Vector model:

1) $n \rightarrow 1\ 2\ 3 \ldots$

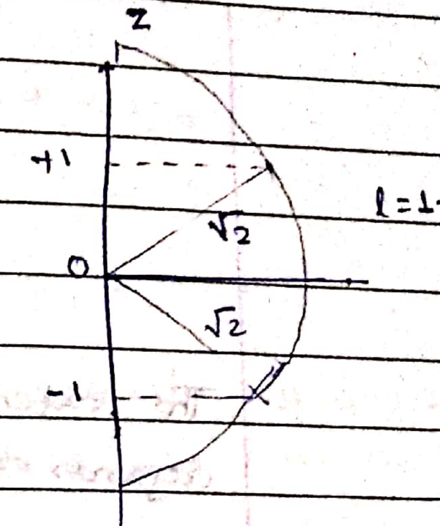
K L M ...

2) Angular momentum $l$

$l = 0, 1, 2, \ldots (n-1)$

s p d ...

$\Delta l = \pm 1$




3) space quantisation:

$\vec{l}$ : vector

magnitude : $\sqrt{l(l+1)} = l^*$

$\bar{l} = \sqrt{l(l+1)}\,\hbar$

$= l^* \hbar$

It can take values from $-l$ to $+l$ and magnetic quantum number $= m_l$.

Degeneracy $= (2l+1)$

4) Spin Angular momentum:

$s = s^* \hbar \qquad s = -\frac{1}{2}, +\frac{1}{2}$.

$m_s$ : magnetic spin quantum number.

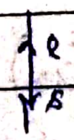
Degeneracy for spin $= 2s+1$.

If $l$ and $s$ are in one direction

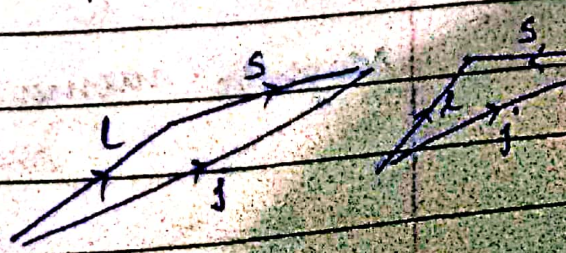
$j = l+s$


If $l$ and $s$ are in opposite "

$j = l-s$.




$j$ = total angular momentum



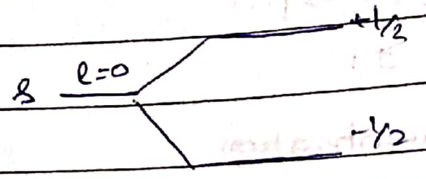

$j = \pm \frac{1}{2}, \pm \frac{3}{2} \ldots$

Term for $l=0$

$^2S_{1/2}$

L-S Coupling : $J = l+s$.

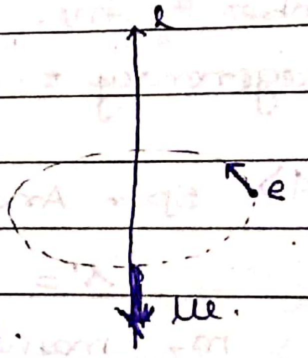
The coupling occurs because of orbital angular momentum mag. field arises and the spinning of $e^-$ also cause a magnetic field and these magnetic fields couple together.




≡ splitting occurs due coupling and extent of coupling depends on energy separation

The extent of coupling and the separation of energy levels depends on g-factor.

Bohr Magneton




The electron in a circular loop produces a current in opposite direction and this leads to magnetic field and magnetic moment.

Current, $i = e/cT$. (CGS unit, in MKS unit remove c).

$T =$ Time period $= \frac{2\pi r}{v}$.

Then

$i = \left(\frac{ev}{c\,2\pi r}\right)$

Magnetic moment, $\mu_l = iA$

$= \frac{e}{c}\left(\frac{v}{2\pi r}\right)\pi r^2$

$= \frac{evr}{2c}$

$\mu_e$: $\perp$ to area but is opp. to $l$. because $e^-$ carr...

$$\frac{\mu_e}{|l|} = \frac{e\omega r^2}{2c}\,\frac{1}{m\omega r^2} = \frac{e}{2mc} = \text{independent of orbit}$$

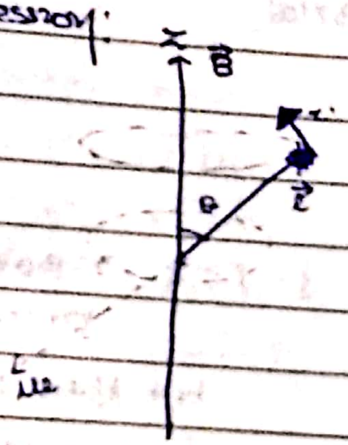
$$\therefore \mu_e = \frac{e}{2mc}|l|$$

$$\mu_e = \frac{e}{2mc}\left(\sqrt{l(l+1)}\,\hbar\right)$$

$\hbar e/2mc \equiv$ Independent of the orbit.

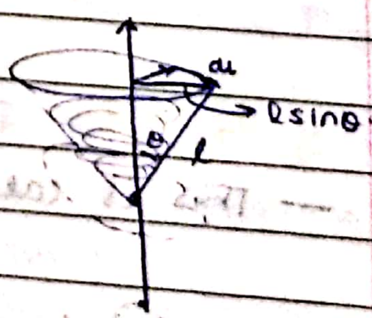
$\equiv$ Bohr magneton $= 0.928\times10^{-20}$ erg/cm

Larmor Precession:




$\vec{l}$ - Starts precessing about magnetic field and the precession has certain frequency called Larmor frequency $\omega_L$.

θ: angle between magnetic field B and angular momentum vector l.




$$\mu_e = -\frac{e}{2mc}\vec{l}$$

The interaction with B produces torque:

$$\vec{\tau} = \vec{\mu}_e \times \vec{B}$$

$\omega \rightarrow$ Angular velocity.

$$\omega dt = \frac{|dl|}{|l|\sin\theta}$$

$$\omega = \frac{|dl|}{dt}\,\frac{1}{\sin\theta} = \frac{\tau}{|l|\sin\theta}$$

$$\tau = \omega|l|\sin\theta$$

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$$\omega_L = \frac{|\mu_l| B \sin\theta}{|l| \sin\theta}$$

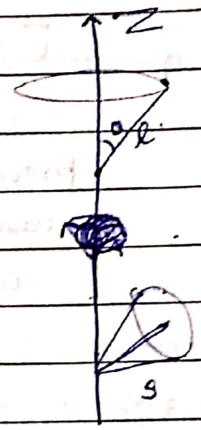
$$= \frac{|\mu_l| B}{l}$$

or $\omega_L = \left(\frac{e}{2mc}\right) \vec{B}$

B – perturbation due to magnetic field.

If $B = 10T$;

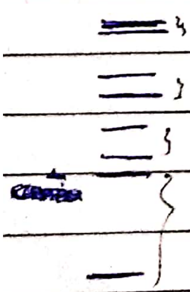
$$\omega_L = \frac{1.606 \times 10^{-19}}{2 \times 9.1 \times 10^{-31} \times 3 \times 10^{8}} \times 10 = 10^{11}\ Hz.$$




$j = l + s$ : Both of them can precess independently but there comes a quality, total angular momentum j which ~~does~~ remains conserved in always remains in Z direction.

— This is called L-S coupling or spin orbit coupling

Doublets



Spin orbit coupling & Doublets:

Alkali Metal

| | |
|---|---|
| H | |
| Li | $2s^1$ |
| Na | $3s^1$ |
| K | $4s^1$ |
| Cs | $5s^1$ |

≡ single e- in outermost orbit

They behave like hydrogen atom because of one e- in outermost orbit. Alkali metals always show doublet.

- Doublet separation increases with ↑ in atomic number.
- doublet separation in alkaline earth metals are larger than corresponding alkali metals.
- Within each element doublet separation ↓ on going to higher ...

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Spin orbit interaction.

Interaction

$l^* = \sqrt{l(l+1)}$ $\quad l = 0,1,2\ldots$

$s^* = \sqrt{s(s+1)}$ $\quad s = +1/2, -1/2$

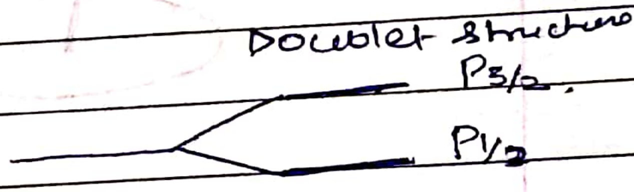
$j^* = \sqrt{j(j+1)}$

Eg: $l = 1$ —— P.

$j = (l+s) - (l-s)$

$= 3/2, 1/2.$

$l = 1.$




$l = 0$ ——

| Orbital | $l$ | $s$ | $j$ | Term |
|---|---|---|---|---|
| s | 0 | $1/2$ | $1/2$ | $^2S_{1/2}$ |
| p | 1 | $1/2$ | $1/2$ $3/2$ | $^2P_{3/2}$ $^2P_{1/2}$ → All are doublet structure |
| d | 2 | $1/2$ | $3/2$, $5/2$ | $^2D_{3/2}$ $^2D_{5/2}$ |
| f | 3 | $1/2$ | $5/2$, $7/2$ | $F_{5/2}$ $F_{7/2}$ |

H
Na
K
Rb
Cs

↓ Doublet splitting increases.

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The fine structure level corresponding to $j = l - 1/2$ ... deeper than the corresponding level $j = l + 1/2$.

Doublet structure depends on

$Z, l, j$

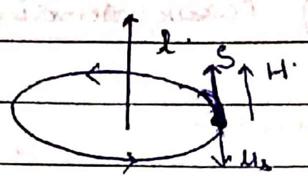
$\propto Z$

$\propto 1/l$.

Normal order of doublet fine structure:

Energy order: $^2P_{3/2}$ $^2P_{1/2}$.

one configuration



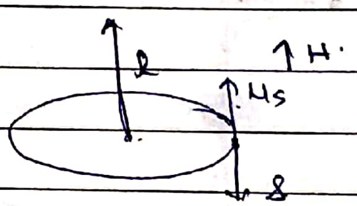
$l = l^* \hbar$

higher energy

$\mu$ is antiparallel to $H$ and hence it will tend to align parallel to $H$.

$j = l + s$

2nd configuration



$j = l - s$.

lower energy

- $\mu$ is $\parallel$ to $H$.

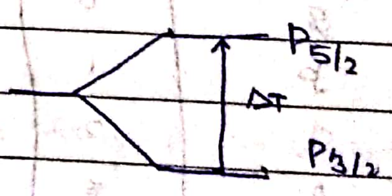
Out of two, the one with lower $j$, has lower energy. because classically $\mu_s$ and $H$ are parallel for lower $j$ and antiparallel for ~~h~~ larger $j$.

★ Exception: Cesium (Cs) 7/2 lies below 5/2.

Splitting - ?

$\Delta T = ?$

$\Delta T \equiv$ depends on strength of interaction



Semi-Classical approach:

$\boxed{Z, l}$:

$l = l^* \hbar$ $\equiv$ angular mom is quantized.

$l^* = \sqrt{l(l+1)}$.

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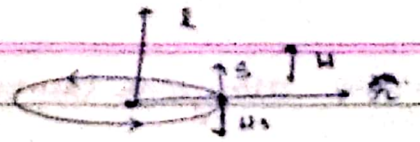


Electric field $\vec{E} = \frac{Ze}{r^3}\vec{r}$

$$\vec{H} = \frac{E \times v}{c}$$

$$\vec{H} = \frac{Ze}{cr^3}\,\vec{r}\times\vec{v}$$

Bohr Assumption

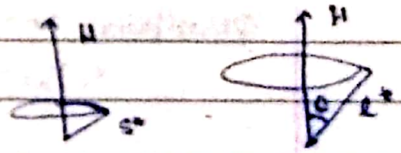
Bohr quantum $2\pi m\,\vec{r}\times\vec{v} = l^* h$

$$H = l^* \frac{h}{2\pi}\frac{Ze}{mc}\frac{1}{r^3}$$ Under this magnetic field the spin precesses called Larmor precession

Larmor Precession frequency    This for spin motion

$\omega_s = 2\omega_L$

Spin precesses faster than angular momentum around H



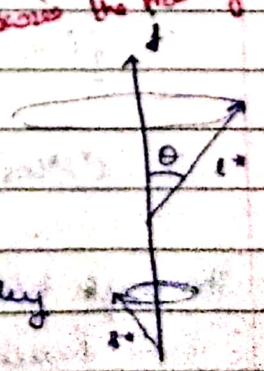
Precession = angle remains conserved

Larmour precession frequency for spin momentum: $\omega_L$ = magnetic field × ratio of magnetic and [illegible]

$$\omega_L = |H| \cdot 2 \cdot \frac{e}{2mc}$$

$$= l^* \frac{h}{2\pi}\frac{Ze}{mc}\frac{1}{r^3}\,2\,\frac{e}{2mc}$$

$$\boxed{\omega_L = l^* \frac{h}{2\pi}\frac{1}{r^3}\frac{Ze^2}{m^2c^2}}$$ → Solve the ordinary larmor precession



$J$ = conserved

These angle can only be conserved if they have common axis.

Interaction Energy

$$\Delta W_{l,s} = \omega_L' \times s^* \frac{h}{2\pi}\cos(l^*, s^*)$$ ??

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Because of relativistic correction, along with Larmor precession $\omega_L$ a relativity precession of half $\omega_r = \frac{\omega_L}{2}$ magnitude and opp direction :

$$\therefore \omega_L' = \omega_L - \omega_r = \text{ordinary precession}$$

$$\therefore \Delta W_{l,s} = \frac{1}{2}\left(l^* \frac{h}{2\pi}\frac{1}{r^3}\frac{Ze^2}{m^2c^2}\right)\cdot s^*\frac{h}{2\pi}\cos(l^*,s^*)$$

≡ energy due to coupling of two momenta.

$$\text{or} \quad \Delta W_{l,s} = \frac{h^2}{8\pi^2}\frac{Ze^2}{m^2c^2}\, l^* s^* \cos(l^*,s^*)\frac{1}{r^3}$$

$$\langle \Delta W_{l,s}\rangle = \left(\frac{h^2}{8\pi^2}\frac{Ze^2}{m^2c^2}\right)\langle l^* s^* \cos(l^*,s^*)\rangle \langle 1/r^3\rangle$$

Quantum mechanically,

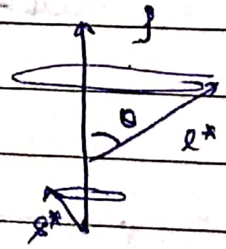
$$\langle 1/r^3\rangle = \frac{Z^3}{a^3 n^3 l(l+1)(l+1/2)}$$

$a_1$ : Radius of 1st orbit

$l$ → angular quantum no.

$n$ → principal q.n.

angle b/w $l^*$ & $s^*$




from vector diagram

$$j^{*2} = l^{*2} + s^{*2} + 2 l^* s^* \cos(l^*, s^*).$$

$$l^* s^* \cos(l^*,s^*) = \frac{j(j+1) - s(s+1) - l(l+1)}{2}$$

The angle b/w $l^*$ and $s^*$ remains conserved all the time and hence average is same as the usual value

$$\therefore \Delta W_{l,s} = \frac{Ze^2}{2m^2c^2}\,\frac{h^2}{4\pi^2}\,\frac{Z^3}{a^3 n^3 (l+1)(l+1/2)}\left(\frac{j(j+1) - s(s+1) - l(l+1)}{2}\right)$$

Page No.

Date: / /

Rydberg constant $R = \frac{2\pi m e^4}{ch^3}$

fine structure constant, $\alpha = \frac{4\pi^2 e^4}{c^2h^3}$

$$\Delta \omega_{l,s} = \left(\frac{R\alpha^2 Z^4 ch}{n^3 l(l+1)(l+1/2)}\right)\left(\frac{j(j+1) - l(l+1) - s(s+1)}{2}\right)$$

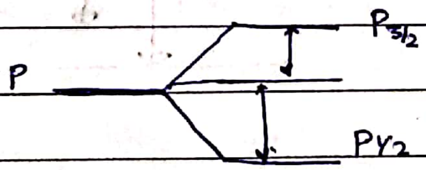
or $$\frac{\Delta \omega_{l,s}}{hc} = a \, \frac{j(j+1) - l(l+1) - s(s+1)}{2}$$

Where $\boxed{a = \frac{R\alpha^2 Z^4}{n^3 l(l+1)(l+1/2)}}$

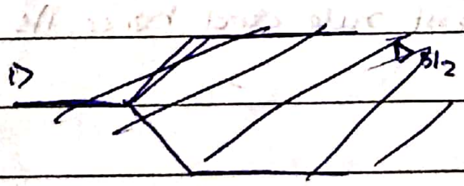
$$\Delta T = \frac{\Delta \bar{\omega}_{l,s}}{hc} = a \, \frac{j(j+1) - l(l+1) - s(s+1)}{2} = -\Gamma$$

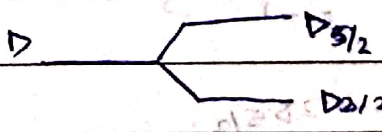
Term $T = T_0 - \Gamma$ ↓ Centre of term

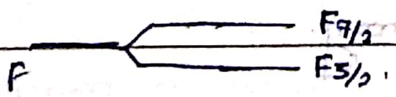
$\Delta T \propto Z$ ∴ $Z \uparrow$ ≡ Separation ↑.




- The splittings are asymmetric because of different j values.
- splitting ↓ as $l$ ↑.




For p term:

$$\Delta \bar{\omega}\Big|_{P_{3/2}} = a \, \frac{3/2 \times 5/2 - 2 - 1/2 \times 1/2}{2} = a/2$$

$$\Delta \bar{\omega}\Big|_{P_{5/2}} = 3a/2$$

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