Atomic Physics

Unit : IV Atomic Spectra

Selection Rules :-

An $\bar{e}$ cannot jump from one energy level to all other energy levels. A transition of an $\bar{e}$ between two levels is possible only if certain rules called Selection Rules.

Angular momentum no (or) K

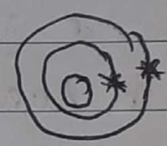
There are 3 types :-

i) Selection Rule for L
(ii) Selection rule for J
(iii) Selection rule for S

i) Selection Rule for L :-

One Orbit to other Orbit jump.

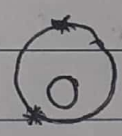
$\Delta L = \pm 1$



ii) Selection Rule for J :-

One position to change of other position → spectral lines

$\Delta J = \pm 1$ (or) 0



$0 \rightarrow 0$ is excluded

iii) Selection Rule of S :-

$\Delta S = 0$ Various S position is not merge. It is not inuse of selection rule of 'S'.

$\Delta m_l = 0 \rightarrow \Delta m_s = 0$

This Rule is used for Zeeman effect and X ray Spectra and light Spectra.

It is used as a energy level diagram drawn.

Interval Rule:-

Lande Discovered a Rule

The interval in freq. between the different energy levels. It States that the freq. interval between two levels with total angular momenta $(J+1)$ and J respectively is proportional to $(J+1)$.

$$J \propto (J+1)$$

J → energy level
J+1 → freq

Intensity Rule:-

Whether an allowed transition is weak (or) Strong is determined are known as intensity Rules.

* Transitions for which L and J change in same way. (Same Direction.)

$\Delta J = \Delta L \rightarrow$ Strong

$\Delta J \neq \Delta L \rightarrow$ Weak transitions

$\Delta L = -1, \Delta J = -1$ Strong

* L and J Opposite direction (ie) forbidden

$$\Delta L = -\Delta J$$

$$\left.\begin{array}{ll} \Delta L = -1, & \Delta J = +1 \\ \Delta L = +1, & \Delta J = -1 \end{array}\right\} \text{forbidden.}$$

* Transitions for which L and J increase

$L \rightarrow L+1$ and $J \rightarrow J+1$

less intense than those for which L and J decrease (ie, $L \rightarrow L-1$ and $J \rightarrow J-1$).

$\Delta L = 1, \Delta J = 0$ less intense

$\Delta L = +1, \Delta J = +1$ weak

$\Delta L = +1, \Delta J = 0$ Very weak

Fine Structure of Sodium D lines:~

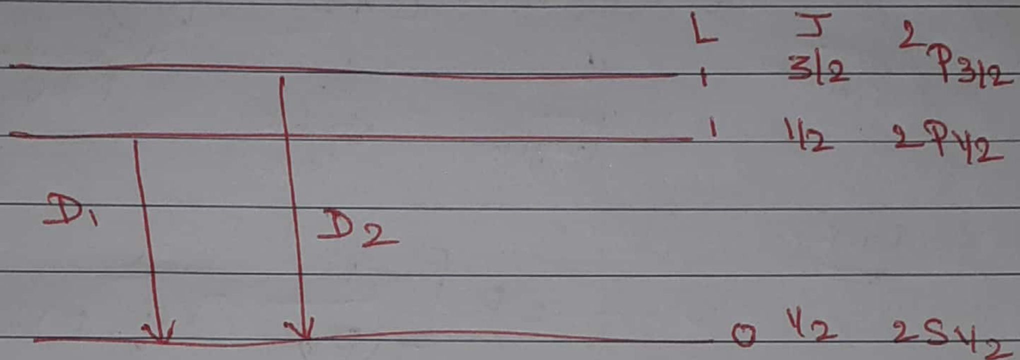
சோடியம் D-வரிகளின் நுண்வரி அமைப்பு:

Na → One electron system.

Bohr theory → Principal Series in D line

principal Series due to transitions is

P state to the S state.



Upper State P :~

$L = 1$; $J = L \pm S = 3/2$ (or) $1/2$, hence the two possible terms.

$^2P_{3/2}$, $^2P_{1/2}$

Lower State S :~

$L = 0$ $J = 1/2$; only one term possible.

fig:- (two possible in P state, One possible S state).

They are,

(i) $^2P_{1/2} \rightarrow {}^2S_{1/2}$ gives the D_1 line of Wave length 5896 A°

(ii) $^2P_{3/2} \rightarrow {}^2S_{1/2}$ gives the D_2 line of wave length 5890 A°.

applying the Selection Rules of $\Delta L = \pm 1$ and $\Delta J = \pm 1$ (or) 0 both are transitions are allowed. This explains the doublet fine structure of the sodium lines.

Alkali Spectra :-

Li, Na, K → Outer Orbit → One $\bar{e}$

Hydrogen → 1 $\bar{e}$

Outer orbit → one electron → metals spectrum → same

This is called Alkali Spectra.

Same series for Hydrogen in below.

→ Ritberg const.

$$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{p^2} - \frac{1}{q^2}\right]$$

wave number, wave length, stable part, change part.

G.F :-

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

α, β - Metals characteristic const.

Different Series in Alkali Spectra :-

(i) Principal Series :-

$p = 1$; $q \geq 2$

$$\bar{\nu}_p = R\left[\frac{1}{(1-\alpha)^2} - \frac{1}{(q-\beta_p)^2}\right]$$

(ii) Sharp Series :-

$p = 2$; $q \geq 2$

$$\bar{\nu}_s = R\left[\frac{1}{(2-\alpha)^2} - \frac{1}{(q-\beta_s)^2}\right]$$

(iii) Diffuse series :-

$p = 2$; $q \geq 3$

$$\bar{\nu}_d = R\left[\frac{1}{(2-\alpha)^2} - \frac{1}{(q-\beta_d)^2}\right]$$

(iv) Fundamental (or) Bergmann Series :-

$p = 3$; $q \geq 4$

$$\bar{\nu}_f = R\left[\frac{1}{(3-\alpha)^2} - \frac{1}{(q-\beta_f)^2}\right]$$

//.

Spectral term:- (நிறமாலை எண்ணுருக் கூறு)

One energy level to Other energy level move to Spectral lines. transistion is named as as Spectral term. (பெயரிடு).

2 types

Ⓘ One $\bar{e}$ System

eg Li, Na, K, Hydrogen. alkali metals

Many electron System. Ⓘⓘ

eg:- alkaline. 2 $\bar{e}$ (or) more $\bar{e}$

Outer Orbit 1 $\bar{e}$

$l, s, j = L, S, J$

$S = s \pm \frac{1}{2}$

Multiplicity $r = (2S+1)$

$r = 2$

Ground நிலை 2 line.

~~$L = 0$~~

~~$J = L + \frac{1}{2} = \frac{1}{2}$~~

; eg:- $L = 1$

$J = L \pm S$

$J = 1 \pm \frac{1}{2}$

$J = 3/2, \frac{1}{2}$

ie, Two lines.

Ⓘⓘ

$l, s, j = L, S, J$

two $\bar{e}$ system $S = 0$ (or) 1 value is One line (or) three line.

three $\bar{e}$ System $S = \frac{1}{2}$ (or) $3/2$ 2 line (or) 4 line.

Notation of Spectral terms:- (நிறமாலைக் கூறின் குறியீடு)

Vector L value is 0, 1, 2, 3, 4.

S, P, D, F, G ... Capital letter.

J Value is written by Subscript

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at the lower right of the letter representing the particular value L of the atomic state Multiplicity r is left superscript.

eg:-

$L = 1; \ S = 1/2$ Spectrum term, $^2P_{1/2}, {^2P_{3/2}}$

$L = 1$, P multiplicity $r = (2S+1)$ (doublet)

$r = (2 \cdot 1/2 + 1) = 2$ (upper)

i.e.,

$J = L \pm S$

$J = 1 \pm 1/2 = 3/2$ (or) $1/2$ (lower)

$^2P_{3/2}$ → Read "doublet P three halves"

left superscript — subscript

$L = 2; \ S = 1$ and $J = 2$ written $^3D_2$ (or) $3D_2$

Read "triplet D two"

Zeeman Effect:-

If a source of light producing line spectrum is placed a mag. field, the spectral lines are split up into components. When the splitting occurs into 2 (or) 3 lines, it is called normal Zeeman effect explained by classical theory. (1896)

The splitting of spectral line into more than three components in ordinary weak mag. fields is called as anomalous Zeeman effect. Cannot explained by classical theory.

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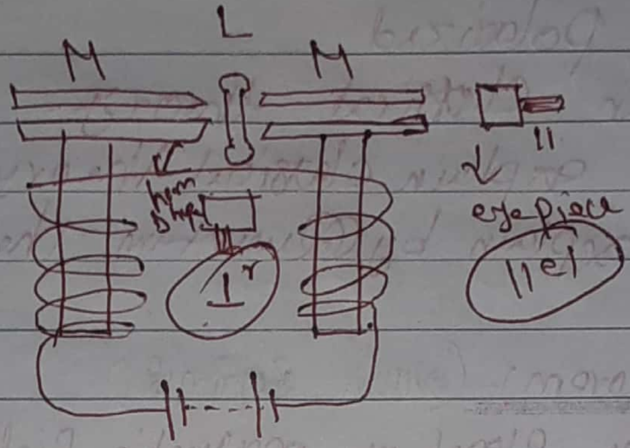
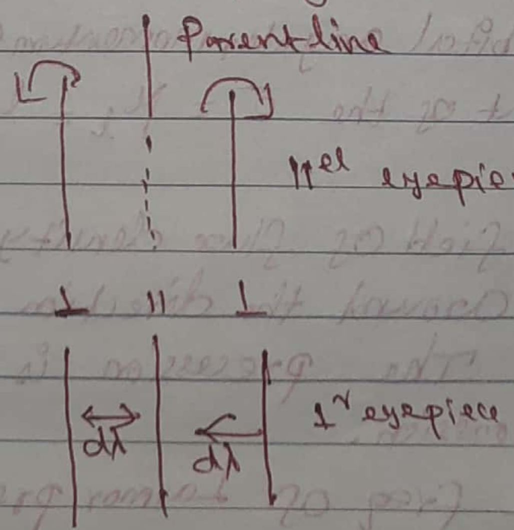
Zeeman Effect - Experimental Study :-
(ஜீமன் விளைவு - சோதனை முறை).



MM → Strong Magnet
L → Sodium vapour Lamp.
hig resolving power of Spectrograph.
longitudinally drilled in hole pieces.
camera eye piece.

(i) $\|^{el}$:-

Parent line → It is not present in Original line near two sides of line. 1 wave length high, other is low. It is opposite direction circularly polarised. It is called as Longitudinal Zeeman effect.



(ii) $\perp^r$:-

3 lines.

Parent line → one line.

both side two lines. outer 2 lines $\perp^r$, Center ∥el.

3 lines are Polarized.

Z.E : Explain classical theory.

A.Z.E : Not explain classical theory

But explain by Quantum theory.

Larmor's theorem :- (லார்மர் தேற்றம்)

The effect of magnetic field on an $\bar{e}$ moving in an orbital 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 $\omega = Be/2m$.

Debye's Quantum Mechanical explanation of the Normal Zeeman effect :~

Debye explained the normal Zeeman effect without taking into account the concept of electron spin. We neglect the spin motion of electron.

Orbital angular momentum of the $\bar{e}$ $= L = l\hbar$ → ①

Magnetic moment of the $\bar{e}$ $= \mu_l = \dfrac{l\hbar e}{2m} = \dfrac{e}{2m} L$ → ②

Magnetic field of flux density, B the vector l precession around the direction of the mag. field as axis. The precession is known as Larmor precession.

The freq of Larmor precession $\omega = \dfrac{Be}{2m}$ → ③

The addition energy of the $\bar{e}$ due to this precessional motion,

$$\Delta E = \mu_l B\cos\theta \left(\frac{el\hbar}{2m}\right) B\cos\theta$$

$$= \frac{Be\hbar l\cos\theta}{2m}$$

Since $\frac{Be}{2m} = \omega$, $l\cos\theta$ = projection l on $B = m_l$

$$\Delta E = m_l \frac{e\hbar B}{2m} = m_l \omega \hbar \rightarrow (4) \quad \{\because l\cos\theta = m_l\}$$

Now m_l can have $(2l+1)$ values of $+l$ to $-l$. This is called as "Zeeman levels".

E_0' & E_B' represent the energy level $l=1$ presence of mag. field, then,

$$E_B' = E_0' + \Delta E' = E_0' + m_l' \frac{e\hbar}{2m} B \rightarrow (5)$$

E_0'' & E_B'' represent the energy level $l=2$, without mag. field,

$$E_B'' = E_0'' + \Delta E'' = E_0'' + m_l'' \frac{e\hbar}{2m} B \rightarrow (6)$$

The quantity of energy radiated in the presence of Mag. field is,

$$\underbrace{E_B'' - E_B'}_{h\nu} = \underbrace{(E_0'' - E_0')}_{h\nu_0} + \underbrace{(m_l'' - m_l')}_{\Delta m_l}\frac{e\hbar}{2m} B$$

$$h\nu = h\nu_0 + \Delta m_l \frac{e\hbar}{2m} B. \quad \{\because \hbar = \frac{h}{2\pi}\}$$

$\div h$

$$\nu = \nu_0 + \Delta m_l \frac{eB}{4\pi m} \rightarrow (7)$$

$\nu \rightarrow$ freq. of the radiation emitted with the mag. field.

$\nu_0 \rightarrow$ freq. of the radiation in the absence of mag. field.

ie, Selection rule for, m_l is $\Delta m_l = 0$ (or) ± 1.

3 possible lines.

(i) $\Delta m_l = 0$

$\nu_1 = \nu_0$ for $\Delta m_l = 0 \rightarrow (8)$

ii) $\nu_2 = \nu_0 + \frac{eB}{4\pi m}$ for $\Delta m_l = +1 \rightarrow (9)$

iii) $\nu_3 = \nu_0 - \frac{eB}{4\pi m}$ for $\Delta m_l = -1 \rightarrow (10)$

$\frac{eB}{4\pi m} \rightarrow$ lorentz Unit.

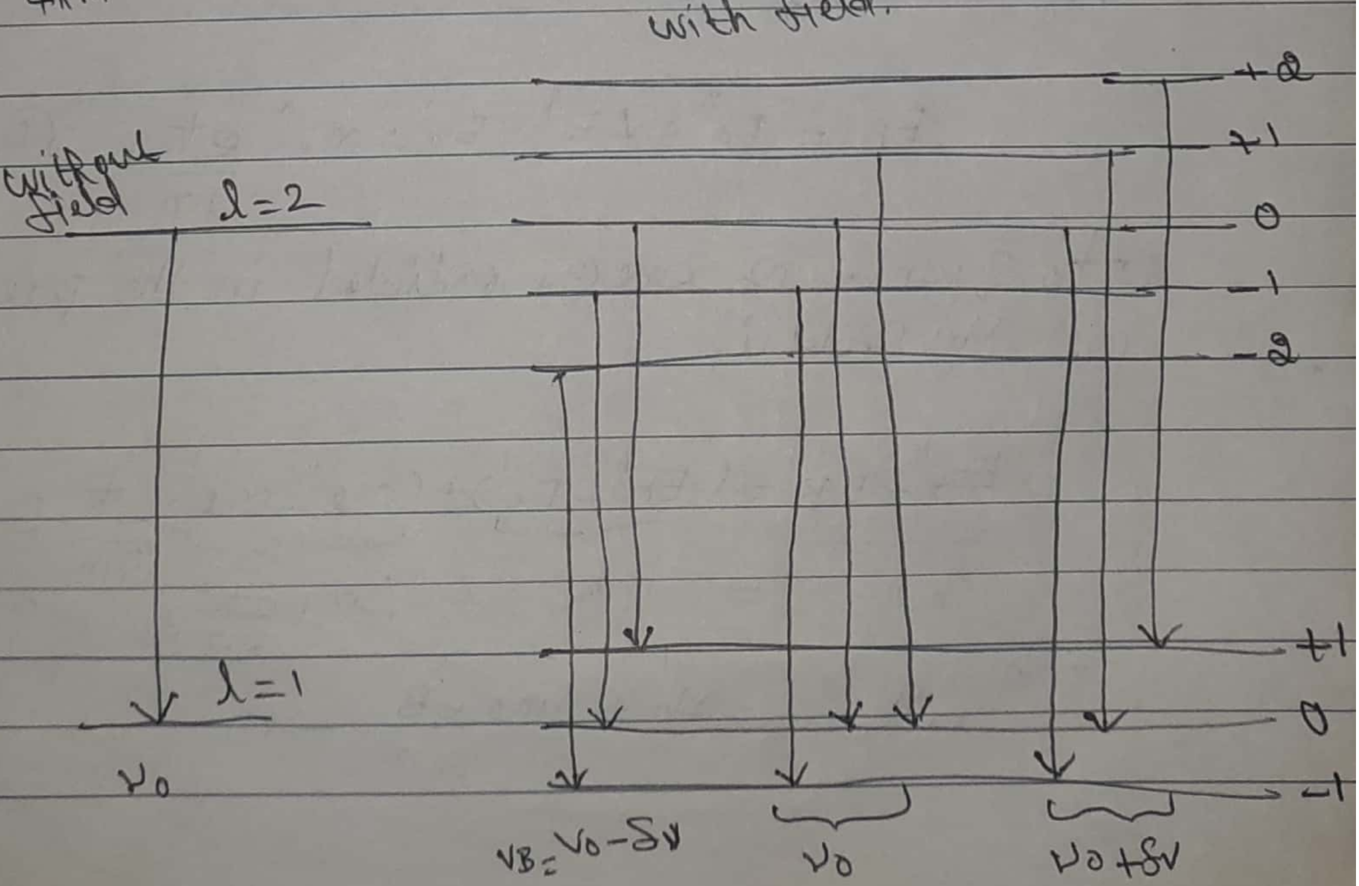
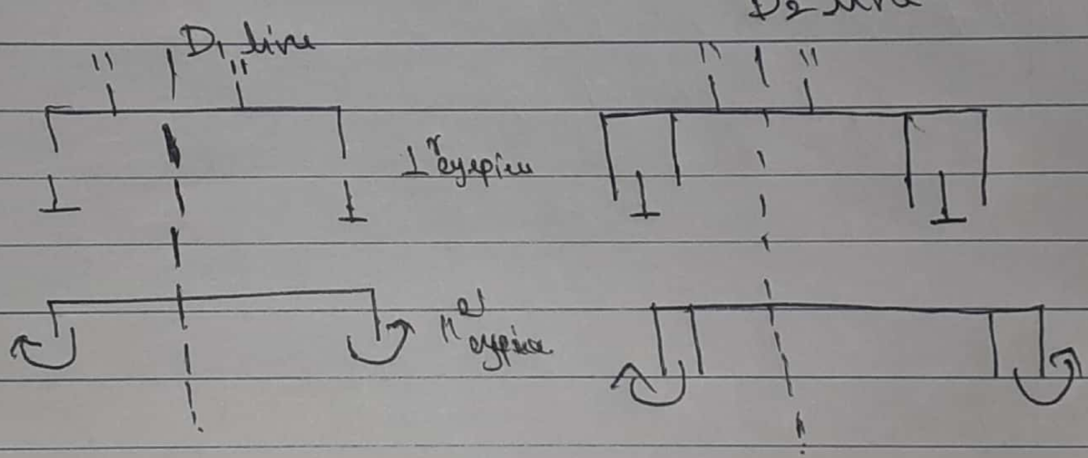


fig (i)

fig (1) represents the Zeeman effect.
9 nine possible transistions.
They are grouped into only 3 different frequency components as indicated by equn (8) & (9), (10)

Anamolous Zeeman effect:-

Normal Z.E = 3 line.
A.N.E ⇒ more than lines.
Na ⇒ D line.



1) D₁ line ⇒ ⊥ʳ ⇒ 4 lines.
Parent line → both sides ⇒ equal ⇒ polarised.
(In side) lines 2 ∥ˡ ⇒ π Components
(Out side) 2 lines ⊥ʳ ⇒ σ Components
* D₁ line ⇒ ∥ˡ :- opposite Circularly polarised (outside lines to see them)

2.) D₂ line ⇒ ⊥ʳ ⇒ 6 lines., Polarised.
Inside 2 lines - ∥ˡ, 4 lines → ⊥ʳ
* D₂ line ⇒ ∥ˡ → Outside 4 lines Circularly Polarized.
Inside no lines.

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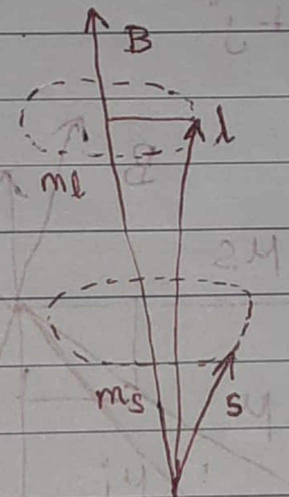
Paschen - Back Effect: (பாசென் பேக் விளைவு)

Paschen and Back found that whatever be the anomalous Zeeman pattern of a given line in a weak magnetic field, the pattern always approximates the normal Zeeman triplet as the field strength is progressively increased. This reduction may occur either through the coalescence of lines (or) through the disappearance of certain lines. This transition phenomenon is called Paschen - Back Effect.

Explanation:-



Two parts:~

(i) l, B

(ii) S, B

$$\Delta E = (\Delta E)_l + (\Delta E)_s$$

$$= \frac{Beh}{4\pi m}\left[l\cos(l,B) + 2s\cos(s,B) \right]$$

$$= \frac{eh}{4\pi m} B\left[m_l + 2m_s \right]$$

frequency change, $\boxed{\Delta \nu = \frac{eB}{4\pi m}\,\Delta(m_l + 2m_s)}$

i.e., $(m_l + 2m_s) \rightarrow$ strong field ~~Quantum~~ number.

$\Delta m_l = 0$ (or) ± 1; $\Delta m_s = 0$

i.e., $\Delta(m_l + 2m_s) = 0$ (or) ± 1

Strong mag. field $\rightarrow$ split up to 3 components $\rightarrow$ usual $\rightarrow$ characteristic of the normal Zeeman Effect.

Anamolous Zeeman Effect - Theoritical Explanation :-
(முரணிய சீமன் விளைவு - கொள்கை விளக்கம்)

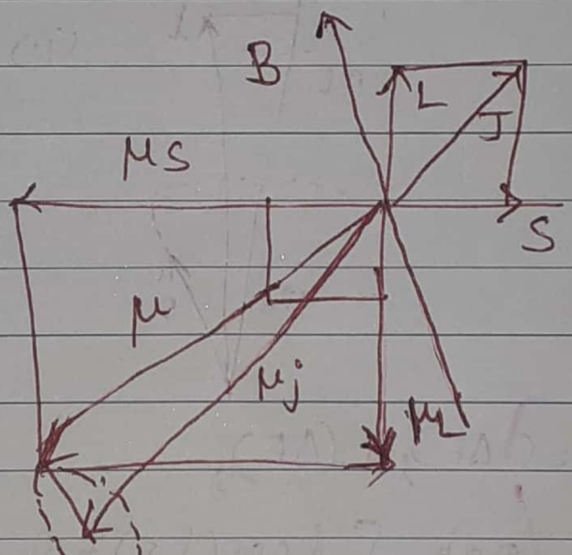
The total angular momentum $\left.\right\} J = L + S \rightarrow (1)$

$L \rightarrow$ Orbital, $S \rightarrow$ Spin.

Magnetic moment due to Orbital motion $\mu_l = \frac{l e \hbar}{2m} \rightarrow (2)$

Magnetic moment due to spin motion $\mu_s = \frac{2 s e \hbar}{2m} \rightarrow (3)$

Since L and S precess about j, μ_l and μ_s must also precess about j.



μ_j = Component of μ_l along the direction of j + component of μ_s along the direction of j

$$= \frac{e\hbar}{2m} l \cos(l, j) + \frac{e\hbar}{2m} 2s \cos(s, j) \rightarrow (4)$$

$$= \frac{e\hbar}{2m} \left[l \cos(l, j) + 2s \cos(s, j) \right] \rightarrow (5)$$

According to cosine law,

$$\cos(l,j) = \frac{l^2+j^2-s^2}{2lj} \rightarrow (6)$$

and,

$$\cos(s,j) = \frac{s^2+j^2-l^2}{2sj} \rightarrow (7)$$

hence,

$$\mu_j = \frac{e\hbar}{2m}\left[\frac{l^2+j^2-s^2}{2j} + \frac{s^2+j^2-l^2}{j}\right]$$

$$= \frac{e\hbar}{2m}\left[\frac{3j^2+s^2-l^2}{2j}\right]$$

$$= \frac{e\hbar}{2m} j\left[1+\frac{j^2+s^2-l^2}{2j^2}\right] \rightarrow (8)$$

Where $j^2 = j(j+1)$ is

$$\mu_j = \frac{e\hbar}{2m} j\left[1+\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\right] \rightarrow (9)$$

The quantity $\boxed{1+\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)} = g} \rightarrow (10)$

is called the Lande g factor.

Hence,

$$\mu_j = \frac{e\hbar}{2m} \cdot j \cdot g \rightarrow (11)$$

The additional energy ΔE due to the action of the magnetic field on this atomic magnet.

$$\Delta E = \mu_j B \cos(j,B) = \frac{e\hbar}{2m} \cdot j \cdot g \cdot B \cos(j,B) \rightarrow (12)$$

$\therefore$ Since $j\cos(j,B) = m_j$

$$\Delta E = \frac{e\hbar}{2m} B \cdot g \cdot m_j \rightarrow (13)$$

The quantity $\frac{e\hbar}{2m}B$ is Called Lorentz Unit.

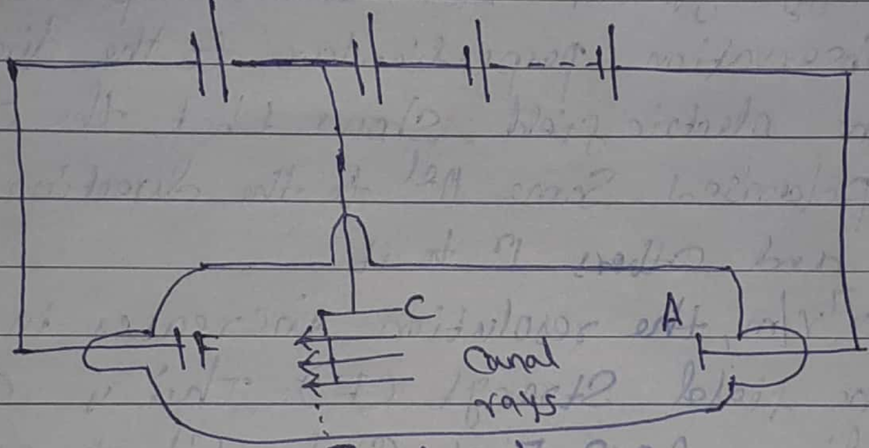
Since m_j has $(2j+1)$ values, a given energy level is split up into $(2j+1)$ Sublevels with the application of magnetic field.

Selection rule $\Delta m_j = 0$ (or) ± 1

Stark Effect

The Stark effect is the electrical analogue of the Zeeman effect 1896 discovered by Zeemaneffect. There is only a Magnetic field. So the spectral lines, apply the Electrical field splitting spectral lines. discovered by Stark effect. There is used by the Hydrogen Spectrum.

Experimental Study:~



Spectrometer (ro)

A → Anode, C → Cathode, F → electrode.

Generaly → discharge tube → cathode hole → Canal rays.

Anode (A) & Cathode (C) Suitable pressure
Cathode hole → Canal rays – Cylindrical.

Otherwise :- Cathode, Electrode } gap Small (few millimeters) → high voltage.

Orbital :→

This studied by → longitudinally & transversely

Electric field → ⊥r & ||el direction.

Result:-

The lines of Balmer Series of the Hydrogen Spectrum are given below.

(i) All hydrogen lines from Symmetrical pattern.

(ii) Depends on Quantum number n.

(iii) The no. of. lines and the total width of pattern increases with n.

(iv) the no. of Components H_β greater than that of the H_α line.

(v) $\parallel^{ly}$ H_γ greater than that of H_β.

(vi) Observation perpendicular to the direction of the electric field shows that the components are polarised. Some $\parallel^{el}$ to the direction of the field and others $\perp^r$ to it.

(vii) 10^7 V/m, the resolution increases in proportion to the field Strengt (E). This is called as linear (or) First Order Stark effect.

(viii) When E exceeds 10^7 V/m. there are shifts in the line pattern which are proportional to E^2. This is called as Second Order Stark effect.