CHAPTER 1

Historical Background

1.1 Newtonian Mechanics

Newtonian mechanics or classical mechanics in its simplest form, known as the laws of mechanics is written in terms of particle trajectories. In fact, the trajectory underlies the structure of classical physics and the particle underlies the model of physical reality. The underlying assumptions and philosophical implications of classical physics are so familiar that we have never given them a second thought. Classical physics ascribes to the universe an Objective Reality, an existence external to and independent of human observers.

Our central assumption about the nature of classical universe is that, it is predictable. Knowing the initial conditions of a system, however complicated it might be, we can use Newton's laws to predict its future. This notion is the essence of determinism that supported Newtonian mechanics for more than three centuries.

Newtonian mechanics has taken such strong roots and everybody believed that everything in this universe can be explained on the basis of these laws. Many scientists have predicted the end of science as they thought that there is nothing new to know and nothing more to investigate. In fact, Prof. John Trowbridge at Harvard University, the then Head of the Department, felt compelled to warn bright students away from physics. He told them that the essential business of Science is over. All that remains is to dot a few 'i's and cross a few 't's, a task best left to second rate.

In 1994, Albert Michelson, the future recipient of the Noble Prize told the audience in one of the conferences that "it seems probable that most of the underlying principles have been firmly established and that further advances are to be sought chiefly in the rigorous application of these principles to all phenomena which come under our notice. The future truths of physics are only to be looked for, in the sixth place of decimals".

However, these ideas did not lost long and with the discovery of x-rays, radioactivity and electron in the last decade of the 19th century, the scientists had to think afresh about the universe.

Röentgen discovered x-rays in his laboratory at Wurtzburg in 1895. For this discovery, he received Rumford medal of the Royal Society in 1896 and the first Nobel Prize in physics in 1901. Henry Bacquerel in 1896 trying to reproduce Röentgen's x-rays, accidentally discovered radioactivity in potassium uranyl sulphate, a phosphorescent rock available in his laboratory. For this discovery, he shared the 1903 Noble prize in physics with the Curies.

In 1897, the British Physicist J. J. Thompson demonstrated that the beam that leaves the cathode, the so-called cathode rays, consists of a beam of negatively charged discrete particles. By balancing this beam between an electric and magnetic field, Thompson was able to measure the charge to mass ratio of these particles, the currently accepted value being 1.7588×10^{11} Coulombs/Kilogram ($C.Kg^{-1}$). Thompson also estimated the charge on the electron by utilizing the observation by C. T. R. Wilson (of the Wilson cloud chamber) that a charged particle acts as nucleus around which water vapour condenses. Thus by performing an early version of the famous oil drop experiment of Millikan, Thompson calculated the charge on the electron to be about 1×10^{-19}C and its mass to be about 6×10^{-31} Kg. Although Thompson's charge to mass measurement was quite accurate, his determination of charge itself was in error by 50%. Consequently, his calculation of the electronic mass was in error by 50%. Nevertheless, he did show that an electron was much lighter than the lightest atom and so it should be a subatomic particle. A little over 10 years later, Millikan refined the electron charge as 1.60×10^{-19} C almost getting the modern value of 1.6022×10^{-19} C.

Although these experiments did not lead immediately to the realization of the inadequacy of the classical physics, they showed that the atom was far more complex than had previously been thought. It was a major challenge to classical physics to provide a structure for the atom, but this was a challenge to which classical physics never rose.

J. J. Thompson
(1856-1940)

Thompson Studied Engineering at Owens College where he developed interest in Science. In 1876, he went to Cambridge University on a scholarship and remained there for the rest of his life. In 1884, he succeeded Lord Rayleigh as the Cavendish Professor of Physics and Director of the Cavendish laboratory. Thompson was an excellent teacher and administrator. Seven Nobel Prize Winners were trained under Thompson at the Cavendish. In 1919, he resigned his Directorship in favour of Ernest Rutherford, in part because of his lack of sympathy for the new Physics of Niels Bohr. Thompson was awarded the Nobel Prize in Physics in 1906 and was knighted in 1908.

1.2 Black Body Radiation

When a body is heated it emits thermal radiation, and the nature of this radiation depends on the temperature of the emitting body. When the heating element of an electric stove is turned on, it emits radiation. This radiation can be detected by placing one's hand at some distance above the heating element. If the stove is on low heat, the radiation can be detected by feeling only and not by sight. If the heat is turned up, the stove element will begin to glow first red, then white and if the temperature could be raised high enough, even blue. This change in colour is evidence that the frequency distribution of the radiation emitted by the hot body is changing with temperature.

In order to study such radiation, it was found that a particularly desirable system was one known as a "black body". When radiation falls on a surface, some of the radiation is reflected and some is absorbed. The absorptivity of a surface is defined as the fraction of the light incident on the surface that is absorbed, and a black body is defined as one that has an absorptivity of unity. That is, it absorbs all the radiation that is incident upon it. In addition, it has been shown (Kirchhoff's law) that the ratio of emissive power, 'E', to the absorptivity, 'A' i.e.

$$\frac{E_0}{A_0} = \frac{E}{A}$$

is a constant for a given temperature.

Now, since the absorptivity of a black body has been defined as unity ($A_0 = 1$), we see that the total emissive power of any surface must be given by, $E = AE_0$ where E_0 = total emissive power of a black body. Since 'A' is necessarily less than unity for any surface other than a black body, it is obvious that no surface can emit more strongly than a black body. *Therefore, it is seen that a black body is both the most efficient absorber and also the most efficient emitter of radiant energy.*

Many experiments were carried out on the black body radiation. The apparatus used for the study of black body radiation consists of a well insulated cavity with a small opening in one of the walls, and this type of furnace is kept at constant temperature. This furnace is called an isothermal enclosure and the radiation is observed as it passes through the small hole or opening. In 1858, Kirchhoff was able to show that if the walls and contents of the cavity are kept at a constant temperature at equilibrium, the stream of radiation in one direction must be the same as that in any other direction. It must be the same at any point in the enclosure and makes no difference of what material the walls are composed.

In 1879, Stefan had given an empirical relation for the rate of emission of radiant energy per unit area of a surface. *(The law was experimentally discovered by Stefan in 1879 and derived by Boltzman in 1884 based on the principles of thermodynamics)*

$$E = e\sigma T^4$$

where E = Rate of emission of radiant energy per unit area, (or the total emissive power), T = Absolute temperature, e = emissivity of the surface, σ = Stefan-Boltzman constant. (Emissivity is defined as E/E_o and for a black body emissivity, $E_o = 1$).

A problem that was of considerable interest at that time was the distribution of energy in the spectrum as a function of wavelength and temperature. In 1894, Willy Wien has provided another useful piece of information in the form of displacement law. It says that the wavelength that corresponded to the maximum of the energy distribution of the black-body radiation, obeys the relation,

$$\lambda_{\max} T = \text{Constant.}$$

This is a consequence of the theoretical attempts made to calculate the shapes of the energy spectra as a function of wavelength.

In an attempt to find an expression for the monochromatic emissive power, Wien utilised the classical methods of thermodynamics to obtain the equation

$$E_\lambda = \frac{a}{\lambda^5} f\left(\lambda T\right)$$

where ‘a’ is constant and f(λT) is a function of λ & T.

In order to determine the function f((λT), it was necessary to consider the mechanism by which the radiation is emitted. Since, Kirchhoff had shown that the nature of the walls, and therefore the nature of the radiator, is not important in an isothermal enclosure, any reasonable model can be chosen. Wien chose oscillators of molecular size and applied the laws of classical electromagnetic theory. He obtained the equation,

$$E_\lambda = \frac{a}{\lambda^5} e^{-b/\lambda T}$$

where ‘a’ and ‘b’ are constants.

Another theoretical attempt to determine a distribution law was made in 1900 by Rayleigh, by applying the equipartition principle to electromagnetic field. This calculation consists of two parts. In the first, one calculates the number of oscillators in an enclosure that correspond to a wavelength, λ. The second part, in accord with the classical equipartition principle, involves associating an energy, KT with each oscillator. Jean commented on some of the mistakes in the calculation and their combined effort, resulted in the form of a modified equation, known as Rayleigh-Jeans equation,

$$E_\lambda = \frac{2\pi kT}{c\lambda^4}$$

Almost simultaneously in 1899, Lummer and Pringsheim made the experimental determination of the energy distribution from a black body at various values of the temperature. The results are shown in Fig. 1.2.1.

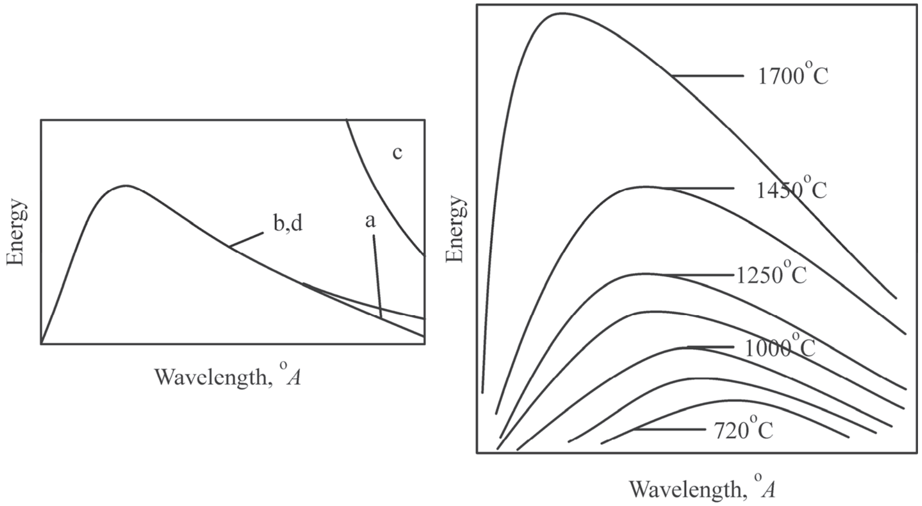


Fig. 1.2.1 Comparison of the three radiation laws with the experimental data. (a) Wien (b) Planck and (c) Rayleigh-Jeans with (d) the dotted experimental curve.

Wien equation gives excellent agreement with experiment in the region of short wavelengths and the Rayleigh-Jeans equation appears to be asymptotically correct at long wavelengths. This equation is clearly not correct, since, it predicts an impossible situation, namely, at shorter and shorter wavelengths the radiation intensity should increase without bound. This paradox known as the "*ultraviolet catastrophe*", dealt a terrible blow to the 19th century classical physics. Hence, neither of the equations is consistent with the experimental curves over the complete spectral range.

Many attempts were made to propose equations to fit into the total experimental spectrum. Such an attempt by Max Planck has brought out the most revolutionary hypothesis of the era.

For the same reason, Wien was able to choose any type of energy radiator that he wished, Planck too made such a choice. It had to be a system capable of emitting and absorbing radiation, and among those the simplest type for the purpose of calculation is a set of simple harmonic oscillators. Now, according to classical ideas, an oscillator must take up energy continuously and emit energy continuously. However, in order to find a formula that would fit the experimentally determined spectrum of a black body radiator, Planck found it necessary to postulate that such an oscillator cannot take up energy continuously as demanded by classical theory, but rather it must take energy in discrete amounts.

These amounts are integral multiples of a fundamental energy unit ε_o that is, 0, ε_o , 2 ε_o , ... n ε_o .

Using this idea, Planck was able to derive the equation,

$$E_\lambda = \frac{2\pi c}{\lambda^4} \frac{\varepsilon_o}{e^{\varepsilon_0/kT} - 1}$$

for the monochromatic emissive power of a black body. Here, 'c' is the velocity of light and 'k' is the Boltzman constant. Since the Wien equation is of thermodynamic origin, and therefore correct, it is necessary for the distribution law of Planck to contain the temperature in the combination, T or (T/ν) or (ν/T).

Consequently, it can be seen that the quantum of energy, ε_o must be proportional to 1/λ or ν. We find that ε_o = hν, where h = Planck's constant. By making the substitution for ε_o.

$$E_\lambda = \frac{2\pi c^2}{\lambda^5} \frac{1}{e^{ch/\lambda kT} - 1}$$

Whereas the energy distribution laws for black body radiation deduced from classical concepts had consistently failed to explain the experimental data, the quantum hypothesis of Planck succeeded. The hypothesis involves no extension of classical ideas, but it is a radical change from the prevalent line of thought of that time. Quite in contrast to the classical idea that an oscillator can absorb and emit energy continuously from wavelengths of zero to infinity, Planck proposed that the energy must be emitted or absorbed, only in discrete amounts. This implies that any system capable of emitting radiation must have a set of energy states, and emission can take place only when the system changes from one of these energy states to another. Intermediate energy states do not occur. Thus, we may find an oscillator emitting an energy of 2hν, but not 0.5 hν.

Physical Basis for the Success

The physical basis for the success of the quantum hypothesis may be, due to the fact that, at a particular temperature there may not be sufficient energy available to excite the higher frequency oscillators. It is because, based on the quantum hypothesis, they can be excited only by absorbing not less than one quantum of energy, hν. On the classical theory, the oscillators could be excited in a continuous manner. Therefore, at the temperature T, when the mean thermal energy available is kT, even the highest frequency oscillators could be excited with a frequency 'ν' (and by equipartition, an energy kT) and so contribute to the radiation from the emitter. Planck's quantum hypothesis therefore has the effect of damping out the high-frequency oscillators, just as we realised was necessary.

Black body radiation is a fundamental problem, and we have arrived at a solution by making a radical alteration to classical theory. Therefore, we should expect to discover ramifications of hypothesis in other parts of physics and chemistry.

It was not long before Planck's hypothesis had another application. In 1905, in order to explain photoelectric effect, Albert Einstein postulated that light energy had to be quantized.

1.3 The Photoelectric Effect

In 1887, Hertz observed photoelectric effect and the first outstanding application of quantum theory was in its explanation by Albert Einstein in 1905. It should be noted that though Planck introduced the idea that radiation must be emitted in quanta or bundles of energy, he however believed that, after being so emitted, the radiation spread in waves. Einstein extended Planck's idea further and introduced the important concept that the radiation energy is not only emitted in quanta but the quanta also preserved their identity until they were finally absorbed.

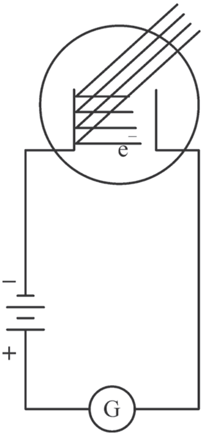


Fig. 1.3.1 Schematic diagram of apparatus for investigating the photoelectric effect.

Photoelectric effect is the ejection of electrons from various materials when irradiated by visible or ultraviolet light. This effect is the basis of photoelectric cell, an extremely sensitive instrument used for detection and measurement of radiation. An arrangement that can be used for this study is shown in Fig.1.3.1.

Laws of photoelectricity, established from experimental facts are as follows:

(a) The total photoelectric current is proportional to the intensity of the light striking the surface.

(b) For each particular metal used to form the surface, there exists a threshold frequency or (wavelength) such that, at frequencies below the threshold, no electrons are emitted, no matter how great the intensity might be.

(c) The maximum energy of the emitted electrons is independent of the light intensity.

(d) The maximum energy of the emitted electrons is linearly dependent on the frequency of the incident light. Fig.1.3.2.

Item (a) is quite expected, item (b) involving discontinuity is surprising, item (c) is totally unexpected and item (d) is an unexplained phenomenon.

Clearly, the photoelectric effect must require an explanation radically different from classical electromagnetic theory. Einstein's celebrated note of 1905 provided the correct explanation. Going even further than Planck, who limited himself to the introduction of discontinuity in the mechanism of absorption and emission, Einstein postulated that light radiation itself was discontinuous, consisting of beam of corpuscles, named as photons. A photon is thus a single quantum of electromagnetic radiation and has the energy, hν.

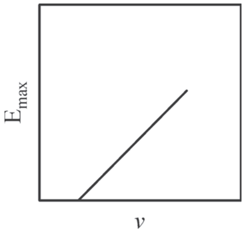


Fig. 1.3.2 Variation of the maximum energy of the photoelectrons with frequency of the incident radiation.

According to the Einstein's explanation, when a photon strikes a metal surface, a given electron on the surface would receive either all of its energy 'hν' or no energy at all. Again as the electron escapes from the metal, it uses up certain energy, W, in overcoming the surface forces, called the work function. Moreover, if the electron originates below the surface, additional amount of energy may be used up in reaching the surface. So, for an electron originating at the surface or one which loses no energy in reaching the surface, the Kinetic Energy (K.E.) after leaving the surface will be the maximum.

Obviously, this K.E. is the difference between hν and W.

So $(½)\ mv^2 = h\nu - w$

$= h\nu - h\nu_0$

So $(½)\ mv^2_{max}$ = stopping potential $= h\nu - w$ or $h\nu - h\nu_0$.

Thus, we can see that if the energy of the incident photon is less than the energy needed by the electron to escape from the surface, no emission can take place, regardless of the intensity of the incident light, i.e., the number of photons, which strike the surface per second.

According to classical physics, electromagnetic radiation is an electric field oscillating perpendicular to its direction of propagation, and the intensity of the radiation is proportional to the square of the amplitude of the electric field. As the intensity increases, so does the amplitude of the oscillating electric field.

The electrons at the surface of the metal oscillate along with the field. As the intensity (amplitude)of the field increases, the electrons oscillate more violently and eventually break away from the surface with a kinetic energy that depends on the amplitude (intensity) of the field. This nice classical picture is at complete variance with the experimental observations. Further, this classical picture predicts that the photoelectric effect should occur for any frequency of the light as long as the intensity is sufficiently intense.

1.4 The Compton Effect

The Compton effect provided further evidence for the quantum nature of radiation. If photons are really particles, they should possess a momentum, 'p', equivalent to hν/c. This momentum should be observable by allowing a beam of light to fall on a beam of electrons, when a transfer of momentum should be observed as a scattering of the electrons by the light beam, or as a scattering of the photons by the electrons. Compton performed this experiment using x-rays as the light beam in 1922, and the results he obtained were in complete agreement with the predictions.

It has been observed that when monochromatic X-rays impinge on elements of low atomic weight, the scattered X-rays were found to be of longer wavelength than those of the impinging beam. This phenomenon cannot be explained based on the classical theory, because as per this theory monochromatic light falling upon matter should be scattered without change in frequency.

However, the effect could be satisfactorily explained as resulting from an impact between the X-ray photon and the electron. Because of this collision, the electron recoils and the photon is scattered. In the process the electron gains momentum and the photon loses momentum. The decrease in momentum of the photon is manifested in the form of lowering of its frequency or increase in its wavelength.

It has also been shown that only one value of the wavelength shift is observed at a given scattering angle: this implies that the momentum transfer takes place only in a discrete manner and not continuously.

The photoelectric effect is stronger than Compton effect when X-rays of energy less than 0.1 MeV are used. In the process of the photoelectric effect, the energy of an X-ray photon is completely given up to an electron of the atomic system. Since it is impossible for a photon to give up all its energy to a free electron, the photoelectric effect can take place only when photons strike bound electrons. At higher X-ray energies (about 0.1 MeV) the Compton Scattering becomes more important. In this case, an X-ray photon is scattered and not really absorbed, since it does not lose a very large fraction of its energy. At still higher energies, above 1 MeV (wavelengths less than

0.0120 Å), the process of pair formation plays a part in the absorption of X-rays. As the photon energy increases this process becomes more important than either photoelectric absorption or Compton Scattering.

Gamma rays are very short electromagnetic waves whose energy range overlaps that of X-rays and extends to several MeV. Under suitable conditions, a gamma-ray-photon converts itself into a pair of material particles, a positive electron and a negative electron. The former is called the positron, while the word electron is used only for negative electrons. In this process of pair formation discovered by Anderson in 1932, two particles each of mass m_0 are created out of the energy of the gamma-ray, if the initial energy is at least equal to $2m_0c^2$. According to Einstein's mass-energy relation $E = mc^2$, the energy required to create an electron is 0.511 MeV. Thus, pair formation cannot take place until the energy of the photon is at least 1.022 MeV the threshold energy for pair formation. Experimentally also this is found to be true. If the initial photon energy is greater than this threshold value, the excess appears as kinetic energy shared equally by the positron and the electron.

1.5 Atomic Spectra

At a time when people were engaged with the problems of black body radiation, a similar development was taking place in the field of atomic spectra.

1. *It was observed that when an electric discharge is passed through an element in the gaseous state, light will be emitted*
2. *Analysis of this light by a prism or grating spectrometer gives a series of sharp lines of a definite wavelength, which prove to be characteristic of the particular element.*

In the case of light element such as hydrogen, this line spectrum turns out to be simple, but for heavier elements, it is more likely to be extremely complex. As the experimental data accumulated, people observed some sort of orderliness, and so, tried to obtain empirical relations to predict the sequence of lines.

1. In 1883, Liveing and Dewar realised that several possible series exist in the spectra of alkali and alkaline earth metals but could not discover an empirical relation to present the order.
2. In 1885, Balmer discovered the equation.

$$\lambda = \frac{bn^2}{n^2 - 4}$$

where '*b*' is a numerical constant and '*n*' is an integer, e.g. 3, 4, 5......etc. The agreement between the observed values, of the lines in the hydrogen spectrum and their values calculated by the Balmer formula, turns out to be extremely good.

$$\nu = \frac{c(n^2 - 4)}{bn^2} = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

The above equation can be expressed as

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

where R = Rydberg constant.

The Rydberg constant has been found to be specific for a given element and very nearly constant for all elements. The difference in its value is due to the atomic weight of the element, and it has been found to have a value of 109,677.58 cm^{-1} for hydrogen.

At the time when the Balmer series was discovered, the known portion of the electromagnetic spectrum was the visible region (4000 to 8000 Å) alone. After this discovery, the same general type of other series were discovered. The Lymann series was found in the ultraviolet region and the Paschen, Brackett and Pfund series were found in the infrared.

The general equation can be written as:

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where	$n_1 = 1$	Lyman series	u.v.
	$n_1 = 2$	Balmer series	Visible
	$n_1 = 3$	Paschen series	Near IR
	$n_1 = 4$	Brackett series	Far IR
	$n_1 = 5$	Pfund series	Far IR
and	$n_2 > n_1$		

Although the early developments in atomic spectra were significant, they were nevertheless empirical. For the most part, they were restricted to classifying and correlating the observed data by means of empirical relations, and there was no clue how these spectral lines arouse.

1.6 Atomic Models

The origin for the spectral lines could be the atoms, is a reasonable assumption. But, how the atoms are able to emit such characteristic lines has remained a matter of speculation because of the absence of any satisfactory concept of the structure of the atom. Subsequently things became clear.

1. With the discovery of radioactivity and the emission of positive, negative and a number of combinations of these particles, it became clear that atom is composed of these newly found particles. So immediately the next question will be, how many of each category are there and how they are arranged in an atom.
2. Basing on the available data at that time, J. J. Thompson proposed a model of the atom with the positive charge distributed uniformly throughout a sphere of diameter 10^{-8} cm. The electrons are embedded in the sphere in equilibrium positions and when disturbed, they oscillate about these equilibrium positions.

   Though it is a crude model, it could account for the occurrence of spectral lines, but it could not explain the scattering of 'α' particles (${}_{2}^{4}He^{2+}$).

   One of the ways by means of which these ‘α’ particles can be observed is by the scintillations they cause on a fluorescent screen coated with zinc sulphide. When a thin gold foil is placed in the path of the ‘α’ particles, naturally a change in pattern on the screen is expected, compared to the one obtained without the gold foil in the path. However, the immediate question will be “How it will change?” Therefore, Thompson calculated theoretically and concluded that the average deflection of the ‘α’ particles should be small and the probability of the large scale scattering is essentially zero. But, Geiger and Marsden noted experimentally that about 1 in 8000 ‘α’ particles, incident on a gold foil, is deflected through an angle greater than 90^0. This is in complete disagreement with Thompson’s model and his predictions.
3. To resolve this, Rutherford proposed a new model of an atom in which the positive charge is concentrated in a small volume at the centre of the atom. The electrons are then assumed to move around this centre of positive charge in various orbits, as the planets in the solar system. This is an improvement over the Thompson’s model as it accounts for the wide angle scattering of the ‘α’ particles in the gold leaf experiment. However, it also met with some difficulties.
   (a) The electrons could not be considered to be stationary because the unlike charges of the electron and the nucleus cause them to come together.
   (b) If the electrons are assumed to be moving around the nucleus, another problem arises. When an electric charge is accelerated, it emits or absorbs radiation. If the electrons are pictured as moving around the nucleus, they are subject to centripetal acceleration. According to the principles of electromagnetic theory, the electrons therefore must radiate energy. The only place for this continuous supply of energy is

the atom itself, and eventually the electron should spiral into the nucleus and in essence run down. Hence, Rutherford's model is not the final answer.

1.7 The Bohr Atom

Through many models were proposed, the model proposed by Niels Bohr (1913) for the hydrogen like atom, is unique in gaining universal recognition. Using the structural ideas of the Rutherford atom, Bohr was successful in quantitatively applying the concepts of quantum theory to explain the origin of line spectra as well as the stability of the atom.

Bohr was able to overcome the difficulties encountered in the earlier model, by applying the quantum concept of discrete energy states.

Assumptions

1. The electron in an atom is restricted to move in a particular stable orbit, and as long as it remains in this orbit, it will not radiate energy.
2. Using the quantum principle, that an oscillator will not emit energy except when it jumps from one energy state to another, Bohr postulated that when the electron jumps from a stable energy state of energy E_1 to another state of lower energy E_2, a quantum of radiation is emitted, with an energy equal to the difference between the two states.

$$h\nu = E_1 - E_2$$

3. In the final form of the theory, Bohr assumed the orbits to be circular with a size such as to satisfy the quantum condition that the angular momentum, p, of the electron is an integral multiple of the quantity h/2π. Thus

$$p = \frac{nh}{2\pi} = mvr.$$

$$\therefore \qquad v = \frac{nh}{2\pi mr}$$

where m and v are the mass and velocity of the electron. '*h*' is the Planck's constant and 'n' is a positive integer known as a quantum number.

For a quantitative treatment of a one electron system, the force of attraction between the electron and the nucleus is considered to arise from the electrostatic attraction between the positive charge of the nucleus and the negative charge of the electron, thus $F = Ze^2/r^2$, where Z is the atomic number of the element and 'r' is the distance between the nucleus and the electron.

This electrostatic attraction should be equal to the centripetal force resulting from the motion of the electron about the nucleus

$$\therefore \qquad \frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

$$\therefore \qquad \text{r} = \frac{Ze^2}{mv^2}$$

But according to the quantum condition

$$p = n.\frac{h}{2\pi} = mvr$$

Hence, substituting the value of 'v' in the above equation

$$r = \frac{n^2h^2}{4\pi^2 \quad mze^2}$$

for the hydrogen atom, Z = 1 and if the electron is considered to be in the ground state (n = 1) the radius of the atom can readily be calculated to be r = 0.529 A^0.

Energy of the Electron in the Atom

The total energy of the electron of the atom is made up of its kinetic and potential energies. If zero of potential energy is defined as the energy of the electron when it is at rest at an infinite distance from the nucleus, its potential energy with respect to the nucleus at any distance 'r' is found to be

$$v = \int_{\alpha}^{r} F.dr = \int_{\alpha}^{r} \frac{Ze^2}{r^2}dr = \frac{-Ze^2}{r}$$

The kinetic energy, $T = \frac{1}{2}mu^2 = \frac{Ze^2}{2r}$

$\therefore$ Total energy of the electron = T + V

$$= \frac{-Ze^2}{r} + \frac{Ze^2}{2r} = \frac{-Ze^2}{2r}$$

$\therefore$ The energy of the electron in the n^{th} quantum state

$$E_n = \frac{-ze^2}{2r_n} = \frac{-ze^2 \times 4\pi^2 mze^2}{2n^2h^2}$$

$$= \frac{-2\pi^2 me^4 z^2}{n^2h^2}$$

Thus the transition between two energy states of energy E_1 and E_2 an be written as

$$\nu = \frac{E_2 - E_1}{h} \qquad or \qquad \overline{\nu} = \frac{2\pi^2 m e^4 z^2}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

If $n_2 = 2$, it is exactly same as the Balmer equation. The constant term in the above equation has given a reasonable agreement with the Rydberg constant. This gave overwhelming support to Bohr's theory.

Now that it has been shown that the equation for the wave number developed by Bohr is same as that found by Balmer, it is now possible to explain the origin of spectral series.

In the equation

$$\overline{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$n_1 = 2$ arises from the fact that the electron transitions are to the second shell. In a similar manner, an analogous relation exists between $n_1 = 1$ and the Lymann series and $n_1 = 3$, 4 and 5 for the Paschen, Brackett and Pfund series, respectively.

Extensions of the Bohr's Theory

Even though Bohr's theory could predict the energies of the spectral lines of the hydrogen like atoms, it met with some difficulties also.

1. It could not explain the fine structure in the line spectrum of the hydrogen-like atom. When Bohr proposed the theory, only single lines were observed and the theory successfully predicted them. But as better instruments and techniques are developed, it was realised that what were thought to be single lines, were actually a collection of several lines close together. This implies that there are several energy levels close together rather than a single level for each quantum number 'n'. This would require new quantum numbers and there is no way to obtain them directly from Bohr model.

   This problem was solved by Sommerfeld when he considered in detail the effect of elliptical orbits for the electron. For an elliptical orbit, both the angle 'ϕ' and the radius vector 'r' can vary.

   Summerfeld found that the degeneracy in this atomic model can be removed by considering the relativistic change in the mass of the electron during its motion around the nucleus. As the electron revolves around the nucleus, its velocity changes continuously, depending on its proximity to the nucleus. From the special theory of relativity it is known that the mass of a particle increases as its velocity increases. If this effect is taken into consideration, a small difference in energy is found to exist between a circular orbit and an elliptical orbit. This difference is a function of 'nϕ', and can be related to the physical picture of energy level in the Bohr atom by considering each major energy level to be composed of several sub-levels lying very close together.

The change in mass of the electron produces slight changes in the effective columbic forces operating between the electron and the nucleus. If this effect is taken into consideration, a small difference in energy is found to exist between orbits of different eccentricities, which will be reflected as fine structure in the spectrum.

The explanation of the fine structure of the spectrum of hydrogen is a notable achievement of the Sommerfeld's modification. But, the greatest single contribution of the Sommerfeld's concept, however, lies in the subdivision of the original Bohr stationary states into several sub-states of slightly differing energies as characterized by orbits of different eccentricities. Inherent also in the concept of elliptical orbits is the concept of penetrating orbits. We shall see later that these features form the basis to the modern concepts of electronic configuration.

Zeeman Effect

When the source emitting the spectral lines was placed in a strong magnetic field, a further splitting of lines was noticed. In order to account for this phenomenon called the Zeeman effect, a third quantum number known as the magnetic quantum number was postulated.

An electron in space requires three coordinates to describe its position. This has three degrees of freedom and should require three quantum numbers to describe its energy. Without a spatial reference, the arrangement of the orbital plane of the electron is completely arbitrary, and this third degree of freedom is degenerate.

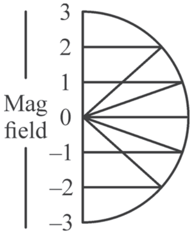


Fig. 1.7.1 Space quantization in a magnetic field.

However, in the presence of an external field, the orbital plane of the electron will precess about the direction of the field, and thereby remove the degeneracy. The possible positions the orbital plane (Vector representing the orbital angular momentum) can assume in space are limited (Space quantisation) and the magnitude of its component in the direction of the magnetic field is given in terms of the magnetic quantum number 'm'.

The third quantum condition, similar to that of the angular momentum is

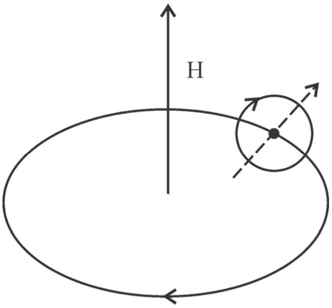
$$P_z = m\frac{h}{2\pi}$$

The magnetic quantum number may have any integral value including zero from $-l$ to $+l$ giving a total of $2l + 1$ values.

The possible values of m when $l = 3$ are shown in Fig.1.7.1. Positive values of 'm' describe the components of orbital angular momentum oriented in the direction of the applied magnetic field, and the negative values represent those oriented in the opposite direction.

Spin

The presence of 'double lines' in the spectra of alkali metals was attributed to the axial spin of the electron by Goudsmit and Uhlenbeck (1925).



A simplified account of the way in which this property leads to new energy levels can be understood, if we remember that a spinning electron behaves as a small magnet. Now, the electron moving around in its orbit produces a magnetic field just as an electric current in a coil of wire produces a field. The arrow marked 'H' represents this field. Since the electron, because of the axial spin behaves as a small magnet, there will be an interaction between the two magnetic fields. The field produced by the axial spin either reinforces or opposes the field 'H' depending on the direction of the spin whether it is clockwise or anticlockwise.

This interaction will produce energy changes, wherein, a single energy level representing a non-spinning electron moving in an orbit, becomes two energy levels close together. Additional electron transitions are therefore possible, and new lines appear in the spectrum. Goudsmit and Uhlenbeck showed that the spectroscopic observations required that the angular momentum associated with the spin of the electron is given by $m_s.h/2\pi$, where m_s is called the ' Spin quantum number' and can have the value $+1/2$ or $-1/2$.

1.8 Failure of the Old Quantum Theory

The success achieved by the Bohr-Sommerfeld theory in explaining the atomic spectrum of hydrogen prompted its extension to other systems. Although it achieved some success in accounting for the spectra of such hydrogen like species as singly ionized helium (He^+), doubly ionized lithium (Li^{2+}) and triply ionized beryllium (Be^{3+}), it failed to predict the spectral lines and spectral intensities in the case of many electron atoms. Apart from this, there are certain other unsatisfactory features in the theory. For instance, there is no justification for the assumption that an electron can move in only those orbits wherein the angular momentum of the electron is an integral multiple of h/2π. Further whenever it has become necessary to explain an experimental observation a new quantum number has been introduced; thus, the introduction of the various quantum numbers is arbitrary.

Finally, the theory contributed virtually nothing to an understanding of the geometry of the molecules.

The unsatisfactory features in the old quantum theory led scientists to search for new mechanics for the treatment of atomic systems that would relieve the wave particle conflict and introduce quantized energy. As a consequence of some more efforts in this direction culminated in the formulation of ‘matrix mechanics’ by Heisenberg and ‘Wave mechanics’ by Schrödinger. Afterwards, Schrödinger and Eckart have shown that both matrix mechanics and wave mechanics lead to the same conclusions. Now these two forms of mechanics are covered by the term ‘quantum mechanics’: that means matrix mechanics and wave mechanics are merely two different mathematical treatments of quantum mechanics. Of these two forms, since wave mechanics are easy to understand and can explain all the phenomena in chemistry, this method is widely used in quantum chemistry.

Quantum mechanics, not only could explain the phenomena associated with chemistry, it helped to amalgamate physics, chemistry and material science. Earlier also the attempts of Newton were successful in applying common laws to the celestial and terrestrial objects alike. Similarly, Mayer and others have unified the laws of heat and mechanics, while Faraday and Maxwell have shown that electricity, magnetism and optics are closely related. Einstein was responsible for bringing together space, time, matter and gravity. The scientific community is eagerly awaiting for a theory which can explain everything in the atomic, nuclear and sub nuclear levels and beyond that includes the bigger than the biggest and the smaller than the smallest, known to us at this point of time.

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