B}{\hbar}\ \vec{L} \times \vec{B} \qquad (\text{I.4.37})$$

i.e.

$$d\vec{L} = -\frac{\mu_B}{\hbar}\ \vec{L} \times \vec{B}\ dt \qquad (\text{I.4.38})$$

$d\vec{L}$ in Equation (I.4.38) represents an infinitesimal change in $\vec{L}$ in a time interval dt. Since $\vec{L} \times \vec{B}$ is perpendicular to $\vec{L}$, $d\vec{L}$ is perpendicular to $\vec{L}$. This means that in a time interval dt, the magniutuide of $\vec{L}$ does not change but only its direction. The change $d\vec{L}$ is perpendicular to the plane containing $\vec{L}\ and\ \vec{B}$, this means that

$\vec{L}$ and therefore $\overrightarrow{\mu_l}$ is precessing around $\vec{B}$ as shown in Figure (I.4.7). The projection of the vector $\overrightarrow{L}$ on the plane perpendicular to $\vec{B}$ moves through an angle $d\emptyset$, in time dt equal to

$$d\emptyset = \frac{\left|d\vec{L}\right|}{L\ sin\theta} = \frac{\mu_B}{\hbar}\frac{\left|\vec{L}\right|B\ sin\theta\ dt}{\left|\vec{L}\right|sin\theta} = \frac{\mu_B}{\hbar}B\ dt$$

$$= \frac{\mu_B}{\hbar}\ B\ dt \qquad \text{(I.4.39)}$$

Therefore the precessional angular velocity

$$\omega_L = \frac{d\emptyset}{dt} = \frac{\mu_B}{\hbar}B \qquad \text{(I.4.40)}$$

This phenomenon of precession of a magnetic moment about $\vec{B}$, is called Larmour precession. Since μ_z is quantized Equation (I.4.35), it means $\overrightarrow{\mu_l}$ and $\vec{L}$ can therefore have only certain orientations with respect to the B field, i.e., Z axis. For a given value of l, m_l can take any one of $(2l+1)$ values and therefore there are $2l+1$ orientations possible for the magnetic moment. Figure (I.4.8) illustrates the possible orientations of the atomic magnet for $l = 1$ with the magnetic field $\vec{B}$ along Z axis. Since $\mu_{l_z} = -\mu_B\ m_l$, μ_{l_z} can be $+\mu_B\ \ 0\ or - \mu_B$ corresponding to $m_l = -1, 0\ or + 1$ respectively.

In a magnetic field each of the $2l+1$ orientations will have a different energy, since the magnetic potential energy is equal to $-\overrightarrow{\mu_l} \cdot \vec{B} = \mu_{l_z}B$. The energy will be a minimum where μ_{l_z} is a maximum and therefore the state $m_l = -l$ will have the lowest energy and the energy will increase with increasing values m_l until the maximum energy is obtained for the state $m_l = +l$. This is illustrated in Fig. (I.4.9). The difference in energy between successive sublevels is equal to

$$\Delta E = \mu_B\ B$$

A level which is $(2l+1)$ fold degenerate in the absence of the field $\vec{B}$, is split into $(2l+1)$ levels in the presence of $\vec{B}$ and this is called the Zeeman splitting of the energy level. The spectral lines due to transitions from the degenerate level will split in the presence of the magnetic field and this effect is called Zeeman Effect.

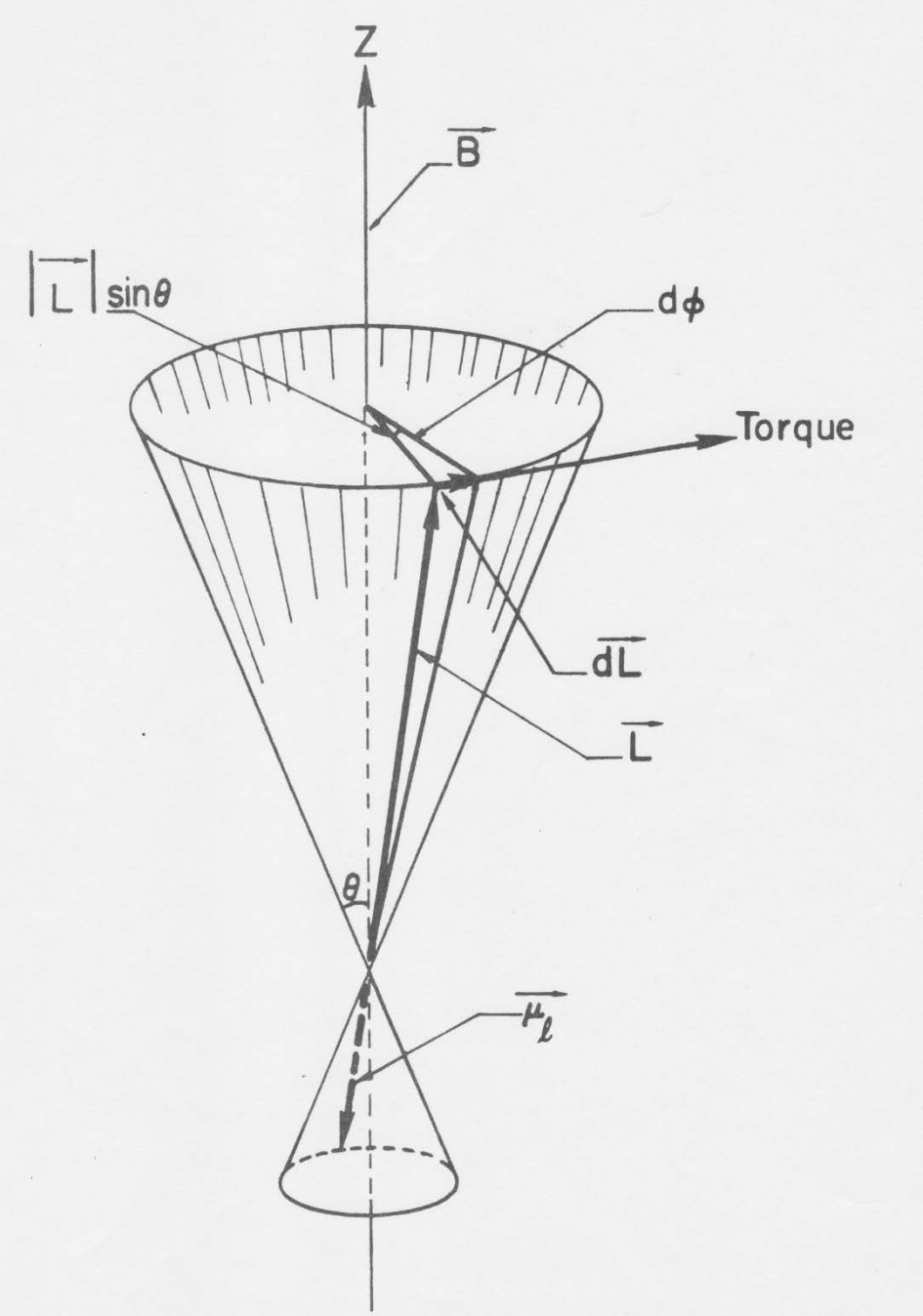


Fig. I-4.7 Precession of $\vec{L}$, the angular momentum around the external magnetic field $\vec{B}$.

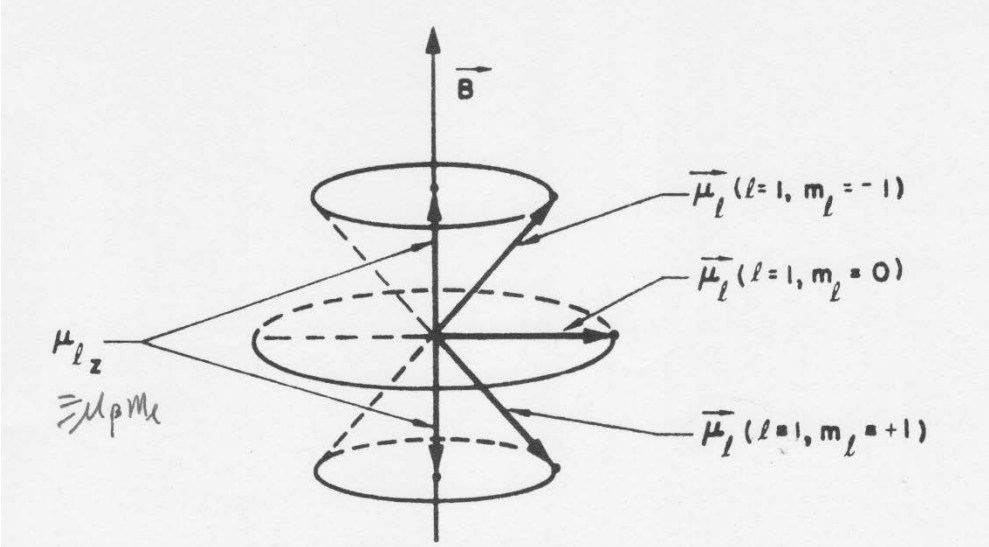


Fig. I-4.8 Spatial quantization of $\vec{\mu}_\ell$ for ℓ = 1.

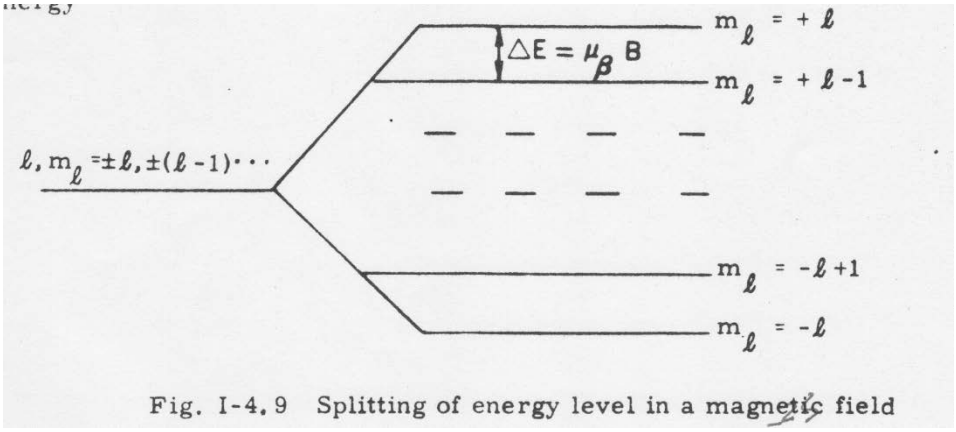


Fig. I-4.9 Splitting of energy level in a magnetic field

I.4.7 Spin Angular Momentum

Till now, we considered only the orbital angular momentum. However the electron has an intrinsic angular momentum called the spin-angular momentum. The existence of spin angular momentum was first postulated by Goudsmit and Uhlenbeck to explain the spectrum observed with one electron atoms.

Later on Dirac, in developing a relativistically corrected system of quantum mechanics, accounted for the existence of a spin angular momentum and an associated magnetic moment. He showed that the magnitude of the spin angular momentum is equal to

$$\left|\vec{S}\right| = \sqrt{s(s+1)}\,\hbar \qquad \text{(I.4.41)}$$

where the spin quantum number s $= \frac{1}{2}$ for an electron and the magnetic moment due to spin is equal to

$$\overrightarrow{\mu_s} = -\frac{l}{m}\vec{S} \qquad \text{(I.4.42)}$$

where $\vec{S}$ = spin angular momentum vector. It must be realized that the spin angular momentum is a quantum mechanical entity and has no classical analogue. The magnetic moment is usually also written in the form

$$\overrightarrow{\mu_s} = -g_s \frac{\mu_B}{\hbar}\vec{S} \qquad \text{(I.4.43)}$$

where g_s is called the spin g factor and is taken to be equal to 2. The Z-component of spin angular momentum is equal to

$$s_z = m_s\hbar \qquad \text{(I.4.44)}$$

where $m_s = +\frac{1}{2}\ or\ -\frac{1}{2}$ for electrons. Therefore the Z component of the magnetic moment due to spin is given by

$$\mu_{s_z} = -g_s\,\mu_B\,m_s \qquad \text{(I.4.45)}$$

Thus we see that the quantum state of an electron in a central field is not only specified by the three quantum numbers n, l, m_l which define the spatial part of the wavefunction but also by a fourth quantum number which defines the spin state of the electron. The total wavefunction should be therefore written as a product of the spatial part ψ_{n,l,m_l} and the spin part $\sigma(\,m_s)$. For our purposes, it is not necessary to know the explicit form of the spin part of the wavefunction. Hereafter, when we write $\psi_{n,l,m_l,\,m_s}$ for the wavefunction we mean the product of space and spin parts. Whenever we specified the quantum state of the electron.

We saw earlier that the energy of the electron in a given state depends only on the quantum number n. Actually there is a magnetic interaction between the spin and orbital angular momentum called the spin-orbit interaction, which makes the energy depend upon n, l and another quantum number j which specifies the total angular momentum the same way as the quantum number l specifies the orbital angular momentum. The total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

is the vector sum of orbital and spin angular momentum and for the case of one electron system the quantum number j can be $l + \frac{1}{2}$ or $l - \frac{1}{2}$. Thus, the spin-orbit interaction partially removes the degeneracy of energy levels which were $2\ n^2$ fold degenerate, and splits it into sublevels whose energies depend now on $n, l, and\ j$. Since the spin-orbit interaction is very small of the order of $\frac{1}{10{,}000}$ eV, the various levels corresponding to different l and j for a given value of n, lie very close to each other and for this reason, the spectral lines form groups of closed spaced lines. This close spacing of lines is referred to as the fine structure of the spectral lines. A quantum state now (in the presence of spin-orbit interaction) is defined by the four quantum numbers $n, l, j\ and\ \ m_j$ and not by $n, l, m_{l,}\ m_s$. What we mean by this, is that the wavefunction we obtain by including the spin-orbit interaction is not an eigenfunction of $\overrightarrow{L_z}$ and $\overrightarrow{S_z}$ but is an eigenfunction $\left|\vec{J}^2\right|$ and $\vec{J}_z$.

We will now describe the spectroscopic notation to describe the one electron states. The electronic state is denoted by writing the value of the principal quantum number n followed by a letter to denote the value of the orbital angular momentum quantum number l as follows:

Value of l	Letter designation
0	S
1	P
2	D
3	F
4	G
5	h

For example, if we say the electron is in $2s$ state we mean $n = 2$ and $l = 0$ for the state in which the electron is. Usually the electron in a given state, say $2s$, is called an $2s$ electron. If it is in $3p$ state it is called an $3p$ electron.

The total number of electronic states for a given value of n, can be shown to be $2\,n^2$. For, there are n values of l ranging from 0 to $n-1$. For each value of l there $(2l+1)$ values of m_l. In addition there are two independent values of m_s.

To summarize, we saw in this chapter that we were able to apply quantum mechanical principles to a particle in three dimensional space. We treated the hydrogen atom (an electron moving under the influence of a nucleus fixed at the origin) quantum mechanically and arrived at results which fitted the experimental values exactly. We found we had to give up the classical ideas of describing the position of the electron as in the Bohr atom and talk of the probability of find the electron at various positions around the nucleus. Later on in the chapter we arrived at expressions for the magnetic moment of the electron, using Bohr model of the atom and then stated without proof that the same expressions hold good even if we use rigorous quantum mechanical techniques. We discussed the existence of an intrinsic or spin angular momentum in addition to the orbital angular momentum. We considered the effect of spin-orbit interaction on the splitting of energy levels and characterized quantum states by a new set of four quantum numbers. We defined the total angular momentum of the electron.

I.4.8 Complex Atoms

Till now we considered problems in which only one particle is involved. Even in the case of hydrogen atom, we considered the nucleus to be fixed and the electron to be the only particle in the problem capable of motion. We will now discuss qualitatively the more complex atoms which contain more than one electron. A neutral atom is said to have an atomic number Z if it has Z electrons around the nucleus. The problem of a complex atom is a dynamical problem where each of the Z electrons is acted on by the nucleus as well as the other (Z-1) electrons. This problem is too difficult to solve analytically. Only approximate methods are possible. The most useful approximation is to replace the force acting on an electron (which force depends on the coordinates of this electron as well as the coordinates of all other electrons belonging to the given atom) by an average force which is a central force. As we saw earlier, the central field problem is similar to hydrogen atom problem and therefore each of the Z electrons will be described by hydrogen-like wavefunctions characterized by the four quantum

numbers $n,\ l,\ m_{l,}\ m_s$. It is natural to expect that all the Z electrons will therefore remain in the state $n = 1$ in the normal state, since this will correspond to the lowest energy for the atom as a whole. But, there is an interaction between the electrons which is described by Pauli's Exclusion Principle. According to this principle no two electrons can occupy the same quantum state. Since each quantum state is characterized by the four quantum numbers $n,\ l,\ m_{l,}\ m_s$, no two electrons can have the same set of four quantum numbers.

Now we can examine how the electrons are distributed among the available quantum states in a complex atom. The two guiding principles are: (1) there can be only one electron in each quantum states and (2) subject to principle 1, the electrons occupy the lowest energy states.

I.4.9 Electronic Structure of Atoms

We now begin the study of the periodic table and the electronic structure of the atoms.

$Z = 1$: Hydrogen: As we already saw in our earlier studies, the single electron is in a state n =1, $l = 0,\ m_{l,} = 0\ and\ \ m_s = \pm\frac{1}{2}$. The ionization energy of the atom which is required to remove one electron from the atom to infinity is 13.6 eV. The average distance of the electron from the nucleus is approximately $\frac{3}{4}$ Å.

$Z = 2$: Helium: Helium has two electrons. There are two states for n=1, corresponding to $l = 0,\ m_{l,} = 0\ and\ \ m_s = +\frac{1}{2}$ and $l = 0,\ m_{l,} = 0\ and\ \ m_s = -\frac{1}{2}$. Therefore, both the electrons occupy the $1s$ states. It must be pointed out that the wavefunction for either of the two electrons, is not the same as for the electron in hydrogen atom, since we must take into account the electrostatic repulsion between the two electrons. The ionization potential is 24.58 volts band because of this large ionization potential, helium is an inert element. The amount of energy involved when helium gives up or takes another electron is very high and therefore helium does not form a chemical compound with other elements. The electron configuration for Helium is $1s^2$.

$Z = 3$: Lithium: Lithium has three electrons. Only two of these can go to the $1s$ state. So the third electron goes into $2s$ states. It might be asked why $2s$ state and not $2\ p$ state, since energy is dependent only on the principal quantum number n. The two $1s$ electrons are localized near the nucleus and their wavefunctions (and therefore the position probability density) are spherically symmetric. The third electron therefore moves around this spherical core. The wavefunction of an electron in a state of lower angular momentum is large close to the nucleus compared with that for an electron in a state of higher angular momentum. Therefore the $2s$ electrons spend more time close to the nucleus where the screening due to the two $1s$ electrons is less effective. On the other hand, the electron in a state of higher angular momentum is kept away from the nucleus and therefore the energy of the electron in $2s$ state is lower than the energy of the electron in the $2p$ state. Actually this is a general result which applies to all values of n higher than $n = 1$. For a given value of n, states of smaller l have lower energy. All states having the same l value within a shell, are said to belong to the same subshell.

The electron configuration of lithium is therefore $1s^2 2s$. The ionization potential of lithium is only 5.39 volts. Low ionization mans that positive ions are formed with very little expenditure of energy and this is the reason why lithium is strongly active in forming chemical compounds. The number of electrons that an element gives up or takes in forming a chemical compound is called the valency of the element. Thus we see that the valency of lithium is one and lithium is electro-positive. Since the second ionization energy, i.e., the energy required to remove a second electron from lithium, is very large (75.6 eV), lithium always goes into chemical compound with a valency of one.

$Z = 4$: Beryllium: The electron configuration is $1s^2 2s^2$. Beryllium has a valency of 2; the ionization potential is 9.32 volts.

$Z = 5$: Boron: The electron configuration is $1s^2 2s^2 2p$. Boron has a valency of 3 and therefore, Boron is said to be trivalent. The ionization potential of Boron is 8.30 Volts.

$Z = 6$: Carbon: The electronic structure of carbon is $1s^2 2s^2 2p^2$ and therefore is tetravalent. The ionization potential is 11.26 volts.

$Z = 7$: Nitrogen through $Z = 9$: Florine: We fill the $2p$ sates as the atomic number increases until we have filled five $2p$ states corresponding to Fluorine. All of these atoms are electro-negative which means that these elements form compounds by taking up additional electrons. The energy with which the additional electron is bound to Fluorine is equal to 4.2 eV. The common way of expressing this is to say that Fluorine has an electron affinity of 4.2 eV. The concept of electron affinity is similar to ionization potential for electro-positive elements.

$Z = 10$: Neon: Neon has a closed shell since all the $2p$ states are filled giving rise to an electron configuration $1s^2 2s^2 2p^6$. Therefore, Neon is inert.

$Z = 11$: Sodium to $Z = 18$: Argon: In this case the shell $n = 3$ is filled the same way as $n = 2$ until we complete the subshell $3p$. The electron configuration corresponding to Argon is the completed subshell $3p$ and this element is an inert element although the shell $n = 3$ is not completely filled because the ionization energy of the closed subshell structure $3p$ is high.

$Z = 19$: Potassium and Z=20: Calcium: Instead of filling $3d$ subshell, Potassium and Calcium have the $4s$ states occupied since the energy of $4s$ subshell is lower than that of $3d$.

$Z = 21$: Scandium through $Z = 30$: Zinc: The energy of $3d$ subshell lies between $4s$ and $4\ p$ subshells and therefore $3d$ levels get filled up. For copper, $Z = 29$, the $4s$ subshell is higher than $3d$ and so we end up having 10 electrons in $3d$ subshell and one electron in $4s$ subshell.

The elements with incomplete $3d$ subshells while the 4s subshells are occupied are called transition elements. All these transition elements are very similar in chemical properties since the $3d$ subshells do not affect the ionization energy.

$Z = 21$: Gallium through $Z = 36$: Krypton: The $4p$ shells get filled up for these elements.

Having seen how the electronic structure of elements up to $Z = 36$ is arrived at it is a simple matter to know the electronic structure of the remaining elements. Table (I.4.1) gives the electronic structure of all the known elements while Appendix II gives the periodic table. We see from an examination of Table

(I.4.1) and the periodic table that the regularities of chemical properties are precisely predicted by quantum mechanics.

TABLE 1.4.1

ELECTRON CONFIGURATION OF THE ELEMENTS

H	$1s$	Cr	$\ldots. 3d^5 4s$
He	$1s^2$ Spherical distribution.	Mn	$\ldots. 3d^5 4s^2$
Li	$1s^2 2s$	Fe	$\ldots. 3d^6 4s^2$
Be	$.. 2s^2$	Co	$\ldots. 3d^7 4s^2$
B	$.. 2s^2 2p$	Ni	$\ldots. 3d^8 4s^2$
C	$.. 2s^2 2p^2$	Cu	$\ldots. 3d^{10} 4s$
N	$.. 2s^2 2p^3$	Zn	$\ldots. 3d^{10} 4s^2$
O	$.. 2s^2 2p^4$	Ga	$\ldots. 4s^2 4p$
F	$.. 2s^2 2p^5$	Ge	$\ldots. 4s^2 4p^2$
Ne	$.. 2s^2 2p^6$ ← spherical distribution	As	$\ldots. 4s^2 4p^3$
Na	$.. 3s$	Se	$\ldots. 4s^2 4p^4$
Mg	$.. 3s^2$	Br	$.. 4s^2 4p^5$
Al	$.. 3s^2 3p$	Kr	$.. 4s^2 4p^6$
Si	$.. 3s^2 3p^2$	Rb	$.. 4s^2 4p^6 5s$
P	$.. 3s^2 3p^3$	Sr	$.. 4s^2 4p^6 5s^2$
S	$.. 3s^2 3p^4$	Y	$.. 4s^2 4p^6 4d\ 5s^2$
Cl	$.. 3s^2 3p^5$	Zr	$.. 4s^2 4p^6 4d^2 5s^2$
A	$.. 3s^2 3p^6$	Nb	$.. 4s^2 4p^6 4d^4 5s$
K	$.. 3s^2 3p^6 4s$	Mo	$\ldots. 4d^5 5s$
Ca	$.. 3s^2 3p^6 4s^2$	Ma	$\ldots. 4d^6 5s$
Sc	$.. 3s^2 3p^6 3d\ 4s^2$	Ru	$\ldots. 4d^7 5s$
Ti	$\ldots. 3d^2 4s^2$	Rh	$\ldots. 4d^8 5s$
V	$\ldots. 3d^3 4s^2$		

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TABLE 1.4.1 (Continued)

Pd	.... $4d^{10}$	Yb	.. $4f^{13}5s^{2}5p^{6}5d^{1}6s^{2}$
Ag	.... $4d^{10}5s$	Lu	.. $4f^{14}5s^{2}5p^{6}5d^{1}6s^{2}$
Cd	.... $4d^{10}5s^{2}$	Hf	.. $5s^{2}5p^{6}5d^{2}6s^{2}$
In	.... $4d^{10}5s^{2}5p$	Ta	.. $5d^{3}6s^{2}$
Sn	.... $4d^{10}5s^{2}5p^{2}$	W	.. $5d^{4}6s^{2}$
Sb	.... $4d^{10}5s^{2}5p^{3}$	Re	.. $5d^{5}6s^{2}$
Te	.... $4d^{10}5s^{2}5p^{4}$	Os	.. $5d^{6}6s^{2}$
I	.... $4d^{10}5s^{2}5p^{5}$	Ir	.. $5d^{7}6s^{2}$
Xe	.... $4d^{10}5s^{2}5p^{6}$	Pt	.. $5d^{9}6s$
Cs	.... $4d^{10}5s^{2}5p^{6}6s$	Au	.. $5d^{10}6s$
Ba	.... $4d^{10}5s^{2}5p^{6}6s^{2}$	Hg	.. $5d^{10}6s^{2}$
La	.... $4d^{10}5s^{2}5p^{6}5d\ 6s^{2}$	Tl	.. $5d^{10}6s^{2}6p$
Ce	.... $4d^{10}4f\ 5s^{2}5p^{6}5d^{1}6s^{2}$	Pb	.. $5d^{10}6s^{2}6p^{2}$
Pr	.... $4d^{10}4f^{2}5s^{2}5p^{6}5d^{1}6s^{2}$	Bi	.. $5d^{10}6s^{2}6p^{3}$
Nd	.... $4d^{10}4f^{3}5s^{2}5p^{6}5d^{1}6s^{2}$	Po	.. $5d^{10}6s^{2}6p^{4}$
Pm	.... $4d^{10}4f^{4}5s^{2}5p^{6}5d^{1}6s^{2}$	At	.. $5d^{10}6s^{2}6p^{5}$
Sa	.... $4d^{10}4f^{5}5s^{2}5p^{6}5d^{1}6s^{2}$	Ry	.. $5d^{10}6s^{2}6p^{6}$
Eu	.... $4d^{10}4f^{6}5s^{2}5p^{6}5d^{1}6s^{2}$	Fr	.. $5d^{10}6s^{2}6p^{6}7s$
Gd	.... $4d^{10}4f^{7}5s^{2}5p^{6}5d^{1}6s^{2}$	Ra	.. $5d^{10}6s^{2}6p^{6}7s^{2}$
Tb	.... $4d^{10}4f^{8}5s^{2}5p^{6}5d^{1}6s^{2}$	Ac	.. $5d^{10}6s^{2}6p^{6}6d^{1}7s^{2}$
Ds	.... $4d^{10}4f^{9}5s^{2}5p^{6}5d^{1}6s^{2}$	Th	.. $5d^{10}6s^{2}6p^{6}6d^{2}7s^{2}$
Ho	.. $4f^{10}5s^{2}5p^{6}5d^{1}6s^{2}$	Pa	.. $5d^{10}6s^{2}6p^{6}6d^{3}7s^{2}$
Er	.. $4f^{11}5s^{2}5p^{6}5d^{1}6s^{2}$	U	.. $5d^{10}6s^{2}6p^{6}6d^{4}7s^{2}$
Tm	.. $4f^{12}5s^{2}5p^{6}5d^{1}6s^{2}$		

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Problems: Chapter I. 4

1. For a box 1 cm on a side, how many electron states exist with total momentum $P\left(=\hbar\sqrt{k_x^2+k_y^2+k_z^2}\right)$ less than 10^{-25} Kg-meter/sec?
2. Consider an electron in a three dimensional rectangular box of dimension $2\text{Å} \times 2\text{Å} \times 4\text{Å}$.
   a. Find the energy and degeneracy of the lowest degenerate state
   b. Calculate the probability of find the electron in the second lowest energy state in an elementary rectangular volume (no interpretation) $0.01\ \text{Å} \times 0.01\text{Å} \times 0.2\text{Å}$ center around the center of the box
3. Determine the normalization constant for the radial part of the wavefunction of an electron in the 1s state of Hydrogen atom. Hint: $\int_0^\infty y^2 e^{-y^2}\, dy = \frac{\sqrt{\pi}}{4}$
4. Show that normalizing the total wave function, for the hydrogen atom,

$$R_{n,l,m_l}(r)\ \Theta_{n,l,m_l}(\theta)\ \Phi_{n,l,m_l}(\emptyset),$$

where

$$\Phi(\emptyset) = \mathrm{A}\, e^{\pm i m_l \emptyset}$$

results in $A^{-1} = \sqrt{2\pi}$

5. Consider an electron bound within a spherical region of space of radius b, so that $U = 0$ from $r = 0\ to\ r = b\ and\ U \to \infty\ at\ r = b$. Separate the Schrödinger equation in spherical coordinates to obtain three ordinary differential equations for $R(r),\ \Theta(\theta), \Phi(\emptyset)$ as was done for the H-atom. Are any of these three equations familiar? This problem demonstrates that there are important similarities among all problems with a spherically symmetric potential energy function.
6. Prove that, to show the variation of electronic charge density as a function of radial distance, r_1 , from the nucleus in the hydrogen atom, we must plot

$$\left|R_{n,l}\right|^2 r^2$$

rather than just

$$\left|R_{n,l}\right|^2$$

7. Calculate the probability that an electron in the 1s state will lie in an elementary volume contained between the following coordinates $= 0.5\text{Å}\ and\ 0.5001\ \text{Å}, \theta = 30^0\ and\ 30.01^0\ and\ \emptyset = 45^0\ and\ 45.01^0$. [Hint: Consider the elementary volume to be so small that integration is not required]
8. Show that the most probable radius for the electron in the ground state of hydrogen is 'a' by finding the value of r for which dP/dr is a maximum.
9. What is the angular momentum of an " f " electron?
10. How many " f " electrons can be placed in the $n = 4$ "orbit"?
11. Show that the operator for z-component of angular momentum is $\frac{\hbar}{i}\frac{\partial}{\partial\emptyset}$
12. Show that the total number of electron states in a shell characterized by quantum number n is equal to $2n^2$.
13. How many valence electrons (electrons not in a filled n-shell) are there for an atom with 32 electrons?
14. An electron moving in a central filed (i.e. under the influence of a positive charge fixed at the origin) is in a state $l = 2$. A magnetic field is applied along the Z-direction of magnitude 10,000 ampere-turns/meter. Show in a figure the spatial quantization of both $\overrightarrow{\mu_l}$ and $\vec{L}$. Also what is the splitting in energy level (in eV or cm^{-1}) of the $(2l + 1)$ degenerate state due to the magnetic field? What is the value of Larmour frequency?