

Review of Bohr's theory of hydrogen atom

Introduction : Atomic physics deals with atom as an isolated system of electrons and an atomic nucleus. It is primarily concerned with the arrangement of electrons around the nucleus and the processes by which these arrangements change. An atom is the smallest particle of an element that has the properties characterizing that element. One of the first breakthroughs in the study of an atom was achieved by Sir Ernest Rutherford in 1911. He established that the mass of the atom is concentrated in its nucleus. He also proposed that the nucleus has a positive charge and is surrounded by negatively charged electrons. The existence of electrons was already discovered in 1897 by J. J. Thomson. This theory of atomic structure was complemented by Niels Bohr in 1913 who explained the origin of spectral lines of hydrogen atom. Bohr proposed the following postulates.

Postulates of Bohr's theory

- (1) In an atom the electrons move in circular orbits with the nucleus at its centre. As long as electrons revolve in these orbits, they do not emit radiation (energy). These orbits are called the **stationary orbits**.
- (2) Electrons can revolve in only those specific stationary orbits for which the orbital angular momentum of the electron about the nucleus is an integral multiple of \hbar ($\hbar = h/2\pi$). Thus an electron in the n th orbit will have an angular momentum ($L = mvr$) given by $mvr = n\hbar$ where $n = 1,2,3,\dots$ the mass, v the velocity of the electron and r the radius of the orbit.
- (3) When an electron jumps from one stationary orbit of higher energy to another orbit of lower energy, it radiates the excess energy as a quantum, corresponding to which a spectral line is emitted. If E_i and E_f are the energies of an electron in the two orbits, then $E_f - E_i = h\nu$.

Using the Bohr's postulates, the expressions for the radius of the electron orbit, energy of the electron and the wavelength of the emitted spectral line can be obtained.

(1) Expression for radius of an electron orbit: Consider an atom of atomic number Z , with charge on the nucleus as Ze . Let m be the mass and v the linear velocity of the electron. Let the radius of the electron orbit be r . The electrostatic force provides the necessary centripetal force that keeps the electron in the orbit.

$$\text{Thus } \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \quad \dots(1) \quad \text{or} \quad mv^2 r = \frac{Ze^2}{4\pi\epsilon_0} \quad \dots(2)$$

$$\text{From the Bohr's quantization rule } mvr = \frac{nh}{2\pi} \quad \dots(3) \quad \text{or} \quad m^2 v^2 r^2 = \frac{n^2 h^2}{4\pi^2} \quad \dots(4)$$

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Dividing (4) by (2) $\frac{m^2 v^2 r^2}{m v^2 r} = \frac{n^2 h^2}{4\pi^2} \times \frac{4\pi\epsilon_0}{Ze^2}$ This gives $r = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$. The radius of the Bohr orbit is directly proportional to the square of the quantum number n.

(2) Expression for orbital velocity of the electron : From the Bohr's quantization

rule $mvr = \frac{nh}{2\pi}$ (1) where $r = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$ (2)

Equation (2) in (1) gives $mv \left(\frac{n^2 h^2 \epsilon_0}{\pi m Z e^2} \right) = \frac{nh}{2\pi}$ or $v = \frac{Ze^2}{2n h \epsilon_0}$

From the above equation v is found to be inversely proportional to n which shows that velocity of an electron in the outer orbit is less than that in the inner orbit.

(3) Expression for energy of the electron: The total energy (E) of an electron in an orbit is the sum of its potential energy (E_P) and kinetic energy (E_K) where

$$E_P = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots(1) \quad \text{and} \quad E_K = \frac{1}{2}mv^2 \quad \dots(2)$$

From the Bohr's postulate $\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2}$ or $mv^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$... (3)

Substituting for mv^2 from (3) in (2) we get $E_K = \frac{1}{2} \times \frac{Ze^2}{4\pi\epsilon_0 r}$ (4) .

Total energy of the electron in the nth Bohr orbit is $E = E_P + E_K$

$$\text{or } E = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{1}{2} \times \frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{or } E = \frac{Ze^2}{4\pi\epsilon_0 r} \left[-1 + \frac{1}{2} \right] = -\frac{Ze^2}{8\pi\epsilon_0 r}. \text{ Thus } E_n = -\frac{Ze^2}{8\pi\epsilon_0 r}$$

As $r = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$ we get $E_n = -\frac{mZ^2 e^4}{8\epsilon_0^2 n^2 h^2}$ J or $E = -\frac{13.6Z^2}{n^2}$ eV (for H - atom, Z = 1)

Note : 1. The significance of negative sign in the expression for energy is that (1) the electron is bound to the nucleus and external energy is required to remove the electron from the atom. (2) Also E is inversely proportional to n^2 . With increase in n, numerically energy decreases but due of negative sign, E increases with increase in n and electrons in outer orbits will have greater energy. (n = 1 is the ground state and n = 2,3,4 ...are excited states).

2. To calculate the radius of an electron orbit in case of H - atom, orbital velocity of the electron and its energy the following constant values are used.

$$m = 9.1 \times 10^{-31} \text{ kg}, e = 1.6 \times 10^{-19} \text{ C}, \epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}, h = 6.63 \times 10^{-34} \text{ Js}, Z = 1.$$

The radius of the electron in the first Bohr orbit (n = 1) = 0.53Å.

The velocity of the first Bohr orbit (n = 1) is $v = 2.18 \times 10^6 \text{ ms}^{-1}$.

The energy of the electrons are $E_1 = -13.6\text{eV}$ (n = 1), $E_2 = -3.4\text{eV}$ (n = 2),.....

Origin of spectral lines

Expression for the wave number of the emitted spectral line

A spectral line of an element results when an electron in the atom jumps from higher energy level (outer orbit) to the lower energy level (inner orbit). If E_1 and E_2 are the two energy levels corresponding to inner orbit n_1 and outer orbit n_2 respectively, then from the

$$\text{Bohr's postulate } h\nu = E_2 - E_1 \quad \text{or} \quad h\nu = -\frac{mZ^2e^4}{8\varepsilon_0^2n_2^2h^2} - \left(-\frac{mZ^2e^4}{8\varepsilon_0^2n_1^2h^2}\right)$$

$$\text{or } \nu = \frac{mZ^2e^4}{8\varepsilon_0^2h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]. \text{ If } \lambda \text{ is the wavelength of the emitted radiation, then } \nu = \frac{c}{\lambda}$$

$$\frac{c}{\lambda} = \frac{mZ^2e^4}{8\varepsilon_0^2h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{or} \quad \frac{1}{\lambda} = \frac{mZ^2e^4}{8\varepsilon_0^2c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ As } \frac{1}{\lambda} = \bar{\nu} \text{ is called the wave number}$$

$$\text{of the emitted spectral line. It is given by } \bar{\nu} = \frac{mZ^2e^4}{8\varepsilon_0^2c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\text{For hydrogen atom } Z = 1. \text{ Thus } \bar{\nu} = \frac{me^4}{8\varepsilon_0^2c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{or} \quad \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $R_H = \frac{me^4}{8\varepsilon_0^2ch^3}$ is a constant called **Rydberg constant (R_H)** for hydrogen atom (Here

the nucleus is assumed to have infinite mass and hence is at rest. Here m stands for mass of the electron). The value of $R_H = 1.09678 \times 10^7 \text{m}^{-1}$.

Bohr gave the explanation of spectral series of hydrogen atom based on his postulates as follows.

When energy is given to the electron in the ground state of an atom, it will rise to one of the permitted higher

energy states (outer orbits). As the electrons are unstable in these states, it will return to ground state either in a single jump or a series of jumps. Each such transition of electron from higher to lower energy state will result in the emission of electromagnetic radiation of a particular wavelength. This corresponds to a line in the spectrum.

Note : A number of spectral lines in the hydrogen spectrum are observed even though hydrogen atom has a single electron. The reason is the following

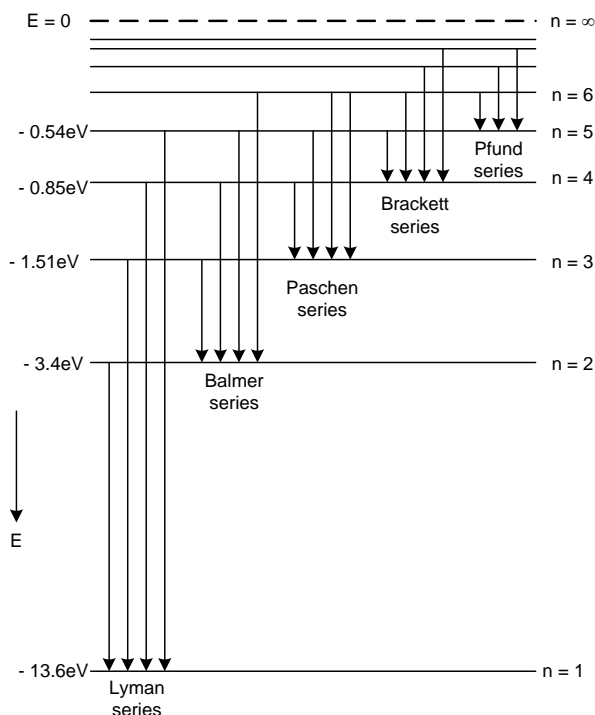
A hydrogen gas has a large number of atoms. If energy is supplied externally to a large number of hydrogen atoms, all the electrons may not be excited to the same higher energy state. Therefore different electrons undergo different transitions.

Spectral series of H - atom			
Name of the spectral series	Transition		Region of EM spectrum
	From n_2	To n_1	
Lyman	2,3,4,...	1	Ultraviolet
Balmer	3,4,5,...	2	Visible
Paschen	4,5,6,...	3	Infrared
Brackett	5,6,7,...	4	Farinfrared
Pfund	6,7,8,...	5	ExtremeIR

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Energy level diagram is a diagram indicating the different energy states corresponding to different values of quantum numbers (n) and the transitions of electrons between different energy states producing different spectral series.

In the Energy level diagram, horizontal lines correspond to different energy values of the stationary states of the electrons. Vertical lines are drawn to show the different transitions of electrons between the orbits. The first excitation energy is $-3.4 - (-13.6) = 12.09\text{eV}$. The ionization energy of H - atom is 13.6eV .



Bohr's correspondence principle : For large

values of n, the successive energy values differ very little. Thus the principle says - the behavior of an atomic system as predicted by quantum theory tends asymptotically to that expected in classical theory in transitions involving states of large quantum numbers.

Variation of Rydberg constant with nuclear mass

In Bohr's theory, it was assumed that mass of nucleus is so heavy (nearly infinity) that it remains at rest and the electron revolves round it in circular orbits. This is not true as the mass of the nucleus is only 1836 times the mass of the electron. With a finite mass of the nucleus, both the nucleus and the electron revolve about their common centre of mass with the same angular frequency.

With this correction to Bohr's theory, the mass of the electron, m is replaced by reduced mass of the system given by $\mu = \frac{mM}{M+m} = \frac{m}{1+\frac{m}{M}}$ where M is the mass of the nucleus.

The expression for Rydberg constant should be written as

$$R = \frac{\mu e^4}{8\epsilon_0^2 ch^3} = \frac{me^4}{8\epsilon_0^2 ch^3} \left(\frac{1}{1+\frac{m}{M}} \right).$$

This shows that Rydberg constant varies with mass of the nucleus.

If R_∞ is the Rydberg constant when nucleus is at rest with its mass close to infinity and R_M is the Rydberg constant when nuclear mass is finite then

$$R = R_M = \frac{R_\infty}{1+\frac{m}{M}}.$$

Here $R_\infty = \frac{me^4}{8\epsilon_0^2 ch^3}$. The transition between two energy levels which

results in the emission of a spectral line of a particular wave number is given by

$$\bar{\nu} = R_M Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = \frac{R_\infty}{1+\frac{m}{M}} Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right].$$

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- (a) The reduced mass $\mu < m$. It increases with increasing nuclear mass M and becomes equal to electronic mass as $M \rightarrow \infty$. For example in case of Hydrogen and Helium, by considering the effect of finite mass of the nucleus, the values of R_H and R_{He} are $1.09677 \times 10^7 m^{-1}$ and $1.09722 \times 10^7 m^{-1}$. As $R_{He} > R_H$ the spectral lines of Pickering series of He^+ should have slightly higher wave numbers or shorter wavelengths than the corresponding lines of the Balmer series of hydrogen. These values agree well with the experimental values giving justification for the motion of the nucleus.
- (b) Using the values of R_{He} and R_H , the ratio of mass of the electron to that of mass of the proton i.e. m/M_H was found to be $1/1840$ which is in excellent agreement with the values obtained by other methods.
- (c) The variation of R with M also resulted in the discovery of heavy hydrogen, called deuterium whose nuclear mass is nearly double that of hydrogen nuclear mass. The spectrum of the H atom were found to have faint lines on the shorter wavelength sides of the spectral lines. This observation was attributed to the presence of isotope of hydrogen called deuterium whose Rydberg constant was found to be $R_D = 1.09707 \times 10^7 m^{-1}$. The wave numbers calculated using this agreed with the experimental values.

Limitations of Bohr's theory

1. It applies only to one-electron atoms, particularly hydrogen atom.
2. As the electron revolves at a high speed, relativistic correction has to be applied to its mass which is not considered in the Bohr's theory.
3. The fine structure of the spectral lines could not be explained by Bohr's theory.
4. When applied to hydrogen like atoms, (singly ionised helium, doubly ionised lithium etc... which contain one electron around the nucleus like hydrogen) the Bohr's theory does not yield proper results.
5. The Bohr's theory gives the frequency of the spectral lines but does not give any information about their relative intensities.
6. Spectra of heavy elements and their chemical properties could not be explained based on this theory.

Sommerfeld's modification of the Bohr atomic model

Spectral lines of the Balmer series of hydrogen spectrum actually consist of a number of very fine lines. These lines were found when observed through an optical instrument of high resolving power. These lines are called **fine structure** of the spectrum. They could

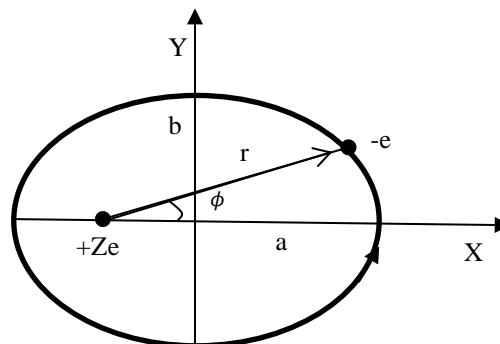
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not be explained by Bohr's theory. Sommerfeld modified Bohr's theory. According to Sommerfeld,

1. The path of electrons around the nucleus, in general is elliptical with the nucleus at one of its foci. The circular orbit is only a special case of an elliptical orbit.
2. The velocity of the electron is very high and is different at different points of elliptical path. This causes variation of mass of the electrons. Thus relativistic variation of mass of the electron need to be considered. This results in splitting of spectral lines giving rise to fine structure.

Concept of elliptical orbits

Periodic motion under the inverse square law force leads to elliptic orbits. It was therefore postulated by Sommerfeld that, in an atom an electron moves in an elliptic orbit with the nucleus located at a focus. In an



elliptic orbit, an electron can be located by two coordinates r (the radius vector) and ϕ (the azimuth angle) as shown. If p_r and p_ϕ be the resolved components of the momentum p of the electron along the radial direction and perpendicular to it, then according to sommerfeld, the two quantum conditions are

$$\int p_r dr = n_r \hbar \quad \dots(1)$$

$$\text{and } \int p_\phi d\phi = n_\phi \hbar \quad \dots(2)$$

where n_r and n_ϕ are called the radial quantum number and azimuthal quantum number respectively which take only positive integral values and are such that $n = n_r + n_\phi$ where n is the principal quantum number.

Here $p_r = \frac{n_r \hbar}{2\pi}$ and $p_\phi = \frac{n_\phi \hbar}{2\pi}$

If ϵ is the eccentricity of the ellipse with semi major axis as a and semi minor axis as b , it can be shown that $n = \frac{n_\phi}{\sqrt{1-\epsilon^2}}$ or $\sqrt{1-\epsilon^2} = \frac{n_\phi}{n}$ (3)

Also as $b = a\sqrt{1-\epsilon^2}$, we have $\sqrt{1-\epsilon^2} = \frac{b}{a}$ (4)

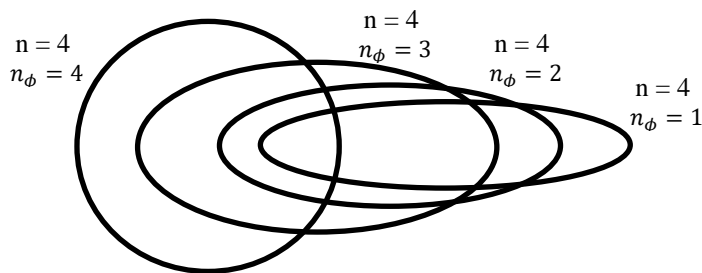
From (3) and (4) $\frac{b}{a} = \frac{n_\phi}{n}$ (5) This condition determines the allowed elliptical orbits. This relation indicates that when $n_\phi = n$, $b = a$, the orbit is circular. n_ϕ cannot be zero because the ellipse degenerates to a straight line. Also n_ϕ cannot be greater than n since in such a case $b > a$. Hence for a given value of n , n_ϕ can only assume n different values. This means only n elliptical orbits of different eccentricities are allowed.

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For example

$n = 4$, we have $n_\phi = 1, 2, 3, 4$

i.e. four possible orbits with three elliptical of different eccentricities and one circular for $a = b$.

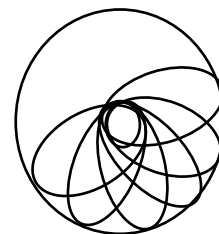


It can be shown that with the introduction of elliptical orbits for electrons, the energy of electron expression is $E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 n^2 h^2}$. This expression does not depend on n_ϕ but only on n . Thus introduction of elliptic orbits does not give rise to new energy levels. Thus Sommerfeld proposed the relativistic correction to explain the fine structure.

Relativistic correction to Sommerfeld's elliptical orbits Since the velocity of an electron in the innermost Bohr orbit is 0.007 times the velocity of light, the electron in the elliptic orbit must undergo variation of mass according to the relation $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$

Where m_0 is the rest mass and m is the mass when electron moves with velocity v close to c .

The application of relativistic correction leads to the fact that there is a slow precession of the plane of the major axis about an axis through its one of the foci. This represents a Rosette curve as shown.

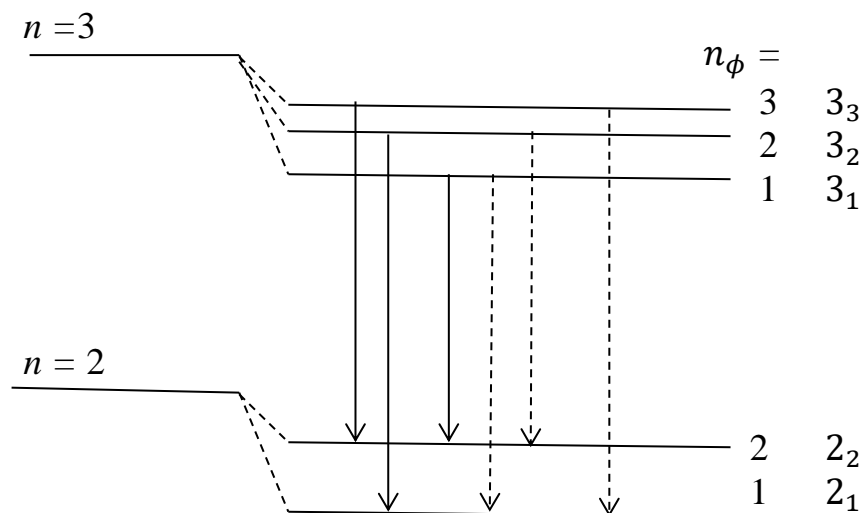


Applying the relativistic correction, the energy of the electron in a particular quantum state represented by n and n_ϕ is found to be $E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 n^2 h^2} \left[1 + \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{n_\phi} - \frac{3}{4} \right) \right]$ where α is the fine structure constant given by $\alpha = \frac{e^2}{2\epsilon_0 ch} = \frac{1}{137}$.

The expression for E_n is found to depend on both n_ϕ and n . Transitions corresponding to various n_ϕ values is found to occur. Since the energy difference of these values are very small, the frequency of the resulting spectral lines will be very close. Thus a group of closely associated lines appear instead of a single line as explained in Bohr's theory. The selection rule for the transition is $\Delta n_\phi = \pm 1$ which suggests a finite number of close lines.

Fine structure of H_α line : The transitions corresponding to the fine structure of H_α line of Balmer series of Hydrogen atom are as shown. H_α line results from the transition of the electron from $n = 3$ to $n = 2$. For $n = 3$, there are three possible energy levels and for $n = 2$, there are two possible energy levels. Six transitions are possible between them as

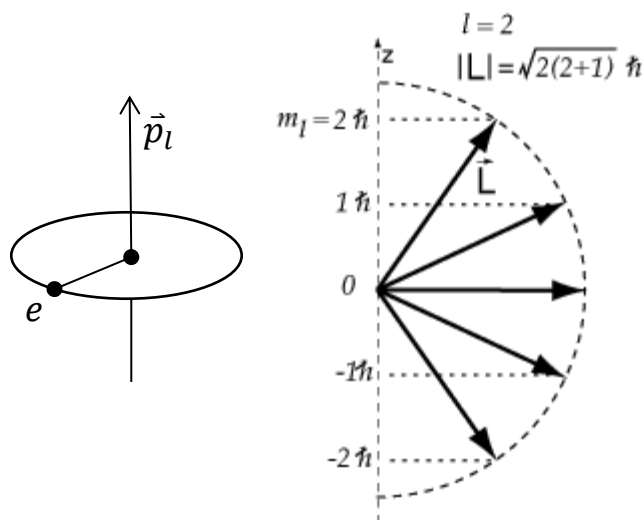
shown. But by selection rule $\Delta n_\phi = \pm 1$, only three transitions are allowed. (continuous vertical lines). The dotted lines are forbidden. This agrees with the experimental results. Sommerfeld's theory was able to explain the fine structure.



Failures of Sommerfeld theory : (1) It fails to predict the number of lines in the fine structure. (2) It failed to give information regarding the relative intensities of the lines. (3) It fails to explain the Zeeman effect and the Stark effect. (4) These theories could not be applied to many electron systems. To explain these drawbacks Vector atom model was proposed.

The Vector Atom Model

The main contributors for this model are Bohr, Sommerfeld, Uhlenbeck, Goudsmith, Pauli, Stern and Gerlach. The two main features of vector atom model are (1) spatial quantization and (2) electron spin.



(1) Space quantization :

According to spatial quantization, the orientation of the electron orbits in space is quantized. The plane of the orbit in space or the direction of orbital angular momentum can take only certain selected orientations with respect to a preferred direction which could be an external magnetic field (B). ($B \rightarrow 0$),

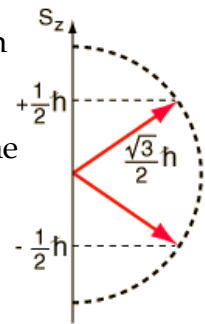
The magnitude of orbital angular momentum of the electron is given by

$L = p_l = l \frac{h}{2\pi} = l\hbar$ where l is the orbital quantum number. The associated magnetic moment is called the orbital magnetic moment μ_l . For a given value of principal quantum number n , l can take n values from 0 to $(n - 1)$. Thus for $n = 3$, $l = 0, 1, 2$. For a given value

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of l , an orbit in space can have $(2l + 1)$ orientations in space with respect to external magnetic field. Then according to the space quantization rule, only those orientations of \vec{p}_l are possible for which its components along the field direction can have values given by $p_l \cos\phi = m_l \frac{h}{2\pi} = m_l \hbar$ where ϕ is the angle between p_l and the external field direction in space, m_l is the magnetic quantum number for orbital motion and can have the possible values of $0, \pm 1, \pm 2, \pm 3, \dots \dots \pm l$. i.e. m_l can have $(2l + 1)$ values. For example, in case of $l = 2$, $m_l = +2, +1, 0, -1, -2$.

(2) Spinning electron hypothesis: According to electron spin hypothesis proposed by Uhlenbeck and Goudsmit, an electron in addition to orbital motion has a spin motion. The spin motion is quantized. The magnitude of the spin angular momentum is $p_s = s \frac{h}{2\pi} = s \hbar$ where s is the spin quantum number. The value of $s = 1/2$. The associated magnetic moment is called the spin magnetic moment μ_s . The spin angular momentum has two orientations with respect to external magnetic field i.e. either parallel or antiparallel to field.



Magnetic moment due to the orbital motion of the electron - Expression for Bohr magneton

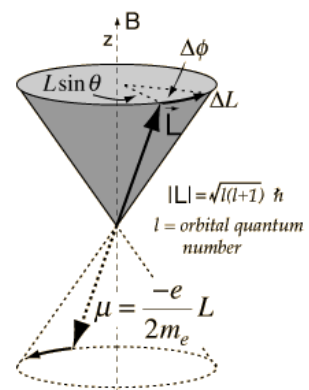
The orbital motion of the electron is equivalent to a current loop which produces a magnetic field perpendicular to the plane of the orbit. The magnetic field is characterized by a magnetic dipole moment. The magnetic moment associated with the current loop is $\mu_l = IA$.

But the current is $I = \frac{e}{T}$ and $A = \pi r^2$ where r is the radius of the electron orbit and T is the time period of revolution of the electron.

Thus the magnetic moment is $\mu_l = \frac{e}{T} \pi r^2$

If v is the orbital velocity of the electron, then $\frac{2\pi r}{v} = T$. Substituting for T in the above equation, we get $\mu_l = e \pi r^2 \left(\frac{v}{2\pi r} \right) = \frac{e v r}{2}$

If we multiply and divide the above equation by m , we get $\mu_l = \frac{e}{2m} (m v r)$



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or $\mu_l = \frac{e}{2m} p_l$ where $p_l = m v r$ called the orbital angular momentum of the electron. As $p_l = l\hbar$, we get $\mu_l = \frac{e}{2m} l\hbar = \left(\frac{e\hbar}{2m}\right) l$

The magnetic moment is $\mu_l = \left(\frac{e\hbar}{2m}\right) l = \mu_B l$

Where $\mu_B = \frac{e\hbar}{2m_e} = \frac{eh}{4\pi m_e}$. (since $\hbar = \frac{h}{2\pi}$)

μ_B is called the Bohr magneton. Its value is $9.273 \times 10^{-24} \text{ JT}^{-1}$.

The ratio $\frac{\mu_l}{p_l} = G$ is called the gyromagnetic ratio given by $G = \frac{e}{2m}$ or $G = g_l \frac{e}{2m}$

where g_l is called the lande's splitting factor and is equal to 1 for orbital motion of the electron.

Note : The electron also possess spin magnetic moment given by $\mu_s = \left(\frac{e\hbar}{2m}\right) 2s$

As $s = \frac{1}{2}$, thus $\mu_s = \left(\frac{e\hbar}{2m}\right)$

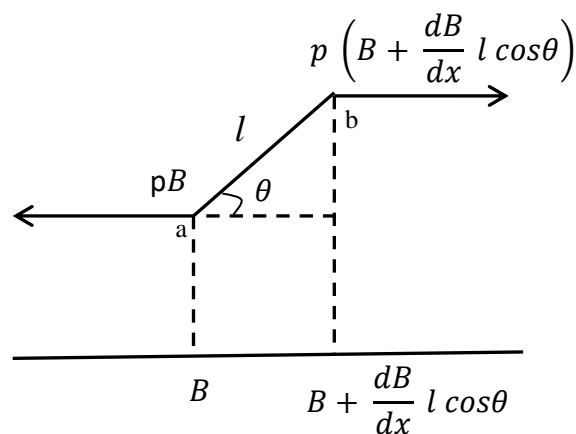
Stern - Gerlach Experiment

In 1921 Otto Stern and W. Gerlach of Germany performed an experiment in which atomic beams were deflected in a non-homogeneous magnetic field. The experiment provides a direct proof of (i) existence of two spin states ($\pm 1/2$) of the electron and (ii) the postulate of space quantization.

Principle : According to the vector atom model, every atom is regarded as an elementary magnet where the magnetic moment arises from the orbital and the spin motion of the electron. If such an atomic magnet is placed in a non-homogeneous magnetic field, each pole of the magnet experiences a different force. This results in translational displacement of the atom when it moves in the magnetic field. Thus the atom deviates from its straight line path.

Theory: Let l be the length of an atomic magnet (ab) with p as its pole strength placed inclined at an angle θ in a non homogeneous magnetic field which changes along x axis as

$\frac{dB}{dx}$. The forces on the two poles at a and b are pB and $p \left(B + \frac{dB}{dx} l \cos\theta \right)$ respectively.



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Couple acts on the magnet and a translatory force F_x acts on the atomic magnet given by

$$F_x = p \frac{dB}{dx} l \cos\theta \quad \text{or} \quad F_x = p l \cos\theta \frac{dB}{dx} = M \cos\theta \frac{dB}{dx} \quad \dots(1) \quad \text{where } M = p \times l$$

called the atomic magnetic moment.

Let m be the mass of the atom, v its velocity of motion normal to the field, L the length of the path in the field and t the time of flight.

$$\text{The acceleration of the atom is } a_x = \frac{F_x}{m} \quad \dots(2) \quad \text{and} \quad t = \frac{L}{v}$$

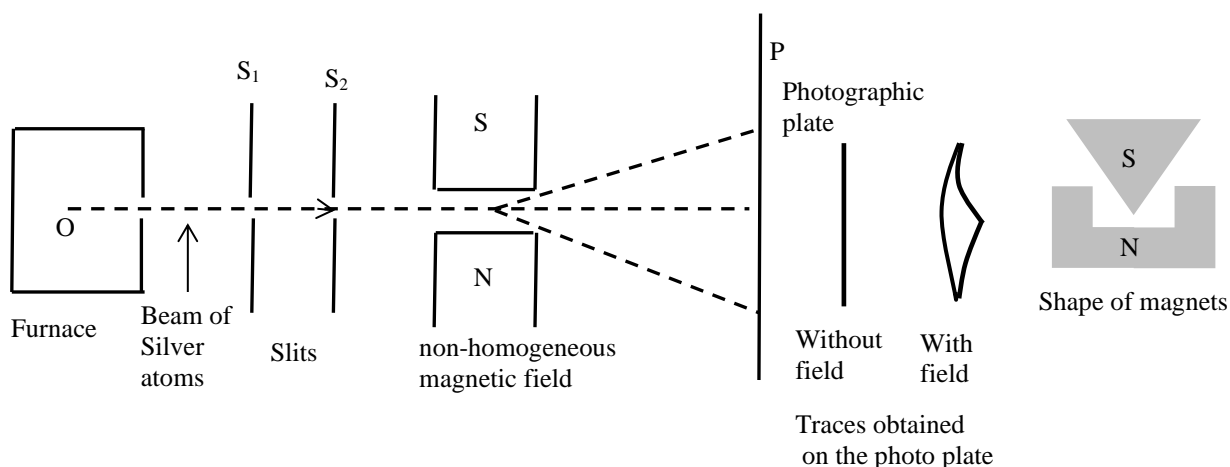
$$\text{Substituting for } F_x \text{ from (1) in (2), } a_x = \frac{M \cos\theta}{m} \frac{dB}{dx} \quad \dots(3)$$

The displacement D_x of the atom along the field direction at the end of the time t is given by $D_x = \frac{1}{2} a_x t^2 \quad \dots(4)$

$$\text{Substituting for } a_x \text{ from (3) and } t \text{ in (4)} \quad D_x = \frac{1}{2} \frac{M \cos\theta}{m} \frac{dB}{dx} \left(\frac{L}{v}\right)^2$$

or $D_x = \frac{1}{2} \frac{\mu}{m} \frac{dB}{dx} \left(\frac{L}{v}\right)^2$ where $\mu = M \cos\theta$ is the resolved magnetic moment in the field direction. If m , L , $\frac{dB}{dx}$ and v are known, by measuring D_x we can calculate μ .

Experimental description



O is the electric oven in which metallic silver is heated to produce a beam of silver atoms. The velocity of the beam is controlled by temperature of the oven. The atomic rays collimated by slits S_1 and S_2 will enter a non-homogeneous magnetic field produced by magnets one with a sharp knife edge and other with a groove parallel to knife edge as shown. P is the photographic plate. The complete apparatus is placed in an evacuated chamber.

When the magnetic field is switched off, a sharp line was traced by the atomic beam on the plate P. On switching on the field, a double trace was obtained on plate P as shown. Since there are two possible values of m_s ($= \pm 1/2$), the beam splits up into two. From the

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trace the deviation D_x of the beam was measured accurately. Knowing $m, L, \frac{dB}{dx}$ and v the value of μ was calculated for silver. It was found to be equal to one Bohr magneton for silver. This confirms the electron spin concept of the vector model.

Stren and Gerlach's experiment also provides a direct proof of the idea of space quantization. Since $J = j = 1/2$ in the present case, there are $(2J + 1)$ or two possible orientations of J in the magnetic field. Hence the beam splits into two in the magnetic field.

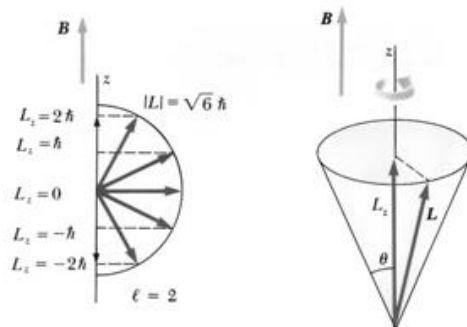
Quantum numbers associated with the vector model of the atom

In vector atom model, for each of the component parts like orbital and spin motion, orbital and spin angular momentum, a quantum number is assigned. They are the set of integers or half integers characterizing the energy states of an electron in an atom. Each electron in an atom is described by four different quantum numbers. They are n, l, s and J . In a strong magnetic field three more quantum numbers arise. They are m_l, m_s and m_j .

1. **Principal Quantum Number (n):** It specifies the energy of an electron and the size of the orbital. It can take only integral values i.e. $n = 1, 2, 3, \dots, \infty$. All orbitals that have the same value of n are said to be in the same shell (level). For a hydrogen atom with $n = 1$, the electron is in its *ground state*; if the electron is in the $n = 2$ orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2 .
2. **Orbital Quantum Number (l):** It specifies the shape of an orbital with a particular principal quantum number. It takes integral values between 0 and $n - 1$ i.e. $l = 0, 1, 2, 3, \dots, n - 1$. This quantum number divides the shells into smaller groups of orbitals called subshells (sublevels). Usually, a letter code is used to identify l to avoid confusion with n . For $l = 0, 1, 2, 3, \dots$, the letters are $s, p, d, f \dots$ respectively. The orbital angular momentum is quantized and is given by $p_l = l \frac{h}{2\pi} = l\hbar$. According to wave mechanics $L = p_l = \sqrt{l(l+1)} \hbar$.
3. **Spin Quantum number (s):** It has a magnitude of $1/2$. An electron can spin in only one of two directions (sometimes called *up* or *down*). The spin angular momentum is quantized and is given by $p_s = s \frac{h}{2\pi} = s\hbar$. According to wave mechanics $p_s = \sqrt{s(s+1)} \hbar$.
4. **Total angular Quantum number (j):** It is the resultant of orbital and the spin motion and is given by $j = l + s = l \pm 1/2$. It is $l + s$ when s is parallel to l and $l - s$ when s is antiparallel to l . The total angular momentum is quantized and is given by $p_j = j \frac{h}{2\pi} = j\hbar$. According to wave mechanics $p_j = \sqrt{j(j+1)} \hbar$.

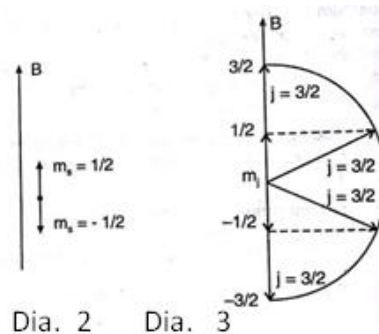
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5. **Magnetic Quantum Number (m_l)** : It specifies the orientation in space of an orbital of a given energy (n) and shape (l). It is the projection of the orbital vector l on the external field direction, i.e. L_z . It is an integer and can have any of the $(2l + 1)$ values from $-l$ to $+l$. This quantum number divides the subshell into individual orbitals which hold the electrons; there are $2l + 1$ orbitals in each subshell. Thus the s subshell has only one orbital, the p subshell has three orbitals, and so on. If $l = 2$, then $m_l = -2, -1, 0, +1, +2$ as shown.



6. **Magnetic Spin Quantum Number (m_s)** : It specifies the orientation of the spin axis of an electron. It is the projection of the spin vector s on the external field direction. It can have $2s + 1$ from $-s$ to $+s$ excluding zero. m_s can have only two values $+\frac{1}{2}$ or $-\frac{1}{2}$. (Dia. 2)

7. **Magnetic total angular momentum Quantum number (m_j)** : It is the projection of the total angular momentum vector j on the external field direction. It can have $2j + 1$ from $-j$ to $+j$ excluding zero. (Dia 3)



Spectral terms and their notations

The different energy states of the atom between which transitions can take place are referred in spectroscopic study as spectral terms. The fine structure is explained in terms of spectral terms. In the classification of the spectral terms by the use of the vector atom model, it is convenient to divide atoms into two main categories,

(a) **One electron systems** are those having only one valance or optical electron like hydrogen atom and hydrogen like atoms such as alkali atoms. Even though in such atoms there are several electrons, except one all other electrons are in closed shells which do not contribute to the angular momentum of the atom. Only the valance electron contributes to the spectral properties. The state of the atom is determined by this single free electron, the values of l, s and j referring to the electron are equal to L, S and J defining to the whole atom. Hence $S = s = \pm \frac{1}{2}$ and the multiplicity of the state is $r = (2S + 1) = 2$. Thus the system gives double terms with the exception of ground term which correspond to normal state of the atom i.e. to $L = 0$. Here the possible values of J are only two. i.e. $J = L +$

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$\frac{1}{2}$ and $L - \frac{1}{2}$. Now if $L = 0$, $J = \pm \frac{1}{2}$. The net angular momentum is always positive, the only value of $J = +\frac{1}{2}$ which means a singlet. If $L = 1$, $J = 1 \pm \frac{1}{2}$ i.e. $3/2$ and $1/2$ (doublet).

(b) **Many electron systems** are those with more than one valance or many electrons interlocked in closed shells which contribute to the total angular momentum and the spectral properties Eg. Alkaline earths. As many free electrons determine the state of the atom, the vectors L, S and J defining the state of the atom will be the resultant of the vectors l, s and j of these electrons. Hence the value of S is not always half, may be $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ according to the number of electrons involved and their orientations i.e. parallel or antiparallel. Also the multiplicity r is no longer 2 for all cases, but is 1 when $S = 0$ and 2 when $S = \frac{1}{2}$ so on. Thus the possible values of J for a given value of L may be one, two, three etc., which means each state may be a singlet or multiplet. For example in a two electron system since $S = 0$ or 1 , the state can be only a singlet or a triplet. In a three electron system, as $S = \frac{1}{2}$ or $\frac{3}{2}$, each state can be a doublet or a quartet. In general odd electron systems have even number of terms, while even electron systems have odd number of terms.

Notations of spectral terms: The states of the system in which values of L vectors are $0, 1, 2, 3, 4, \dots$ Are symbolically represented by the capital letters S, P, D, F, G,.... respectively. The value of J is written as a subscript to this symbol and the multiplicity of the state r written as a left superscript. For example the spectral terms corresponding to $L = 1$ and $S = \frac{1}{2}$ are written as ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$. This is because for $L = 1$, the letter is P and multiplicity is $r = (2S + 1) = (2 \times \frac{1}{2} + 1) = 2$ which is the left superscript. Also as $J = L \pm S = 1 \pm \frac{1}{2} = \frac{1}{2}$ or $\frac{3}{2}$ which represent the subscripts.

Selection rules : They specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. In vector atom model three selection rules, one each for L, S and J have been devised.

The selection rule for L is given by $\Delta L = \pm 1$ (not zero). i.e. only these lines are observed for which the value of L changes by ± 1 .

The selection rule for S is given by $\Delta S = 0$. It means that states with different S do not combine with each other. However both theoretical and experimental observations show that this rule is not strictly adhered but is only approximate.

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The selection rule for J is given by $\Delta J = \pm 1$ or 0 ($0 \rightarrow 0$ is excluded). i.e. spectral lines arise only when transitions occur for which J changes by ± 1 .

Note : In the presence of a magnetic field, the orbital magnetic quantum number m_l either does not change or changes by ± 1 i.e. $\Delta m_l = 0, \pm 1$. Similarly $\Delta m_s = 0$.

The intensity rules have been devised to supplement the selection rules, in order to predict the intensity of lines that occur. They are

(a) The transitions are strong, giving intense lines in which L and J change in the same sense and the transitions are weak when changes in L and J are different. For example $\Delta L = -1, \Delta J = -1$ (intense line) $\Delta L = -1, \Delta J = 0$ (less intense)

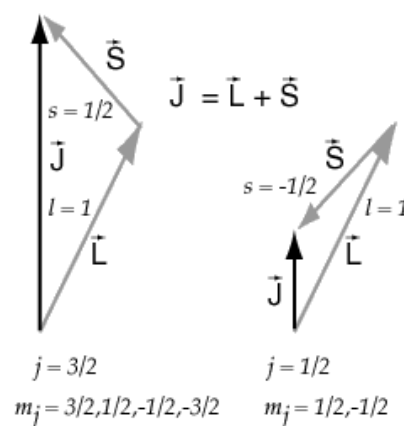
(b) Transition in the decreasing sense ($L \rightarrow L - 1$) is stronger than a transition in the increasing sense ($L \rightarrow L + 1$) i.e. $\Delta L = +1, \Delta J = +1$ (weaker) $\Delta L = +1, \Delta J = 0$ (weakest).

(c) The case of oppositely directed transitions does not occur, in general and is forbidden i.e. $\Delta L = -1, \Delta J = +1$ or $\Delta L = +1, \Delta J = -1$ (no line).

Coupling schemes

In atoms, with two or more electrons the orbital and spin angular momenta of all its electrons can be added in two ways depending on the interaction or coupling between the orbital and spin angular momenta. They are (a) the L - S coupling and (b) the j - j coupling.

(a) L-S Coupling or Russell-Saunders Coupling: For multi-electron atoms where the spin-orbit coupling is weak, it can be presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum L. Likewise, the individual spin angular momenta are presumed to couple to produce a resultant spin angular momentum S. Then L and S combine to form the total angular momentum.



$$L = L_1 + L_2 + L_3 + \dots, \quad S = S_1 + S_2 + S_3 + \dots \quad \text{and} \quad J = L + S.$$

This kind of combination is visualized in terms of a vector model of angular momentum. When $L > S$, J can have $(2S + 1)$. When $L < S$, J can have $(2L + 1)$. This coupling scheme is applicable in case of light atoms.

(b) j - j Coupling : For heavier elements with larger nuclear charge, the spin-orbit interactions become as strong as the interactions between individual spins or orbital

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angular momenta. In those cases the spin and orbital angular momenta of individual electrons tend to couple to form individual electron angular momenta.

$$J_1 = L_1 + S_1, \quad J_2 = L_2 + S_2, \quad J_3 = L_3 + S_3 \dots \text{ and } J = J_1 + J_2 + \dots$$

Pauli exclusion principle

The Pauli exclusion principle (Nobel Prize 1945) states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**. This is an example of a general principle which applies not only to electrons but also to other particles of half-integer spin (fermions). It does not apply to particles of integer spin (bosons).

In the modern view of atoms, the space surrounding the dense nucleus may be thought of as consisting of orbitals, or regions, each of which comprises only two distinct states. The Pauli exclusion principle indicates that, if one of these states is occupied by an electron of spin one-half, the other may be occupied only by an electron of opposite spin, or spin negative one-half.

The principle implies that each electron in an atom has a set of unique quantum numbers $n, l, m_l, \text{ and } m_s$. Two electrons cannot have the same four quantum numbers. The following table gives the distribution of electrons in various states.

n	l	m_l	m_s	Number of electrons in subshell with spectroscopic notation		Total number of electrons in the shell = $2n^2$
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$1s^2$	2
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$2s^2$	8
2	1	-1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6	$2p^6$	
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2	$3s^2$	18
3	1	-1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6	$3p^6$	
3	2	-2, -1, 0, +1, +2	$+\frac{1}{2}, -\frac{1}{2}$	10	$3d^{10}$	

Expression for maximum number of electrons in a shell

For a given sub shell, the values of n and l are fixed. Only the values of m_l and m_s can change. m_l can take $(2l + 1)$ values from $-l$ to $+l$. For each value of m_l , m_s can have

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two values namely $+\frac{1}{2}, -\frac{1}{2}$. Thus the maximum number of electrons in any sub shell with orbital l is equal to $2(2l + 1)$.

Thus the total number of electrons with principal quantum number n is equal to sum of electrons in the constituent n sub shells and is given by

$$\begin{aligned}\sum_{l=0}^{l=(n-1)} 2(2l + 1) &= 2 \sum_{l=0}^{l=(n-1)} (2l + 1) \\ &= 2[1 + 3 + 5 + 7 + \dots \{2(n - 1) + 1\}] \\ &= 2[1 + 3 + 5 + 7 + \dots (2n - 1)]\end{aligned}$$

The quantity in bracket has n terms whose average value is $\frac{1}{2}[1 + (2n - 1)]$

Therefore the maximum number of electrons in a filled shell

$$\begin{aligned}N_{max} &= 2(n \text{ average values}) \\ &= 2(n) \frac{1}{2}[1 + (2n - 1)] = n[1 + (2n - 1)] = n + 2n^2 - n\end{aligned}$$

$$\text{Thus } N_{max} = 2n^2$$

Thus a closed K - shell holds two electrons, a closed L - shell holds eight electrons, a closed M - shell holds eighteen electrons and so on.

Spectra of alkali elements (Sodium D line)

The alkali elements like sodium, potassium, lithium etc. contain one valance electron in the outermost shell and hence is hydrogen like. The spectra of these elements are similar to that of hydrogen and are called alkali spectra. The frequency of a spectral line in the alkali spectra is given by $\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{(n_1 - \alpha)^2} - \frac{1}{(n_2 - \beta)^2} \right]$

$$\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{(n_1 - \alpha)^2} - \frac{1}{(n_2 - \beta)^2} \right]$$

where α and β are the characteristic constants of the given element and $n_1 = 1, 2, 3, \dots$ and $n_2 = 1, 2, 3, \dots$ Depending on the values of n_1 and n_2 we obtain the following series.

(1) When $n_1 = 1$ and $n_2 = 1, 2, 3, 4, \dots$ we get the **sharp series** and its frequency is

$$\text{given by } \bar{\nu} = R \left[\frac{1}{(1 - \alpha)^2} - \frac{1}{(n_2 - \beta_s)^2} \right].$$

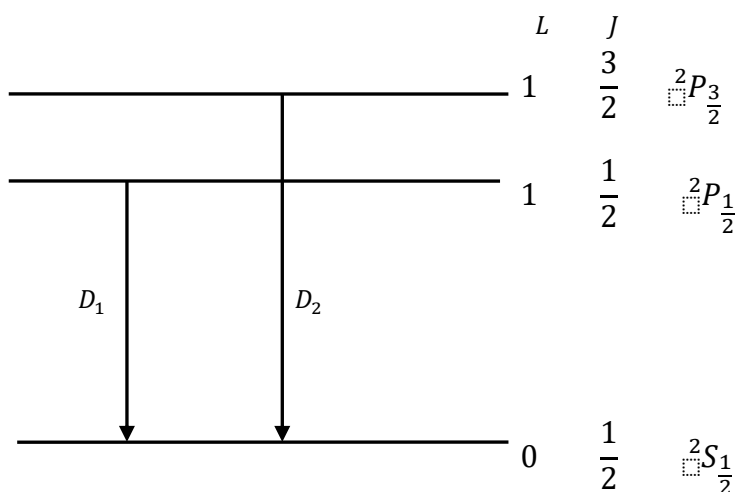
(2) When $n_1 = 2$ and $n_2 = 2, 3, 4, 5, \dots$ we get the **principal series** and its frequency is

$$\text{given by } \bar{\nu} = R \left[\frac{1}{(2 - \alpha)^2} - \frac{1}{(n_2 - \beta_p)^2} \right].$$

(3) When $n_1 = 3$ and $n_2 = 3, 4, 5, \dots$ we get the **diffuse series** and its frequency is

$$\text{given by } \bar{\nu} = R \left[\frac{1}{(3 - \alpha)^2} - \frac{1}{(n_2 - \beta_d)^2} \right].$$

(4) When $n_1 = 4$ and $n_2 = 4, 5, 6, \dots$ we get the **fundamental series** and its frequency is given by $\bar{\nu} = R \left[\frac{1}{(4-\alpha)^2} - \frac{1}{(n_2-\beta_f)^2} \right]$.



Fine structure of Sodium D line

The atomic number of sodium is 11. Ten out of the 11 electrons are interlocked in the closed shells. Only the eleventh electron contributes to the

angular momentum of the atom resulting in the optical spectrum of the sodium atom.

The D-line belongs to the principal series. They are due to transitions from a *P* state to *S* state. For the upper *P* state, $L = 1, J = L \pm S = \frac{1}{2} \text{ or } \frac{3}{2}$. Hence the two possible terms are

${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$. For the lower *S* state, $L = 0, J = \frac{1}{2}$, so that only one term ${}^2S_{\frac{1}{2}}$ is possible. The

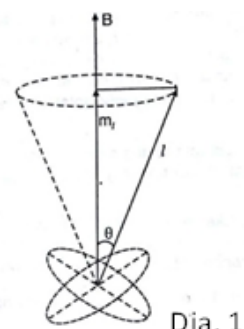
diagram above shows the two possible transitions between the two terms of the *P* state and the single term of the *S* state. They are (1) ${}^2P_{\frac{1}{2}} \rightarrow {}^2S_{\frac{1}{2}}$ which results in the *D*₁ line

of wavelength 5896 Å and (2) ${}^2P_{\frac{3}{2}} \rightarrow {}^2S_{\frac{1}{2}}$ giving the *D*₂ line of wavelength 5890 Å . Now

applying the selection rules $\Delta L = \pm 1$ and $\Delta J = \pm 1 \text{ or } 0$ (excluding $0 \rightarrow 0$), both the transitions are allowed. This explains the doublet fine structure of the sodium *D* line.

Larmor precession :

Larmor theorem : The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion a precessional motion of the entire orbit about the direction of the magnetic field with angular velocity ω given by $\omega = \frac{Be}{2m}$.



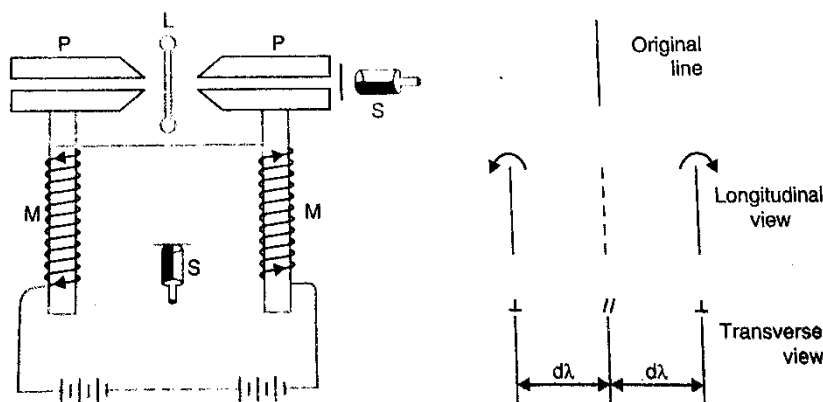
Explanation : Diagram 1 shows two positions of the vector \vec{l} as it precesses about the magnetic field at constant inclination and the corresponding positions of the electronic orbit. Just as a mechanical top precesses in a gravitational field, an electron in an orbit precesses in a magnetic field. This is called Larmor precession.

Zeeman Effect

Zeeman effect is a magneto-optical phenomenon discovered by Zeeman in 1896. If a source of light producing line spectrum is placed in a magnetic field, the spectral lines are split into components. This phenomenon is called Zeeman effect. They are of two kinds, (a) Normal Zeeman effect and (b) Anomalous Zeeman effect.

Experimental study of Zeeman effect.

The arrangement is as shown in the diagram. MM is a strong electromagnet which produces strong magnetic field. Its conical pole pieces PP have longitudinal holes drilled through them. A source of light L (say sodium vapour lamp) producing line spectrum is placed between the pole pieces. The spectral lines are observed with the help of a spectrograph S of high resolving power. The Zeeman effect is observed in two ways.



The spectral lines are observed with the help of a spectrograph S of high resolving power. The Zeeman effect is observed in two ways.

- (1) The spectral line is viewed without the application of magnetic field. Now the magnetic field is applied and the spectral line is viewed longitudinally through the hole drilled in the pole pieces and hence parallel to the direction of the magnetic field. The spectral line is found to split into two components one with the longer wavelength and the other with the shorter wavelength than the original line. The original line is absent. These two lines are symmetrically situated on either side of the original line. Analysing the two lines with the nicol prism, both are found to be circularly polarized in opposite directions. This is called **Normal longitudinal Zeeman effect**.
- (2) When the spectral line is viewed along the transverse direction, i.e. perpendicular to the magnetic field, it is found to split into three components. The central line has the same wavelength as that of the original line and is plane polarized with the vibrations parallel to the direction of the field. The outer lines are symmetrically positioned about the central line and both these lines are plane polarized with the vibrations perpendicular to the magnetic field. The displacement of either of the two outer lines from the central line is called Zeeman shift. This is called **Normal transverse Zeeman effect**.

Normal Zeeman Effect

The splitting of a spectral line into two or three components in a magnetic field is called the Normal Zeeman effect. The experimental arrangement is explained above.

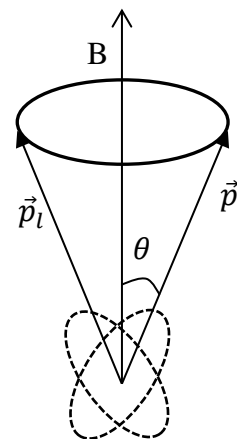
Quantum mechanical explanation of Normal Zeeman effect

Debye's explanation of Normal Zeeman effect : Debye explained the Normal Zeeman effect without taking into account the concept of electron spin. By neglecting the spin motion, the orbital angular momentum of the electron is

$$p_l = \frac{lh}{2\pi} \dots(1)$$

$$\text{The magnetic moment is given by } \mu_l = \frac{e}{2m} p_l \dots\dots(2)$$

In the presence of an external magnetic field of flux density B, the vector l precesses around the direction of magnetic field as the axis. This precession is the Larmor precession. The potential energy of the electron due to interaction between orbital magnetic moment and the magnetic field B is given by $U_m = -\mu_l \cdot B$



If θ is the angle between B and p_l , then μ_l has a direction opposite to p_l ,

$$\text{thus } U_m = \mu_l B \cos\theta \dots(3)$$

$$\text{The frequency of the Larmor precession is } \omega = \frac{Be}{2m} \dots(4)$$

The diagram shows two positions of the vector p_l as it precesses about the electronic orbit. The effect of this precession is to change the energy of the system by an amount ΔE which is the potential energy gained by the electron, given by $\Delta E = \mu_l B \cos\theta \dots(5)$

$$\text{Substituting (2) and (1) in (5) } \Delta E = \frac{e}{2m} p_l B \cos\theta = \frac{e}{2m} \frac{lh}{2\pi} B \cos\theta$$

$$\Delta E = \frac{Be}{2m} \frac{h}{2\pi} l \cos\theta . \text{ But } \frac{Be}{2m} = \omega \text{ and } l \cos\theta \text{ is the projection of } l \text{ on } B = m_l.$$

$$\text{Thus } \Delta E = m_l \frac{eh}{4\pi m} B = m_l \omega \frac{h}{2\pi} \dots(6)$$

Now m_l can have $(2l + 1)$ values from $+l$ to $-l$. Therefore, an external magnetic field will split a single energy level into $(2l + 1)$ levels. The d - state ($l = 2$) is split into 5 sublevels and the p - state ($l = 1$) is split in to 3 sublevels as shown.

Let E'_0 be the energy of the level $l = 1$ in the absence of magnetic field and E'_B be the energy of this level in the presence of the field.

$$\text{Then } E'_B = E'_0 + \Delta E' = E'_0 + m'_l \frac{eh}{4\pi m} B \dots(7)$$

Let E''_0 be the energy of the level $l = 2$ in the absence of magnetic field and E''_B be the energy of this level in the presence of the field. Then

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$$E_B'' = E_0'' + \Delta E'' = E_0'' + m_l'' \frac{eh}{4\pi m} B \dots(8)$$

The quantity of radiation emitted in the presence of magnetic field is

$$E_B'' - E_B' = (E_0'' - E_0') + (m_l'' - m_l') \frac{eh}{4\pi m} B$$

$$\text{or } h\nu = h\nu_0 + \Delta m_l \frac{eh}{4\pi m} B$$

$$\text{or } \nu = \nu_0 + \Delta m_l \frac{eB}{4\pi m} \dots(9)$$

where ν is the frequency of radiation emitted in the presence of magnetic field and ν_0 is the frequency of emitted radiation in the absence of field.

The selection rule for m_l is

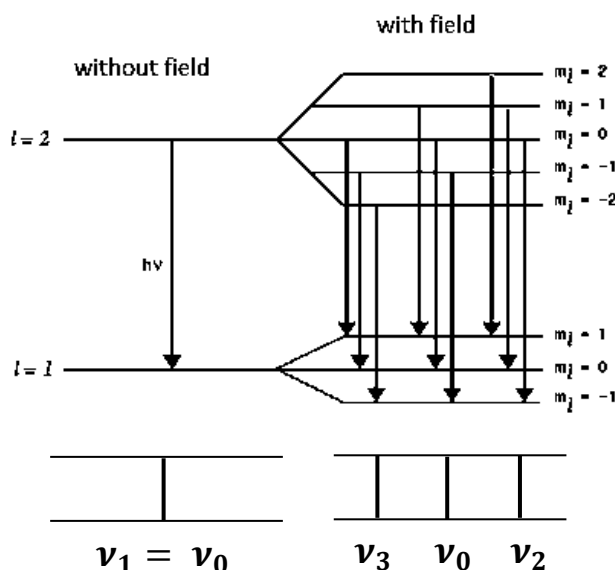
$\Delta m_l = 0$ or ± 1 . Hence we have three possible lines.

They are

$$\nu_1 = \nu_0 \text{ for } \Delta m_l = 0 \dots(10)$$

$$\nu_2 = \nu_0 + \frac{eB}{4\pi m} \text{ for } \Delta m_l = +1 \dots(11)$$

$$\nu_3 = \nu_0 - \frac{eB}{4\pi m} \text{ for } \Delta m_l = -1 \dots(12)$$



The diagram above represents Normal Zeeman effect. Although there are nine possible transitions, they are grouped into only three different frequency components as indicated by equations (10), (11) and (12).

The frequency shift is given by $d\nu = \pm \frac{eB}{4\pi m}$

$$\text{As } \nu = \frac{c}{\lambda}, \quad d\nu = -c \frac{d\lambda}{\lambda^2} \quad \text{or} \quad d\lambda = -\frac{\lambda^2}{c} d\nu$$

Thus the Zeeman shift in terms of wavelength is $\Delta\lambda = d\lambda = \pm \left(\frac{\lambda^2}{c}\right) \frac{eB}{4\pi m}$.

Anomalous Zeeman Effect

The splitting of a spectral line into more than three components in ordinary weak magnetic field is called Anomalous Zeeman effect. The quantum mechanical analysis of this effect is done by using spin of the electron along with orbital motion. Thus there are two angular momentum vectors L and S associated with an electron. The total angular momentum vector is

$$J = L + S \quad \dots(1)$$

The magnetic moment due to orbital motion is

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$$\mu_l = L \left(\frac{e h}{4\pi m} \right) \dots (2)$$

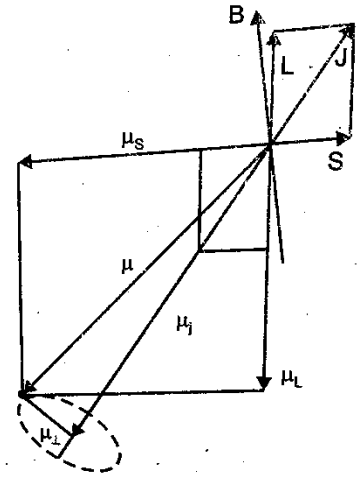
Similarly the magnetic moment due to spin motion is

$$\mu_s = 2S \left(\frac{e h}{4\pi m} \right) \dots (3)$$

μ_l and μ_s are directed opposite to L and S respectively due to negative charge of the electron.

The resultant magnetic moment μ is not along J , since L and S precess around J , μ_l and μ_s must also precess about J .

To find the resultant magnetic moment of the electron, each of these vectors μ_l and μ_s is resolved into two components, one along J and the other perpendicular to it. The value of the perpendicular component of each vector, averaged over a period of the motion will be zero, since it is constantly changing direction.



The effective magnetic moment of the electron will be $\mu_j =$ component of μ_l along J + component of μ_s along J .

$$\mu_j = \frac{e h}{4\pi m} L \cos(L \cdot J) + \frac{e h}{4\pi m} 2S \cos(S \cdot J) = \frac{e h}{4\pi m} [L \cos(L \cdot J) + 2S \cos(S \cdot J)]$$

But, according to cosine law, $\cos(L \cdot J) = \frac{L^2 + J^2 - S^2}{2LJ}$ and $\cos(S \cdot J) = \frac{S^2 + J^2 - L^2}{2SJ}$

$$\text{Thus } \mu_j = \frac{e h}{4\pi m} \left[\frac{L^2 + J^2 - S^2}{2J} + \frac{S^2 + J^2 - L^2}{J} \right] \dots (4)$$

$$\mu_j = \frac{e h}{4\pi m} \left[\frac{3J^2 + S^2 - L^2}{2J} \right] \quad \text{or} \quad \mu_j = \frac{e h}{4\pi m} J \left[1 + \frac{J^2 + S^2 - L^2}{2J^2} \right]$$

Writing $J^2 = J(J+1)$, $L^2 = L(L+1)$ and $S^2 = S(S+1)$

$$\mu_j = \frac{e h}{4\pi m} J \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \dots (5)$$

The quantity $1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = g$(6) It is called **Lande g factor**. Its value depends on L , S and J .

$$\text{Hence } \mu_j = \frac{e h}{4\pi m} gJ \quad \dots (7)$$

If the atom is placed in a weak magnetic field, the total angular momentum vector J precesses about the direction of the magnetic field as axis.

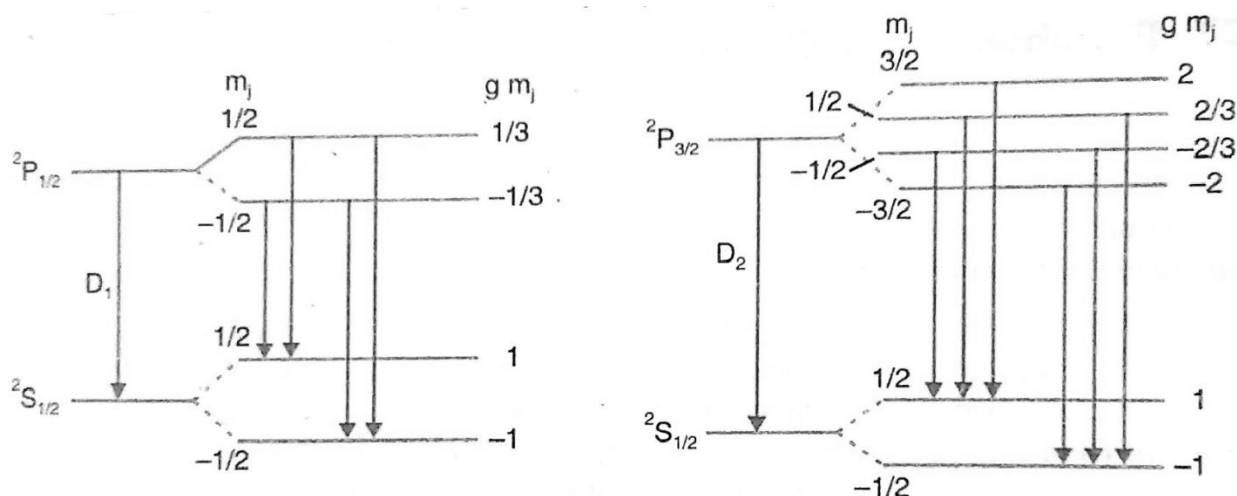
The change in energy or the additional energy ΔE due to the action of the magnetic field on the atomic magnet is $\Delta E = \mu_j B \cos(J, B) = \frac{e h}{4\pi m} gJ B \cos(J, B)$.

But $J \cos(J, B) =$ the projection of vector J on the direction of the magnetic field $= m_j$.

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$$\Delta E = \frac{e h}{4\pi m} B g m_j \quad \dots (8)$$

The quantity $\frac{e h}{4\pi m} B$ is called a Lorentz unit. It is the unit of energy used for expressing the splitting of the energy levels in a magnetic field.



Since m_j has $(2J + 1)$ values, a given energy level is split up into $(2J + 1)$ sublevels with application of the magnetic field. When this m_j is subjected to the selection rule $m_j = 0$ or ± 1 , we get the transition shown in the above diagram for the sodium D-lines.

The ground state $^2S_{1/2}$ splits into two sublevels. Here, $l = 0$, $S = \frac{1}{2}$, $J = \frac{1}{2}$, Hence $g = 2$.

Since m_j can take $+\frac{1}{2}$ and $-\frac{1}{2}$, gm_j can have the values $+1$ and -1 . The following table gives the values for the quantum numbers necessary for the determination of splitting factor gm_j for each of the energy levels of the sodium D - lines.

The longest wavelength component $^2P_{1/2} \rightarrow ^2S_{1/2}$ splits into four lines. The shortest wavelength component $^2P_{3/2} \rightarrow ^2S_{1/2}$ splits into six lines.

State	L	S	J	g	m_j	$m_j g$
$^2S_{1/2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	2	$\frac{1}{2}, -\frac{1}{2}$	1, -1
$^2P_{1/2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$^2P_{3/2}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$2, \frac{2}{3}, -\frac{2}{3}, -2$

The introduction of electron spin has led to complete agreement between the experimental results and the theory of Anomalous Zeeman effect.