SARDAR PATEL UNIVERSITY

Vallabh Vidyanagar-388120

B.Sc. (Semester - 6)
Subject: Physics
Course: US06CPHY22
Atomic and Molecular Spectroscopy
(Four Credit Course –4 Hours per week)
(Effective from June-2020)

UNIT- I Spectra of Atom

Spectrum of Hydrogen atom and spectral series, Observation of Hydrogen spectrum, Failure of electromagnetic theory of radiation, Bohr’s theory and spectrum of Hydrogen atom, Franck-Hertz Experiment, short coming of Bohr’s theory, Larmor’s theorem, Stern-Gerlach Experiment, Fine structure of Hydrogen lines, Positronium, Different series in Alkali spectra: main features, Ritz combination principle, explanation of salient features of Alkali spectra, Related Numerical.

UNIT- II Spectra of Molecule

Separation of Electronic and Nuclear Motion: The Born-Oppenheimer approximation, Types of molecular energy states and associated spectra, Types of spectra, Salient features of rotational spectra, The molecule as a rigid rotator: Explanation of rotational spectra (Rotational energy only), Diatomic molecule as a Non-rigid rotator, Validity of the theory: Determination of the inter-nuclear distance (Bond length) and moment of inertia, Isotope effect in rotational spectra, Rotational spectra of polyatomic molecules, Related Numerical.

UNIT- III Infrared Spectroscopy

Salient features of vibrational - Rotational spectra, Vibrating diatomic molecule as a harmonic oscillator, Vibrating diatomic molecule as an harmonic oscillator(without force content for HCl molecule), Molecule as a vibrating rotator: fine structure of Infra red bands: Ignoring interaction of vibrational and rotational energies, Molecule as a vibrating rotator: fine structure of Infra red bands: considering interaction of vibrational and rotational energies, Applications of vibrational spectroscopy, General experimental arrangement for studying infra red spectra, Related Numerical

UNIT-IV Raman Spectra

Raman Effect and its salient features, experimental study, Apparatus, Result, Raman effect in liquids, Raman effect in gases, Raman effect in solids, Intensity of Raman lines, Polarization of Raman lines, Nature of Raman Effect, Relation between the Raman and infra red absorption spectra, Importance of Raman effect, Applications of Raman Effect in Physics: Molecular structure, Nature of liquid state, Crystal Physics, Nuclear Physics, Classical theory of Raman Effect, Quantum theory of Raman Effect, Related Numerical.

Books Recommended:

1. Elements of Spectroscopy
   S L Gupta, V Kumar, R C Sharma, (30th Edition)
   Pragati Prakashan, Meerut
2. Atomic Physic J B Rajam (7th Edition)
   S. Chand publication, Delhi
3. Molecular structure and Spectroscopy
   G Aruldhas PHI Private Limited, Delhi

UNIT- I SPECTRA OF ATOM

SPECTRUM OF HYDROGEN ATOM AND SPECTRAL SERIES:

To study the spectrum of hydrogen, an electric discharge is maintained in hydrogen. When the intensity of the current is low, a very complicated spectrum is observed. It contains a few brilliant lines forming a series superimposed on a large number of weaker lines. The few brilliant and well ordered lines are attributed to atomic hydrogen and weaker ones to the hydrogen molecule for the hydrogen atom is the simplest one and it should therefore, emit the simplest spectrum. The weaker lines are attributed to molecular hydrogen because under normal circumstances hydrogen exists in the molecular state and when electric discharge is maintained, some molecules dissociate and the resultant atoms give rise to simplest spectral lines. The above argument is confirmed by the fact that as the intensity of the current is raised, the brilliant lines gain in intensity while weaker ones disappear. Previously, atomic hydrogen showed only four lines but at the time of Balmer, it showed nine lines forming a series. The photographic investigation showed that the series is extended convergence limit in the ultraviolet region. The separation and intensity of spectral lines decrease towards the violet end (shorter wavelength side) of the spectrum. The convergence limit of a series is now known to correspond to ionization of the atom. The first line of the series, known as Balmer series (after the name of Balmer), has the wavelength 6562-80A. After keeping constant watch on the regularity of the spectral lines.

Balmer gave an empirical relation for the wavelength of the spectral lines which reads as follows:

$$\lambda = \frac{n^2}{n^2-4} b \qquad 1$$

Where λ is the wavelength of a line for a definite value of n defined by n=3, 4, 5, 6...and b is a constant the value of which is equal to 3645.6 Å. Balmer declared that in this series no line of longer wavelength than H_α (first line of Balmer series) would be found and the series should converge at λ=3645.6 Å, since the term $\frac{n^2}{n^2-4}$ approaches to unity as n becomes large.

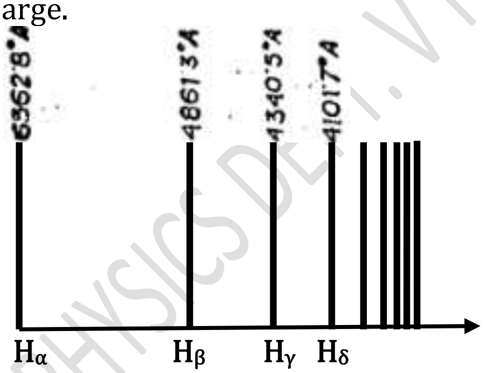


Figure: 1, Lines of Balmer series

Figure-1 depicts the first few lines of Balmer series. The lines in successive order are known as H_α, H_β, H_γ, H_δ..... and so on. The figure-1 also indicates the fact that intensity and separation of spectral lines diminish towards the converging limit. Balmer compared the predictions of his relation with the best available experimental values for wavelengths of spectral lines. The wavelengths of four lines in the visible region (as measured by

Angstrom) and five lines in ultra violet region 9measured by Huggins) confirmed the accuracy of this relation with the discrepancy of 1 part in 1000.

Balmer's empirical relation after Rydberg's contribution is modified as

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

ν̄ is the wave number and R is a constant computed so that formula represents the observed frequencies and is called the "Rydberg constant" after the name of the Swedish spectroscopist.

[The above equation 2 is the result of the contribution done by Rydberg in the formulation of series relation. The equation 1 can be deduce from equation 2 by writing 2 as

$$\frac{1}{\lambda} = \frac{R}{4}\frac{n^2-4}{n^2}$$

$$\lambda = \frac{n^2}{n^2-4}\text{b}, \quad \text{where b}=\frac{4}{R}$$]

The figure indicates the accuracy of spectroscopic measurements. In equation-2, n assumes values greater than 2, i.e. 3,4,5,6,...,∞ for H_α, H_β, H_γ, H_δ,.... lines. Later on relation (2) got its generalization, which now runs as follows:

$$\bar{\nu} = R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

The beauty of the equation-3 is that it not only gave the wave number of Balmer lines but also predicted the wave number of other lines which were later observed.

With the condition that n_2 assumes values greater than n_1 and n_1 takes a definite value for a definite series starting from one and ending at five for entire hydrogen spectrum. Now due to the development of more refined techniques, the following five series have been observed in the spectrum of atomic hydrogen:

1. Lyman series: In the year 1906, Lyman discovered a series similar to Balmer series in the extreme ultraviolet region of the spectrum. The series is represented by the relation written below:

$$\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{{n_2}^2}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

With n=2, 3, 4.... i.e., by replacing n_1 by 1 and n_2 by the integral number greater than one. The first line of Lyman series has the wavelength 1215.7 Å and the convergence limit of this series is $\bar{\nu} = R$, λ=917.4 Å. The extreme ultraviolet region extends from 4 Å to nearly 1000 Å. But the region in which lines of Lyman series have been observed ranges from 500 Å to 1000 Å. It is to be noted that in the ultraviolet region Lyman series is the only one series observed and studied so far.

2. Balmer series: As mentioned before, this series marked the beginning of spectroscopy. The lines of this series are most easily observable and lie in the visible region of the spectrum. The lines in the visible part are photographed by any spectrograph and lines falling near ultraviolet are photographed with quartz spectrograph. The Balmer formula gives the wave number (or wavelength) of any line of this series. The series starts with the line of wavelength 6562.8Å and converges at the line of wavelengths $\lambda=\frac{4}{R}$ (3645.6 Å). The Balmer relation, here, we rewrite for the sake of symmetry:

$\bar{\nu} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ ………..5

With n=3, 4, 5… ∞.

Here n of relation (3) has been replaced by 2 and n_2 by n which assumes values greater than 2.

3. Paschen series: The series lies in the infrared region of the spectra. The following relation determines the wave number of different lines depending upon the possible values of n.

$\bar{\nu} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ ………..6

Where n=4, 5, 6… ∞.

The wavelength of the first line of this series is 18751 Å and converges at the line with wavelength $\lambda = \frac{9}{R}$ (8256.6 Å). The lines of this series were observed after the prediction of their existence in the infrared region.

4. Brackett series: This series was observed when it was first predicted theoretically. It exists in the infra red region of theoretically. It exists in Infra red region of the spectra. The wave numbers of different lines are expressible by the relation

$\bar{\nu} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$ ………..7

With n= 5, 6…∞.

The series has the convergence limit at the line with wavelength $\lambda = \frac{16}{R}$ (14678.4 Å) and the wavelength of first line is 40500 Å.

5. Pfund series: The lines of this series rest in the far infra red region of the spectrum (25μ to 0.4 mm). The wave number of any line of this series can be computed from the relation.

$\bar{\nu} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$ ………..8

With n= 6, 7…∞

The first line of the series has the wavelength 74000 Å and series converges at $\lambda = \frac{25}{R}$ (22935.0 Å).

It is to be noted that Brackett series overlaps the Paschen and Pfund series.

6. Humphry series: This series is observed in far infra red region of the spectrum (25μ to 0.4 mm). The wave number of a line of this series is given by

$\bar{\nu} = R\left(\frac{1}{6^2} - \frac{1}{n^2}\right)$ ………..9

Where n= 7, 8…∞

The first line of the series has the wavelength 12360 Å and series converges at $\lambda = \frac{36}{R}$ (32816.8 Å).

OBSERVATION OF HYDROGEN SPECTRUM:

The Lyman series is not observed in the quartz spectrograph, inspite of the fact that quartz transmits ultraviolet light down to 2000 Å due to the reasons:

(i) Quartz becomes opaque and must be replaced by one of the rare crystals (fluorite) which transmits light of still shorter wavelengths.

(ii) Ordinary photographic plates do not respond due to the fact that gelatin absorbs so strongly that it does not penetrate into emulsion.

(iii) Air becomes opaque demanding the evacuation of whole apparatus. But as we know that Lyman series lies beyond the limit of fluorite; therefore Lyman used concave gratings which depend upon the reflection power of the material on which ruling is done rather than on the transparency of the substance.

A noteworthy point in the investigation of infrared spectrum is that glass prism is opaque in this region and must be replaced by rock salt prism or a grating. In this region photographic plates also fail completely in receiving the radiation and in place of photographic plate bolometer or thermocouple is used.

FAILURE OF ELECTROMAGNETIC THEORY OF RADIATION:

In the field of practical spectroscopy the work done by Balmer, Rydberg and others was very iniquitous but the entire work was empirical in nature and therefore provided ne information about the nature of the mechanism in the atom responsible for the emission of spectral lines of characteristic frequencies. After practical findings the next attempt was to study the nature of the mechanism involve. Now since the work of Hertz and Maxwell gave rise to electromagnetic theory of radiation and this theory successfully explained a number of facts about the radiant energy, so the first step was to apply the electromagnetic theory to explain the, origin of the spectral lines. In this theory the atom is supposed to be an antenna of very small dimensions just like the antenna of radio transmitter. The atomic antenna radiates the energy of high frequency and such emission may be considered identical with emission in the spectra only in some respects. We know that a transmitting antenna made of a straight piece of wire has a fundamental frequency of vibration and a series of harmonics of higher frequency. But this series cannot be compared to the series spectrum of hydrogen because the higher antenna harmonics are the multiples of the fundamental frequency. Hence the series of harmonics does not show the convergence limit, the characteristic of hydrogen spectrum observed. Furthermore, the atomic antenna radiates only one series of spectral lines while five series are observed in hydrogen spectrum.

The next attempt is to modify the transmitter concept of atomic radiator as was done, taking into consideration the atom model due to Rutherford in which it is assumed that an electron revolved round the hydrogen nucleus. Now taking the analogy from planetary motion, it is argued that electrons will continue to revolve in circular or elliptic orbits. The energy given to the system by the discharge process by the impact of free electrons throws the atomic electron into a distant orbit which we assume circular in shape for the sake of convenience. Had the revolving electron of the atomic hydrogen been exactly identical to the planet revolving round the sun, it would have had a definite frequency of revolution. But the electron is a charged particle, so it behaves differently compared to a planet (planet is a neutral body). The electron loses energy continuously at a rate given by electromagnetic theory and, as the time passes on, its energy will decrease and it will come closer to nucleus, increasing thereby its frequency of revolution. Finally, the electron will merge into the nucleus and the atom will lose its stable configuration. If the merging of the electron into the nucleus somehow or the other is checked, even then the electron will radiate energy of continuously increasing frequencies. The result of this will be the continuous spectrum of hydrogen atom and not the well defined and sharp lines; as are actually observed. The prediction based on electromagnetic theory thus contradicts the observed facts and justifies its failure to explain the hydrogen spectrum.

It is important to note that, here three pillars of classical physics-namely. Newton's laws motion Coulomb's law of electric force and electromagnetic theory is employed in order to explain the spectrum of H-atom. But the results the emission of continuous spectrum and spiraling of electron into the nucleus are against the observed fact of discrete H spectrum and stability of atom.

This contradiction only means the laws of physics that are valid in macroscopic world do not hold well in microscopic world of atom. The classical theory fails in world of the atomic and subatomic dimensions because it deals with the systems in terms of the abstract concept of ‘pure particles’ and ‘pure waves’. But in microscopic world the particles and waves manifest their dual character and this dual character becomes imperceptible in macroscopic world on account of smallness of Plank’s constant.

The laws of Physics when applied to explain the stability of the atoms and spectrum gives wrong results and the same laws when applied to Rutherford scattering give the famous Rutherford formula. But the quantum mechanical analysis of alpha particle scattering from thin foils coincidently yields exactly the same result. To understand this, let us estimate the de-Broglie wavelength of alpha particle whose speed is 2x 10^7 m/sec.

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{6.6\times10^{-27}\times2\times10^{7}} = 5\times10^{-15}m$$

The distance of closest approach in the case of gold foil is 30x 10^{-15} m which is six time of de-Broglie wavelengths. Hence, it is reasonable to regard the a-particle as classical particle in Rutherford.

BOHR'S THEORY AND SPECTRUM OF HYDROGEN ATOM:

The hydrogen atom was the target of the first theoretical attack aimed to explain the observed facts about the spectra of different elements and of hydrogen itself because of the fact that the atom of hydrogen is the lightest and, therefore should possess the simplest structure. The fact is confirmed by the simplicity of the spectrum observed.

In the year 1913, Bohr pronounced a model for the Balmer. hydrogen atom for which he was guided by Rutherford's large angle a particle scattering experiment, electronic charge determination experiment of Millikan and J. J. Thomson's experiment for the determination of the positive charge. These experiments suggest that positive charge and total mass of the atom are contained in its core (mass of the electrons being negligible). The positive charge of the core, i.e., of the nucleus of the atom, is equal to Z units, the atomic number of the element. The electrons which are equal to Z in number revolve round the nucleus and are attracted by the nucleus. With this basic concept for the atom in mind and Planck's postulate for energy emission (this postulate was made by Planck while explain in the energy distribution in the spectrum of black body which could not be explained by classical mechanics) which states, “Radiant energy is not emitted or absorbed by matter in a continuous fashion but in the form of discrete packets or quanta (also known as photons) of energy of magnitude hν, where h is Planck's constant and ν is the frequency of radiation” ($h=662\text{x } 10^{-34}$ joule sec), he attacked the problem and derived a theoretical relation which not only provides an explanation for the hydrogen spectrum but also accounts for the spectra of hydrogen like atoms. To avoid the running down of the electron into the nucleus due to the Coulombian attraction and electromagnetic radiation, Bohr developed his theory on the basis of following assumptions:

1. Bohr's first assumption:

Bohr's first assumption is that if Z is the atomic number of an element, (the charge on the nucleus is Ze) then Z electrons revolve in circular orbits (circular orbits are assumed for the sake of simplicity). The force of attraction between nucleus and electron is balanced by centrifugal force. This balance keeps the electrons in closed circular orbits and maintains the stability of the configuration, the conditions expressed as

$$-\frac{Ze^2}{4\pi\epsilon_0 r^2} = -\frac{mv^2}{r} \qquad 1$$

Or

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r} \qquad 2$$

The minus sign in equation 1 on the left side is because the electrostatic force is that of attraction and on the right side is because the force and acceleration are in opposite directions.

Further,

$$\mathrm{r} = \frac{Ze^2}{4\pi\epsilon_0\, mv^2} \qquad 3$$

Where m and v are mass and velocity of the atomic electron and r is the radius of the circular orbit. Equation 3 suggests that every value of r is possible, depending of course upon the velocity of moving electron. Therefore, classically we speak that every circular orbit is permissible.

For kinetic energy of the electron we write

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$= \frac{1}{2}\frac{Ze^2}{r}\frac{1}{(4\pi\epsilon_0)} \qquad 4$$

If the potential energy of the system is taken as zero when the electron is at infinity, then the potential energy of the system when the electron is at a distance r from the nucleus is written as

$$\text{P.E.} = -\int_{\infty}^{r} -\frac{Ze^2}{(4\pi\epsilon_0)r^2}\,dr$$

$$= -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \qquad 5$$

Hence, the total energy of the system will be

$$\mathrm{E} = \text{K.E.} + \text{P.E.} = \frac{1}{4\pi\epsilon_0}\left[\frac{Ze^2}{2r} - \frac{Ze^2}{r}\right]$$

$$= -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{2r} \qquad 6$$

The interesting point about the total energy of the system is that the kinetic energy taken with negative sign equals the total energy of the system.

According to the classical electromagnetic theory, the frequency of energy radiation is equal to the orbital frequency which we write using equation 3:

$$v = \left[\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{mr}\right]^{\frac{1}{2}} = \omega r$$

In above relation, ω is the angular velocity of the electron. Hence,

$$f = \text{orbital frequency} = \frac{\omega}{2\pi} = \left[\frac{Ze^2}{(4\pi\epsilon_0)m}\right]^{\frac{1}{2}}\frac{1}{2\pi r^{3/2}} \qquad 7$$

As we have already said that r can assume any value, f will be continuous, suggesting thereby continuous emission of energy and hence the continuous spectrum-a contradiction of the, experimentally observed facts. The contradiction was overcome in his second assumption.

2. Bohr's second assumption: Bohr next assumed (in order to avoid running down of the system due to radiation) that only certain discrete orbits are permissible: all classically possible orbits, defined by equation (3), are not allowed. When in these states, the atom possesses stability, unexplainable on the basis of classical mechanics and electrodynamics, of such a sort that every spontaneous change from a stationary state of motion result in a transition to another state. The allowed orbits are called privileged or stationary orbits because they have got the privilege of not radiating energy while electron revolves in these stationary orbits. The words "stationary state" does not mean that electrons are at rest. By stationary means that the motion of the particles is periodic, the energy of system being constant. In the above statement "spontaneous is essential is the essential word in the above statement. If an atom is temporarily exposed to radiations of a wavelength which it cannot absorb, its state of motion is altered; but after the period of disturbance the atom returns to its original state of motion. When an atom is initially at rest it absorbs a quantum of energy, it recoils and the energy of the quantum is divided in giving the atom kinetic energy of translation, and in increasing its internal energy.

To define the allowed orbits, the incentive is taken from Planck's quantum hypothesis which suggests that Planck's constant h somehow determines the energy levels and has the dimensions of an angular momentum. This coincidence leads to the guess that the angular momentum of the revolving electron must be proportional to some multiple of Planck's constant h. Bohr found that desired results are obtained when the quantum condition which states that "allowed orbits are those for which the total angular momentum is an integral multiple of h/2π", where is Planck's constant. Mathematically, we write

$$mvr = \frac{nh}{2\pi} \qquad 8$$

Where n is any positive integer and is called principal quantum number; the factor $\frac{1}{2\pi}$ is justified partly by the success of the theory and partly by desired transition from quantum theory to classical theory.

The condition specified by equation (8) is called Bohr's quantum condition and this limits the number of orbits which are allowed by eqn. (3). According to this condition only those values of r are allowed for which eqn. (6) is satisfied.

3. Explanation of energy radiation:

To explain the energy radiation, Bohr assumed that emission of radiation by an atom or molecule takes place during a transition from a stationary state to another energy state of lower energy. The quantum of energy thus emitted can be completely absorbed by a similar atom whose initial energy state is exactly identical to the final energy state of the radiating atom. The absorbed energy raises the atom to higher energy state. The quantum of energy radiated, in its interaction with spectroscopic instruments, behaves as if it consisted of wave-train of monochromatic wavelength whose wavelength is given by

$$E_2 - E_1 = h\upsilon = \frac{ch}{\lambda} \qquad 9$$

Where E_1 and E_2 are the energies of initial and final states, ν and λ are the frequency and wavelength of monochromatic radiations, respectively. For energy emission E_2 has greater value than E_1. The condition expressed by equation (9) is called Einstein's frequency condition.

Further, if E_0, denotes the energy of the atom in its ground state, i.e., for the normal unexcited level, it can absorb the radiation of frequency ν only when

$$h\nu = E_n - E_0$$

Where E_n is one of the higher energies of the atom such as E_1, E_2, etc. which are possible when the atom is excited by an arc, spark, or electric discharge. The lines in the absorption spectrum of the atom will, therefore, have the frequencies given by

$$\nu_1 = \frac{E_1 - E_0}{h}$$

$$\nu_2 = \frac{E_2 - E_0}{h}$$

$$\nu_3 = \frac{E_3 - E_0}{h}$$

$$\nu_4 = \frac{E_4 - E_0}{h}$$

…………………..

$$\nu_n = \frac{E_n - E_0}{h} \qquad 10$$

This explains why emission spectrum has more lines than absorption spectrum.

Calculation of possible energy values of the stationary states of the atom:

To calculate the possible energy values E_n of the stationary states of the atom in terms of the physical constants and the dimensions of the atom.

Taking the more general case of an element with atomic number Z we write for the velocity of an electron in nth orbit as given by equation 3,

$$\upsilon_n{}^2 = \frac{Ze^2}{4\pi\epsilon_0 m r_n} \qquad 11$$

Where υ_n is the velocity of the electron in nth orbit, the radius of which is equal to r_n. Further from equation 8,

$$\upsilon_n{}^2 = \frac{n^2h^2}{4\pi^2m^2\, r_n{}^2} \qquad 12$$

Equating the two values of equations 11 & 12

$$\frac{n^2h^2}{4\pi^2m^2\, r_n{}^2} = \frac{Ze^2}{4\pi\epsilon_0 m r_n}$$

$$r_n = (4\pi\epsilon_0)\frac{n^2h^2}{Ze^2m^2} \qquad 13$$

Substituting the value of r in equation 6

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2}\frac{2\pi^2 m Z^2 e^4}{n^2h^2} \qquad 14$$

Equation 14 the energy of the system when the electron is in nth orbit is given by

$$E_{n_1} = -\frac{1}{(4\pi\epsilon_0)^2}\frac{2\pi^2 m Z^2 e^4}{n_1{}^2 h^2}$$

$$E_{n_2} = -\frac{1}{(4\pi\epsilon_0)^2}\frac{2\pi^2 m Z^2 e^4}{n_2{}^2 h^2}\text{; respectively}$$

Therefore, when the electron jumps from orbit number n_2 to orbit number n_1, the energy of definite frequency will be radiated as is determined by the operation of assumption 3, that is

$$E_{n_2} - E_{n_1} = hv = \frac{2\pi^2 m Z^2 e^4}{(4\pi\epsilon_0)^2 h^2}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$

Or

$$v = \frac{2\pi^2 m Z^2 e^4}{(4\pi\epsilon_0)^2 h^3}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right] \qquad 15$$

And wavelength corresponding radiation is given by

$$\frac{1}{\lambda} = \frac{2\pi^2 m Z^2 e^4}{(4\pi\epsilon_0)^2 c h^3}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right] \qquad 16$$

Or

Wave number $\bar{v} = RZ^2\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$

Where R is known as Rydberg constant and is defined by

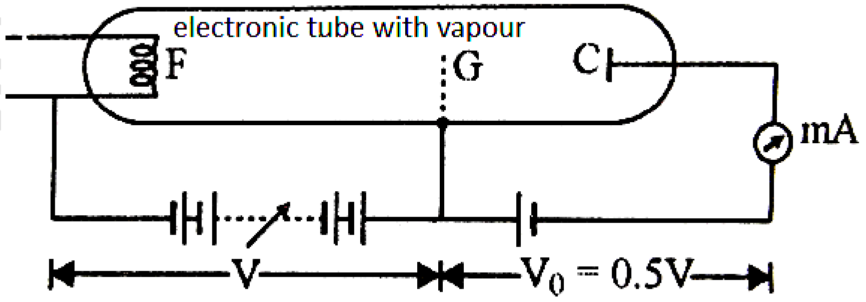
$$R = \frac{2\pi^2 m e^4}{(4\pi\epsilon_0)^2 c h^3} \qquad 17$$

Substituting values of respective quantities in equation 17, we find the value of Rydberg constant is $1.097 \times 10^7 m^{-1}$

This relation is identical to given by Balmer basis of the hydrogen spectrum.

FRANCK-HERTZ EXPERIMENT:

Principle: The principle of this experiment is based upon the fact that a bombarding of electron which has transferred some of its energy to the orbital electron moves comparatively slowly and can be stopped by means of a relatively smaller retarding potential than that which would have to be applied if the collision had not taken place.



F-Filament C-Cathode G-Grid
mA-current meter V-voltage

Figure-1. Franck-Hertz Experiment

Construction and working: A special electronic tube is taken containing vapour of an element at a low pressure whose excitation potentials are required.

Working: The electrons are generated thermionically by heating the filament F and then accelerated through the vapours towards the grid G maintained at a positive potential, as shown in figure-1. After crossing the grid G, these electrons face a small retarding potential of about 0.5 volt between grid G and collector C.

The current through the tube is noted as a function of the acceleration potential. As the acceleration potential is increased from zero, the current at C will increase until V reaches a characteristic excitation potential of the vapour. At this point electron under goes inelastic collision with atoms of the vapour and kinetic energy is reduced to zero.

If the collision takes place near the grid, there is then no chance for electron to acquire enough kinetic energy to overcome the retarding potential and reach to collector. Therefore, just beyond this there is sharp fall in current.

Subsequently, as the potential is further increased there is a corresponding current rise again, since in the stronger field, electrons can make inelastic collision early and still undergo enough acceleration to get over the 0.5 volt barrier.

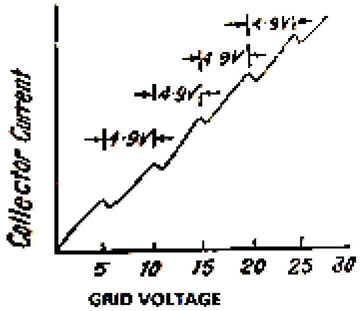


Figure-2. Graphical results of Franck-Hertz experiment

Further falls may also be observed at roughly the values of V which are an integral multiple of first value as shown in figure-2.

These are due to electrons making two or more inelastic collisions of the same kind, the energy of electrons in falling is proportional to V. The separation of successive peaks is 4.9V for Hg (Mercury).

Result and Analysis: Franck and Hertz also studied the radiation given off by the excited Hg atoms retarding to their normal states and found a line at 2537 Å. Corresponding photon energy is evaluating as

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3\times10^{8}}{2537\times10^{-10}\times1.6\times10^{-19}}\ eV = \frac{1.242\times10^{4}}{2537} = 4.89 \approx 4.9\ eV$$

This supports the view that Hg atom cannot exist in intermediate energy states and energy levels are quite sharp and quantized.

The voltage corresponding to the peaks in the current are called excitation potentials as illustrated in figure-2.

When voltage is very high, the electrons may cause inelastic collisions in which the atom is completely ionized. Thus there is an additional drop in the current at the voltage corresponding to the ionization potential voltage.

Shortcomings of Bohr’s theory:

The Bohr’s theory does not give the following information:

1. Bohr’s theory does not give any idea of the distribution and arrangement of electrons in the atom.
2. In this theory we have two rival theories namely, classical and quantum theory. The equilibrium is governed by classical laws, while the emission of radiation is explained by quantum rules.
3. The theory predicts only the frequency of different spectral lines but does not gives any information about the intensities of different lines. Moreover, it is quite inadequate in explaining the multiplicity and fine structure of spectral lines.
4. With the help of Bohr’s theory it is difficult to treat dynamical problem of atoms containing more than one valence electron.

LARMOR’S THEOREM:

This theorem deals with the behaviour of a system of particles; the particles are such that they have some ratio of charge to mass (in sign as well as in magnitude) in the presence of constant uniform magnetic field, B. In order to give the description of motion of particles in such a system, it is supposed that particles, in absence of magnetic field, move under the forces which depend only on the co-ordinates.

Definitions: When a uniform magnetic field is applied, the size and shape of the orbit is not changed but the electron starts precession of an electron is called ‘Larmor’s precession’ and the relation expressing the frequency of Larmor’s precession is called Larmor’s theorem.

It involves the simple assumption that the nucleus remains stationary and excluding it for other purposes from the system, it is possible to predict the motion of the electron about the nucleus, even though the two particles have widely different e/m ratios.

Statement: The general statement of the theorem is: “The motion of the system is the same as it would be in the absence of the field, except that a uniform rotation around the direction parallel to the magnetic field is superposed, provided the effects proportional to the square and higher power of B are neglected.”

The above consideration leads to following angular frequency for the electron about the field direction:

$$\omega_L = \frac{e}{2m}\boldsymbol{B} \qquad 1$$

Or with a frequency

$$v_L = \frac{e}{4\pi m}\boldsymbol{B} \qquad 2$$

And can be easily derived as follows:

The potential energy of an atomic magnet associated with magnetic moment is given by

$$\text{P.E.} = -\mu \mathbf{B} \cos\theta \qquad 3$$

Where, θ is the angle which the angular momentum vector makes with the field direction. The angle θ, according to rule of space quantization, is given by

$$l\,cos\theta = m_l \qquad 4$$

On the other hand, the revolving electron with charge –e and mass m gives rise to the magnetic moment of magnitude,

$$\mu = -\frac{elh}{4\pi m} \qquad 5$$

Combining now equations 3, 4 and 5,

$$P.E. = \frac{elh}{4\pi m}\boldsymbol{B}\frac{m_l}{l}$$

$$= \frac{eBh}{4\pi m}m_l \qquad 6$$

The additional energy of the system according to quantum mechanics must be the form

$$m_l h v_L = \frac{eBh}{4\pi m}m_l$$ [Since m_l is an integer]

$$v_L = \frac{eB}{4\pi m} \qquad 7$$

Where, v_L thus indicates the frequency of Larmor precession.

The theorem outlined above is of considerable importance as it facilities the calculation of energy of the atomic levels in the presence of magnetic field.

STERN AND GERLACH EXPERIMENT:

In 1921, O. Stern and Gerlach performed an experiment which directly reveals the essential features of vector atom model. The atom is regarded as a small elementary magnet. The magnetism of the atom arises due to the spin and orbital motion of the electrons. When this atomic magnet is placed in a homogeneous magnetic field, its poles are acted upon by equal and opposite forces so it gets aligned in the direction of the field. In this case the magnet does not experience any translatory force. But when this atomic magnet is placed in a non-uniform magnetic field, the magnet not only aligns in the direction of magnetic field but also experiences a translatory force.

Principle: If these atomic magnets are allowed to move in a direction normal to the field, they move in a straight line path without displacement in a homogeneous field and in a curved path in an inhomogeneous field (curved path is due to displacement). This is the principle of the experiment.

Experimental arrangement: The substance under investigation is heated in an electrical oven O. The substance (K) on heating emits atomic rays in all directions with velocity determined by temperature of emitting substance.

The sharp atomic beam is then allowed to pass through a non uniform magnetic field. The non-uniform magnetic field is made available with the help of specially constructed pole-pieces and the sharpness of the beam is obtained with the help of slits S_1 and S_2 as illustrated in Fig. 1. The atomic beam is then made to strike on a plate which records the path of the rays. The magnetic field is made as intense and as non-uniform as possible.

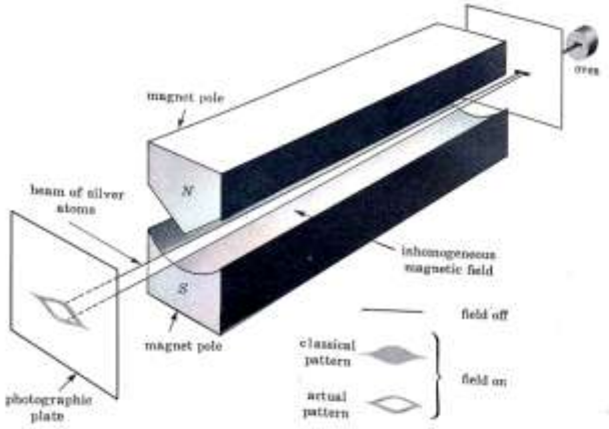


Figure 1 Experimental arrangement

Method: To measure the deflection of atomic rays very accurately each part of the apparatus is carefully aligned. Then to prevent the collisions of atoms in the beam with the atoms and molecules of any residual gas, the chamber is completely evacuated with the help of charcoal.

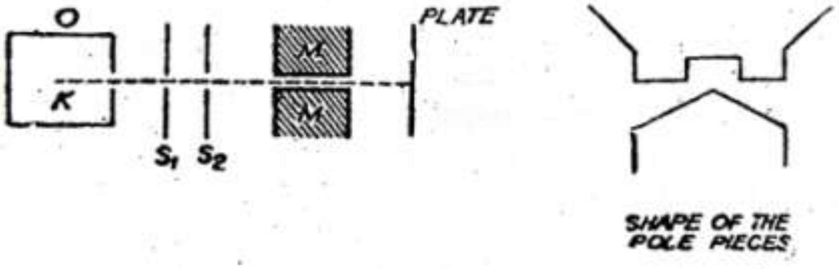


Figure 2 Schematic arrangement of experimental and shape of the pole-pieces of the magnet

The displacement of atomic rays is then measured by measuring the repulsion, at various points between the pole-pieces, of a thin bismuth wire which is mounted parallel to the edge of the knife edge pole piece. Then the traces of atomic Plate rays are developed by various using various methods. Meissner and Scheffers, to measure the displacement D_x, in case of alkali metals, allowed the deflected beam to strike the hot tungsten filament instead of a plate. The atoms on striking the filament lost Shape of the ionization produced electrons and a pole pieces current ionization current. This ionization was measured at different positions and by noting the position of maximum current, the magnetic deviation was accurately determined. The expression for the displacement may be derived as follows:

We suppose that **p** is the pole strength and $\boldsymbol{l}$ is the effective length of the atomic magnet and the field has a gradient $\frac{dB}{dx}$ in positive X-direction. Now we say that an elementary atomic magnet dx with magnetic moment $= \mathbf{p}\, \boldsymbol{l}$ is placed in a non-uniform field as illustrated in figure 3.

If the field strength at the end A of the magnet is B, then at the other end it will be $\mathbf{B}+\frac{d\boldsymbol{B}}{dx}\,l cos\theta$. The magnitude of the force at pole A is p$\mathbf{B}$ while at C is $p\left(\mathbf{B}+\frac{dB}{dx}\,l cos\theta\right)$. The force p Figure -3 the field gradient atomic magnet AC will rotate the magnet in the field direction p$\frac{d\boldsymbol{B}}{dx}\,l cos\theta$ will act along the positive X-direction. This force is responsible for the deviation of the straight line path. The additional force will give acceleration to the atomic magnet of magnitude.

$$f_x = \frac{\text{force}}{\text{mass}} = \frac{\text{p}\frac{d\boldsymbol{B}}{dx} l cos\theta}{M} \qquad 1$$

Where, M is the mass of the atom.

So, the displacement D_x of the atoms at the temperature of the field

$$= \frac{1}{2} f_x t^2 \qquad 2$$

Where, t is the time taken by the atom to cover the distance d in the normal direction of the field.

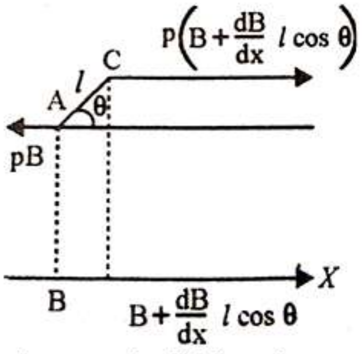


Figure-3. The field gradient

So,

$$D_x = \frac{1}{2} f_x \left(\frac{d}{v}\right)^2 \qquad 3$$

Where v is the velocity of the atoms at the temperature of the experiment and is given by

$$v = \left(\frac{3kT}{M}\right)^{1/2}$$

k is Boltzmann's constant.

Therefore,

$$D_x = \frac{1}{2}\frac{pl}{M}\frac{d\boldsymbol{B}}{dx} cos\theta \left(\frac{d}{v}\right)^2 \qquad 4$$

$$= \frac{1}{2}\frac{\mu}{M}\frac{d\boldsymbol{B}}{dx} cos\theta \left(\frac{d}{v}\right)^2 \qquad 5$$

Where, μ = p$l$cosθ, that is the resolved component of magnetic moment in the field direction.

Now since $D_x \propto \frac{d\boldsymbol{B}}{dx}$, to get greater deviation the field must be more non-uniform.

When $\frac{d\boldsymbol{B}}{dx} = 0$, that is, when field is uniform, $D_x = 0$. It means that in a uniform field there is no translatory motion in the field direction.

Result and analysis: The traces obtained in the case of silver are shown in Figure-4. A straight line trace is obtained without field and a double trace with some irregularities on applying the field. The irregularity in the double trace is due to the irregularity of the

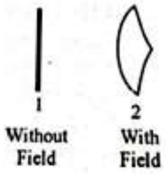


Figure-4

magnetic field near the knife-edge of the poles of magnet. The double trace gets converged because field gradient decreases transversely. No doubt there is some diffusiveness due to the velocity distribution of atomic particles. By knowing d, v, dB/dx and measuring D_x, the value of μ can be calculated. In the case of silver, the value of magnetic moment comes to be one Bohr magnetron. The other results are given below:

(a) In the case of Cu, Au, H, Li, Na, K, we get double traces. The separation D_x, corresponds to the value of $\mu=\pm1$.

(b) In the case of Zn, Cd, Hg we get no separation with the $\mu = 0$.

(c) In nickel, three distinct traces are visible; one at its original position and other two traces show the separation corresponding to $\mu > 1$.

(d) In the case of cobalt, the separation comes out to be such that $\mu > 6$.

(e) In case of iron, separation indicates that μ is greater than 6.

With the help of these results the important features of vector atom model can be easily explained.

1. Spin of the electron: In the case of silver, the single trace of path splits up into two lines, showing the value of $\mu = \pm1$, by magnetic field. If we consider the ground state of the silver atom and neglect the electron spin, then L = 0, S = 0 and J = 0. Since J has only zero value, the splitting of the line will not take place and μ will be zero because $= m_J\, g$, where m_J is total magnetic angular momentum quantum number and g is Lande's splitting factor. But if we admit the existence of electron spin and give it a value, then naturally $u = m_J g$ (g = 1 for orbital motion and g=2 for spin motion) will have two values +1 and -1. So the results obtained are in complete agreement with theory.

2. The Quantisation of Space: Classically speaking, the atomic magnets can orient themselves in any direction. If this is the case, then we should get diffused path in place of two distinctly visible traces. But due to the quantisation of the spin all possible orientations are not allowed but only certain discrete orientations are permissible. If we consider the atom belonging to one electron system and its ground state then L = 0 and J = S, and the possible orientations will be (2J+1) = 2 (increase of one electron spin S being). Therefore, in case of one electron system, i.e., in case of silver, we must get double trace. But in the case of many electron systems, the number of traces depends upon value of S. This explains the results obtained in the case of Stern-Gerlach experiment in the following way:

(a) H, Li, Na, K, Cu, Ag belong to one electron system having the values of $S = ½$, L = 0, for ground state. In this case 2J+1 = 2, hence two traces are possible. Further, since $\mu= m_J\, g$; g=2, $m_J = -J, J$; $\mu = \pm1$which is in agreement with experimental data.

(b) Zn, Cd and Hg have two *s* electrons in their outermost orbit and their normal state is represented by the term $^1S_0$ which means J = 0. Therefore, $m_J = 0$ and $\mu= 0$. This means again that the application of the field brings no effect.

(c) Finally, in the case of Ni, Co and Fe, the effect is clear due to the large value of electron spin.

The Stern-Gerlach experiment not only confirms the essential features of vector atom model but also confirms the well established fact that diamagnetic substances do not have any resultant magnetic moment while paramagnetic do have, as is clear from the result obtained.

FINE STRUCTURE OF HYDROGEN LINES:

Having explained the action of magnetic field on small atomic magnets in Stern-Gerlach experiment, we may visualize the fine structure doubling of spectral lines on the basis of a magnetic interaction between the spin and angular moment of atomic electrons. An electron revolving round a proton finds itself in a magnetic field because, in its own frame of reference, the proton is circling about it. This magnetic field then acts upon the electron's own magnetic moment to produce a kind of internal Zeeman Effect. The magnetic energy V_m of a magnetic dipole moment μ in a magnetic field of flux density **B** is

$$V_m = -\mu\cdot\mathbf{B} \qquad 1$$

$$= \pm\frac{e\hbar}{2m}\boldsymbol{B} \qquad 2$$

where $\frac{e\hbar}{2m}\boldsymbol{B}$ is spin magnetic moment in the direction of **B**. Depending upon the orientation of its spin vector, the energy of the electron in a given atomic state will be higher or lower by the $\frac{e\hbar}{2m}\boldsymbol{B}$ than its value in the absence of spin orbit interaction, The result is the splitting of every quantum state (except S state) into two separate sub-states and, consequently, the splitting of every Spectral line into two component lines.

"The assignment of s=½ is only one that conforms fine structure doubling."

Let us now have the estimate of magnetic flux density and magnetic energy in fine structure doubling. The circular wire loop of radius r that carries the current i has a magnetic field of flux density at its centre.

$$\boldsymbol{B} = \frac{\mu_0 i}{2r} \qquad 3$$

Where, μ_0 is the permeability of the vacuum. An orbital electron say in a hydrogen atom 'sees' itself circled f each second by a proton of charge +e for a resulting flux density of

$$\boldsymbol{B} = \frac{\mu_0 f e}{2r} \qquad 4$$

In ground state of hydrogen atom $f = 6.8\times10^{15}$ cps and 5.3×10^{-11} meter, so that **B**=13 Tesla (abbreviation T) 5

It shows very strong magnetic field.

The value of Bohr magnetron is

$$\frac{e\hbar}{2m} = 9.27\times10^{-24}\ \text{J/T} \qquad 6$$

Hence, magnetic energy V_m of such electron is

$$V_m = \pm \frac{e\hbar}{2m}\boldsymbol{B}$$

$$= 9.27 \times 10^{-24}\ \text{J/T} \times 13\text{T}$$

$$= 1.2 \times 10^{-22}\ \text{Joules}$$

The wavelength shift in such a change in energy is about 2Å for a spectral line of unperturbed wavelength 6563Å, somewhat more than the observed splitting of the originating in the n=3→ n=2 transition. However, the flux density of the magnetic field at the orbits of higher order is less than for ground state orbit, which accounts for the discrepancy.

POSITRONIUM:

The fundamental particle positron, during the slowing down, may combine with the electron from one of the atoms. The slowing down positron takes place due to its interaction with electron in a substance. The combined structure Positronium, as it is called, revolves round the common centre of gravity. Thus the system is very much identical to the hydrogen atom and so the formulae derived for hydrogen atom may be applied for this system.

Hence the orbital radius is given by

$$r_n = \frac{\hbar^2}{e^2}\frac{(m+m)}{m^2}\frac{n^2}{Z}(4\pi\epsilon_0) \qquad 1$$

For ground state,

$$r_0 = \frac{2\hbar^2(4\pi\epsilon_0)}{me^2} \approx 1\text{Å}$$

Thus, the orbital radius increases by a factor two. The energy of dissociation is given by

$$E = -\frac{1}{(4\pi\epsilon_0)^2}\frac{e^4}{2\hbar^2}\frac{m^2}{(m+m)} = \frac{m^2e^4}{4\hbar^2}\frac{1}{(4\pi\epsilon_0)^2} \qquad 2$$

This is one half of the ionization potential of the hydrogen atom (The results are not accurate because in Positronium both the particles move with very high velocity and hence relativistic correction is necessitated).

The Positronium exists in two states depending upon the state of spin orientation. These are ortho-Positronium in which the spins of two particles are parallel and para-positronium in which spins are anti-parallel. In para-positronium as two particles have their spins are anti-parallel, the system is unstable one with a life time 1.25×10^{-10} second. The para – positronium decays into two photons. The ortho-Positronium is stable enough and has a life time of the order of 1.4×10^{-7} second. It decays into three γ-photons so as to maintain the conservation of spin. The ground level of ortho-Positronium lies above the ground state of para-positronium by only 0.84×10^{-2} eV. The difference between the life times of two photons accelerates the annihilation process.

DIFFERENT SERIES IN ALKALI SPECTRA:

MAIN FEATURES: The alkali spectra are studied taking the following facts into account: (i) the physical appearance of the lines, for instance, sharp or diffuse; (ii) a physical change in the spectral lines when emitting atoms are subjected to some physical change, for example, the compression of the gas; (iii) the behaviour of the line, when emitting atom, is subjected to a magnetic field, etc.

It can be concluded that alkali spectra can be grouped into 4 chief series as given below:

1. Principal series: The series arises from the transitions between various P-levels and lowest S-level. The lowest S-level has the lowest possible value for the energy and represents the ground state of the atom. The wave number of the series is given by the relation

$$\bar{\nu}_P = \frac{R}{(1+\mu_S)^2} - \frac{R}{(m+\mu_P)^2}; m \geq 2.$$

2. Sharp series: This type of series comes from the transitions from S-levels (exclusive of the lowest) to the lowest of the P-levels. The wave number is expressed as

$$\bar{\nu}_S = \frac{R}{(2+\mu_P)^2} - \frac{R}{(m+\mu_S)^2}; m \geq 2.$$

3. The diffuse series: It arises from the transitions between the various D-levels and the lowest P-level. The wave number is expressed by the relation

$$\bar{\nu}_D = \frac{R}{(2+\mu_P)^2} - \frac{R}{(m+\mu_D)^2}; m \geq 3 .$$

4. Fundamental Series or Bergmann Series: The fundamental series arises from the transitions from various F-levels to the lowest D-level. The wave number is expressed by the relation

$$\bar{\nu}_F = \frac{R}{(3+\mu_D)^2} - \frac{R}{(m+\mu_F)^2}; m \geq 4 .$$

Here μ_S, μ_P, μ_D and μ_F are the characteristic constants of sharp, principal, diffuse and fundamental series, respectively. The abbreviated forms for writing the wave number of each series are as follows:

1. $(1, \mu_S) \leftarrow (m, \mu_P)$; with $m \geq 2$ Principal series
2. $(2, \mu_P) \leftarrow (m, \mu_S)$; with $m \geq 2$ Sharp series
3. $(2, \mu_P) \leftarrow (m, \mu_D)$; with $m \geq 3$ Diffuse series
4. $(3, \mu_D) \leftarrow (m, \mu_F)$; with $m \geq 4$ Fundamental series

It is to be noted that the series takes its name from the nature of the current term. The first term here is no doubt bigger than the second term, but the second term corresponds to more excited state.

The transitions between sharp and sharp level, and diffuse and sharp level, etc. are forbidden due to the selection principle, $\Delta l = \pm 1$.

To have the proper transitions it is essential here that the second term must be numerically less than the first; that is why the first member of principal series and sharp series correspond to m=2. Further, since $\mu_s > \mu_p > \mu_D > \mu_F$, lowest possible values of m come out to be 2 in case of principal and sharp series.

The other important features of the series are
1. The sharp and diffuse series have a common limit.
2. The wave number interval between this common limit and the limit of the principal series is equal to that of first line of principal series.

RITZ COMBINATION PRINCIPLE:

The structure of formulae for H-series persuaded Rydberg to think that combination of terms giving two spectral lines of a series might correspond to a spectral line of a new series. This idea of Rydberg was generalized in 1908 by Ritz and is known as Ritz combination principle and stated as follows:

If $\bar{\nu}_1$ and $\bar{\nu}_2$ are the wave numbers of two lines in the spectrum of certain atom, it often happens that lines also occur at the wave numbers $\bar{\nu}_1 + \bar{\nu}_2$ or $\bar{\nu}_1 - \bar{\nu}_2$.

Taking, for example, the H_α and H_β lines of Balmer series of hydrogen spectrum and combining the terms representing these lines, we write

$$\left.\begin{aligned}
\bar{\nu}_\alpha &= R_H\left[\frac{1}{2^2}-\frac{1}{3^2}\right]\\
\bar{\nu}_\beta &= R_H\left[\frac{1}{2^2}-\frac{1}{4^2}\right]\\
\bar{\nu}_\beta - \bar{\nu}_\alpha &= R_H\left[\frac{1}{3^2}-\frac{1}{4^2}\right]
\end{aligned}\right\} \qquad 1$$

This last relation represents first line of Paschen series. The second line of this series is obtained by combining H_γ, and H_α of Balmer series and so on. In similar fashion, the lines of other series may also be obtained.

Now, if we recall the structure of series formulae representing hydrogen lines, we notice that the fixed terms of second, third, fourth and fifth series are the 1st, 2nd, 3rd and 4th running terms of 1st series. Similarly, the fixed terms of 3rd, 4th and 5th series are the 1st, 2nd and 3rd running terms of 2nd series. This suggests that lines of a new series may also be obtained by changing the fixed term of a series. This is another way of stating Ritz principle. Further, the structure of the four chief series (sharp, principal, diffuse and fundamental) formulae state that 1st term is fixed and 2nd (current) term varies. But by varying the 1st term as the 2nd, we may get new series as in the case of hydrogen. The chief series

Sharp series : $\bar{\nu}_S = (2, \mu_P) \leftarrow (m, \mu_S)$; m≥2 2a
Principal series : $\bar{\nu}_P = (1, \mu_S) \leftarrow (m, \mu_P)$; m≥2 2b
Diffuse series : $\bar{\nu}_D = (2, \mu_P) \leftarrow (m, \mu_D)$; m≥3 2c
Fundamental series : $\bar{\nu}_F = (3, \mu_D) \leftarrow (m, \mu_F)$; m≥4 2d

Now by changing the fixed terms, we get the combination lines as
$(3, \mu_P) \leftarrow (m, \mu_S)$; $m \geq 3$ 3a
$(3, \mu_P) \leftarrow (m, \mu_S)$; $m \geq 4$ 3b
Combination principal series is
$(2, \mu_S) \leftarrow (m, \mu_P)$; $m \geq 3$ 4a
$(3, \mu_S) \leftarrow (m, \mu_P)$; $m \geq 4$ 4b
and so on

Since all the fixed terms occurring in the representations (3) and (4) are included in the running terms of the representation (2), the predicted series are simply combinations (sum or difference) of the terms of chief series. Therefore, the resultant series are called combination series and the possibility of their occurrence is known as Ritz combination principle (note that, each combination is not allowed due to the operation of selection rules and quantum conditions). In the spectra of alkaline earth, series and lines have been observed not only for triplet-triplet and singlet-singlet combinations, but also for triplet-singlet and singlet-triplet combinations. The triplet-singlet or singlet-triplet combinations are called inter-combination lines or series.

The principle maintains itself in the whole realm of spectroscopy, both in optical and X-ray regions, as an exact physical law within the accuracy of spectroscopic measurements. The principle is used to prove that in the equation $E = hc/\lambda$, the quantity hc is constant over the entire range within the accuracy of our measurements. The exactness of the principle has been tested by considering its application to iron spectrum by Mergers.

EXPLANATION OF SALIENT FEATURES OF ALKALI SPECTRA:

The electronic configuration of alkali metals is such that the core of an inert gas is surrounded by an s electron, for example for:

Li = [He] $+2s^1$
Na = [Ne] $+3s^1$
K = [Ar] $+ 4s^1$
Rb = [K] $+5s^1$
Cs = [Xe] $+ 6s^1$

The configuration is thus identical to hydrogen as core electrons do not play any part in optical spectra; only valence electrons, also called optical electrons, govern the characteristics of optical spectra.

Let us discuss the characteristics of alkali spectra taking the example of Na-atom. The optical 3s electron of sodium when excited jumps to higher energy states, such as 3s 3P, 45, 3D, 4S, 5S, 4D, etc. depending upon the amount of excitation energy. According to Bohr-Sommerfeld theory and quantum mechanical theory all substrates belonging to a given n in hydrogen have same value of energy. But this l degeneracy is removed in a multi-electron system because of shield of nuclear charge and penetration of atomic core. The term value is written as

$$T = \frac{RZ_0{}^2}{n_{eff}{}^2}$$

Where Z_0 is effective nuclear charge outside the core and n_{eff}^2 is effective quantum number. As Z_0 is greater than one and $n_{eff} < n$, the term value is increased. As a result energy levels in alkali atoms lie lower than the corresponding hydrogen levels. However, for large n, Z_0 is equal to unity and $n_{eff} \to n$; the corresponding levels approach the hydrogen levels.

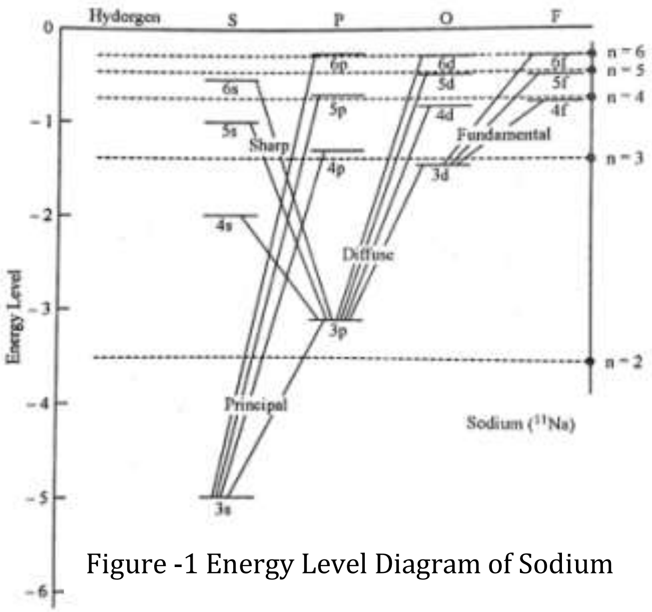


Figure -1 Energy Level Diagram of Sodium

Further, on account of the dependence of energy on l value, on account of shielding of nuclear Charge, the levels with a given n have energy in algebraically increasing order of t. It means that the levels S, P, D... for a given n are less and less negative and thus these levels lie lower than the corresponding hydrogen levels. The l dependence of energy is important to the extent that the 45 level lies lower than the 3D orbit of the same orbit; similarly 5S lies lower than the 4D and 4F levels.

When an optical electron, for example in case of sodium atom, is excited and then it returns to ground level, it gives rise to all 4 chief series as

Sharp series $n^2S \rightarrow 3^2P$, n = 4, 5, 6….
Principal series $n^2P \rightarrow 3^2S$, n = 3, 4, 5….
Diffuse series $n^2P \rightarrow 3^2D$, n = 3, 4, 5….
Fundamental series $n^2F \rightarrow 3^2D$, n = 4, 5, 6….

As sodium source contains a large number of atoms, all possible excited states are available for transition, hence all the series are simultaneously observed. The lines of sharp series were relatively sharp and hence the name "sharp series". The lines of the P series were observed both in emission and absorption spectra of sodium for very small excitations, hence the name "principal series". The diffuse series lines were found to be somewhat diffused; hence the name "diffuse". The frequencies of the fundamental series are in infra-red region and come very close to that of the "fundamental" hydrogen atom; therefore we call it fundamental series. Details of sodium spectrum are shown in Fiure-1.

Now, that in the case of sodium sharp and diffuse series have same convergence limit (3p →$3^2P_{1/2,\,3/2}$). The wave number difference between this limit and principal series limit (3p →$3^2S_{1/2}$) is equal to the first line ($3^2P_{1/2}$ →$3^2S_{1/2}$) of the principal series. Similarly, the wave number difference between the diffuse series limit (3p →$3^2P_{1/2,\,3/2}$) and fundamental series limit (3d →$3^2P_{3/2,\,5/2}$) is equal to the wave number of first line ($^2D_{1/2}$ → $^2P_{1/2}$) of diffuse series.

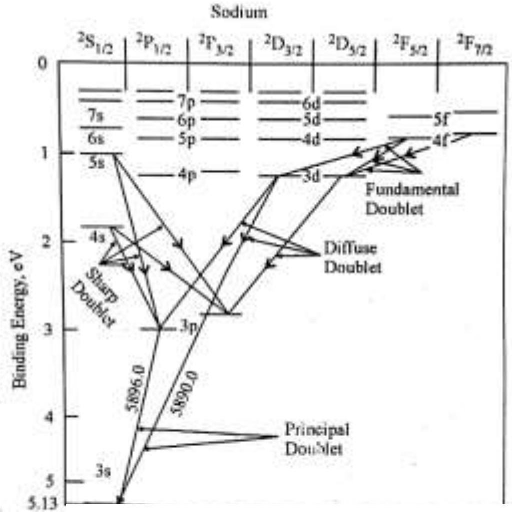


Figure-2 - Doublet character of Na-spectrum.

Doublet Structure in Alkali Spectra (Fine Structure):

As mentioned earlier, doublet separation decreases with increasing l and increasing n. Thus, the 3P doublet is wider than 3D; 3D wider than 4F; also the 3P doublet is wider than the 4P and 4P wider than the 5P, and so on. Now when electrons make transitions from one of the excited states to a lower state, spectral lines result.

The transitions $n^2S_{1/2}$ →$m^2P_{1/2,\,3/2}$ and $n^2P_{3/2,\,1/2}$ →$m^2S_{1/2}$ gives rise to doublet. Thus every line of the sharp series ($n^2S_{1/2}$ →$m^2P_{1/2,\,3/2}$) and the principal series ($n^2P_{1/2,\,3/2}$ →$3^2S_{1/2}$) is doublets. The two transitions $3^2P_{3/2}$ →$3^2S_{1/2}$ and $3^2P_{1/2}$ →$3^2S_{1/2}$ are the first members of principal series and are the prominent yellow lines of sodium referred to as the sodium D lines doublet. The diffuse and fundamental series start from doublet levels and end on doublet levels; so we would expect to find a quartet. But the selection rules only permit triplets. The component lines of diffuse and fundamental series are triplets but known as doublets. The following points are also noted in regard to alkali spectra. The doublet character is shown in Figure-2.

(a) In the principal series, the difference of the wave numbers of the components of a doublet decreases rapidly as we pass towards higher frequency side.
(b) The wave number difference$\Delta\bar{\nu}_S$, of sharp series doublets remains constant as the series can be followed.
(c) In the diffuse series the wave number difference $\Delta\bar{\nu}$ between the shorter components of doublet and satellite also remains constant.
d) The wave number difference between the doublet of sharp series and doublet separation in diffuse series is equal, i.e. $\Delta\bar{\nu}_S = \Delta\bar{\nu}_d$
(e) The wave number difference of the first doublet in principal series is equal to$\Delta\bar{\nu}_l$. Figure-2 explains the above noted facts.

In case of principal series, the difference of lines of a doublet is simply $mP_{1/2} - mP_{3/2}$

which decreases as m increases. In the case of sharp and diffuse series different doublets have the same final orbits, i.e., $^2P_{1/2}$ and $^2P_{3/2}$ Hence the doublet separation is constant and equal.

In the states having the same values of n, l and s, the energy is the same. But there is small energy difference due to the orientation of spin vector with respect to the field direction, i.e. due to spin orbit interaction. This spin orbit interaction as we know gives rise to a new quantum number j upon which the final value of energy depends, but by a very little For given values of n, l and s, J can take two values right from $l+s$ to $l-s$ with a difference of one, because $s = 1/2$. But the S sate itself is not double because for S state $l=0$; so the possible value of j is only one, i.e., ½. Hence in alkali spectra every component level is double, excluding S level.

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QUESTION BANK 2020-21

Unit: I [Spectra of Atom]

Part: I: Multiple Choice Questions:

1. The separation components of light can be established either by _________or by_________
   (a) reflection ,diffraction (b) refraction , diffraction
   (c) refraction, interference (d) refraction, polarization
2. Stern and Gerlach's experiment directly reveals the essential features of ___________
   (a)bombardment of electrons (b) bombardment of neutrons
   (c) vector atom model (d) Liquid drop model
3. In ortho-Positronium, the spin of two particles is __________________
   (a) anti parallel (b) perpendicular
   (c) parallel (d) None of above
4. The prism method to get spectra has advantage of greater ______________.
   (a) Greater light intensity (b) Resolving power
   (c) clarity (d) None of above
5. The grating method to get spectra has advantage of greater ____________.
   (a) light intensity (b) Greater resolving power
   (c) clarity (d) None of above
6. The separation components of light can be established either by__________ or by____________
   (a) reflection ,diffraction (b) refraction , diffraction
   (c) refraction, interference (d) refraction, polarization
7. Thermopile and bolometer are used to investigate spectra in the____________ region.
   (a) ultra violet region (b) Visible region
   (c) micro wave region (d) Far infra red region
8. Para-Positronium in which the spin of two particles are ___________
   (a) anti parallel (b) neutral
   (c) zero (d) parallel
9. The spectrum directly examined by a spectroscope is known as ____________spectrum.

(a) emission (b) discontinuous
(c) absorption (d) All of above

10. Wien displacement law is represented by relation__________________.
(a) $2\lambda T = a\ constant$ (b) $\lambda T = a\ constant$
(c) $\lambda / T = a\ constant$ (d) $1/\lambda T = a\ constant$

11. The band spectra also known as ______________________.
(a) Atomic spectra (b) electronic spectra
(c) molecular spectra (d) wide spectra

12. In spectroscopy, reciprocal value of the wave length is called _____________
(a) absorption (b) intensity
(c) Wave number (d) Periodic time

13. Balmer's exact empirical relation for wave length and spectral lines is _______
(a) $\lambda = \frac{n^2}{n^2-4} b$ (b) $\lambda = \frac{n^2}{n-4} b$
(c) $\lambda = \frac{n}{n^2-4} b$ (d) $\lambda = \frac{n}{n-4} b$

14. Paschen series lies in the __________________region.
(a) visible region (b) ultra violet region
(c) micro wave region (d) infra red region

15. Stern and Gerlach's experiment directly reveals the essential features of __________
(a) bombardment of electrons (b) bombardment of neutrons
(c) vector atom model (d) Liquid drop model

16. In ortho-Positronium, the spin of two particles is _______________
(a) anti parallel (b) perpendicular
(c) parallel (d) None of above

Part: II: Short Questions

1. Define line spectra & Band Spectra
2. Write Bohr's two assumptions to explain the spectrum of Hydrogen.
3. Write Ritz combination principle.
4. What is Positronium?
5. Enlist various series have been observed in the spectrum of atomic Hydrogen.
6. Explain Salient features of Alkali spectra in brief.

Part: III: Long Questions

1. Discuss Bohr's theory to explain the spectrum of Hydrogen atom.
2. Discuss atoms of alkaline elements in detail.
3. Explain Bohr's theory to explain the spectrum of Hydrogen.
4. Discuss the Larmor's theorem.
5. Explain Stern Gerlach experiment in detail.
6. Discuss 1. Frank – Hertz experiment and 2. Ritz combination principle.
7. Discuss atoms of alkaline elements.

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