COURSE BY
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QUANTUM MECHANICS

CC 11

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For the course content, see the syllabus.

5th Semester

The Propagation of Wave-packets :

In general, the form of the simple plane wave is, $e^{i(kx-\omega t)}$; $\omega = 2\pi\nu$, $k = \frac{2\pi}{\lambda}$.

So; form will be: $e^{2\pi i(x/\lambda - \nu t)}$
$= e^{ik(x-ct)}$

Superposition of waves with amplitude $g(k)$ of these simple waves,

$$f(x,t) = \int_{-\infty}^{\infty} dk.\, g(k)\, e^{ik(x-ct)} = f(x-ct)$$

This is the same shape that we started with except that instead of being localised at

$x=0$; it's now localised at $x-ct=0$. Thus a wave packet of light waves propagates without distortion with vel. c.

Now $\omega = \omega(k) = ck$ (speed of light in free space)

As $\omega = \omega(k)$;

$$f(x,t) = \int dk\, g(k)\, e^{ikx - i\omega(k)t}$$

Let's consider a wave packet which is strongly localised at $k=k_0$ (in k space about k_0).

$$\omega(k) = \omega(k_0) + (k-k_0)\left.\frac{d\omega}{dk}\right|_{k=k_0} + \frac{1}{2}(k-k_0)^2 \left.\frac{d^2\omega}{dk^2}\right|_{k=k_0} + \ldots$$

[Taylor ser. exp. wrt k_0;

$\omega(k) = \omega(k-k_0+k_0)$]

The 1st term is const. (independent of k). The 2nd term the quantity $\frac{d\omega}{dk}$ is the grp. vel, which describes the propagation of the wavepacket

$$\left.\frac{d\omega}{dk}\right|_{k=k_0} = v_g$$

$$\left.\frac{d^2\omega}{dk^2}\right|_{k=k_0} = \beta$$

With $k' = k-k_0$; the wave packet has the time dependence; $e^{i(kx-\omega t)}$ ~~$e^{ik_0x}\, e^{ik'\omega}$~~

$$= e^{i(k_0+k')x}\, e^{-i[\omega(k_0) + k' v_g + \frac{1}{2}k'^2\beta]t}$$

$$= \exp i[(k_0x - \omega(k_0)t) + k'x - k'v_g t - \frac{1}{2}\beta k'^2 t]$$

Let; $g(k') = e^{-\alpha k'^2}$

So, $f(x,t) = e^{i(k_0x-\omega(k_0)t)} \int_{-\infty}^{\infty} dk'\, e^{-\alpha k'^2}\, e^{ik'(x-v_gt)}\, e^{-\frac{\beta t k'^2}{2}}$

$$= e^{i(k_0x-\omega(k_0)t)} \left[\int_{-\infty}^{\infty} dk' \exp\left[-\left(\alpha + \frac{i\beta t}{2}\right)k'^2 + i(x-v_gt)k'\right]\right]$$

$$\boxed{\text{std. integral: } \int e^{-\alpha x^2 + \beta x}\, dx = \sqrt{\frac{\pi}{\alpha}}\, \exp\left(\frac{\beta^2}{4\alpha}\right)}$$

$$\therefore f(x,t) = e^{i(k_0x-\omega(k_0)t)} \sqrt{\frac{\pi}{\alpha + \frac{i\beta t}{2}}}\, \exp\left[\frac{-(x-v_gt)^2}{4\left(\alpha + \frac{i\beta t}{2}\right)}\right]$$

So; $$|f(x,t)|^2 = \frac{\pi}{(\alpha^2 + \beta^2t^2/4)^{1/2}} \exp\left[\frac{-(x-v_gt)^2}{2(\alpha^2+\beta^2t^2/4)}\right]$$

This represents a wave packet whose peak is travelling with vel. v_g, but doesn't have a definite width. The quantity that was 'α' at $t=0$; now becomes $\alpha^2 + \frac{\beta^2 t^2}{4}$; i.e. the packet is spreading; since the width is ~~prop~~; $\left(\alpha^2 + \frac{\beta^2 t^2}{4}\right)^{1/2} = \alpha\left(1 + \frac{\beta^2 t^2}{4\alpha^2}\right)^{1/2}$

($\alpha \uparrow \rightarrow$ Rate of spread $\downarrow$).

$f(x,t) = \int dk\, g(k)\, e^{i(kx - \omega(k)t)}$.

This represent a particle with mom. p and KE $= p^2/2m$; $v_g = \frac{d\omega}{dk} = \frac{p}{m}$.

$E = \hbar\omega$, $p = \hbar k$

so in terms of p; we can write 1st eq.,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p)\, e^{\frac{i}{\hbar}(px - Et)}$$

(Normalisation const.)

Now $\psi(x,t)$ is the gen. sol^n of the PDE;

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \frac{i\hbar}{\sqrt{2\pi\hbar}} \int dp\, \phi(p) \cdot \left(-\frac{iE}{\hbar}\right) e^{\frac{i}{\hbar}(px - Et)}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p) \cdot \frac{p^2}{2m} e^{\frac{i}{\hbar}(px - Et)}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$$

$$= -\frac{\hbar^2}{2m}\left(\frac{i}{\hbar}p\right)^2 \cdot \Psi(x,t)$$

$$= \frac{p^2}{2m}\Psi(x,t).$$

$\left[i\hbar\left(-\frac{iE}{\hbar}\right) = E = p^2/2m\right]$

$\Rightarrow i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$. (Time dep. Sch. eq.)

~~the~~ wave f^n in mom. space:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p)\, e^{ipx/\hbar}$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(\hbar k)\, e^{ikx}$$

Inv. Fourier trans:

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ipx/\hbar}$$

$$\phi(\hbar k) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ikx}$$

Now; $\int dp\, \phi^*(p)\, \phi(p) = \int dp\, \phi^*(p) \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ipx/\hbar}$

$= \int dx\, \psi(x). \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi^*(p)\, e^{-ipx/\hbar}$

$= \int dx\, \psi(x)\, \psi^*(x).$

$\Rightarrow \int \phi^*(p)\, \phi(p)\, dp = \int \psi^*(x)\, \psi(x)\, dx = 1.$

This is Perseval's theorem.

It states that if a f^n is normalised to 1, then its F.T. is also normalised to 1.

Now,

$\langle p \rangle = \int dx\, \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi$

$= \int dx\, \psi^* \, -i\hbar \frac{d}{dx} \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p)\, e^{ipx/\hbar}$

$= \int dx\, \psi^* \left(-i\hbar \frac{i}{\hbar}\right) \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p)\, e^{ipx/\hbar}$

$= \int dp\, \phi(p)\, \phi^*(p)$; As; $\phi^*(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{ipx/\hbar}$

so; $\boxed{\langle p \rangle = \int \phi^*(p)\, \phi(p)\, dp}$

Now: $\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int dp.\, \Phi(p,t)\, e^{ipx/\hbar}$

Now; $x = i\hbar \frac{\partial}{\partial p}$ (similar to $p = -i\hbar \frac{\partial}{\partial x}$)

As; $\langle x \rangle = \int dp\, \Phi^*(p,t) \left(i\hbar \frac{\partial}{\partial p}\right) \Phi(p,t)$

(can be shown)

Gaussian functions

$\psi(x) = \frac{1}{(\pi\sigma^2)^{1/4}}\, e^{-x^2/2\sigma^2}$

~~In mom. space~~ By F.T.; (inv.)

$\alpha(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x)\, e^{-ikx}\, dx.$

(As; $\psi(x) = \frac{1}{\sqrt{2\pi}} \int dk\, \alpha(k)\, e^{ikx}$)

$\Rightarrow \alpha(k) = \frac{1}{\sqrt{2\pi}} \frac{1}{(\sigma^2\pi)^{1/4}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2} - ikx}\, dx$

$= \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{(\sigma^2\pi)^{1/4}} \left(\frac{\pi}{1/2\sigma^2}\right)^{1/2} \exp\left[\frac{(-ik)^2}{4/2\sigma^2}\right].$

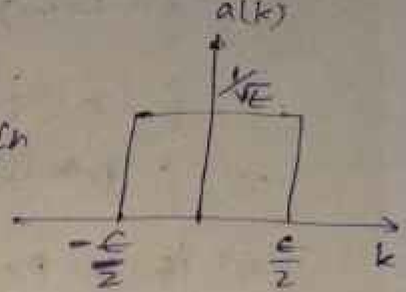
$= \frac{1}{\sqrt{2}} \frac{1}{(\sigma^2\pi)^{1/4}} (\sigma^2 2)^{1/2} \exp\left[\frac{-k^2\sigma^2}{2}\right]$

$\Rightarrow \alpha(k) = (\sigma^2/\pi)^{1/4} \exp\left(-\frac{k^2\sigma^2}{2}\right).$

so; it's also Gaussian in k-space.

1. Lets consider the ~~ramp~~ f^n in k space;

$$a(k) = \frac{1}{\sqrt{\epsilon}} \text{ for } k \text{ in } -\frac{\epsilon}{2} \text{ to } \frac{\epsilon}{2}$$
$$= 0 \text{ for } |k| > \frac{\epsilon}{2}.$$

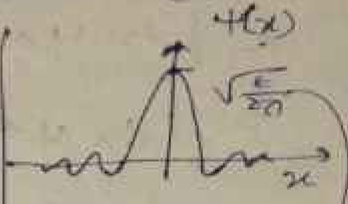


The fourier transform of the f^n is,

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\epsilon/2}^{\epsilon/2} \frac{1}{\sqrt{\epsilon}} e^{ikx} dk$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{\epsilon}} \frac{e^{ix\frac{\epsilon}{2}} - e^{-ix\frac{\epsilon}{2}}}{ix}$$

$$\Rightarrow \psi(x) = \sqrt{\frac{2}{\pi}} \frac{1}{x\sqrt{\epsilon}} \sin\frac{\epsilon x}{2} = \sqrt{\frac{2}{\pi\epsilon}} \frac{1}{x} \sin\left(\frac{\epsilon x}{2}\right)$$



$$\left[\sqrt{\frac{2}{\pi\epsilon}} \cdot \frac{\epsilon}{2} \lim_{z\to 0} \frac{\sin z}{z} = \sqrt{\frac{\epsilon}{2\pi}} \right.$$

~~Parseval's theorem~~ Parseval's formula:

$$\int_{-\infty}^{\infty} |a(k)|^2 dk = \int_{-\epsilon/2}^{\epsilon/2} \frac{1}{\epsilon} dk = 1.$$

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \frac{2}{\pi\epsilon} \left(\frac{\epsilon}{2}\right)^2 \int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} \, dz$$

$$\left(z = \frac{\epsilon x}{2} \Rightarrow dx = \frac{2}{\epsilon} dz \right).$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} dz = 1.$$

$$\int_{-\infty}^{\infty} |a(k)|^2 dk = \int_{-\infty}^{\infty} |\psi(x)|^2 dx$$

Now, $a(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \sqrt{\frac{2}{\pi\epsilon}} \frac{\sin\frac{\epsilon x}{2}}{x} e^{-ikx} dx.$

width of $a(k)$: ϵ width of $\psi(x)$: $\frac{1}{\epsilon}$ order

'0' obtained at $x = \pm\frac{2\pi}{\epsilon}$.

so, $\Delta k \Delta x \simeq \epsilon \cdot \frac{1}{\epsilon} = 1$

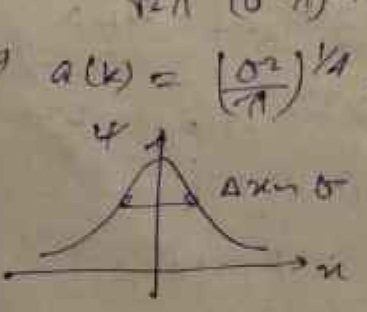
(connection with Heisenberg uncertainity principle)

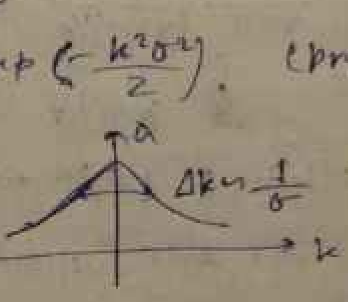
② Gaussian function: $\psi(x) = \frac{1}{(\sigma^2\pi)^{1/4}} e^{-x^2/2\sigma^2}$

F.T. of this f^n:

$$a(k) = \frac{1}{\sqrt{2\pi}} \frac{1}{(\sigma^2\pi)^{1/4}} \int_{-\infty}^{\infty} e^{-x^2/2\sigma^2} e^{ikx} dx$$

$$\Rightarrow a(k) = \left(\frac{\sigma^2}{\pi}\right)^{1/4} \exp\left(-\frac{k^2\sigma^2}{2}\right). \text{ (prev. page)}$$





$\Delta k \Delta x = 1$ here also.

Also: $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} |a(k)|^2 dk = 1$ (here also)

Q. A particle whose norm. wavefn is

$\psi(x) = 2\alpha\sqrt{\alpha}\, x\, e^{-\alpha x}$; $x<0$

$= 0$; $x<0$.

(a) Find x for the peak of $P(x) = |\psi(x)|^2$.

(b) Calculate $\langle x\rangle$, $\langle x^2\rangle$

(c) Find prob. b/w $x=0$ and $x=\frac{1}{\alpha}$.

(d) Calculate $\phi(p)$ and use this to calculate $\langle p\rangle$ and $\langle p^2\rangle$.

$\rightarrow$ (a) $P = \psi^*\psi = 4\alpha^3 x^2 e^{-2\alpha x}$

The peak occurs for $\frac{dP(x)}{dx} = 0$

So: $2x e^{-2\alpha x} + x^2(-2\alpha) = 0$.

$\Rightarrow$ ~~$\cancel{x + \alpha x = 0} \Rightarrow -x = $~~

$1 - \alpha x = 0. \Rightarrow x = 1/\alpha$.

(b) $\langle x\rangle = \int_0^\infty \psi^* x \psi\, dx = \int_0^\infty x P(x)\, dx$

$= \int_0^\infty 4\alpha^3 x^3 e^{-2\alpha x} dx$

$= \frac{4\alpha^3}{(2\alpha)^4} \int_0^\infty (2\alpha x)^3 e^{-2\alpha x} d(2\alpha x)$

$\Rightarrow \langle x\rangle = \frac{1}{4\alpha}\Gamma(4) = \frac{3}{4\alpha}\cancel{4}! = \frac{3!}{4\alpha}$

$\langle x^2\rangle = \int_0^\infty x^2 P(x)\, dx = \frac{4\alpha^3}{(2\alpha)^5}\int_0^\infty (2\alpha x)^4 e^{-2\alpha x} d(2\alpha x)$

$= \frac{1}{8\alpha^2}\Gamma(5) = \frac{4!}{8\alpha^2} = \frac{3!}{2\alpha^2}$

So; $\langle x\rangle = \frac{3!}{4\alpha} = \frac{3}{2\alpha}$, $\langle x^2\rangle = \frac{3!}{2\alpha^2} = \frac{3}{\alpha^2}$ (Ans).

(c) Prob. $P_1 = \int_0^{1/\alpha} P(x)\, dx = 4\alpha^3 \int_0^{1/\alpha} x^2 e^{-2\alpha x} dx$

$\Rightarrow P_1 = 4\alpha^3\left[x^2 \frac{e^{-2\alpha x}}{-2\alpha}\Big|_0^{1/\alpha} + \frac{1}{2\alpha}\int_0^{1/\alpha} 2x e^{-2\alpha x} dx\right]$

$= 4\alpha^3\Big[\frac{-1}{2\alpha^3} e^{-2} + \frac{1}{2\alpha}\frac{2x e^{-2\alpha x}}{-2\alpha}\Big|_0^{1/\alpha}$

$+ \left(\frac{1}{2\alpha}\right)^2 2\int_0^{1/\alpha} e^{-2\alpha x} dx\Big]$.

$=$

(d). $\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_0^\infty 2\alpha\sqrt{\alpha}\, x \cdot e^{-\alpha x} \cdot e^{-\frac{ipx}{\hbar}}\, dx.$

$= \frac{2\alpha\sqrt{\alpha}}{\sqrt{2\pi\hbar}}$

$z = \left(\alpha + \frac{ip}{\hbar}\right)x.$

Q show that the F.T. of the fn $f(x) = Ae^{-\alpha|x|}$ is given by $F(k) = \frac{A}{\sqrt{2\pi}} \frac{2\alpha}{\alpha^2+k^2}$ which is a Lorentzian distribution.

$\rightarrow$ $F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A e^{-\alpha|x|} e^{-ikx} dx.$

$= \cancel{\sqrt{\frac{2}{\pi}} A \left[\frac{e^{-\alpha x}}{-\alpha}\right]_0^{\infty} \left.\frac{e^{-(\alpha+ik)x}}{-(\alpha+ik)}\right|_0^{\infty}}$

$= \cancel{\sqrt{\frac{2}{\pi}} A \frac{1}{\alpha+ik}}$

$= \frac{A}{\sqrt{2\pi}} \left[\int_{-\infty}^{\infty} e^{-\alpha|x|} \cos x \, dx + i \underbrace{\int_{-\infty}^{\infty} e^{-\alpha|x|} \sin x \, dx}_{0}\right].$

$= \frac{A}{\sqrt{2\pi}} 2 \int_0^{\infty} e^{-\alpha x} \cos x \, dx.$

$= \sqrt{\frac{2}{\pi}} A \left.\frac{e^{-\alpha x}(-\alpha \cos kx + k \sin kx)}{\alpha^2+k^2}\right|_0^{\infty}$

$\therefore F(k) = \sqrt{\frac{2}{\pi}} A \frac{\alpha}{\alpha^2+k^2} = \frac{A}{\sqrt{2\pi}} \frac{2\alpha}{\alpha^2+k^2}$ (proved.)

Hence show that $\int_{-\infty}^{\infty} \frac{e^{ikx}}{\alpha^2+k^2} dk = \frac{\pi}{\alpha} e^{-\alpha|x|}$

$\int_{-\infty}^{\infty} \frac{dk}{(\alpha^2+k^2)^2} = \frac{\pi}{2\alpha^3}$

$\int_{-\infty}^{\infty} \frac{e^{ikx}}{\alpha^2+k^2} dk = \underbrace{\int_{-\infty}^{\infty} \frac{\cos kx}{\alpha^2+k^2} dk}_{\text{even}} + i \underbrace{\int_{-\infty}^{\infty} \frac{\sin kx}{\alpha^2+k^2} dk}_{\text{odd}}$

$= 2\int_0^{\infty} \frac{\cos kx}{\alpha^2+k^2} dk$

$\int_{-\infty}^{\infty} \frac{dk}{(\alpha^2+k^2)^2} = 2\int_0^{\infty} \frac{dk}{(\alpha^2+k^2)^2}$

Let; $k = \alpha \tan\theta$
so; $\alpha^2+k^2 = \alpha^2 \sec^2\theta$.
$dk = \alpha \sec^2\theta \, d\theta$

$k = \alpha\tan\theta$	θ
0	0
∞	$\pi/2$.

$= 2\int_0^{\pi/2} \frac{\alpha \sec^2\theta \, d\theta}{\alpha^4 \sec^4\theta}$

$= \frac{2}{\alpha^3} \int_0^{\pi/2} \cos^2\theta \, d\theta$

$= \frac{2}{2\alpha^3} \int_0^{\pi/2} (1+\cos 2\theta) d\theta$

$= \frac{2}{2\alpha^3} \left[\frac{\pi}{2} + \underbrace{\left.\frac{\sin 2\theta}{2}\right|_0^{\pi/2}}_{0}\right]$

$= \frac{\pi}{2\alpha^3}$ (proved.)

Linear Harmonic Oscillator:

1D time indep-endent sch. eq. :

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \quad ; \quad V(x) = \frac{1}{2}m\omega^2 x^2 \text{ (1D LHO)}, \; k = m\omega^2$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2 x^2\right]\psi(x) = 0$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2 x^2}{\hbar^2}\right]\psi(x) = 0.$$

Put ; $\alpha = \frac{m\omega}{\hbar}$ and $\beta = \frac{2mE}{\hbar^2}$

En. is measured in $\frac{\hbar\omega}{2}$

~~Aega~~ $\frac{\beta}{\alpha} = \frac{2E}{\hbar\omega} = \lambda$

Then the amplitude A of LHO of en. $\frac{\hbar\omega}{2}$ is ; $A = \sqrt{\frac{\hbar}{m\omega}}$

$$E = \frac{1}{2}kA^2 = \frac{1}{2}m\omega^2A^2$$

$$\frac{\hbar\omega}{2} = \frac{1}{2}m\omega^2A^2$$

$$\Rightarrow A = \sqrt{\frac{\hbar}{m\omega}}$$

Let; $x = \sqrt{\frac{\hbar}{m\omega}}\, y \Rightarrow y = \sqrt{\frac{m\omega}{\hbar}}\, x$

$$\Rightarrow y = \sqrt{\alpha}\, x$$

$$\frac{d\psi}{dx} = \frac{d\psi}{dy}\frac{dy}{dx} = \sqrt{\alpha}\frac{d\psi}{dy}$$

$$\frac{d^2\psi}{dx^2} = \sqrt{\alpha}\frac{d^2\psi}{dy^2}\frac{dy}{dx} = \alpha\frac{d^2\psi}{dy^2}$$

So, $\alpha\frac{d^2\psi}{dy^2} + (\beta - \alpha^2x^2)\psi(x) = 0$

$$\frac{\beta}{\alpha}\alpha - \alpha\cdot\alpha x^2 = \lambda\alpha - \alpha\cdot y^2 = \alpha(\lambda - y^2)$$

$$\Rightarrow \frac{d^2\psi}{dy^2} + (\lambda - y^2)\psi(y) = 0$$

All the eig. fn of the sys. belongs to bnd states of (+)ve energy and must vanish for $|y| \to \infty$.

Try Asymptotic soln for $y \gg \lambda$;

$$\frac{d^2\psi}{dx^2} - \lambda^2\psi(y) = 0.$$

soln of this is, $\psi(y) = e^{\pm y^2/2}$ — $e^{+y^2/2}$ blows for $|y| \to \infty$.

So; $\psi(y) = e^{-y^2/2}$

In ~~order~~ order to solve ~~the diff~~ for total $\psi(y)$ let's try a soln valid for all values of y; $\psi = B\, e^{-y^2/2} H(y)$ — B: const, H(y): ~~Hermite~~ polynomial

$$\frac{d\psi}{dy} = -By\,e^{-y^2/2}H(y) + Be^{-y^2/2}\frac{dH}{dy}$$

$$\frac{d^2\psi}{dy^2} = -Be^{-y^2/2}H(y) + By^2e^{-y^2/2}H(y) - Bye^{-y^2/2}\frac{dH}{dy} + Be^{-y^2/2}\frac{d^2H}{dy^2}$$

$$= Be^{-y^2/2}\left[\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (y^2-1)H(y)\right].$$

Substituting it,

$$B e^{-y^2/2}\left[\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (y^2-1)H\right] + (\lambda - y^2) B e^{-y^2/2} H = 0.$$

$$\Rightarrow \frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (\lambda-1)H = 0.$$

Write, $\lambda - 1 = 2n$; $\underline{\lambda = 2n+1}$.

So $$\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + 2nH = 0.$$

It's the Hermite diff. eq. soln: $H = H_n(y)$.

$$\underline{H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n} e^{-y^2}}$$ (Hermite Polynomials)

$\lambda = 2n+1$, $n = 0, 1, 2, \dots$ (n: quantum no.)

$\Rightarrow \frac{2E}{\hbar\omega} = 2n+1 \Rightarrow \underline{E_n = (n+\frac{1}{2})\hbar\omega}$

$\psi_n = B_n H_n(y) e^{-y^2/2}$; $y = \sqrt{\frac{m\omega}{\hbar}}\, x$

$n = 0 \Rightarrow E_0 = \frac{\hbar\omega}{2} \Rightarrow$ Lowest val. of en. of LHO

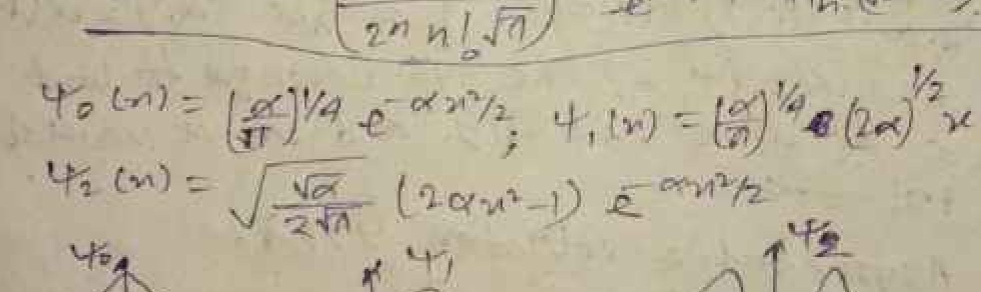
It's called ~~zero~~ zero point energy.

Normalised: $\cancel{\left(\frac{\sqrt{m\omega/\hbar}}{2^n n! \sqrt{\pi}}\right)^{1/2} e}$ $\left(\alpha = \frac{m\omega}{\hbar}\right)$

$$\underline{\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}}\right)^{1/2} e^{-\alpha x^2/2} H_n(\sqrt{\alpha}\, x)}$$

$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$; $\psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha)^{1/2} x\, e^{-\alpha x^2/2}$

$\psi_2(x) = \sqrt{\frac{\sqrt{\alpha}}{2\sqrt{\pi}}}\,(2\alpha x^2 - 1)\, e^{-\alpha x^2/2}$

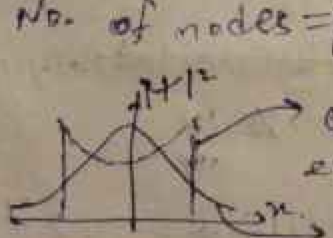


⇓ 1 max

⇓ 1 node, 1 max, 1 min (2 peaks)

⇓ 2 nodes, 2 max, 1 min. (3 peaks)

No. of nodes $= \boxed{n}$, No. of peaks $= \boxed{n+1}$.

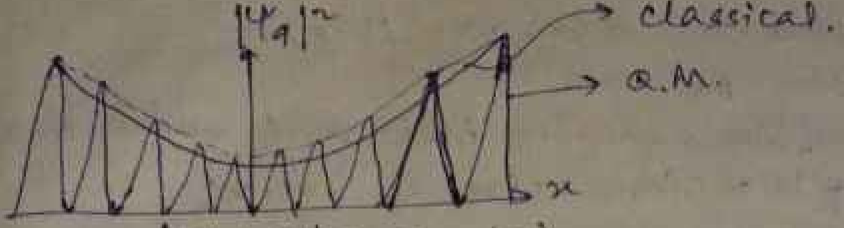


→ classical prob. dist. for same en. $\frac{\hbar\omega}{2}$ of the oscillator.

→ Q.M. ⇓ (No agreement b/w the two)

max at $x=0$ ⇓ min. at $x = 0$.

Large n: classical ⟺ Q.M.



(10 peaks, 9 nodes)

Since the lim. of the classical motion are given by $x = \pm\sqrt{\lambda}$.

Position of the particle; $x = \sqrt{\lambda}\sin\omega t$.

Speed " " " ; $v = \omega\sqrt{\lambda}\cos\omega t$.

Fraction of the total time spent by the particle in interval dt is; $\frac{dt}{T} = \frac{1}{T}\frac{2\,dx}{v}$

Prob. in interval dx;

$P(x)dx = \frac{dx}{\pi\sqrt{\lambda - x^2}}$

(2 for to & fro motion)

[Acc. to classical theory)

Now, if n is large the Hermite Polynomial can be approximated to, $H_n(y) \sim \frac{2^{n+1}}{\sqrt{2\cos\alpha}}\left(\frac{n}{2e}\right)^{n+2} e^{n\alpha^2}\cos\left[\left(2n+\frac{1}{2}\right)x - n\pi/2\right]$.

where α is smallest possible ang. whose sine is $x/\sqrt{2n}$

$$|\psi_n|^2 = \frac{1}{2^n n!\sqrt{\pi}} e^{-y^2} H_n^2(y) = \frac{2}{\pi\sqrt{2n-y^2}}\cos^2\left[\left(2n+\frac{1}{2}\right)\frac{y}{\sqrt{2n}} - n\pi/2\right].$$

$$\Rightarrow P(y) = \frac{1}{\pi\sqrt{\lambda - y^2}}$$

Orthogonality of eig. f^n of LHO:

cond.: $\int_{-\infty}^{\infty} \psi_m^* \psi_n\, dx = \delta_{mn} = 0$ if $m \neq n$.

Selection rule: It can be shown that, $\int_{-\infty}^{\infty} \psi_m x \psi_n\, dx$ determines the prob. that a quantum of en. $\hbar\omega$ is emitted in a transition b/w the states m and n. Since the int. vanishes for $m \neq n \pm 1$; we have the selection ~~rule~~ rule; $\Delta n = \pm 1$.

Parity: $PE = \frac{1}{2}kx^2 \rightarrow$ ev. f^n of x.

$$\frac{d^2\psi}{dx^2} + [\lambda - U(x)]\psi(x) = 0.$$

eig. val. x: $\frac{d^2}{dx^2}$ and $U(x)$

Put; $x = -x'$; $[U(x) = U(-x)]$.

So; $\frac{d^2}{dx'^2}\psi + [\lambda - U(x')]\psi(x') = 0$.

At $|x| \to \infty$; $\psi(x) \to 0$. (b.c.)
(also: $|x'| \to \infty$)

The problem remains invariant ~~under~~ to the symmetry transformation; $x \to -x'$.

If $\psi(x)$ is an eig. f^n of LHO then $\psi(-x)$ is also an eig. f^n of it.

For non degen. state; $\psi(x)$, $\psi(-x)$ are lin. dependent.

So, there must exist a no. c s.t. $\underline{\psi(-x) = c\psi(x)}$

Put $x = -x$; $\psi(x) = c\psi(-x) = c \cdot c\psi(x)$

$\Rightarrow c^2 = 1 \Rightarrow c = \pm 1$.

Hence, $\psi(-x) = \pm\psi(x)$
- $\psi(-x) = \psi(x)$ (sym.) (even parity)
- $\psi(-x) = -\psi(x)$ (odd parity). (asym.)

Expectation values:

$\langle x \rangle = \int_{-\infty}^{\infty} \psi_0^* x \psi_0 \, dx = \int_{-\infty}^{\infty} x \, e^{-\alpha x^2} dx$. const.
$\quad x \to$ odd, $e^{-\alpha x^2} \to$ even.

$\Rightarrow \langle x \rangle = 0$.

$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} \psi_0^* \frac{d\psi_0}{dx} dx$; $\psi_0^* \to$ even
$\frac{d\psi_0}{dx} \to$ odd

$\Rightarrow \langle p \rangle = 0$.

$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0^* x^2 \psi_0 \, dx$

$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$.

$= 2\sqrt{\frac{\alpha}{\pi}} \int_0^{\infty} \frac{1}{2\alpha\sqrt{\alpha}} z^{1/2} e^{-z} dz$

$\alpha x^2 = z$
$x = \sqrt{\frac{z}{\alpha}}$
$x\,dx = \frac{dz}{2\alpha}$

$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$

$\Rightarrow \langle x^2 \rangle = \frac{1}{2\alpha}$

$\langle p^2 \rangle = -\hbar^2 \int_{-\infty}^{\infty} \psi_0^* \frac{d^2}{dx^2} \psi_0 \, dx$

$\Rightarrow \langle p^2 \rangle = \frac{1}{2}\hbar^2 \alpha$

$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{1}{\sqrt{2\alpha}}$

$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \hbar\sqrt{\frac{\alpha}{2}}$

So, $\Delta x \Delta p = \frac{1}{\sqrt{2\alpha}} \hbar \sqrt{\frac{\alpha}{2}} = \frac{\hbar}{2}$ (min. bcz the wave f^n is gaussian)

3D Harmonic Oscillator:

$V(r) = \frac{1}{2}kr^2 = \frac{k}{2}(x^2 + y^2 + z^2)$
(spherically sym.)

$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{1}{2}kr^2\psi = E\psi$

$E = \frac{\hbar\omega}{2}\lambda$; r measured in unit $\left(\frac{\hbar}{m\omega}\right)^{1/2}$; $\omega = \sqrt{\frac{k}{m}}$

So: $\nabla^2\psi + (\lambda - r^2)\psi = 0$. (Same thing done in 1 D).

$\Rightarrow \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + (\lambda - r^2)\psi = 0$.

Sep. of var.: $\psi(x,y,z) = \psi_1(x)\,\psi_2(y)\,\psi_3(z)$.

So; $\left(\psi_2\psi_3 \frac{d^2\psi_1}{dx^2} + \psi_1\psi_3\frac{d^2\psi_2}{dy^2} + \psi_1\psi_2\frac{d^2\psi_3}{dz^2}\right)$

$+ \underbrace{(\lambda - x^2 - y^2 - z^2)}_{(\lambda_1+\lambda_2+\lambda_3)}\psi_1\psi_2\psi_3 = 0$

$\Rightarrow \left[\frac{1}{\psi_1}\frac{d^2\psi_1}{dx^2} + \lambda_1 - x^2\right] + \ldots\ldots = 0$.

So; $\frac{d^2\psi_1}{dx^2} + (\lambda_1 - x^2)\psi_1 = 0 \Rightarrow \lambda_1 = 2n_1 + 1$
and $\psi_1 = \text{const.}\, H_{n_1}(\sqrt{\alpha}x)\, e^{-\frac{\alpha x^2}{2}}$

$\frac{d^2\psi_2}{dy^2} + (\lambda_2 - y^2)\psi_2 = 0 \Rightarrow \lambda_2 = 2n_2 + 1$
and $\psi_2 = \text{const.}\, H_{n_2}(\sqrt{\alpha}y)\, e^{-\frac{\alpha y^2}{2}}$

$\frac{d^2\psi_3}{dz^2} + (\lambda_3 - z^2)\psi_3 = 0 \Rightarrow \lambda_3 = 2n_3 + 1$
and $\psi_3 = \text{const.}\, H_{n_3}(\sqrt{\alpha}z)\, e^{-\frac{\alpha z^2}{2}}$

So; $\psi(x,y,z) = \psi_1\psi_2\psi_3 = \frac{\alpha^{3/4}}{\sqrt{2^n\, n_1!\, n_2!\, n_3!}}\, e^{-\alpha r^2/2}\, H_{n_1}(\sqrt{\alpha}x)\, H_{n_2}(\sqrt{\alpha}y)\, H_{n_3}(\sqrt{\alpha}z)$

where;
$n = n_1 + n_2 + n_3$.

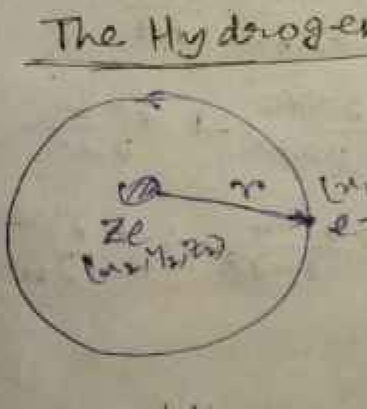
$E_{n_1 n_2 n_3} = (2n_1 + 1 + 2n_2 + 1 + 2n_3 + 1)\frac{\hbar\omega}{2}$

$\Rightarrow E_n = \left(n + \frac{3}{2}\right)\hbar\omega$.

Degree of degen. is $\frac{1}{2}(n+1)(n+2)$.

The Hydrogen Atom:

(1 electronic sys.)
H, He^+, Li^{2+}, ...



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

P.E. $\Rightarrow V(r) = -\int_0^r \vec{F}(r)\cdot d\vec{r}$

$\Rightarrow V(r) = -\frac{Ze^2}{r}$

(Spherically sym.)

Total Ham.:

$H_T = -\frac{\hbar^2}{2}\left[\underset{\substack{\Downarrow\\ e^-}}{\frac{1}{m_1}}\nabla_1^2 + \underset{\substack{\Downarrow\\ p}}{\frac{1}{m_2}}\nabla_2^2\right] + V(x_1, x_2, y_1, y_2, z_1, z_2)$ (for H atom). — (1)

(6 co-ordinates)

Sch. eq.: ~~$E_T\psi_T$~~ $H_T\psi_T = E_T\psi_T$. — (2).

So, $-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right) -$

$\frac{\hbar^2}{2m_2}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right) + [V(x_1,y_1,z_1,x_2,y_2,z_2) - E]\psi_T = 0$ — (3)

rel. co-ordinate

$V = V(x_1-x_2,\, y_1-y_2,\, z_1-z_2)$

$x, y, z \to$ relative co-ordinates

$X, Y, Z \to$ COM co-ordinates

$x = x_1 - x_2,\ y = y_1 - y_2,\ z = z_1 - z_2$ — (4)

$X = \frac{m_1x_1+m_2x_2}{m_1+m_2}$, $Y = \frac{m_1y_1+m_2y_2}{M}$; $Z = \frac{m_1z_1+m_2z_2}{M}$ — (5)

(M)

So, (3) $\to$

$-\frac{\hbar^2}{2}\left[\left(\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2}{\partial x_2^2}\right)\psi_T + \left(\frac{1}{m_1}\frac{\partial^2}{\partial y_1^2}+\frac{1}{m_2}\frac{\partial^2}{\partial y_2^2}\right)\psi_T + \left(\frac{1}{m_1}\frac{\partial^2}{\partial z_1^2}+\frac{1}{m_2}\frac{\partial^2}{\partial z_2^2}\right)\psi_T\right] +$

$(V(x,y,z) - E)\psi_T = 0.$

$\cancel{\frac{1}{m_1}\frac{\partial\psi_T}{\partial x_1} = \frac{1}{m_1}\frac{\partial\psi_T}{\partial X}\frac{\partial X}{\partial x_1} = \frac{1}{m_1}\frac{m_1}{M}\frac{\partial\psi_T}{\partial X}}$

$\cancel{\Rightarrow \frac{1}{m}\frac{\partial^2\psi_T}{\partial x_1^2} = \frac{1}{M}\frac{\partial^2\psi_T}{\partial X^2}\cdot\frac{\partial X}{\partial x_1} = \frac{m_1}{M^2}}$

Now, $x_1 = x_1(x, X)$.

So, $\frac{\partial\psi_T}{\partial x_1} = \frac{\partial\psi_T}{\partial X}\cdot\frac{m_1}{M} + \frac{\partial\psi_T}{\partial x}$ (1)

$\Rightarrow \frac{\partial^2\psi_T}{\partial x_1^2} = \frac{m_1}{M}\frac{\partial^2\psi_T}{\partial X^2}\frac{m_1}{M} + \frac{m_1}{M}\frac{\partial^2\psi_T}{\partial x\partial X}$ (1)

$+ \frac{\partial^2\psi_T}{\partial x^2} + \frac{\partial^2\psi_T}{\partial X\partial x}\cdot\frac{m_1}{M}$

$= \frac{m_1^2}{M^2}\frac{\partial^2\psi_T}{\partial X^2} + \frac{2m_1}{M}\frac{\partial^2\psi_T}{\partial x\partial X} + \frac{\partial^2\psi_T}{\partial x^2}$

Similarly, $\frac{\partial^2\psi_T}{\partial x_2^2} = \frac{m_2^2}{M^2} - \frac{2m_2}{M}\frac{\partial^2\psi_T}{\partial x\partial X} + \frac{\partial^2\psi_T}{\partial x^2}$

So, $\left(\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x_2^2}\right)$

$= \frac{m_1+m_2}{M^2}\frac{\partial^2\psi_T}{\partial X^2} + \left(\frac{2}{M}-\frac{2}{M}\right)\frac{\partial^2\psi_T}{\partial x\partial X} +$

$\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\frac{\partial^2\psi_T}{\partial x^2}$

$= \frac{1}{M}\frac{\partial^2\psi_T}{\partial X^2} + \frac{1}{\mu}\frac{\partial^2\psi_T}{\partial x^2}$; $\frac{1}{\mu} = \frac{1}{m_1}+\frac{1}{m_2}$

$\mu \to$ reduced mass.

So; (same things for y_1, y_2 and z_1, z_2)

$$-\frac{\hbar^2}{2}\left[\frac{1}{M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)\psi_T + \frac{1}{\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_T\right] + V(x,y,z)\psi_T = E_T\psi_T$$

Let; $\psi_T = \psi(x,y,z)\,\phi(X,Y,Z)$ — (6).

So; $$-\frac{\hbar^2}{2}\left[\frac{\psi}{M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)\phi + \frac{\phi}{\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi\right] + V(x,y,z)\psi\phi = E_T\psi\phi.$$

$$\Rightarrow -\frac{\hbar^2}{2M}\cdot\frac{1}{\phi}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)\phi - \frac{\hbar^2}{2\mu}\frac{1}{\psi}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + V(x,y,z) = E_T$$

So; $$-\frac{\hbar^2}{2M}\frac{1}{\phi}\nabla^2_{XYZ}\phi - E_T = +\frac{\hbar^2}{2\mu}\frac{1}{\psi}\nabla^2_{xyz}\psi - V(x,y,z) = -E$$ (Let).

So; $$\nabla^2_{XYZ}\phi + \frac{2M}{\hbar^2}(E_T - E)\phi = 0. \quad \text{— (7)}$$

and $$\nabla^2_{xyz}\psi + \frac{2\mu}{\hbar^2}(E - V(x,y,z))\psi = 0. \quad \text{— (8).}$$

$\phi \rightarrow$ free particle wave f^n (X,Y,Z)

Spherical: $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$.

So; $$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

(r,θ,ϕ)

So; $$\frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{r^2\sin\theta}\frac{\partial\psi}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E - V(r))\psi = 0.$$

Sep. of var: $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$. — (9)

So; $$\frac{2}{rR}\frac{\partial R}{\partial r} + \frac{1}{R}\frac{\partial^2 R}{\partial r^2} + \frac{1}{r^2 Y}\frac{\partial^2 Y}{\partial\theta^2} + \frac{\cos\theta}{r^2\sin\theta\cdot Y}\frac{\partial Y}{\partial\theta} + \frac{1}{r^2\sin^2\theta\, Y}\frac{\partial^2 Y}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E - V(r)) = 0.$$

$$\Rightarrow \frac{2r}{R}\frac{\partial R}{\partial r} + \frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial\theta^2} + \frac{\cot\theta}{Y}\frac{\partial Y}{\partial\theta} + \frac{\operatorname{cosec}^2\theta}{Y}\frac{\partial^2 Y}{\partial\phi^2} + \frac{2\mu r^2}{\hbar^2}(E - V) = 0.$$

$$\Rightarrow \frac{r^2}{R}\left(\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V(r))$$

$$=-\frac{1}{Y}\left[\frac{\partial^2 Y}{\partial\theta^2}+\cot\theta\cdot\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$=\lambda \text{ (let)}.$$

So;
$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[\frac{2\mu}{\hbar^2}(E-V(r))-\frac{\lambda}{r^2}\right]R(r)=0. \quad -(10)$$

$$\frac{\partial^2 Y}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}=-\lambda Y.$$

Let; $Y=\Theta\,\Phi. \quad -(11)$

So;
$$\frac{1}{\Theta}\left(\frac{\partial^2\Theta}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial\Theta}{\partial\theta}\right)\sin^2\theta+\lambda\sin^2\theta$$

$$=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m^2 \text{ (let)}$$

So;
$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0. \quad -(12)$$

and

$$\frac{\partial^2\Theta}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial\Theta}{\partial\theta}+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0. \quad -(13)$$

So; Φ is independent of E and V(r).
(and Θ)

So; ~~Y(θ, φ)~~ $Y(\theta,\phi)$ (angular part of wavefn) is solely determined by the prop. of the spherical sym..

eq. (12) $\rightarrow$ $\Phi(\phi)=N_\phi\, e^{\pm im\phi}$
single valued ✓   Norm. const.

So; $\Phi(\phi=0)=\Phi(\phi=2\pi) \Rightarrow$ ~~$N_\phi = N_\phi e^{\pm 2\pi i m}$~~
or ϕ or $\phi+2\pi$

So; $N_\phi e^{\pm im\phi}=N_\phi\, e^{\pm im(\phi+2\pi)}$

$\Rightarrow e^{\pm 2\pi i m}=1=\cos 2\pi m+i\sin 2\pi m.$

~~m = 0~~   So; $m=0,\pm1,\pm2,\dots$

We can write; $\Phi(\phi)=N_\phi\, e^{im\phi}$; $m=0,\pm1,\pm2,\dots$

Norm: $\int_0^{2\pi}|\Phi(\phi)|^2 d\phi=1 \rightarrow |N_\phi|^2\int_0^{2\pi}d\phi=1 \Rightarrow N_\phi=\frac{1}{\sqrt{2\pi}}$

Hence; $\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi} \quad -(14)$

m is called the magnetic quantum no..

orthogonality: $\int_0^{2\pi}\Phi^*_{m'}\Phi_m\,d\phi=\frac{1}{2\pi}\int_0^{2\pi}e^{i(-m'+m)\phi}d\phi$

for, $m'\neq m$ it's 0.

So; $\int_0^{2\pi}\Phi^*_{m'}\Phi_m\,d\phi=\delta_{m'm} \quad -(15)$

(17) → Sol^n of Θ:

Let; $x = \cos\theta$; $\frac{dx}{d\theta} = -\sin\theta$; $\sin\theta = \sqrt{1-x^2}$

(13) → $\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} \cdot \left(-\frac{\sin\theta}{\sin\theta}\right) = -\sin\theta \frac{\partial \Theta}{\partial x}$

$$\frac{\partial^2 \Theta}{\partial \theta^2} = -\cos\theta \frac{\partial \Theta}{\partial x} - \sin\theta \frac{\partial^2 \Theta}{\partial x^2} \underbrace{\left(\frac{dx}{d\theta}\right)}_{-\sin\theta}$$

$$= -x \frac{\partial \Theta}{\partial x} + (1-x^2) \frac{\partial^2 \Theta}{\partial x^2}.$$

(13) → $(1-x^2) \frac{\partial^2 \Theta}{\partial x^2} - x \frac{\partial \Theta}{\partial x} - \cos\theta \frac{\partial \Theta}{\partial x} + \left(\lambda - \frac{m^2}{1-x^2}\right) \Theta(x) = 0.$

$\Rightarrow (1-x^2) \frac{\partial^2 \Theta}{\partial x^2} - 2x \frac{\partial \Theta}{\partial x} + \left(\lambda - \frac{m^2}{1-x^2}\right) \Theta(x) = 0.$

$\Rightarrow \frac{d}{dx}\left((1-x^2) \frac{d\Theta}{dx}\right) + \left(\lambda - \frac{m^2}{1-x^2}\right) \Theta(x) = 0$ — (16).

(Associated Legendre eq^n).

Sol^n: Associated Legendre polynomial.

So, (degree $= l$) $\underline{\Theta(\theta) = N_\Theta P_l^m(\cos\theta)}$; — (17) | Restriction: $\boxed{\lambda = l(l+1)}$,

l: Azimuthal quantum no. | $l = 0, 1, 2, 3, \ldots$

m has one of the integer values b/w $-l$ to l.

$$P_l^m(x) = \frac{(1-x^2)^{\frac{m}{2}}}{2^l\, l!} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l \quad \text{— (18)}.$$

$m > l \to P_l^m(x) = 0$. (Highest power in x is x^{2l}. If $l+m > 2l$; or $m > l$ all terms will vanish).

Now; $\int_{-1}^{1} |P_l^m(x)|^2 dx = \frac{(l+m)!}{(l-m)!} \frac{2}{2l+1}$ — (19)

(Prop. of associated Legendre polynomial)

Now; $\int_0^\pi |\Theta(\theta)|^2 d\theta = N_\Theta^2 \int_{-1}^{1} |P_l^m(x)|^2 dx = 1.$

$$\Rightarrow N_\Theta = \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}\right]^{1/2}$$

So, $\underline{\Theta_{lm}(\theta) = \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)}$ — (20)

Sol^n of Radial equation ($R(r)$): (Putting $\lambda = l(l+1)$)

$$\frac{\partial^2 R(r)}{\partial r^2} + \frac{2}{r} \frac{\partial R}{\partial r} + \left[\frac{2\mu}{\hbar^2}(E - V(r)) - \frac{l(l+1)}{r^2}\right] R(r) = 0$$

$$V(r) = -\frac{Ze^2}{r} = -\frac{e^2}{r} \text{ ; (H - atom)}$$

Let; $\rho = \gamma r$

so; $\frac{\partial R}{\partial r} = \gamma \frac{\partial R}{\partial \rho}$, $\frac{\partial^2 R}{\partial r^2} = \gamma^2 \frac{\partial^2 R}{\partial \rho^2}$.

so; $\gamma^2 \frac{\partial^2 R}{\partial \rho^2} + \frac{2\gamma}{\rho} \cdot \gamma \frac{\partial R}{\partial \rho} + \left[\frac{2\mu E}{\hbar^2} + \frac{2\mu Z e^2 \gamma}{\rho \hbar^2} - \frac{l(l+1)\gamma^2}{\rho^2}\right] R(\rho) = 0$

$\rightarrow \rho^2 \frac{\partial^2 R}{\partial \rho^2} + 2\rho \frac{\partial R}{\partial \rho} + \left[\frac{2\mu E \rho^2}{\hbar^2 \gamma^2} + \frac{2\mu Z e^2 \rho}{\hbar^2 \gamma} - l(l+1)\right] R(\rho) = 0.$

Eigenvalue of ang. mom. op. L^2 are,

$\lambda \hbar^2 = l(l+1)\hbar^2$; $l = 0, 1, 2, \ldots$

old a.M.: $L = k\hbar$; $k = 1, 2, 3, \ldots$

Also, $L_z = -i\hbar \frac{\partial}{\partial \phi}$, $\Phi(\phi) = e^{im\phi}$

so, $L_z \Phi = -i\hbar \, im \, e^{im\phi} \Rightarrow L_z \Phi = m\hbar \Phi$

so; Eig value of L_z is $m\hbar$; $m = 0, \pm 1, \pm 2, \ldots, \pm l$

or, $m = (-l, l)$ in steps of 1.

Also; $\Theta(\theta) = P_l^m(x) = \frac{1}{2^l l!}(1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l$

Spherical Harmonics:

$$Y_l^m(\theta, \phi) = (-1)^m C_l^m P_l^m(x) e^{im\phi}$$

$$C_l^m = \left(\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}\right)^{1/2}$$

$Y_0^0 = \frac{1}{\sqrt{4\pi}}$, $Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$, $Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm im\phi}$

$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$, $Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{\pm im\phi}$

$Y_l^m(\theta, \phi)$ are the simultaneous eig. f^n of the operators L^2 and L_z belonging to the eig. val. $l(l+1)\hbar^2$ and $m\hbar$.

Radial part: $E < 0 \rightarrow$ (-ve) en. corr. to bnd state (elliptical orbits) in atomic system.

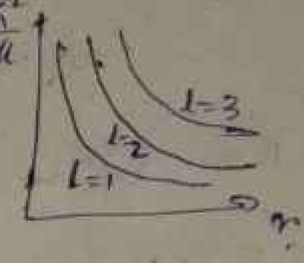
$E > 0 \Rightarrow$ unbound states (+ve en.). Hyperbolic orbits.

consider $E < 0$; i.e. bnd. states for H-atom.

We have; $\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left(\frac{2\mu}{\hbar^2}(E - V(r)) - \frac{l(l+1)}{r^2}\right) R(r) = 0$

$\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} \Rightarrow$ centrifugal contribution.

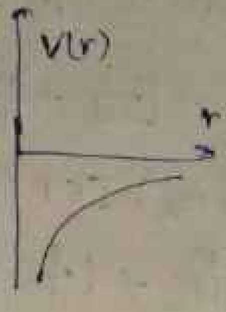
(Repulsive).

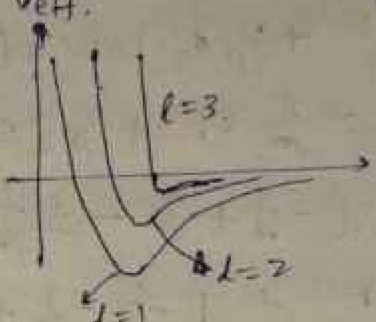


$V(r) = -\frac{e^2}{r}$.

(Attractive)

(coulomb pot.)





Now, $\rho = \gamma r$ leads to,

$$\rho^2\frac{\partial^2 R}{\partial\rho^2} + 2\rho\frac{\partial R}{\partial\rho} + \left[\frac{2\mu E}{\hbar^2\gamma^2}\rho^2 + \frac{2\mu Ze^2\rho}{\hbar^2\gamma} - l(l+1)\right] R(\rho) = 0$$

$$\gamma = \left(\frac{8\mu|E|}{\hbar^2}\right)^{1/2}, \quad n = \frac{Ze^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}$$

So; $\rho^2\frac{\partial^2 R}{\partial\rho^2} + 2\rho\frac{\partial R}{\partial\rho}\left[-\frac{1}{4} + n\rho - l(l+1)\right] R(\rho) = 0$.

$$\frac{2\mu E}{\hbar^2\gamma^2} = \frac{2\mu E}{\hbar^2}\frac{\hbar^2}{8\mu|E|} = -\frac{1}{4}$$

$$\frac{2\mu Ze^2}{\hbar^2\gamma} = \frac{2\mu}{\hbar^2}Ze^2\frac{1}{2}\sqrt{\frac{\hbar^2}{2\mu}}\frac{1}{\sqrt{|E|}} = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

$= n$; $n = \frac{Ze^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2}$

So; $\frac{\partial^2 R}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial\rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right] R(\rho) = 0$.

$\rho \to \infty \Rightarrow$ (asymptotic region) $\frac{\partial^2 R}{\partial\rho^2} - \frac{1}{4}R(\rho) = 0$.

$\Rightarrow R(\rho) = e^{-\rho/2}$ (omitting $e^{\rho/2}$ for having well behaved soln)

So, the general soln will be; $R(\rho) = A(\rho)\, e^{-\rho/2}$

finite order polynomial

$$A(\rho) = \rho^k(c_0 + c_1\rho + c_2\rho^2 + c_3\rho^3 + \dots) = \rho^k F(\rho)$$
$(k \geq 0)$

Take; $R(\rho) = \rho^l F(\rho)\, e^{-\rho/2} = SF$; $S(\rho) = \rho^l e^{-\rho/2}$

$$\frac{\partial S}{\partial\rho} = l\rho^{l-1} - \frac{1}{2}\rho^l e^{-\rho/2} = \frac{lS}{\rho} - \frac{S}{2}$$

$$\frac{\partial^2 S}{\partial\rho^2} = \left(\frac{l}{\rho} - \frac{1}{2}\right)\frac{\partial S}{\partial\rho} + \left(-\frac{l}{\rho^2}\right)S = \left(\left(\frac{l}{\rho} - \frac{1}{2}\right)^2 - \frac{l}{\rho^2}\right)S.$$

$$\frac{\partial R}{\partial\rho} = S\frac{\partial F}{\partial\rho} + \left(\frac{l}{\rho} - \frac{1}{2}\right)SF$$

so; $\frac{\partial^2 R}{\partial \rho^2} = S\frac{\partial^2 F}{\partial \rho^2} + \left(\frac{l}{\rho}-\frac{1}{2}\right)S\frac{\partial F}{\partial \rho} +$

$\left(\frac{l}{\rho}-\frac{1}{2}\right)\left[S\frac{\partial F}{\partial \rho} + \left(\frac{l}{\rho}-\frac{1}{2}\right)SF\right] - \frac{l}{\rho^2}SF.$

Now; $\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$

$\Rightarrow SF'' + \left(\frac{l}{\rho}-\frac{1}{2}\right)SF' + \left(\frac{l}{\rho}-\frac{1}{2}\right)\left[SF' + \left(\frac{l}{\rho}-\frac{1}{2}\right)SF\right]$

$-\frac{l}{\rho^2}SF + \frac{2}{\rho}\left[S\frac{\partial F}{\partial \rho} + \left(\frac{l}{\rho}-\frac{1}{2}\right)SF\right] +$

$\left[-\frac{1}{4}+\frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]SF = 0$

$\Rightarrow F'' + \left[\frac{l}{\rho} - \frac{1}{2} + \left(\frac{l}{\rho}-\frac{1}{2}\right) + \frac{2}{\rho}\right]F' + \left[\left(\frac{l}{\rho}-\frac{1}{2}\right)^2\right.$

$\left. - l/\rho^2 + \frac{2}{\rho}\left(\frac{l}{\rho}-\frac{1}{2}\right) - \frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]F = 0.$

$\frac{1}{\rho}\left[l - \frac{\rho}{2} + l - \frac{\rho}{2} + 2\right]$
$= \frac{1}{\rho}\left[(2l+1)+1-\rho\right]$

$\frac{1}{\rho}\left[\frac{l^2}{\rho} - l + \frac{\rho}{4} - \frac{l}{\rho} + \frac{2l}{\rho} - 1 - \frac{\rho}{4} + n - \frac{l^2}{\rho} - l/\rho\right]$
$= \frac{1}{\rho}\left[-l-1+n\right]$

$\rho\frac{\partial^2 F}{\partial \rho^2} + \left[(2l+1)+1-\rho\right]\frac{\partial F}{\partial \rho} + (n-l-1)F(\rho) = 0$

comparing with;

$x\frac{\partial^2 y}{\partial x^2} + (p+1-x)\frac{\partial y}{\partial x} + (k-p)y = 0$ where,

the solⁿ is $y(x) = L^p_k(x) = \frac{d^p}{dx^p}\left[e^x\frac{d^k}{dx^k}(x^k e^{-x})\right]$

~~Asso~~ (Associated Laguerre polynomials).

$p+1 = (2l+1)+1 \Rightarrow p = 2l+1$; $k-p = n-l-1$
$\Rightarrow k = 2l+1+n-l-1$
$\Rightarrow k = n+l$

Hence; the solⁿ is,

$F(\rho) = L^{2l+1}_{n+l}(\rho).$

so; $R(\rho) = N\rho^l e^{-\rho/2} \cdot L^{2l+1}_{n+l}(\rho)$; $\rho = \gamma r$

$L^{2l+1}_{n+l}(\rho)$ doesn't vanish for $2l+1 \leq n+l$
or $n \geq l+1$.

For, $l=0$; $n \geq 1$.
Lowest value of $n = 1$

n: Principle (total) quantum no.

Now; $n^2 = \frac{Z^2e^4}{\hbar^2}\frac{\mu}{2|E|} \Rightarrow E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 \cdot n^2}$ | $E \propto \frac{1}{n^2}$

$\gamma^2 = \frac{8\mu}{\hbar^2}\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \Rightarrow \gamma = \frac{2\mu Z e^2}{\hbar n}$; $\rho = \gamma r.$

Bohr radius; $a_0 = \hbar^2/\mu e^2$; $E_n = -\frac{Ze^2}{2a_0}\cdot\frac{1}{n^2}.$

1 Hydrogen atom prob.: Radial part:

$$R_{nl}(\rho) = N_r \rho^l e^{-\rho/2} L^{2l+1}_{n+l}(\rho) \; ; \; \rho = \gamma r; \quad \gamma = \frac{2\mu Z e^2}{n\hbar} = \frac{2Z}{na_0}$$

(Stationary states; i.e. time independent)

Normalisation: $N_r^2 \int_0^\infty \rho^{2l} e^{-\rho} \left(L^{2l+1}_{n+l}(\rho)\right)^2 d\rho = 1$

$$\Rightarrow N_r^2 \frac{2n[(n+l)!]^3}{(n-l-1)!} = 1 \rightarrow N_r = \left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{1/2}$$

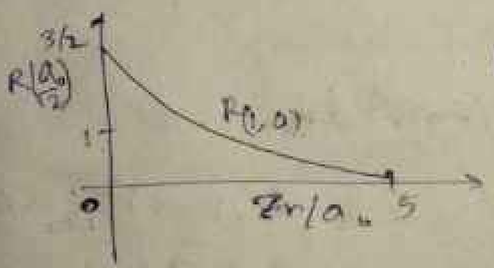
So, $$R_{nl}(\rho) = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \, (\gamma r)^l e^{-\gamma r/2} L^{2l+1}_{n+l}(\gamma r)$$

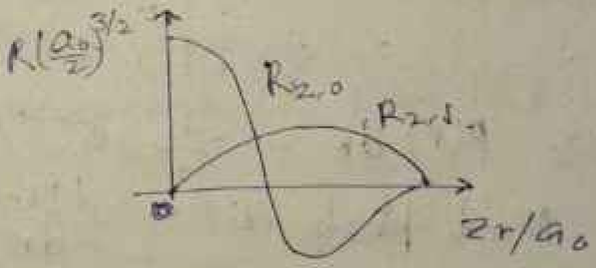
$$\rightarrow R_{nl}(r) = \left(\frac{2Z}{na_0} \frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{1/2} e^{-\frac{Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L^{2l+1}_{n+l}\left(\frac{2Zr}{na_0}\right)$$

$$R_{1,0}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{2,0}(r) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{2,1}(r) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$





complete Normalised Wavefn.:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, \Theta_{l,m}(\theta)\, \Phi_m(\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

$$\rightarrow \psi_{nlm}(r,\theta,\phi) = C_{nlm} \underbrace{e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^l L^{2l+1}_{n+l}\left(\frac{2Zr}{na_0}\right)}_{R_{nl}(r)} \underbrace{P_l^m(\cos\theta)\, e^{im\phi}}_{Y_l^m(\theta,\phi)}$$

$C_{nlm} = N_r N_\theta N_\phi; \; N_\phi = 1/\sqrt{2}$

$$\rightarrow C_{nlm} = \left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \cdot \left(\frac{2l+1}{2}\right) \frac{(l-m)!}{(l+m)!} \frac{1}{2\pi}\right]^{1/2}$$

Gnd. state: $$\psi_{100} = C_{100}\, e^{-Zr/a_0} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$\psi_{100} \Rightarrow$ independent of $\theta, \phi \rightarrow$ spherically sym.

The s-wave f^n ($l=0$) are only ones for which $\psi(r=0) \neq 0$. Time dependent wave f^n

$$\Psi_{nlm} = \psi_{nlm}\, e^{-iE_n t/\hbar}$$

$l=0 \rightarrow s$; $l=1 \rightarrow p$, $l=2 \rightarrow d$, $l=3 \rightarrow f$, ...

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos\theta$$

H-atom ($Z=1$) $\rightarrow$ $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$

Prob. dist. f^n for the e^- relative to the nucleus is; $\psi_{100}^* \psi_{100} = \frac{1}{\pi a_0^3} e^{-2r/a_0}$

Prob. $P = \int |\psi_{100}|^2 \underbrace{r^2 \sin\theta\, dr\, d\theta\, d\phi}_{d\tau}$

$$= \frac{1}{\pi a_0^3}\int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{2\pi \cdot 2}{\pi a_0^3}\int_0^\infty \left(\frac{2r}{a_0}\right)^2 e^{-2r/a_0} d\left(\frac{2r}{a_0}\right)\left(\frac{a_0}{2}\right)^3$$

$$= \frac{4}{8}\Gamma(3) = 1$$

Also; $P(r)\,dr = \frac{4}{a_0^3} e^{-2r/a_0} r^2 dr$

Most prob. dis.: $\frac{dP(r)}{dr} = 0 \Rightarrow 4 \cdot 2r - r^2 \frac{2}{a_0} = 0$

$\Rightarrow r = a_0$ (Bohr Radius)

Also, $E_n = -\frac{Z^2 e^2}{2a_0 n^2}$

$n \rightarrow \infty \Rightarrow E_n \rightarrow 0$

Total no. of states belonging to E_n i.e degree of degen. is $\sum_{l=0}^{n-1}(2l+1) = \frac{2n(n-1)}{2} + n = n^2$

Q. Find the avg. dist. of 1s e^- from the nucleus if the wavef^n for 1s orbital (H-atom) is

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$\rightarrow$ $\langle r \rangle = \int r |\psi|^2 d\tau = \int_0^\infty r^3 e^{-2r/a_0} dr \cdot \frac{4\pi}{\pi a_0^3}$

$\Rightarrow \langle r\rangle = \int_0^\infty \left(\frac{2r}{a_0}\right)^3 e^{-2r/a_0}\, d\left(\frac{2r}{a_0}\right) \left(\frac{a_0}{2}\right)^4 \frac{4}{a_0^3}$

$= \Gamma(4)\, \frac{a_0 \cdot 4}{16} = 3!\, \frac{a_0}{4} \cdot 3\times 2\, \frac{a_0}{4}$

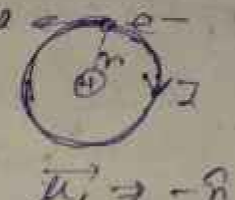
$\Rightarrow \langle r\rangle = \frac{3}{2} a_0$ (Ans.)

Max. occupancy of an orbital $= 2(2l+1)$

Orbit - $2n^2$ $K\to 2,\ L\to 8,\ M\to 18,\ N\to 32$.

Relⁿ b/w $\vec{l}$ and magnetic dip. moment $\vec{\mu}_l$ of an e^-:

$\vec{\mu}_l = I \cdot$ area (due to motion of e^-)



$\Rightarrow \vec{\mu}_l = \frac{-e}{T} \cdot \pi r^2 \hat{n}$

$= \frac{-e}{2\pi} \omega \pi r^2 \hat{n}$

$\Rightarrow \mu_l = -\frac{e}{2} \omega r^2 \hat{n}$

$\vec{\mu}_l \to -\hat{n}$

$\vec{l} \to \hat{n}$

(anti parallel)

$\vec{l} = m\omega r^2 \hat{n}$; $\underline{\vec{\mu}_l = -\frac{e}{2m}\vec{l}}$

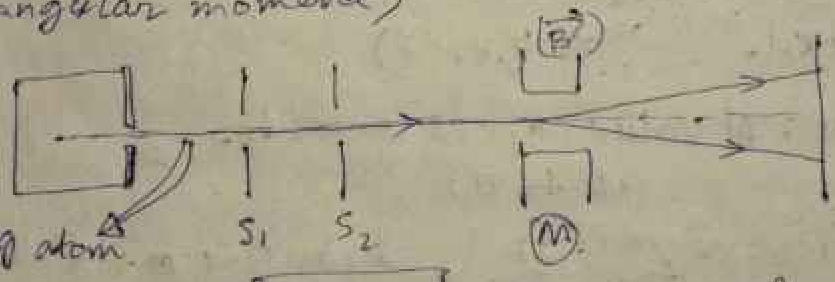
$\vec{l}$ is ~~~~ quantised as $\vec{l} = n\hbar$ so, $\mu_l = \frac{e\hbar}{2m} n$

so; $\mu_l = \mu_B n$ or, $\vec{\mu}_l = -\mu_B \cdot \frac{\vec{l}}{\hbar}$

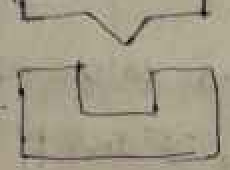
Bohr magneton; $\underline{\mu_B = \frac{e\hbar}{2m}} = 9.27\times 10^{-24}$ J/T or (A-m²)

Stern-Gerlach Expt. : (1921).

(To test whether microparticles had the angular moment)



M: (magnet).



$\vec{B}$: non-uniform.

(Atomic mag. dip. mom. $= \mu_l$)

Torque; $\vec{\tau} = \vec{\mu}_l \times \vec{B}$ while passing through the non uniform mag. field $\vec{B}$.

Pot. En. of interaction; $U = -\vec{\mu}_l \cdot \vec{B}$

Deflecting Force; $\vec{F} = -\nabla U = +\nabla(\vec{\mu}_l \cdot \vec{B})$

$\Rightarrow \vec{F} = (\vec{\mu}_l \cdot \vec{\nabla})\vec{B} + \vec{\mu}_l \underbrace{(\vec{\nabla}\cdot\vec{B})}_{\to 0}$

$\Rightarrow \vec{F} = \left(\mu_{lx}\frac{\partial}{\partial x} + \mu_{ly}\frac{\partial}{\partial y} + \mu_{lz}\frac{\partial}{\partial z}\right)\vec{B}(z)$

$\vec{B} = B(z)\hat{z}$ (Taking the z axis in variation)

So, $\vec{F} = \mu_{lz}\frac{\partial B(z)}{\partial z}\hat{z}$

$\Rightarrow F = -\frac{\mu_B}{\hbar} l\cos\theta \frac{\partial B}{\partial z}\hat{z}$

$\mu_{lz} = \vec{\mu}_l \cdot \hat{z} = -\frac{\mu_B}{\hbar}\vec{l}\cdot\hat{z}$

$= \frac{-\mu_B l\cos\theta}{\hbar}$

$l_z = l\cos\theta$

Displacement $= z$

$\vec{a} = \frac{\vec{F}}{m} = \frac{\mu_{lz}}{m}\frac{\partial B}{\partial z}\hat{z}$

m → mass of atom

$KE = \frac{1}{2}mv^2 = \frac{3}{2}k_BT \Rightarrow v = \sqrt{\frac{3k_BT}{m}}$

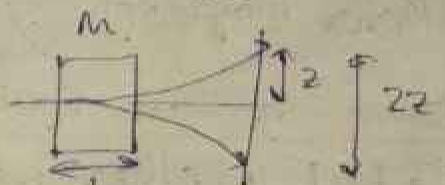
$z = \frac{1}{2}at^2 = \frac{a}{2}\left(\frac{L}{v}\right)^2 = \frac{a}{2}L^2\frac{m}{3k_BT} = \frac{mL^2a}{6k_BT}$

(as $u_z = 0$)

$\Rightarrow z = \frac{mL^2}{6k_BT}\frac{\mu_{lz}}{m}\frac{\partial B}{\partial z}$

$\Rightarrow z = \frac{\mu_{lz}L^2}{6k_BT}\frac{\partial B}{\partial z}$; $z \propto \frac{\partial B}{\partial z}$

If $\vec{B}$ is uniform; $z = 0$.
i.e. no deflection. (also $F = 0$)



From this relⁿ; μ_{lz} can be calculated. → (i.e. l)

Classical: All values of θ possible. (0 to π).

Result: $\vec{F} = -\hat{z}\frac{\mu_B l}{\hbar}\frac{\partial B}{\partial z} \Rightarrow \cos\theta = 1 \Rightarrow \theta = 0$

$= \hat{z}\frac{\mu_B l}{\hbar}\frac{\partial B}{\partial z} \Rightarrow \cos\theta = -1 \Rightarrow \theta = \pi$

$\theta = 0 \Rightarrow \vec{l} \parallel \vec{B}$; $\theta = \pi \Rightarrow \vec{l}$ anti $\parallel \vec{B}$

$l_z = l$; $l_z = -l$.

No. of possible proj. of $\vec{l}$ along $\vec{B}$ (i.e. no of l_z values) is given by $2l+1$.

So, $2l+1 = 2$ by expt. $\Rightarrow l = 1/2 \Rightarrow$ But l is $0, 1, 2, 3, \ldots$ (not accepted).
(as we got 2 strats)

So, we need another type of ang. mom. to explain it. It's the spin ang. mom.

Spin ang. mom. $\Rightarrow \vec{S}$. Quantum no. of $\vec{S} \Rightarrow s$

$(s = \frac{1}{2})$. [from $2s+1 = 2$]
(multiplicity of s).

Ag: $^2S_{1/2}$ $(l=0)$.

$B_z \uparrow$

$\uparrow \vec{S}$; $\theta = 0$; spin up.

$\downarrow \vec{S}$; $\theta = \pi$, spin down

Conclusion of Stern-Gerlach expt.:

1. Concept of spin confirmed by expt.
2. Space quantization. (2 discrete vals of θ).

- H, Li, Na, K, Cu, Au, Ag give ~~the~~ 2 traces.

Ang. mom., mag. dip. mom. and gyromagnetic ratio:
(g-factor)

(a) $\vec{l}, \vec{\mu_l}, g_l$: $\vec{\mu_l} = -g_l \mu_B \frac{\vec{l}}{\hbar}$

$g_l \Rightarrow$ orbital g factor.

$g_l = \frac{\mu_l / \mu_B}{l / \hbar} = 1$ for e^-.

$\vec{l}$: not an intrinsic prop. of e^-. It changes if e^- changes orbit.

(b) $\vec{S}, \vec{\mu_s}, g_s$: Anamolous Zeeman eff. can be explained if spin is considered.

μ_s: spin mag. dip. mom.

s: spin ang. mom.

$\mu_s = -g_s \mu_B \frac{\vec{S}}{\hbar}$; $g_s = \frac{\mu_s / \mu_B}{s / \hbar} = 2$ for e^-.

$\vec{S}$: intrinsic prop. of e^-.

The concept of spin has no classical analogy since, though $\vec{L} = \vec{r} \times \vec{p}$, we don't have similar expression for $\vec{S}$. So, $\vec{S}$ is a quantum ~~concept~~ concept.

(c) $\vec{J}, \vec{\mu_J}, g$: $\vec{J} = \vec{L} + \vec{S} \rightarrow$ Total ang. mom. of e^-.

$\vec{\mu_J}$: Total mag. dip. mom.

$\vec{\mu_J} = -g \mu_B \frac{\vec{J}}{\hbar} \rightarrow g = \frac{\mu_J / \mu_B}{J / \hbar}$

g : Lande g-factor.

Ang. momenta $\vec{l}, \vec{s}, \vec{J}$ as well as mag. dip mom. all precess about the mag. field dirn $\vec{B} = B\hat{z}$.

A. Principal Quantum no. (n):

Shell quantum no. (n): 1, 2, 3, 4, ...

Shell symbol : K, L, M, N, ...

B. Orbital Quantum no. (l).

C. Magnetic Q.N. (m_l).

$l = 0, 1, 2, 3, \ldots (n-1)$

Old Q.M. $\Rightarrow L = l\hbar$ - QM.: $\sqrt{l(l+1)}\,\hbar = L$.

$0, \hbar, 2\hbar, 3\hbar, \ldots$ $\quad$ $0, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar, \ldots$

$\sqrt{(n-1)n}\,\hbar$.

Symbol: $l = 0 \rightarrow s$, $l = 1 \rightarrow p$, $l = 2 \rightarrow d$,
$l = 3 \Rightarrow f$, $l = 4 \rightarrow g$, ...)

E_1 $(n=1) \rightarrow l = 0 \rightarrow 1s$.

E_2 $(n=2) \rightarrow l = 0, 1 \rightarrow 2s, 2p$.

E_3 $(n=3) \rightarrow l = 0, 1, 2 \rightarrow 3s, 3p, 3d$.

E_4 $(n=4) \rightarrow l = 0, 1, 2, 3 \rightarrow 4s, 4p, 4d, 4f$.

...

(En. levels of H-atom).

Space Quantization of $\vec{l}$: Not all val. of θ are allowed.

θ: Orientation of $\vec{l}$ wrt. $\vec{B} = B\hat{z}$.

$m_l = -l, -l+1, \ldots, -1, 0, 1, \ldots l-1, l$

Total $\underbrace{(2l+1)}_{\text{Multiplicity of } l}$ values of m_l.

$\frac{\vec{l}\cdot\vec{B}}{|\vec{B}|} = \vec{l}\cdot\hat{z} = l_z = l\cos\theta \Rightarrow \cos\theta = \frac{l_z}{l}$

Old QM : $\cos\theta = \frac{m_l\hbar}{l\hbar}$ $\rightarrow \cos\theta = \frac{m_l}{l}$ | New Q.M. : $\cos\theta = \frac{m_l\hbar}{\sqrt{l(l+1)}\,\hbar}$ $\rightarrow \cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$.

$l=2$

$m_l = -2, -1, 0, 1, 2 \rightarrow 5$ values

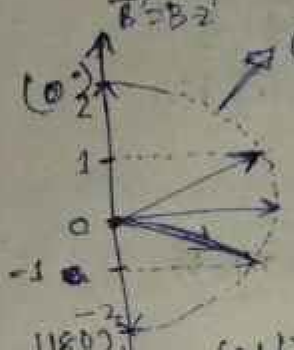
$l=2$: $\sqrt{(l+1)l}\,\hbar = \sqrt{6}\,\hbar$. ; $m_l = -2, -1, 0, 1, 2$.

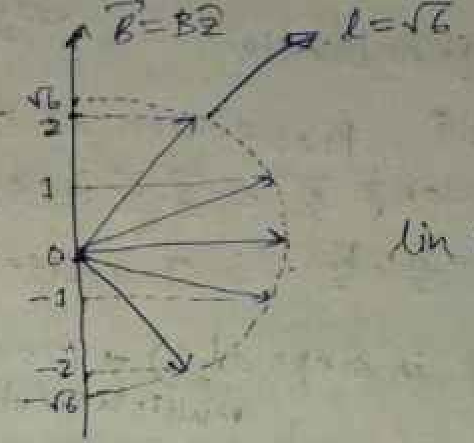
$\cos\theta = \frac{m_l \hbar}{\sqrt{l(l+1)}\hbar} = -\frac{2}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}$

$\Rightarrow \theta = 144.74°c, 114.09°, 90°, 65.91°, 35.26°$

~~Old~~ old: $\cos\theta = -1, -\frac{1}{2}, 0, \frac{1}{2}, 1$
$(l=2)$

$\Rightarrow \theta = 180°, 120°, 90°, 60°, 0$.





Spin

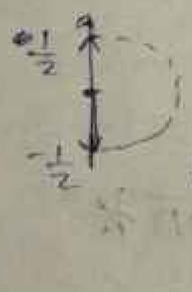
Old: $s\hbar = \frac{\hbar}{2}$

New: $\sqrt{s(s+1)}\,\hbar$. $m_s = -\frac{\hbar}{2}, \frac{\hbar}{2}$

$= \sqrt{\frac{1}{2}(\frac{1}{2}+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$.

OLD: $\cos\theta = \frac{m_s}{s} = -1, 1$

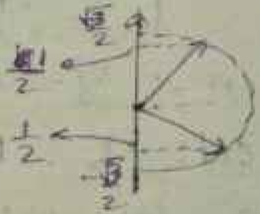
$\Rightarrow \theta = 180°, 0°$



New: $\cos\theta = \frac{m_s}{\sqrt{s(s+1)}}$

$= -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$

$\cos\theta = 125.26, 54.74$.

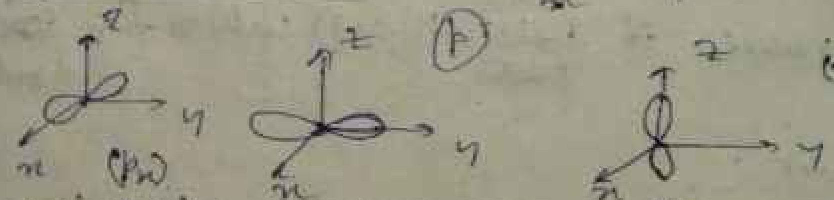


$m_l = 0, l = 0$: (s)

sym about nucleus.

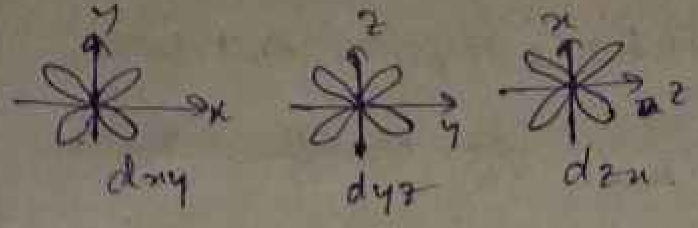
$l=1 \Rightarrow m_l = -1, 0, 1$

(p) (Total 6 lobes)



$l=2 \Rightarrow m_l = -2, -1, 0, 1, 2$: (d)

5 orientations: d_{xy}, d_{zx}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}
$(l, m_l) \Rightarrow$ (2,2) (2,1) (2,-1) (2,-2) (2,0)



Ang. mom. Quantum no.:

($l \to m_l$, $s \to m_s$, $j \to m_j$)

~~old~~ ~~old: $\sqrt{s(s+1)}$~~ old: $s\hbar$. New: $\sqrt{s(s+1)}\,\hbar$

$= \frac{\hbar}{2}$ $\quad = \sqrt{\frac{1}{2}\cdot\frac{3}{2}}\,\hbar$

Space quantisation: $\quad = \frac{\sqrt{3}}{2}\hbar$.

$\vec{B} = B\hat{z}$. Projection of $\vec{s}$ along $\vec{B} = \frac{\vec{s}\cdot\vec{B}}{B} = s_z$

$m_s = -\frac{\hbar}{2}, \frac{\hbar}{2}$. $\quad s^2 \to s(s+1)\hbar^2$, $s_z \to m_s\hbar$

↓

($-s$ to s in steps of 1) $\to$ $(2s+1)$ values

Multiplicity factor for s.

Old: $\cos\theta = \frac{m_s}{s}$

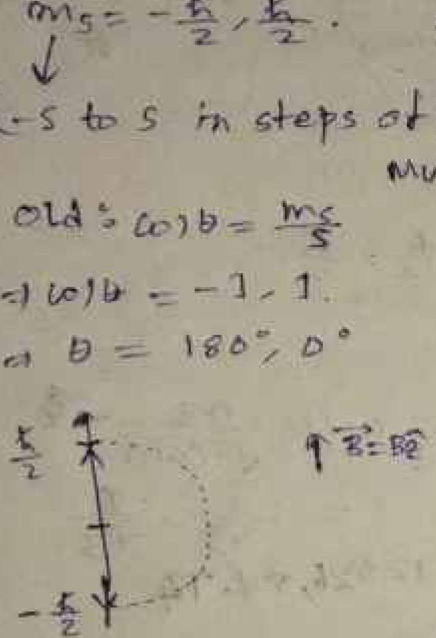
$\to \cos\theta = -1, 1$.

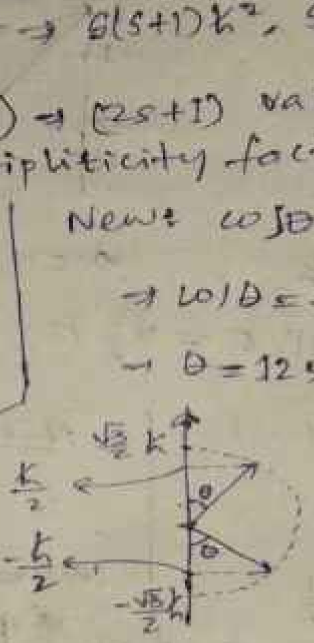
$\to \theta = 180°, 0°$

New: $\cos\theta = \frac{m_s}{\sqrt{s(s+1)}}$

$\to \cos\theta = -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$

$\to \theta = 125.26°, 54.74°$





Total ang. mom.: $\vec{J} = \vec{l} + \vec{s}$

Magnitude: Old: $j\hbar$. New: $\sqrt{j(j+1)}\,\hbar$.

For $l = 0$, $j = s$. $(m_j = m_l + m_s)$.

$l \neq 0 \to j = l+s, l+s-1, \ldots, |l-s|$.

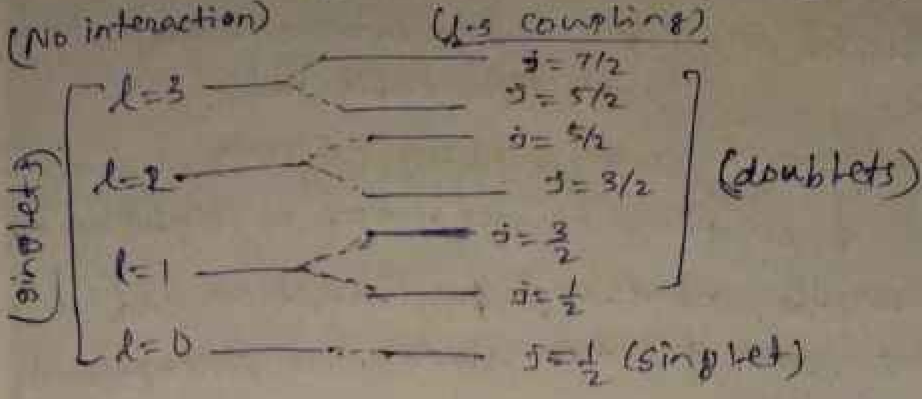
or, $j = |l-s|$ to $l+s$ in steps of 1

$(2l+1)$ values if $l<s$. $(2s+1)$ values for $l>s$.

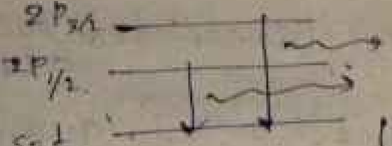
Fine Structure:

For a level $l \neq 0$ will split up into 2 levels (doublet). $j = l \pm \frac{1}{2}$. It's interaction of orbital and spin mag. moments. ~~It's~~ It's called spin-orbit (s-o) interaction or l-s coupling.

$l=0 \to j=\frac{1}{2}$. (singlet). $l=1$; $s=\frac{1}{2}$; $j=\frac{1}{2},\frac{3}{2}$ (doublet.



Selection rules based on Δl, and Δj.



5890Å, 5896Å.
(D_1 - D_2 lines). (Check)
(Na) ~~d_1, d_2 line~~

Space Quantisation: Old: $j\hbar$, New: $\sqrt{j(j+1)}\,\hbar$.
$m_j = -j$ to j in steps of 1.
$(2j+1)$ values.

Old: $\cos\theta = \frac{m_j}{j}$; $(2j+1)$ values. | New: $\cos\theta = \frac{m_j}{\sqrt{j(j+1)}}$; $(2j+1)$ values.

Diff types of interactions within an atom:
$\vec{\mu}_1, \vec{\mu}_2 \to$ mag. dipoles. μ_1, μ_2 interacts with each other.
Total pot. en. of interaction; $\Delta E = -\vec{\mu}_1 \cdot \vec{\mu}_2$

Mag. Dip. mom for orbital ang. mom.: $\vec{\mu}_l = -g_l \mu_B \frac{\vec{l}}{\hbar}$
" " " " spin " " : $\vec{\mu}_s = -g_s \mu_B \frac{\vec{s}}{\hbar}$
" " " " total " " : $\vec{\mu}_j = -g \mu_B \frac{\vec{j}}{\hbar}$

Multielectronic sys., following interactions are possible: (a) Interaction ~~b/w~~ ~~μ_1 and μ_2~~ ~~among~~ b/w $\vec{\mu}_l$s:
Int. en.: $\Delta E_l \propto -\vec{\mu}_{l_1} \cdot \vec{\mu}_{l_2} \propto \vec{l}_1 \cdot \vec{l}_2$
It's called l-l interaction
(b) Interaction b/w $\vec{\mu}_s$s:
$\Delta E_s \propto -\vec{\mu}_{s_1} \cdot \vec{\mu}_{s_2} \propto -\vec{s}_1 \cdot \vec{s}_2$
It's called s-s interaction
(c) Interaction b/w $\vec{\mu}_j$s: (j-j interaction)
$\Delta E_j \propto -\vec{\mu}_{j_1} \cdot \vec{\mu}_{j_2} \propto -\vec{j}_1 \cdot \vec{j}_2$

(2). Interaction b/w $\vec{\mu}_l$ and $\vec{\mu}_s$:

$\Delta E_{ls} \propto -\vec{\mu}_l \cdot \vec{\mu}_s \propto -\vec{l} \cdot \vec{s}$ (l-s interaction) or (spin-orbit int.).

1. Russel-Sanders or L-S coupling scheme:

This type of coupling is executed in light atoms. Here, strength of the l-l interaction and s-s interactions are greater than the strength of l-s interaction.

$\vec{l}$'s couple to form $\vec{L} = \sum_i \vec{l}_i$ (quantized vec. addition)

$\vec{s}$'s couple to form $\vec{S} = \sum_i \vec{s}_i$. (quantized vec. add).

Then; $\vec{L}$ and $\vec{S}$ couple to form, $\vec{L} + \vec{S} = \vec{J}$. (quantized vec. addition).

$2e^-$: $\vec{L} = \vec{l_1} + \vec{l_2}$.

$l_1 = 2$, $l_2 = 1$ → $L = 3$; $l_1 = 2$, $l_2 = 1$ → $L = 2$; $l_1 = 2$, $l_2 = 1$ → $L = 1$.

$\vec{S} = \vec{s_1} + \vec{s_2} + \vec{s_3}$ ($3e^-$). $|\vec{s_i}| = \frac{1}{2}$.

$s_1\ s_2\ s_3$ → $S = \frac{3}{2}$; $1\ 2\ 3$ → $S = \frac{1}{2}$

$\vec{S} = \vec{s_1} + \vec{s_2}$ ($2e^-$).

$1\ 2$ → $S = 1$; $1\ 2$ → $S = 0$.

Total: $j = l + s$; $l = 1$, $j = \frac{1}{2} \Rightarrow j = \frac{3}{2}, \frac{1}{2}$

Ang. Mom: $P_j = \sqrt{j(j+1)}\,\hbar$, $P_l = \sqrt{l(l+1)}\,\hbar$, $P_s = \sqrt{s(s+1)}\,\hbar$

$l = 2$, $s = \frac{1}{2}$

$\Rightarrow P_l = \sqrt{6}\,\hbar$. $P_s = \frac{\sqrt{3}}{2}\hbar$.

$j = |l + s| = \frac{5}{2} \Rightarrow P_j = \sqrt{\frac{5}{2}\cdot\frac{7}{2}}\,\hbar = \frac{\sqrt{35}}{2}\hbar$.

$= |l - s| = \frac{3}{2} \Rightarrow P_j = \sqrt{\frac{3}{2}\cdot\frac{5}{2}}\,\hbar = \frac{\sqrt{15}}{2}\hbar$

Ang. b/w. P_l and P_s is given by;

$$\cos\theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$$

2e⁻ sys.: $\vec{L} = \vec{l_1} + \vec{l_2}$ (coupling of $\vec{l_1}$ and $\vec{l_2}$)

$\vec{L} = |l_1 - l_2|$ to $(l_1 + l_2)$ in steps of 1.

$\Rightarrow 2l_1+1$ values if $l_1 < l_2$ and $2l_2+1$ values if $l_1 > l_2$.

Also; $\vec{S} = \vec{s_1} + \vec{s_2}$ (coupling of $\vec{s_1}$ and $\vec{s_2}$).

$\Rightarrow \vec{S} = |s_1 - s_2|$ to $(s_1 + s_2)$ in steps of 1.

$\vec{J} = \vec{L} + \vec{S}$. $\Rightarrow \vec{J} = |\vec{L} - \vec{S}|$ to $(\vec{L} + \vec{S})$ in steps of 1.

$\Rightarrow 2L+1$ values if $L < S$ and $2S+1$ values if $S < L$.

$l_1 = 1, s_1 = \frac{1}{2}$ (1st e⁻) and $l_2 = 2, s_2 = \frac{1}{2}$ (2nd e⁻).

$\vec{L} = |l_1 - l_2|$ to $(l_1 + l_2) = 1, 2, 3$. (coupling of $\vec{l_1}, \vec{l_2}$)

$\vec{S} = |s_1 - s_2|$ to $(s_1 + s_2) = 0, 1$. (coupling of $\vec{s_1}, \vec{s_2}$)

Now, $\vec{L}$ and $\vec{S}$ couple to form $\vec{J} = \vec{L} + \vec{S}$. ; $\vec{J} = |L - S|$ to $|L + S|$ in unit steps.

$(1,0) \Rightarrow \vec{J} = 1 \Rightarrow 1 = 2.0+1$ values

$(1,1) \Rightarrow \vec{J} = 0, 1, 2 \Rightarrow 3 = 2.1+1$ values

$(2,0) \Rightarrow \vec{J} = 2 \Rightarrow 2.0+1$ values

$(2,1) \Rightarrow \vec{J} = 1, 2, 3 \Rightarrow 2.1+1$ values.

$(3,0) \Rightarrow \vec{J} = 3 \Rightarrow 2.0+1$ values

$(3,1) \Rightarrow \vec{J} = 2, 3, 4 \Rightarrow 2.1+1$ values.

J-J coupling:

This type of coupling is exhibited in heavy atoms. Here, strength of the l-s interaction is greater than the strength of the l-l interaction and s-s interaction.

$\vec{l}$'s couples with $\vec{s}$'s to form $\vec{j}$'s as $\vec{j} = \vec{l} + \vec{s}$. (quantised vec. add.)

Then the $\vec{j}$'s couple as $\vec{J} = \sum_i \vec{j_i}$

2e⁻ $\vec{j_1} = \vec{l_1} + \vec{s_1} = |l_1 - s_1|$ to $(l_1 + s_1)$ in unit steps.

$(2l_1+1)$ values of $l_1 < s_1$ and $(2s_1+1)$ values if $s_1 < l_1$.

$\vec{j_2} = \vec{l_2} + \vec{s_2}$ (coupling of $\vec{l_2}$ and $\vec{s_2}$).

$\Rightarrow \vec{j_2} = |l_2 - s_2|$ to $(l_2 + s_2)$ in unit steps.

$\vec{j_1}$ and $\vec{j_2}$ couples as $\vec{j_1} + \vec{j_2} = \vec{J}$.

$\vec{J} = |j_1 - j_2|$ to $|j_1 + j_2|$ in unit steps.

$2j_1 + 1$ values if $j_1 < j_2$ and $2j_2 + 1$ values if $j_2 < j_1$.

Ex. $l_1 = 1$ (p state), $s_1 = \frac{1}{2}$, $l_2 = 2$ (d state), $s_2 = \frac{1}{2}$.
(1st electron) (2nd electron).

$\vec{j_1} = |l_1 - s_1|$ to $(l_1 + s_1) = \frac{1}{2}, \frac{3}{2}$

$\vec{j_2} = +\frac{3}{2}, \frac{5}{2}$.

$\vec{J} = |j_1 - j_2|$ to $(j_1 + j_2)$ in unit steps.

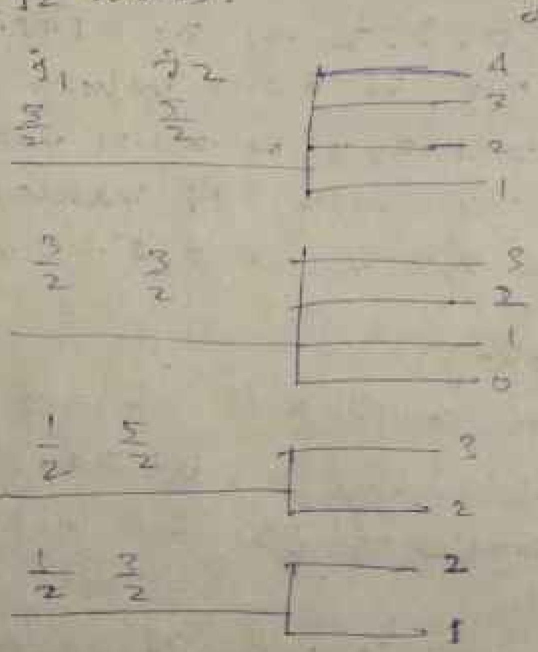
$(\frac{1}{2}, \frac{3}{2}) \Rightarrow \vec{J} = 1, 2 \Rightarrow 2j_1 + 1$ values

$(\frac{1}{2}, \frac{5}{2}) \Rightarrow \vec{J} = 2, 3 \Rightarrow 2j_1 + 1$ values

$(\frac{3}{2}, \frac{3}{2}) \Rightarrow \vec{J} = 0, 1, 2, 3 \Rightarrow 2(\frac{3}{2}) + 1$ values

$(\frac{3}{2}, \frac{5}{2}) \Rightarrow \vec{J} = 1, 2, 3, 4 \Rightarrow 2(\frac{3}{2}) + 1$ values

$\vec{J} \Rightarrow$ total 12 values.



Fine structure of states of Na alkali atoms:

① $l = 0$, $s = \frac{1}{2} \Rightarrow j = \frac{1}{2}$. No. of split levels = 1
(s state) (no splitting)
singlet.

Term of fine st. of alkali atom : $n\,^{2}S_{1/2}$

Principal quantum no.

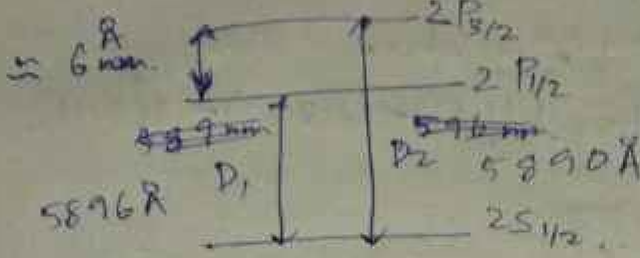
$2s + 1 = 2 \cdot \frac{1}{2} + 1 = 2$.

⊙ $l = 1$, $s = \frac{1}{2} \to j = \frac{1}{2}, \frac{3}{2} \Rightarrow$ no. of split lvl = 2
(p state). (doublet)

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

⊙ $l = 2$, $s = \frac{1}{2} \Rightarrow j = \frac{3}{2}, \frac{5}{2} \Rightarrow$ doublet $\Rightarrow n^2D_{3/2}, n^2D_{5/2}$
(d-state)

⊙ $l = 3$; $s = \frac{1}{2} \to j = \frac{5}{2}, \frac{7}{2} \Rightarrow$ doublet $\to n^2F_{5/2}, n^2F_{7/2}$
(f-state)



(Daniel and Stack)
(book)

Anamolous Zeeman effect:

If $\vec{L}$ and $\vec{S}$ represents the orbital and spin ang. mom. vectors (in units of $\hbar$), then their resultant $\vec{J}$ will be precessed about the dirn of mag. field. There are $2J+1$ possible orientations wrt. the field dirn. It's components in the field dirn being given by $m_J\hbar$; $m_J = -J$ to J in unit steps.

Resultant mag. dip mom. ~~that~~ of $\vec{J}$ is $\vec{\mu}_J$. $\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S$

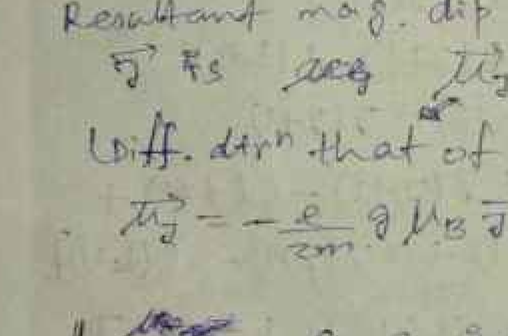
(Diff. dirn that of $\vec{J}$).

$$\vec{\mu}_L = -\frac{e}{2m} g_L \mu_B \vec{L}$$

$$\vec{\mu}_J = -\frac{e}{2m} g \mu_B \vec{J}$$

$$\vec{\mu}_S = -\frac{e}{2m} g_S \mu_B \vec{S}$$

$g_s = 2$. $g_L = 1$ ~~.~~ So, $\frac{\mu_L}{L}$ is half of $\frac{\mu_S}{S}$.



Dirn of $\vec{\mu}_J$ (corr. to $\vec{J}$) is in diff. dirn of $\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S$.

~~So~~ ~~As $\neq \mu_L$~~ $\mu_J \neq \mu_L + \mu_S$

$$\mu_J = \mu_L \cos(L, J) + \mu_S \cos(S, J)$$

As μ_L and μ_S precess about the dirn of J, the resultant $\vec{\mu}$ also precess about $\vec{J}$.

(The comp. ~~of~~ μ_J of μ along $\vec{J}$): $\mu_J = \mu_L \cos(L,J) + \mu_S \cos(S,J)$

~~Here~~ $L^2 \to L(L+1)$, $S^2 \to S(S+1)$, $J^2 \to J(J+1)$.

$$\cos(L,J) = \frac{L(L+1)+J(J+1)-S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}}$$

$$\cos(S,J) = \frac{S(S+1)+J(J+1)-L(L+1)}{2\sqrt{S(S+1)}\sqrt{J(J+1)}}$$

$\vec{S} = \vec{J} - \vec{L}$

$\Rightarrow S^2 = L^2 + J^2 - 2\vec{L}\cdot\vec{J}$

$\Rightarrow 2|\vec{L}||\vec{J}|\cos(L,J) = L(L+1)+J(J+1)-S(S+1)$.

$\vec{L} = \vec{J} - \vec{S}$

$\Rightarrow L^2 = J^2 + S^2 - 2\vec{J}\cdot\vec{S}$

$\Rightarrow 2|\vec{J}||\vec{S}|\cos(S,J) = S(S+1)+J(J+1)-L(L+1)$

Quantum mech. values of μ_J, μ_S are:

$$\vec{\mu}_L = \frac{-e}{2m_e}\underset{\approx 1}{g_L}\vec{L} = \frac{-e\hbar}{2m_e}\sqrt{L(L+1)}$$

similarly, $\mu_S = -\frac{e\hbar}{m_e}\sqrt{S(S+1)}$

So,
$$\mu_J = -\frac{e\hbar}{2m_e}\sqrt{L(L+1)}\,\frac{L(L+1)+J(J+1)-S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}} - \frac{e\hbar}{m_e}\sqrt{S(S+1)}\,\frac{S(S+1)+J(J+1)-L(L+1)}{2\sqrt{S(S+1)}\sqrt{J(J+1)}}$$

$$= -\frac{e\hbar}{2m_e}\frac{1}{\sqrt{J(J+1)}\cdot 2}[L(L+1)+J(J+1)-S(S+1)+2S(S+1)+2J(J+1)-2L(L+1)]$$

$$= \frac{-e\hbar}{4m_e\sqrt{J(J+1)}}[3J(J+1)+S(S+1)-L(L+1)]$$

$$= \frac{-e\hbar}{2m_e}\left[\sqrt{J(J+1)} + \frac{J(J+1)+S(S+1)-L(L+1)}{2\sqrt{J(J+1)}}\right]$$

$$\Rightarrow \mu_J = \frac{-e\hbar}{2m_e}\sqrt{J(J+1)}\underbrace{\left[1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right]}_{g}$$

$$\Rightarrow \mu_J = -\frac{e\hbar}{2m_e}g\sqrt{J(J+1)}$$

g = (Lande g-factor) or, splitting factor.

Thus, the splitting of the atomic en. levels in presence of mag. field of flux B is given by:

$E_B = -\mu_J B \cos(J,B) \Rightarrow E_B = g\mu_B B\sqrt{J(J+1)}\cos(J,B)$

Here, $\sqrt{J(J+1)}\cos(J,B)$ is the comp. of $\vec{J}$ along $\vec{B}$. If $\vec{B}$ is in $\hat{z}$; it's J_z and it has eig. val. m_J. | $\mu_B = \frac{eh}{2m_e}$

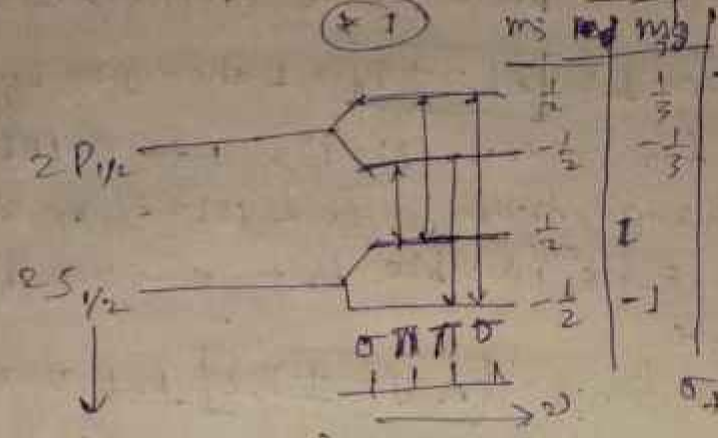
So; $E_B = g\mu_B B m_J$

Selection rule: $\Delta m_J = 0, \pm 1$.

~~$(m_J = m_L + m_S)$~~

~~$J_z = L_z + S_z$~~

(*1)



(Na D1 transition)

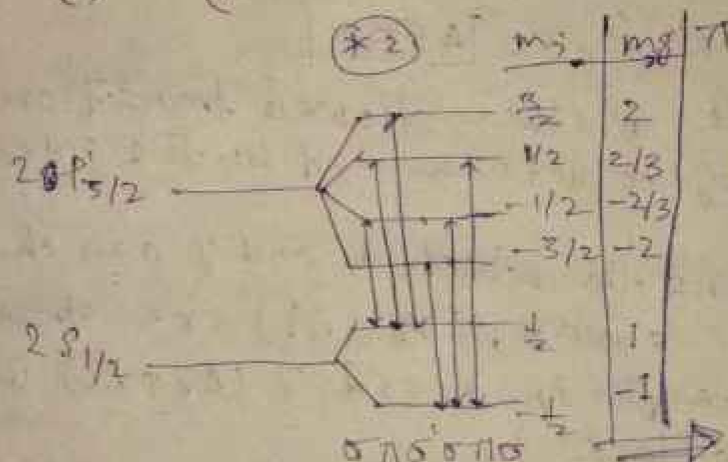
(i). (4 lines)

$\sigma_+ : \Delta m_J = +1$

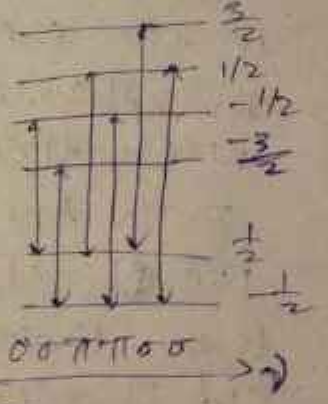
$\sigma_- : \Delta m_J = -1$

$\pi : \Delta m_J = 0$

(*2)



(Na D2 transition)



(6 lines)

Total 10 lines

(*1) $m_J = \frac{1}{2}, J = \frac{1}{2}, L = 1, S = \frac{1}{2}$; $g = 1 + \frac{\frac{3}{4} + \frac{3}{4} - 2}{2 \cdot 3/4} = 1 + \frac{4}{3}\left(\frac{-1}{2}\right)$

so, $m_J g = \frac{1}{2}\left(\frac{2}{3}\right) = \frac{1}{3}$ $\Rightarrow g = 1 - \frac{1}{3} = \frac{2}{3}$

$2S_{1/2} \Rightarrow g = 1 + \frac{\frac{3}{4} + \frac{3}{4} - 0}{2 \cdot 3/4} = 1 + 1 = 2$

(*2) $2P_{3/2} \Rightarrow g = 1 + \frac{\frac{15}{4} + \frac{3}{4} - 2}{2 \cdot 15/4} = 1 + \frac{4}{15 \cdot 2}\left(\frac{9}{2} - 2\right)$

$\Rightarrow g = 1 + \frac{2}{15}\cdot\frac{5}{2} = 1 + \frac{1}{3} \Rightarrow g = 4/3$

$2S_{1/2} \Rightarrow g = 2$

So, $2S_{1/2} \Rightarrow m_J g = 1, -1$, $2P_{1/2} \Rightarrow m_J g = \frac{1}{3}, -\frac{1}{3}$

$2P_{3/2} \Rightarrow m_J g = 2, \frac{2}{3}, -\frac{2}{3}, -2$

1. Spectral Notation: Multiplicity: $2S+1$.

- A state with $L=1$, $S=\frac{1}{2}$, $J=\frac{3}{2}$.

$L=\sum_i l_i$, $S=\sum_i s_i$. Multiplicity $= 2\cdot\frac{1}{2}+1=2$

$L=1 \Rightarrow$ P state. Notation: $^2P_{3/2} \Rightarrow {}^{2S+1}P_J$

- A state with $L=2$ (D), $S=1$ and $J=2$.

Notation: $^{2S+1}D_J \Rightarrow {}^3D_2$ (triplet D two).

Selection rules for L: $\boxed{\Delta L=\pm 1}$ $\Rightarrow$ L changes by ± 1.

So, L can change from 0 to 1 ($\Delta L=1$), 1 to 0 ($\Delta L=-1$), but L cannot change from 0 to 2 ($\Delta L=2$) or 2 to 0, i.e. $S\rightarrow P$ and $P\rightarrow S$ are possible but $S\rightarrow D$ and $D\rightarrow S$ are not possible.

Selection rules for J: $\boxed{\Delta J=\pm 1, 0}$ but $0\rightarrow 0$ excluded.

Selection rule for S: $\boxed{\Delta S=0}$

Intensity rule: whether allowed transition is weak or strong is determined by the intensity rules:

1. Transitions for which L and J can change in the same way; ($\Delta J=\Delta L$) are strong. For other changes in L and J ($\Delta J\neq\Delta L$) we get weak transitions.
2. The transition for which L and J increases (i.e. $L\rightarrow L+1$ and $J\rightarrow J+1$) are less intense than those for which L and J decreases ($L\rightarrow L-1$ and $J\rightarrow J-1$).
3. The transition for which changes in L and J are opposite ($\Delta L=-\Delta J$), are forbidden.

- $\Delta L=-1$, $\Delta J=-1$ (strongest)

$\Delta L=-1$, $\Delta J=0$ (less intense)

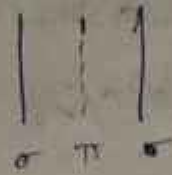
$\Delta L=1$, $\Delta J=1$ (weak)

$\Delta L=1$, $\Delta J=0$ (very weak)

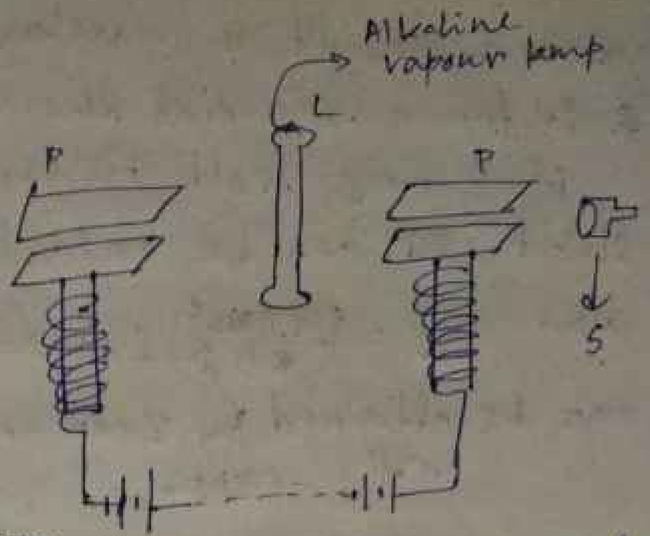
$\left.\begin{array}{l}\Delta L=-1,\ \Delta J=+1\\ \Delta L=1,\ \Delta J=-1\end{array}\right\}$ (forbidden)

Zeeman Effect:

L: Lamp.
S: spectrometer.

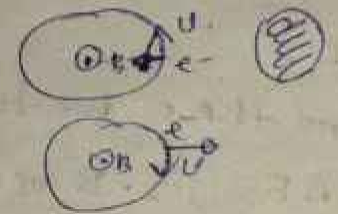


(Normal Zeeman effect)



consider an e^- in the atom moving in circular orbit of radius r with a linear velocity v and angular velocity ω. | e: charge, m_e: mass

centripetal force on e^- towards the center in absence of the mag. field is; $F = \frac{mv^2}{r} = m\omega^2 r$.



In presence of the mag. field, the motion of e^- becomes complex and an extra radial force is added. It's called Lamor precession.

Let; $\delta\omega$ be the change in angular vel. caused by the field. For circular motion in the c/w dir^n; the additional radial force is away from the center.

So; $F - evB = m(\omega+\delta\omega)^2 r$ | $F = m\omega^2 r$, $v = \omega r$

$\rightarrow m\omega^2 r - m(\omega+\delta\omega)^2 r = e(\omega r)B$

$\rightarrow m\omega^2 r - m\omega^2 r - 2m\omega\,\delta\omega\, r = eB\omega r$ (neglecting $\delta\omega^2$)

$\Rightarrow \delta\omega = -\frac{eB}{2m}$

For anti clockwise vel.; $F + evB = m(\omega+\delta\omega)^2 r$.

$\rightarrow \delta\omega = \frac{eB}{2m}$

So; $\delta\omega = \pm\frac{eB}{2m}$

combination of the 2 cases.

Now; $\omega = 2\pi\nu$
and $\delta\omega = 2\pi\delta\nu$

$\Rightarrow \delta\nu = \frac{\delta\omega}{2\pi} = \pm\frac{eB}{4\pi m}$

(change in freq. spectral line).

$\nu = \frac{c}{\lambda} \rightarrow \delta\nu = -\frac{c}{\lambda^2}\delta\lambda \Rightarrow \delta\lambda = -\frac{\lambda^2}{c}\delta\nu$

Zeeman shift in wavelength: $\delta\lambda = \pm \frac{eB\lambda^2}{4\pi mc}$.

So for a spectral line of known wave len. (λ), if B mag. field is applied; the Zeeman shift $\delta\lambda$ can be calculated and measured.

Now, $\frac{e}{m} = \left(\frac{4\pi c}{B\lambda^2}\right)\delta\lambda \Longrightarrow 1.757\times10^{11}\ C/kg$.

can be obtained by Zeemann eff. expt.

Larmor's theorem: The eff. of a mag. field on an e^- moving in an orbit is to super-impose on the orbital motion a precession motion of the entire orbit about the dirn of mag. field with ang. vel. ω given by $\omega = \frac{eB}{2m}$.

Orbital ang. mom.: $L = \frac{lh}{2\pi}$ $(= l\hbar)$.

Mag. mom.: $\mu_L = \frac{lh}{2\pi}\cdot\frac{e}{2m} = \frac{e}{2m}\cdot L$.

$\omega = \frac{eB}{2m}$. Additional en. of the e^- due to this precessional motion is, $\Delta E = \mu_L \cdot B\cos\theta$

$\Rightarrow \Delta E = \frac{eB}{2m}\frac{lh}{2\pi}\cos\theta = \frac{eB}{2m} l\hbar\cos\theta$

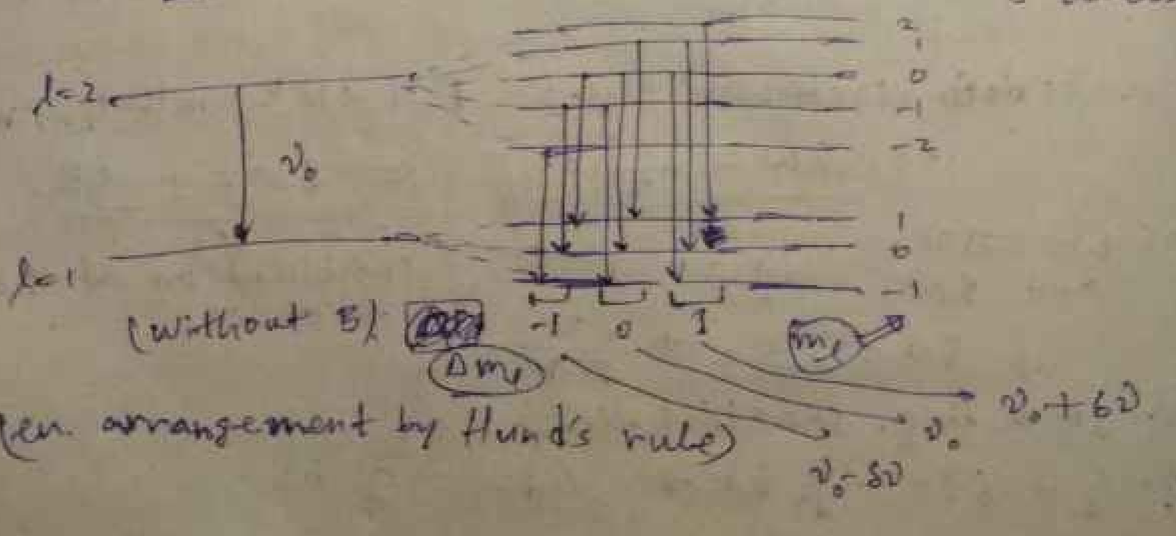
so, $\Delta E = \frac{eB}{2m}\hbar m_l \Rightarrow \Delta E = m_l\omega\hbar$ $(l\cos\theta \to m_l)$

$m_l \to 2l+1$ values from $-l$ to l in unit steps.

So, in an ext. mag. field, the spectral line will split in a single en. level to $(2l+1)$ levels.

For D state; $l=2$; $m_l = -2,-1,0,1,2 \to 5$ values.

$\Delta E = -2\omega\hbar, -\omega\hbar, 0, \omega\hbar, 2\omega\hbar \Rightarrow$ splitting into 5 levels.



(en. arrangement by Hund's rule)

Let, E_0' represent the en. of level $l=1$ in absence of mag. field and E_B' represents that en. in presence of mag. field B. $E_B' = E_0' + \Delta E'$

$\Rightarrow E_B' = E_0' + m_l' \hbar\omega$; $\omega = \frac{eB}{2m}$; $m_l' = -1, 0, 1$

Similarly E_0'' and E_B'' are for the level $l=2$.

So, $E_B'' = E_0'' + \Delta E'' = E_0'' + m_l'' \hbar\omega$;

$m_l'' = -2, -1, 0, 1, 2$.

$E_B'' - E_B' = (E_0'' - E_0') + (m_l'' - m_l')\hbar\omega$

$\Rightarrow h\nu = h\nu_0 + \Delta m_l \, h\frac{\omega}{2\pi}$.

$\Rightarrow \nu = \nu_0 + \Delta m_l \frac{\omega}{2\pi} = \nu_0 + \Delta m_l \frac{eB}{4\pi m}$

$\hookrightarrow$ freq. in absence of mag. field

$\Delta m_l = -1 \Rightarrow \nu = \nu_0 - \delta\nu$, $\Delta m_l = 0 \Rightarrow \nu = \nu_0$;

$\Delta m_l = 1 \Rightarrow \nu = \nu_0 + \delta\nu$; $\delta\nu = \frac{eB}{4\pi m} = \frac{\omega}{2\pi}$.

(Normal Zeeman effect)

Q.

1. Pauli Exclusion Principle: No 2 identical fermions can exist in the same quantum ~~sta~~ state; i.e. can have all their quantum numbers equal.

Quantum no. : (n, l, s, m_l, m_s) ~~j, m_j~~

or (n, l, s, j, m_j)

2 e in 2p : (same orbital) (2 p_x orbital)

n	l	s	m_l	m_s
2	1	1/2	1	1/2
2	1	1/2	1	-1/2

$\rightarrow$ diff.

Aufbau Principle (or, building up principle):

In the gnd state of a neutral atom e tend to occupy orbitals in the increasing order of energies starting from lowest energy orbital to the highest energy orbital. Energy values in ascending series:

~~1s<2s<3s<2p~~ $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \ldots$

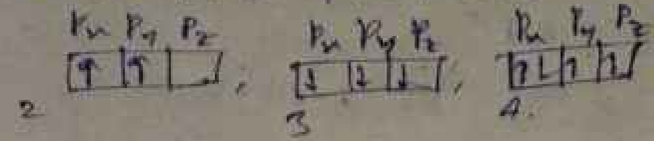
- $(n+l)$ rule
- If $(n+l)$ is same for 2 states; then higher n corresponds to higher energy state.

State $\rightarrow$	4s	3d	6s	4f	4d	5d
$n \rightarrow$	4	3	6	4	4	5
$l \rightarrow$	0	2	0	3	2	2
$n+l \rightarrow$	4	5	6	7	6	7

(4f < 5d)

(4d < 6s)

Hund's rule: Orbital having same 'l' are filled up with same spins first.



1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f

same (n+l) line

Paschen Back Effect:

- Strong magnetic field.
- Result is similar to normal Zeeman effect (3 lines).

In a strong mag. field the coupling b/w $\vec{L}$ and $\vec{S}$ breaks down and total angular mom. vector $\vec{J}$ become insignificant. In that case $\vec{L}$ and $\vec{S}$ become quantized ~~sep~~ separately and precess separately about the mag. field.

Total mag. dip. mom. $\vec{\mu} = \vec{\mu}_l + \vec{\mu}_s$

$$\vec{\mu}_l = -\mu_B \frac{\vec{L}}{\hbar} = -\frac{e}{2m}\vec{L}, \quad \vec{\mu}_s = -2\mu_B \frac{\vec{S}}{\hbar} = -\frac{e}{2m}2\vec{S}$$

So, $\vec{\mu} = -\frac{e}{2m}(\vec{L} + 2\vec{S})$

In presence of mag. field; the change in energy of the atomic levels due to $\vec{L}$ is;

$$\Delta E_l = -\vec{\mu}_l \cdot \vec{B} = -(\mu_l) B \cos(\mu_l, B)$$

$$\Rightarrow \Delta E_l = \frac{e}{2m}|\vec{L}| B \cos(\vec{L}, \vec{B}) = \frac{e\hbar}{2m}\sqrt{l(l+1)}\, B \cos(\vec{L}, \vec{B})$$

Now, $\cos(\vec{L}, \vec{B}) = \frac{L_z}{|L|} = \frac{m_l}{\sqrt{l(l+1)}}$

So, $\Delta E_l = \frac{e\hbar}{2m} m_l B$ $\qquad \cos(\mu_l, B) = -\cos(L, B)$

For $\vec{S}$; $\Delta E_s = 2 \cdot \frac{e\hbar}{2m} m_s B$

$$\Delta E = \Delta E_l + \Delta E_s = \frac{e\hbar}{2m} B (m_l + 2m_s)$$

$\Delta E = h\Delta\nu$; $\quad \Delta\nu = \frac{eB}{4\pi m}(m_l + 2m_s)$

The quantity $(m_l + 2m_s)$ is called the strong field quantum no.

Selection rule: $\Delta m_l = 0, \pm 1, \; \Delta m_s = 0$.

So: $\Delta m_l + 2\Delta m_s = 0, \pm 1$ (selection rule for transition),

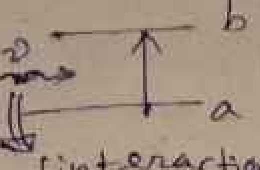
So: in a strong mag. field a given spectral line becomes a triplet that is, shows normal zeeman effect irrespective of its behaviour in a weak mag. field.

② Hamiltonian: $H = H_0 + H_I$

H → total; H_0 → unperturbed; H_I → for interaction; (perturbed)

2 level sys.

$$H_0 = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix}$$



$E = E_0 \cos\nu t$ field.

$$H_I = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

$H = -\vec{\mu}\cdot\vec{E}$.

So; $H_{12} = -\mu_{12} E_0 \cos\nu t$

$H_{21} = -\mu_{21} E_0 \cos\nu t$

$(H_{11} = H_{22} = 0)$

So; $H = H_0 + H_I = \begin{pmatrix} E_a & -\mu_{ab} E_0 \cos\nu t \\ -\mu_{ba} E_0 \cos\nu t & E_b \end{pmatrix}$

$(\psi = c_a\psi_a + c_b\psi_b)$

<u>Stark effect</u>: splitting of en. levels of an atom caused by a uniform electric field (external) $\vec{E}$, is called Stark effect.

H atom: $\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} - eEz\right]\psi = W\psi$

$-eEz$ → extra pot.

z → displacement.

$E = F.z = -eEz$

Unperturbed Hamiltonian:

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

Perturbed (1st order) Hamiltonian: (for 1st order stark effect; only $-eEz$ is taken)

$H' = -eEz$; $z = r\cos\theta$; $H' = -eEr\cos\theta$

1st order perturbation energy in gnd. state:

$E_1' = \int \psi_{100}^* H' \psi_{100} d\tau$,

$= \int \frac{1}{\pi a_0^3} e^{-2r/a_0} (-eEr\cos\theta) r^2 \sin\theta \, dr\, d\theta\, d\phi$

$= \frac{2\pi}{\pi a_0^3} \int_0^\infty e^{-2r/a_0} r^3 dr \int_0^\pi \sin\theta\cos\theta d\theta$ → 0

$(E_1' = \langle\psi_{100}|H'|\psi_{100}\rangle)$,

$\psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$

$\Rightarrow \cancel{E_1' = -\frac{2}{a_0^5} eE}$ $\Rightarrow \underline{E_1' = 0}$

(No 1st order Stark effect for gnd state of H-atom). For 1st order; $E \simeq 10^5$ V/cm.