Week 8 Lecture 1

ANGULAR MOMENTUM IN Q.M.

- MOST IMPORTANT CHAPTER: SECTION 5 (SUMMARY)
- Prepare copies/transparencies for plots of spherical harmonics ≡ "the shapes of atoms"

• EVIDENCE FOR QUANTISATION OF A.M.

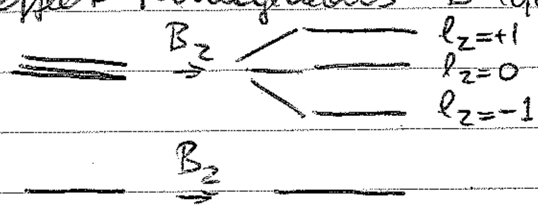
◦ Early experimental evidence atoms in magnetic fields $\vec{B}$

- Zeeman effect homogeneous $\vec{B}=(0,0,B_z)$ potential energy

$E_n = -\frac{13.6\,eV}{n^2}$

$n=2,\ l=1$

$n=1,\ l=0$



$\Delta V = -\vec{\mu}\cdot\vec{B},\ \vec{B}=\begin{pmatrix}0\\0\\B_z\end{pmatrix}$

$\vec{\mu} = -\mu_B g \vec{L}/\hbar$

degeneracy of line spectra lifted! $\Delta V = -\frac{\mu_B g}{\hbar} L_z B_z$

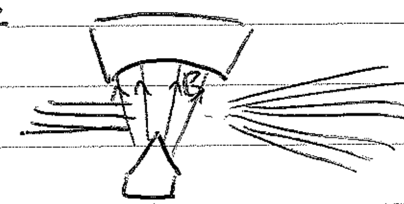
not covered

- Stern-Gerlach inhomogeneous $\vec{B}$

$\Rightarrow$ force on beam of particles

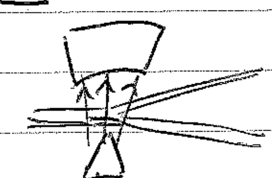
$F_z \sim \frac{\partial B_z}{\partial z} J_z$

classically



continuous distribution

in Q.M. reality e.g.



$S_z=+\frac{1}{2}$

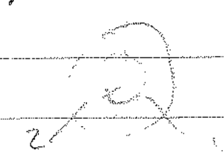
$S_z=-\frac{1}{2}$

Spin $\frac{1}{2}$ Silver atom

ORBITAL A.M. OPERATORS AND ITS COMMUTATORS

Compare with S.H.O: we had only $\hat{a}, \hat{a}^\dagger$ $[\hat{a}, \hat{a}^\dagger] = 1$
all needed!

Classically: $\vec{L} = \vec{r} \times \vec{p}$ $\quad L_x = y p_z - z p_y$



$$\Big\Downarrow \text{ OPERATOR POSTULATE}$$

$$\vec{r} \Rightarrow \hat{\vec{r}} = (x, y, z) = \vec{r}, \quad \vec{p} \Rightarrow \hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar \nabla$$

$$= -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

Q.M. AM operators

$$\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} = -i\hbar\, \vec{r} \times \nabla = -i\hbar \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

In Cart. coordinates

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = y \hat{p}_z - z \hat{p}_y$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = z \hat{p}_x - x \hat{p}_z$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = x \hat{p}_y - y \hat{p}_x$$

ARE THEY HERMITIAN? YES $\hat{\vec{L}} = \hat{\vec{L}}^\dagger$

Why: e.g. $(\hat{L}_z)^\dagger = (x\hat{p}_y - y\hat{p}_x)^\dagger = \hat{p}_y x - \hat{p}_x y$

$$= x\hat{p}_y - y\hat{p}_x$$

SINCE $x = x^\dagger$, $\hat{\vec{p}}^\dagger = \hat{\vec{p}}$

$[x, \hat{p}_y] = 0$ ...

COMMUTATORS USE $[x_i, x_j] = [\hat{p}_i, \hat{p}_j] = 0$

$[x_i, \hat{p}_j] = i\hbar\delta_{ij}$

$$[\hat{L}_x, \hat{L}_y] = [y\hat{p}_z - z\hat{p}_y, z\hat{p}_x - x\hat{p}_z]$$

$\boxed{\text{EXAM QUESTION}}$

DISTRIBUTIVITY: $= [y\hat{p}_z, z\hat{p}_x] - [y\hat{p}_z, x\hat{p}_z] - [z\hat{p}_y, z\hat{p}_x]$

$+ [z\hat{p}_y, x\hat{p}_z]$

$$= y\hat{p}_x \underbrace{[\hat{p}_z, z]}_{-i\hbar} - 0 - 0 + x\hat{p}_y \underbrace{[z, \hat{p}_z]}_{+i\hbar}$$

$$= i\hbar \underbrace{(x\hat{p}_y - y\hat{p}_x)}_{\hat{L}_z} = i\hbar\hat{L}_z$$

OTHER POSSIBILITIES $x \to y \to z \to x$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

- IF $\hat{L}_z$ IS MEASURED PERFECTLY $\Delta L_z = 0$
  THEN $\Delta L_x \neq 0, \Delta L_y \neq 0$
- eigenstate of $\hat{L}_z$ <u>cannot</u> be eigenstate of $\hat{L}_x, \hat{L}_y$ as well

<u>BUT THERE IS ANOTHER OPERATOR</u>

WHICH COMMUTES WITH $\hat{L}_i$ $i = x, y, z$

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

A USEFUL IDENTITY

$$[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$$

$$= \hat{A}\hat{A}\hat{B} - \cancel{\hat{A}\hat{B}\hat{A}} + \cancel{\hat{A}\hat{B}\hat{A}} - \hat{B}\hat{A}\hat{A}$$

$$= [\hat{A}^2, \hat{B}] \checkmark$$

$$[\hat{L}_x^2, \hat{L}_z] = \hat{L}_x \underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar\hat{L}_y} + \underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar\hat{L}_y}\hat{L}_x$$

$$= -i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$$

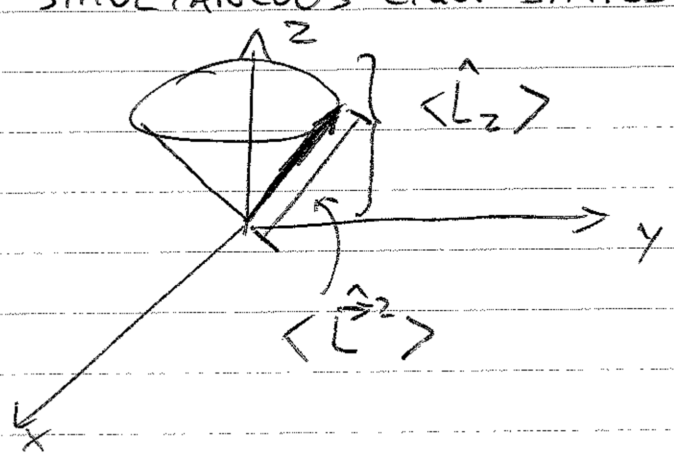
$$[\hat{L}_y^2, \hat{L}_z] = \ldots = +i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$$

$$[\hat{L}_z^2, \hat{L}_z] \stackrel{?}{=} 0$$

$$\boxed{[\hat{\vec{L}}^2, \hat{L}_z] = 0}$$ ALSO $[\hat{\vec{L}}^2, \hat{L}_x] = [\hat{\vec{L}}^2, \hat{L}_y] = 0$

$\Rightarrow$ • can measure $\hat{\vec{L}}^2$ AND $\hat{L}_z$ simultaneously (not L_x, L_y)

• SIMULTANEOUS EIGEN STATES !



end Lecture 1
Week 8

$\hat{\vec{L}}$ IN SPHERICAL COORDINATES

IF WE HAVE SPHERICAL SYMMETRY

$$V(x,y,z) = V(|\vec{r}|)$$

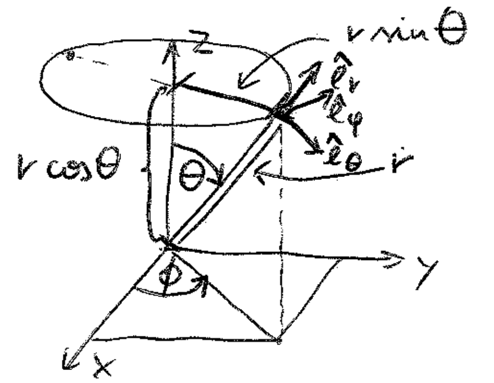
$$\boxed{\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}}$$

V does not depend on θ, ϕ!

$r = 0..\infty$, $\theta = 0..\pi$, $\phi = 0..2\pi$

SEE LECTURE NOTES ALTERNATIVE + MORE COMPLETE DERIVATION:

Recall: $dx\,dy\,dz = r^2 \sin\theta\, dr\, d\theta\, d\phi$



$\vec{L}$ IN SPHERICAL COORDINATES

E.g. $\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

USE CHAINRULE

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$r = \sqrt{x^2+y^2+z^2}, \quad \phi = \arctan(y/x), \quad \theta = \arctan\left(\frac{\sqrt{x^2+y^2}}{z}\right)$$

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2+y^2+z^2}} = \frac{x}{r} = \sin\theta\cos\phi$$

SIMILARLY $\frac{\partial r}{\partial y} = \sin\theta\sin\phi$

$$\frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}, \quad \frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r}$$

$$\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta}, \quad \frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}$$

$$x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} =$$

$$= r\sin\theta\cos\phi\left(\cancel{\sin\theta\sin\phi\frac{\partial}{\partial r}} + \cancel{\frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$- r\sin\theta\sin\phi\left(\cancel{\sin\theta\cos\phi\frac{\partial}{\partial r}} + \cancel{\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$= (\cos^2\phi + \sin^2\phi)\frac{\partial}{\partial\phi} = \frac{\partial}{\partial\phi} \longrightarrow$$ eigenstates $e^{im\phi}$ Periodicity!

$$\Rightarrow \boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}}$$ (relation to rotation around z-Axis!)

$$\boxed{\begin{aligned}
\hat{L}_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
\hat{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
\hat{\vec{L}}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}
\end{aligned}}$$

without proof

NOW LETS LOOK AT 3D ~~TDSE EQN~~ $\hat{H}$

$\hat{L}_{x,y,z} f(r) = 0!$

IT CONTAINS $\frac{1}{2m}\hat{\vec{P}}^2 = -\frac{\hbar^2}{2m}\nabla^2 = E_K$

IN SPHERICAL COORDINATES

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2}$$

"Centrifugal potential"

COMPARE THIS CLASSICAL KINETIC ENERGY

USE $|\vec{p}\cdot\vec{r}|^2 + |\vec{r}\times\vec{p}|^2 = |\vec{r}|^2\,|\vec{p}|^2$ $\quad |\vec{r}|=r$

$$\boxed{\begin{aligned}\frac{\vec{r}}{r}&=\hat{r}\\ \vec{r}\times\vec{p}&=\vec{L}\end{aligned}}$$

$$E_{KIN} = \frac{1}{2m}|\vec{p}|^2 = \frac{1}{2m}\,\frac{|\vec{p}\cdot\vec{r}|^2 + |\vec{r}\times\vec{p}|^2}{r^2}$$

$$= \frac{1}{2m}\left(\left(\vec{p}\cdot\hat{r}\right)^2 + \frac{\vec{L}^2}{r^2}\right)$$

$$= \frac{1}{2m}\,p_r^2 + \frac{\vec{L}^2}{2mr^2}$$

p_r … momentum in radial direction

- IF WE REPLACE $p_r \to \hat{p}_r = -i\hbar\frac{\partial}{\partial r}$ we almost get the Q.M. kinetic operator! except for term $\boxed{-i\hbar\,\frac{\hat{p}_r}{mr}}$

FOR CENTRAL POTENTIALS IN 3D (LIKE H-ATOM)

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2} + V(r)$$

central Pot.

- $\hat{H}$ commutes with $\hat{\vec{L}}^2$ and all $\hat{L}_i$!

$$[\hat{H},\hat{L}_i]=0=[\hat{H},\hat{\vec{L}}^2]$$

FOR central potential!

$\Rightarrow \vec{L}$ conserved

$$\boxed{\frac{d}{dt}\langle\hat{\vec{L}}\rangle=0}$$

END OF Lecture 2 Week 8

Lecture 3 of Week 8 →

Quantisation of orbital A.M. (distinct from spin (internal) A.M.)

Maximum set of commuting operators
$\{\hat{H}, \hat{\vec{L}}^2, \hat{L}_z\}$

EIGENSTATES OF ENERGY ARE ALSO EIGENSTATES OF $\hat{\vec{L}}^2$ AND $\hat{L}_z$

we will find

$$\boxed{\begin{array}{ll} \text{IF} \quad \hat{H}\psi_E(\vec{r}) = E\psi_E(\vec{r}) & \\ \text{then} \quad \hat{\vec{L}}^2\psi_E(\vec{r}) = \hbar^2 l(l+1)\psi_E(\vec{r}) & l = 0, 1, 2, 3, \ldots \\ \text{and} \quad \hat{L}_z\psi_E(\vec{r}) = \hbar m\, \psi_E(\vec{r}) & m = \underbrace{-l, -l+1, \ldots, +l}_{2l+1} \end{array}}$$

VERY IMPORTANT!

TWO APPROACHES AS FOR S.H.O

1) find eigenfunctions by solving TISE $\Rightarrow$ SEPARATION OF VARIABLES
$$\psi = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

2) OPERATOR METHOD THIS LEADS TO THE POSSIBILITY THAT l, m can be half-integer! $\Rightarrow$ Possibility of spin

MATHEMATICAL POSSIBILITY WHICH NATURE MAKES USE OF!

ADDITIONAL NOTES

without proof

$$\hat{L}_x = i\hbar\left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi}\right)$$
$$\hat{L}_y = -i\hbar\left(\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$
$$= -\hbar^2\Big\{ \left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$
$$+ \left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$
$$+ \frac{\partial^2}{\partial\phi^2}\Big\}$$

$$= -\hbar^2\left\{ \frac{\partial^2}{\partial\theta^2} + \underbrace{\cot\theta}_{\frac{\cos\theta}{\sin\theta}}\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\phi^2}\right\}$$

$$= -\hbar^2\left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}$$

$$\Rightarrow \frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2}$$

centrifugal force

compare with classical expression for E_{KIN}

$$\frac{1}{2m}\vec{p}^2 = \frac{1}{2m}p_r^2 + \frac{\vec{L}^2}{2mr^2} \qquad |\vec{p}\cdot\vec{r}|^2 + |\vec{r}\times\vec{p}|^2 = |\vec{r}|^2|\vec{p}|^2$$

$$|\vec{p}|^2 = \underbrace{\frac{|\vec{p}\cdot\vec{r}|^2}{|\vec{r}|^2}}_{=p_r^2} + \frac{\vec{L}^2}{|\vec{r}^2|}$$

$$\hat{L}_z = -i\hbar(x\partial_y - y\partial_x) = x\hat{p}_y - y\hat{p}_x$$

$$\hat{L}_x = -i\hbar(y\partial_z - z\partial_y) = y\hat{p}_z - z\hat{p}_y$$

$$\hat{L}_y = -i\hbar(z\partial_x - x\partial_z) = z\hat{p}_x - x\hat{p}_z \qquad [x,\hat{p}_x] = i\hbar \ldots$$

$$[\hat{L}_x,\hat{L}_y] = [y\hat{p}_z - z\hat{p}_y,\; z\hat{p}_x - x\hat{p}_z]$$

$$= [y\hat{p}_z, z\hat{p}_x] \mp [y\hat{p}_z, x\hat{p}_z]$$

$$-[z\hat{p}_y, z\hat{p}_x] + [z\hat{p}_y, x\hat{p}_z]$$

$$= y\hat{p}_x\underbrace{[\hat{p}_z, z]}_{-i\hbar} - 0 - 0 + x\hat{p}_y\underbrace{[z,\hat{p}_z]}_{i\hbar}$$

$$= i\hbar(x\hat{p}_y - y\hat{p}_x) = \underline{\underline{i\hbar\hat{L}_z}}$$

$$\Rightarrow \hat{\vec{L}} \times \hat{\vec{L}} = i\hbar\hat{\vec{L}} \quad ✓$$

$$[\hat{\vec{L}}^2, \hat{L}_z] = 0$$

<u>Proof</u> $\quad [\hat{L}_x^2, \hat{L}_z]$

$$[\hat{A}^2, \hat{B}] = \underline{\hat{A}^2\hat{B}} \mp \hat{B}\hat{A}^2 + \hat{A}\hat{B}\hat{A} - \underline{\hat{A}\hat{B}\hat{A}} = \hat{A}[\hat{A},\hat{B}] + [\hat{A},\hat{B}]\hat{A}$$

$$= \hat{L}_x[\hat{L}_x,\hat{L}_z] + [\hat{L}_x,\hat{L}_z]\hat{L}_x \quad ①$$

$$= -i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$$

$$[\hat{L}_y^2,\hat{L}_z] = \hat{L}_y\underbrace{[\hat{L}_y,\hat{L}_z]}_{i\hbar\hat{L}_x} + \underbrace{[\hat{L}_y,\hat{L}_z]}_{i\hbar\hat{L}_x}\hat{L}_y = +i\hbar(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y) \quad ②$$

$$[\hat{L}_z^2,\hat{L}_z] = 0 \quad ③$$

$$① + ② + ③ = 0$$

$$\Rightarrow \boxed{[\hat{\vec{L}}^2, \hat{L}_z] = 0}$$

PARTICLE IN CENTRAL POTENTIAL

$$\hat{H}\,\psi_E(r,\theta,\varphi) = E\,\psi_E(r,\theta,\varphi) \qquad r=\sqrt{x^2+y^2+z^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\hat{\vec{L}}^2}{2mr^2}+V(r)$$

COMPLETE SET OF OPERATORS $\{\hat{H}, \hat{\vec{L}}^2, \hat{L}_z\}$ Eigenvalues ~~QU.NRS~~ $\{E_n, \hbar^2 l(l+1), \hbar m\}$

SEPARATION OF VARIABLES

QU.NRS. $\{n, l, m\}$

$$\psi_E(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)Y + R\,\frac{\hat{\vec{L}}^2 Y}{2mr^2} + VRY = ERY$$

multiply with $-\frac{2mr^2}{\hbar^2 RY}$

$$r^2\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)\frac{1}{R} - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right) = \frac{\hat{\vec{L}}^2 Y}{\hbar^2 Y} = l(l+1)$$

BOTH SIDES MUST BE CONST.!

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)+V(r)R+\frac{\hbar^2 l(l+1)}{2mr^2}R = ER}$$

RADIAL EQN.

$$\boxed{\hat{\vec{L}}^2 Y = \hbar^2 l(l+1)\,Y}$$ Angular Eqn.

l could be arbitrary real number, but turns out to be quantised

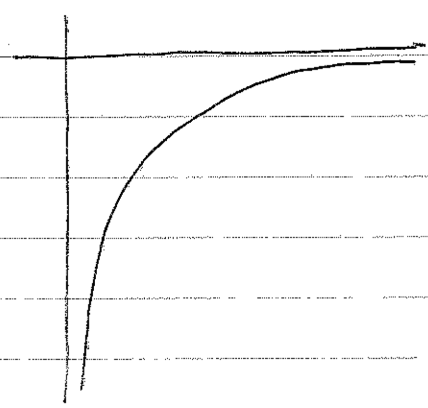
RADIAL EQN.:

$$V_{eff}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}$$

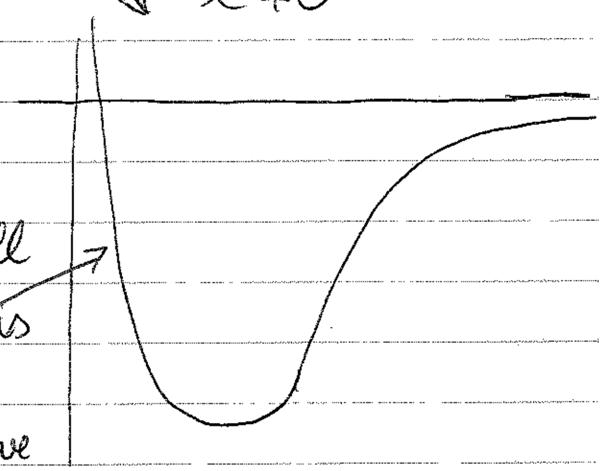
$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

"Zentrifugal potential"

$l=0$ $\qquad\qquad$ $l \neq 0$



For small r V_{eff} is ~~[illegible]~~ repulsive if $l \neq 0$



EXERCISE : GROUNDSTATE W.F. OF HYDROGENATOM

- $Z=1$
- W.F. has spherical symmetry

$\Rightarrow$ no θ, φ dependence

$\Rightarrow \underline{\underline{l=0}}$ "A.M. $=0$"

$\Rightarrow$ ENERGY EIGENSTATE $\psi_{E_1}(r,\theta,\varphi)=\psi_{E_1}(r)$

$\hat{\vec{L}}^2 \psi_{E_1} = \hat{L}_z \psi_{E_1} = 0$

$\Rightarrow$ Radial equ.:

GROUNDSTATE

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2\psi}{dr^2}+\frac{2}{r}\frac{d\psi}{dr}\right)-\frac{Ze^2}{4\pi\epsilon_0 r}\psi = E_1\psi$$

Try $\psi(r) = e^{-r/a}$ $\qquad \psi(r)\to 0$ FOR $r\to\infty$

$$\frac{d\psi}{dr} = -\frac{1}{a}e^{-r/a} \qquad \frac{d^2\psi}{dr^2}=\frac{1}{a^2}e^{-r/a}$$

$$\Rightarrow -\frac{\hbar^2}{2m_e}\frac{1}{a^2}e^{-r/a} - \frac{\hbar^2}{m_e r}\left(-\frac{1}{a}\right)e^{-r/a} - \frac{Ze^2}{4\pi\epsilon_0 r}e^{-r/a}$$

$$= E e^{-r/a}$$

compare

$$e^{-r/a} : \quad E_1 = -\frac{\hbar^2}{2m_e a^2}$$

$$\frac{1}{r}e^{-r/a} : \quad \frac{\hbar^2}{m_e a} = \frac{Ze^2}{4\pi\epsilon_0} \Rightarrow a = \frac{4\pi\epsilon_0\hbar^2}{m_e Z e^2}$$

BOHR RADIUS

$$E_1 = -\frac{\cancel{\hbar^2}}{2\cancel{m_e}}\frac{m_e^{\cancel{2}} Z^2 e^4}{(4\pi\epsilon_0)^2\hbar^{\cancel{4}\,2}} = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2}$$

$2\pi\hbar = h$

$a \sim 5.3\times 10^{-11}$ m

$-E_1 \sim Z^2\, 13.6$ eV

$$E_n = E_1 \frac{1}{n^2}$$

$$|\psi(r)|^2 \Downarrow$$

NORMALISE W.F.

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} dr\, d\theta\, d\varphi\, r^2 \sin\theta\, e^{-2r/a}$$

$$= \left(\int_{\theta=0}^{\pi} \sin\theta\, d\theta\right)\left(\int_{\varphi=0}^{2\pi} d\varphi\right) \int_{r=0}^{\infty} dr\, \underset{u}{r^2}\, \underset{v'}{e^{-2r/a}}$$

$$= \left[-\cos\theta\right]_0^{\pi} \times (2\pi) \times \left\{ \underbrace{-\frac{a}{2} r^2 e^{-2r/a}\Big|_{r=0}^{\infty}}_{=0} - \int_{r=0}^{\infty} dr\, 2r\left(-\frac{a}{2}\right) e^{-2r/a} \right\}$$

$$= 4\pi \left\{ a \int_{r=0}^{\infty} dr\, \underset{u}{r}\, \underset{v'}{e^{-2r/a}} \right\}$$

$$= 4\pi a \left\{ \underbrace{r\left(-\frac{a}{2}\right) e^{-2r/a}\Big|_{r=0}^{\infty}}_{0} - \int_{r=0}^{\infty} dr \left(-\frac{a}{2}\right) e^{-2r/a} \right\}$$

$$= 2\pi a^2 \left[-\frac{a}{2} e^{-2r/a} \right]_{r=0}^{\infty} = \pi a^3$$

$$\text{NORMALISED} \quad \psi(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

$$\boxed{\begin{array}{l}\text{USE:} \\ \int_0^{+\infty} dr\, r^n e^{-r/b} \\ = n!\, b^{n+1}\end{array}}$$

$$\langle r \rangle = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} dr\, d\theta\, d\varphi\, r^2 \sin\theta\, |\psi(r)|^2\, r$$

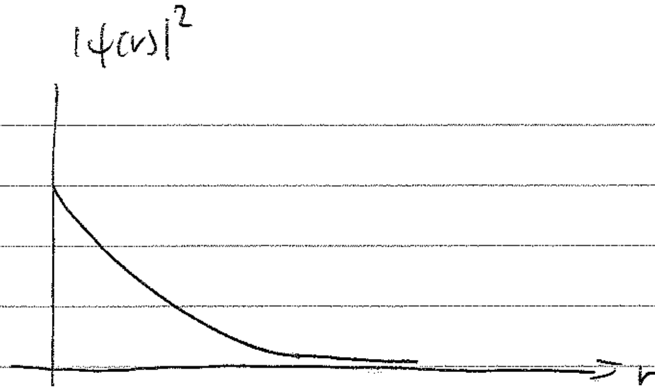
↓ angular integrations

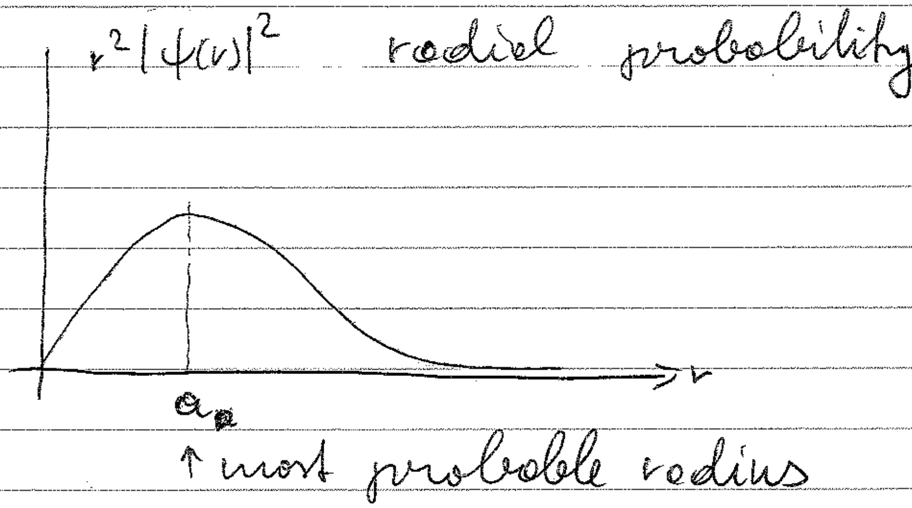
$$= \frac{1}{\pi a^3} 4\pi \int_{r=0}^{\infty} r^3 e^{-2r/a}$$

$$= 4 \times \frac{1}{8} \int_{r=0}^{\infty} \left(\frac{2r}{a}\right)^3 e^{-2r/a} dr = \frac{1}{2} \int_{r=0}^{\infty} \tilde{r}^3 e^{-\tilde{r}} \frac{a}{2} d\tilde{r}$$

$$\tilde{r} = \frac{2r}{a}$$

$$= \frac{a}{4} \int_{r=0}^{\infty} \tilde{r}^3 e^{-\tilde{r}} d\tilde{r} = \frac{a}{4} 6 = \underline{\underline{\frac{3a}{2}}}$$


$|\psi(r)|^2$
r


$r^2|\psi(r)|^2$ radial probability
r
a_0
↑ most probable radius