NOW AS $X(0) = X(a) = 0$ THE x-DEP'T PART IS EXACTLY SAME AS 1D ∞ LI OF BOX SIZE a

$$\Rightarrow \quad E_1 = \frac{\hbar^2 n_1^2 \pi^2}{2ma^2} \quad , \quad X = \sqrt{\frac{2}{a}} \sin \frac{n_1 \pi x}{a}$$

NOTE

SIMILARLY FOR Y AND Z

$$E_2 = \frac{\hbar^2 n_2^2 \pi^2}{2mb^2} \quad , \quad Y = \sqrt{\frac{2}{b}} \sin \frac{n_2 \pi y}{b}$$

$$E_3 = \frac{\hbar^2 n_3^2 \pi^2}{2mc^2} \quad , \quad Z = \sqrt{\frac{2}{c}} \sin \frac{n_3 \pi z}{c}$$

ALTOGETHER

$$\boxed{\begin{aligned} \phi(\vec{x}) &= \frac{2^{3/2}}{\sqrt{abc}} \sin \frac{n_1 \pi x}{a} \sin \frac{n_2 \pi y}{b} \sin \frac{n_3 \pi z}{c} \\ E &= \frac{\hbar^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \end{aligned}}$$

- NOTE : ENERGY EIGENFUNCTIONS LABELLED BY <u>THREE QUANTUM NUMBERS</u> n_1, n_2, n_3

  ϕ_{n_1, n_2, n_3} <u>CORRECTLY NORMALIZED</u>

$$\int_0^a dx \int_0^b dy \int_0^c dz \, |\phi|^2 = 1$$

- LOOK AT <u>EQUAL-SIDED</u> CUBICAL BOX $a = b = c$

  THEN HAVE

$$E_{n_1 n_2 n_3} = \frac{\hbar^2}{2ma^2} \left(n_1^2 + n_2^2 + n_3^2 \right)$$

- <u>GROUND STATE</u> IS $n_1 = n_2 = n_3 = 1$

$$E_{111} = \frac{\hbar^2}{2ma^2} \cdot 3$$

- <u>NEXT STATE</u> IS $n_1 = 2, \, n_2 = 1, \, n_3 = 1$

$$E_{211} = \frac{\hbar^2}{2ma^2} \left(2^2 + 1^2 + 1^2 \right) = \frac{6\hbar^2}{2ma^2}$$

<u>BUT ALSO</u> $n_1 = 1, \, n_2 = 2, \, n_3 = 1$ <u>AND</u>

$n_1 = 1, \, n_2 = 1, \, n_3 = 2$ WITH

$$E_{121} = \frac{6\hbar^2}{2ma^2} \quad , \quad E_{112} = \frac{6\hbar^2}{2ma^2}$$

THUS WE HAVE <u>3 STATES</u> WITH <u>SAME ENERGY</u>. SUCH STATES ARE CALLED

<u>'DEGENERATE STATES'</u>

AND HAVE <u>'3-FOLD DEGENERACY'</u>

THREE DIMENSIONAL TDSE

HAMILTONIAN IS NOW

$$H = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x,y,z)$$

AND TDSE IS

$$H\psi(x,y,z) = i\hbar \frac{\partial \psi(x,y,z)}{\partial t}$$

HOW EASY/HARD THIS IS TO SOLVE DEPENDS ON $V(x,y,z)$. HOWEVER TIME-DEPENDENCE ALWAYS SEPERABLE

$$\psi(\vec{x},t) = \phi(\vec{x})\,T(t)$$

AND SINCE H IS NOT t-DEP'T GET

$$\frac{1}{\phi(\vec{x})} H\phi(\vec{x}) = \frac{i\hbar}{T(t)}\frac{\partial T(t)}{\partial t} = E$$

SO

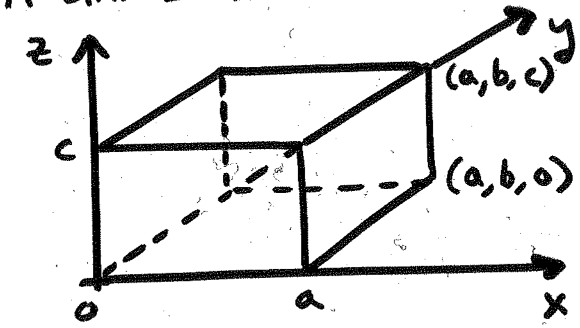
$$T(t) = e^{-iEt/\hbar}$$

$$H\phi(\vec{x}) = E\phi(\vec{x})$$

SIMILAR TO 1-D CASE.

CUBICAL BOX

A SIMPLE EXAMPLE



SIDES OF LENGTH
a x-dir
b y-dir
c z-dir

OUTSIDE BOX $V = \infty \Rightarrow \phi = 0$

INSIDE BOX

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\phi = E\phi$$

TO SOLVE THIS 3D TISE PROCEED BY USING SEPARATION OF VARIABLES

$$\phi(\vec{x}) = X(x)\,Y(y)\,Z(z)$$

$$-\frac{\hbar^2}{2m}\left\{\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)}\right\} = E$$

SO $-\frac{\hbar^2}{2m}X'' = E_1 X$, $-\frac{\hbar^2}{2m}Y'' = E_2 Y$, $-\frac{\hbar^2}{2m}Z'' = E_3 Z$

WITH $\underline{E = E_1 + E_2 + E_3}$

• NOTE THAT ALTHOUGH ENERGIES ARE EQUAL THE **WAVEFUNCTIONS ARE NOT** – IN FACT THEY ARE **ORTHOGONAL**! EG,

$$\int_0^a dx\,dy\,dz\; \psi_{112}(\vec{x},t)^* \psi_{121}(\vec{x},t)$$

$$= \int_0^a dx\,dy\,dz \left(\sqrt{\frac{2}{a}}\right)^6 \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi z}{a} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a}$$

$$= \left(\frac{2}{a}\right)^3 \int_0^a dx \sin^2\frac{\pi x}{a} \underbrace{\int_0^a dy \sin\frac{\pi y}{a} \sin\frac{2\pi y}{a}}_{0} \times \underbrace{\int_0^a dz \sin\frac{2\pi z}{a} \sin\frac{\pi z}{a}}_{0}$$

$$= 0$$

NOW LET'S CONSIDER **3D SHO**

$$V = \frac{1}{2}k_1 x^2 + \frac{1}{2}k_2 y^2 + \frac{1}{2}k_3 z^2$$

IN THIS CASE

$$\frac{(p_x^2 + p_y^2 + p_z^2)}{2m}\phi + \frac{1}{2}(k_1 x^2 + k_2 y^2 + k_3 z^2)\phi = E\phi$$

STILL SEPERABLE ...

SETTING $\phi(\vec{x}) = X(x)\,Y(y)\,Z(z)$ GET

$$-\frac{\hbar^2}{2m}X'' + \frac{1}{2}k_1 x^2 X = E_1 X$$

$$-\frac{\hbar^2}{2m}Y'' + \frac{1}{2}k_2 y^2 Y = E_2 Y$$

$$-\frac{\hbar^2}{2m}Z'' + \frac{1}{2}k_3 z^2 Z = E_3 Z$$

WITH $E = E_1 + E_2 + E_3$

EACH OF THESE IS JUST 1D SHO PROBLEM SO

$$E_1 = \hbar\omega_1(n_1 + 1/2) \qquad \omega_1 = \sqrt{k_1/m}$$

$$E_2 = \hbar\omega_2(n_2 + 1/2) \qquad \omega_2 = \sqrt{k_2/m}$$

$$E_3 = \hbar\omega_3(n_3 + 1/2) \qquad \omega_3 = \sqrt{k_3/m}$$

AGAIN SOMETHING IMPORTANT HAPPENS IF $k_3 = k_2 = k_3 = k$

$$E = \hbar\omega\,(n_1 + n_2 + n_3 + 3/2) \qquad \omega = \sqrt{k/m}$$

GROUND STATE $n_1 = n_2 = n_3 = 0$ $\quad E = 3\hbar\omega/2$ **UNIQUE**

1^{st} EXCITED $\{n_1, n_2, n_3\} \in \{0,0,1\}$ $\quad E = \frac{5}{2}\hbar\omega$ **3 STATES**

2^{nd} " $\{n_1, n_2, n_3\} \in \{0,1,1\}$ **AND** $\{0,0,2\}$ $\quad E = \frac{7}{2}\hbar\omega$ **6 STATES**

IN FACT n^{th} EXCITED STATE

$$E_n = (n + 3/2)\hbar\omega \qquad \text{DEGENERACY} = \frac{(n+1)(n+2)}{2}$$

AS IN CUBICAL WELL CASE ALL THE WAVEFUNCTIONS FOR THESE DEGENERATE STATES ARE ORTHOGONAL

WHY DEGENERACY?

SHO PROBLEM CAN BE ANALYZED IN A DIFFERENT WAY

IF $k_1 = k_2 = k_3 = k$ THEN

$$V = \tfrac{1}{2}k(x^2+y^2+z^2)$$
$$= \tfrac{1}{2}k r^2$$

r = RADIAL COORD OF SPHERICAL POLAR

SO TISE IS

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\phi + V(r)\phi = E\phi$$

WITH $V(r)$ SPHERICALLY SYMMETRIC, AND THIS SYMMETRY GIVES RISE TO THE DEGENERACY OF EXCITED STATES (SIMILARLY THE CUBIC SYMMETRY OF EQUAL SIDED CUBIC BOX GIVES RISE TO ITS' DEGENERACY)

SPHERICAL SYMMETRY AND ANGULAR MOMENTUM

LAST LECTURE OBSERVED THAT SPHERICALLY SYMM. POTENTIALS $V = V(r)$ (AND NOT DEP'T ON θ, ϕ) ARE SPECIAL

TISE

$$\left(\frac{\vec{p}^2}{2m} + V(r)\right)\Phi(r,\theta,\varphi) = E\,\Phi(r,\theta,\varphi)$$

NATURAL TO THINK ABOUT ANGULAR MOMENTUM ...

- CLASSICALLY $\vec{L} = \vec{r} \times \vec{p}$

SO IN CM HAVE

$$\left.\begin{aligned}\vec{L}^2 &= (\vec{r}\times\vec{p})\cdot(\vec{r}\times\vec{p})\\ &= \vec{r}^2\vec{p}^2 - (\vec{r}\cdot\vec{p})^2\end{aligned}\right] \text{STEP } ①$$

SO THAT

$$\vec{p}^2 = \underbrace{\frac{1}{r^2}(\vec{r}\cdot\vec{p})^2}_{\text{THIS JUST } (\hat{r}\cdot\vec{p})^2 \text{ RADIAL PART OF } p^2} + \frac{1}{r^2}\vec{L}^2$$

TANGENTIAL PART DETERMIN BY ANG. MOM'M

$\vec{L}$ IN QM

HAVE TO BE CAREFUL AS COMPONENTS OF $\vec{r}$ AND $\vec{p}$ DON'T COMMUTE

$$[x, p_x] = [y, p_y] = [z, p_z] = i\hbar$$

$$[x, p_y] = [x, p_z] \ldots = 0 .$$

EQUIV.

$$\boxed{[\vec{x}_i, \vec{p}_j] = i\hbar\,\delta_{ij}} \quad i,j = x,y,z$$

REPRESENTATION OF $\vec{p}$ OPERATOR IN TERMS OF CARTESIAN COORDS IS

$$\boxed{\vec{p} = -i\hbar\vec{\nabla}} \qquad \vec{\nabla} = (\partial_x, \partial_y, \partial_z)$$

CLASSICALLY THE ANG. MOM'M $\vec{L} = \vec{r}\times\vec{p}$ SO

OPERATOR $\boxed{\vec{L} = -i\hbar\,\vec{r}\times\vec{\nabla}}$

CHECK THAT WELL-DEFINED...

$$L_x = -i\hbar\,(y\,\partial_z - z\,\partial_y)$$

COMMUTE SO OK

SIMILARLY FOR L_y AND L_z.

ALSO SIMPLE TO CHECK THAT $\vec{L}$ HERMITIAN

CLASSICALLY $L^2 = \vec{L}.\vec{L}$ WAS IMPORTANT

<u>WHAT IS L^2 IN QM?</u>

$$\vec{L}.\vec{L} = (-i\hbar)^2 (\vec{r}\times\vec{\nabla}).(\vec{r}\times\vec{\nabla})$$
$$= -\hbar^2\,\vec{r}.\left[\vec{\nabla}\times(\vec{r}\times\vec{\nabla})\right]$$
$$= -\hbar^2\left\{r^2\nabla^2 - \vec{r}.\vec{\nabla} - (\vec{r}.\vec{\nabla})^2\right\}$$

NEW PIECE (CAME FROM $\vec{\nabla}$ ACTING ON $\vec{r}$)

REARRANGING GIVES

$$\boxed{-\hbar^2\vec{\nabla}^2 = \frac{-\hbar^2}{r^2}\left\{(\vec{r}.\vec{\nabla})^2 + \vec{r}.\vec{\nabla}\right\} + \frac{L^2}{r^2}}$$

MOST USEFUL TO WRITE EXPLICIT FORM IN SPHERICAL POLAR COORDS

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

NEED $r.\nabla$

$$\vec{r}.\vec{\nabla} = x\,\partial_x + y\,\partial_y + z\,\partial_z \quad \text{IN } x, y, z$$

BUT

$$\partial_r = \left.\frac{\partial x}{\partial r}\right|_{\theta,\varphi}\partial_x + \left.\frac{\partial y}{\partial r}\right|_{\theta,\varphi}\partial_y + \left.\frac{\partial z}{\partial r}\right|_{\theta,\varphi}\partial_z$$

$$= \frac{x}{r}\partial_x + \frac{y}{r}\partial_y + \frac{z}{r}\partial_z$$

SO $\vec{r}.\vec{\nabla} = r\,\partial_r$ AND THUS CAN WRITE RADIAL PART OF $\vec{\nabla}^2$ AS

$$\frac{1}{r^2}\left\{(r.\nabla)^2 + r.\nabla\right\}$$

$$= \frac{1}{r^2}\left\{r\,\partial_r\, r\,\partial_r + r\,\partial_r\right\}$$

$$= \frac{1}{r^2}\partial_r\left(r^2\partial_r\right)$$

THUS

$$\boxed{-\hbar^2\nabla^2 = \frac{-\hbar^2}{r^2}\partial_r\left(r^2\partial_r\right) + \frac{L^2}{r^2}}$$

BUT FROM MATHS COURSE KNOW ∇^2 IN SPHERICAL

$$\nabla^2 = \frac{1}{r^2}\partial_r\left(r^2\partial_r\right) + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\right) + \frac{1}{r^2\sin^2\theta}\partial_\varphi^2$$

THE ∂ PARTS EXACTLY MATCH, AND WE CONCLUDE

$$\boxed{L^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\right) + \frac{1}{\sin^2\theta}\partial_\varphi^2\right\}}$$

NOTE: THIS IS INDEED ONLY 'TANGENTIAL' AS IT CONTAINS ONLY ∂_θ, ∂_φ

OF COURSE COULD HAVE CALCULATED L^2 FROM

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

AND EXPRESSIONS FOR L_x ETC

$$L_x = y p_z - z p_y$$
$$L_y = z p_x - x p_z$$
$$L_z = x p_y - y p_x$$

FOR EXAMPLE

$$L_z = -i\hbar\left(x\,\partial_y - y\,\partial_x\right)$$

WHICH CAN BE SIMPLIFIED USING

$$\partial_\varphi = \left.\frac{\partial x}{\partial \varphi}\right|_{r,\theta}\partial_x + \left.\frac{\partial y}{\partial \varphi}\right|_{r,\theta}\partial_y + \left.\frac{\partial z}{\partial \varphi}\right|_{r,\theta}\partial_z$$

$$= -y\,\partial_x + x\,\partial_y$$

THUS

$$\boxed{L_z = -i\hbar\left(x\,\partial_y - y\,\partial_x\right) = -i\hbar\,\partial_\varphi}$$

PROCEEDING SIMILARLY WOULD FIND PREVIOUS EXPRESSION FOR L^2

<u>HOW MANY ANG. MOM'M QUANTUM NUMBERS</u>?

IN CLASSICAL CASE L_x, L_y, L_z, L^2 ARE <u>ALL</u> DEFINED, AND SPECIFYING ANY 3 (SAY L_x, L_y, L^2 OR L_x, L_y, L_z) COMPLETELY DETERMINES ANG. MOM'M

THIS IS <u>NOT</u> THE CASE IN Q.M.

INDEED L_x, L_y, L_z, L^2 DO <u>NOT ALL</u> <u>COMMUTE WITH EACH OTHER</u>...

EG. $[L_x, L_y] = [(y p_z - z p_y), (z p_x - x p_z)]$

$$= y[p_z, z]p_x + (-1)^2 p_y [z, p_z] x$$

(+ ALL OTHERS ZERO)

$$= -i\hbar\, y p_x + i\hbar\, p_y x$$

$$= i\hbar L_z$$

IN FACT, AS YOU SHOULD CHECK FOR YOURSELF

$$\left.\begin{aligned} [L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y \end{aligned}\right\}$$ SO NO 2 OPS. OUT OF L_x, L_y, L_z COMMUTE

WHICH WE CAN WRITE COMPACTLY AS

$$\boxed{[L_i, L_j] = i\hbar\,\epsilon_{ijk} L_k}$$

SO OUT OF L_x, L_y, L_z WE CAN AT MOST HAVE 1 OPERATOR WHICH LEADS TO QUANTUM NUMBER

CONVENTIONAL TO CHOOSE L_z AND COORDINATES SUCH THAT

$$L_z = -i\hbar\frac{\partial}{\partial\varphi}$$

HOWEVER THIS IS NOT YET <u>MAXIMAL</u> COMMUTING SET OF ANGULAR MOM'M OPS...

CONSIDER

$$[L_z, L^2] = [L_z, L_x^2 + L_y^2 + L_z^2]$$
$$= [L_z, L_x^2] + [L_z, L_y^2] + [L_z, L_z^2]$$
$$= L_x[L_z, L_x] + [L_z, L_x]L_x + L_y[L_z, L_y] + [L_z, L_y]L_y$$
$$= L_x(i\hbar L_y) + (i\hbar L_y)L_x + L_y(-i\hbar L_x) + (-i\hbar L_x)L_y$$
$$= 0$$

THUS MAXIMAL SET OF COMMUTING OPS. IS

$$\boxed{L^2, \; L_z}$$

NOTE: CAN EASILY SHOW THAT $[L_x, L^2] = 0$

AND $[L_y, L^2] = 0$ (OBVIOUS BY SYMMETRY!)

SO AN ALTERNATE SET OF COMMUTING OPS WOULD BE L^2, L_x OR L^2, L_y

TISE WITH $V = V(r)$

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r) \right\} \Phi(r,\theta,\varphi) = E\,\Phi(r,\theta,\varphi)$$

RECALL FROM LAST TIME

$$-\hbar^2\nabla^2 = \frac{-\hbar^2}{r^2}\left\{ \partial_r(r^2\partial_r) \right\} + \frac{L^2}{r^2}$$

SO

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r\Phi) + \frac{L^2}{2mr^2}\Phi + V(r)\Phi = E\Phi$$

SINCE L^2 DEPENDS ONLY ON θ, ϕ THIS EQN IS SEPERABLE $\Phi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

SUBST. INTO TISE (AND MULT BY $2mr^2$)

$$\underbrace{\frac{1}{Y}L^2 Y}_{\text{ONLY } \theta,\varphi \text{ DEPENDENT}} = \underbrace{2mr^2(E - V(r)) + \frac{\hbar^2}{R}\partial_r(r^2\partial_r R)}_{\text{ONLY } r \text{ DEPENDENT}}$$

THUS BOTH SIDES MUST EQUAL A CONST. $\hbar^2 K^2$

AND GET 2 EQNS DEPENDING ON r ONLY AND θ, φ ONLY

1) RADIAL EQN.

$$\frac{\hbar^2}{R}\partial_r(r^2\partial_r R) + 2mr^2(E - V(r)) = \hbar^2 K^2$$

THE SOLUTION OF THIS DEPENDS ON $V(r)$

2) ANGULAR EQN.

$$\boxed{L^2 Y(\theta,\varphi) = \hbar^2 K^2 Y(\theta,\varphi)}$$

THIS DOES <u>NOT</u> DEPEND ON $V(r)$. SO <u>SOLUTION IS UNIVERSAL</u> FOR ALL SPHERICALLY SYMM. POTENTIALS

IT IS EIGENVALUE EQN FOR TOTAL ANG. MOM'M SQUARED

• LET'S STUDY THESE ANGULAR EIGENFUNCTIONS...

$$L^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\partial_\theta(\sin\theta\,\partial_\theta) + \frac{1}{\sin^2\theta}\partial_\varphi^2\right\}$$

THUS IN E'VALUE EQN CANCEL $\hbar^2$ AND MULT BY $\sin^2\theta$

$$-\sin\theta\,\partial_\theta(\sin\theta\,\partial_\theta Y) - \partial_\varphi^2 Y = K^2\sin^2\theta\, Y$$

THIS EQN IS (YET AGAIN!) SEPERABLE

$$Y(\theta,\varphi) = P(\theta)\,f(\varphi)$$

AND GET

$$-\frac{\sin\theta}{P}\partial_\theta(\sin\theta\,\partial_\theta P) - K^2\sin^2\theta = \frac{1}{f}\partial_\varphi^2 f$$

THUS BOTH SIDES EQUAL TO CONST. $-m^2$ NOT $(m_{s})^2$
LEADING TO TWO EQNS

A) $$\frac{d^2 f}{d\varphi^2} = -m^2 f$$

B) $$-\frac{\sin\theta}{P}\frac{d}{d\theta}\sin\theta\frac{dP}{d\theta} - K^2\sin^2\theta = -m^2$$

SOLVE φ-EQN (A)

$$f = e^{\pm i m\varphi}$$

TEMPTING TO ARGUE THAT $f(\varphi) = f(\varphi + 2\pi)$
AND THEREFORE m = INTEGER

BUT THIS IS A <u>FALSE ARGUMENT</u>
(EVEN THOUGH CONCLUSION IS CORRECT!)

IN QM THE OBSERVABLE IS $|\psi(r,\theta,\varphi)|^2$

SO ONLY NEED

$$|f(\varphi)|^2 = |f(\varphi+2\pi)|^2$$

(IE, PROB DENSITY SINGLE-VALUED) AND THIS IS TRUE FOR ANY m!

THE CORRECT ARGUMENT IS AS FOLLOWS (SEE E.G. page 322 of Shankar 1st edition)

WE WANT $L_z = -i\hbar\,\partial_\varphi$ TO BE AN OBSERVABLE — THUS IT MUST BE A HERMITIAN OPERATOR.

$$\Rightarrow \int_0^{2\pi} \psi_1^* (-i\hbar\,\partial_\varphi)\psi_2\, d\varphi = \left[\int_0^{2\pi} \psi_2^* (-i\hbar\,\partial_\varphi)\psi_1\, d\varphi\right]^*$$

FOR ALL $\psi_1(\varphi)$ and $\psi_2(\varphi)$

BUT INTEGRATE RHS BY PARTS GIVING

$$\int_0^{2\pi} [(-i\hbar\,\partial_\varphi)\psi_2]\,\psi_1^*\, d\varphi + i\hbar\int_0^{2\pi} \partial_\varphi(\psi_2\,\psi_1^*)\, d\varphi$$

THE ADDITIONAL BOUNDARY TERM

$$i\hbar\int_0^{2\pi} \partial_\varphi(\psi_1^*\,\psi_2)\, d\varphi = i\hbar\left\{\psi_1^*(2\pi)\psi_2(2\pi) - \psi_1^*(0)\psi_2(0)\right\}$$

MUST VANISH IF WE ARE TO HAVE LHS = RHS (IE, HERMITIAN L_z)

BUT THIS IS ONLY TRUE FOR ALL ψ_1, ψ_2 IF

$$\psi_i(0) = \psi_i(2\pi) \quad i = 1,2 \,!$$

$$\Longrightarrow e^{im.2\pi} = 1$$

$$m = 0, \pm 1, \pm 2, \ldots.$$

AFTER ALL!

SO IT IS HERMITIAN NATURE OF L_z THAT FORCES L_z EIGENVALUES TO BE

$$\boxed{\ell_z = m\hbar} \qquad m = 0, \pm 1, \pm 2, \ldots$$

- NOW RETURN TO Θ - EQN

$$-\frac{\sin\theta}{P}\,\partial_\theta(\sin\theta\,\partial_\theta P) - K^2\sin^2\theta = -m^2$$

THIS IS THE 'ASSOCIATED LEGENDRE EQN' YOU HAVE MET IN MATHS METHODS.

ITS SOLUTION IS AN 'ASSOCIATED LEGENDRE POLYNOMIAL' $P_{\ell m}(\cos\theta)$

- WHY IS $K^2 = \ell(\ell+1)$ ℓ = INTEGER ?

IN QM THE WAVEFUNCTION MUST BE NORMALIZABLE. THIS MEANS FOR US THAT

$$1 = \int d(\text{Vol})\,|R(r)\,P(\theta)\,f(\varphi)|^2$$

$$= \int_0^\infty r^2|R(r)|^2 dr \int_0^{2\pi} d\varphi \int_0^\pi |P(\theta)|^2 \sin\theta\, d\theta$$

AND EACH FACTOR MUST BE SEPARATELY NORMALIZABLE. CONVENIENT/CONVENTIONAL TO CHOOSE

$$\int_0^\infty r^2|R(r)|^2 dr = 1$$

$$2\pi\int_0^\pi |P(\theta)|^2\sin\theta\, d\theta = 1$$

AS SHOWN IN MATHS COURSE THE SOL'NS TO ASSOCIATED LEGENDRE EQN ARE ONLY NORMALIZABLE WHEN

① $K^2 = \ell(\ell+1)$ ℓ = INTEGER

= "THE ORBITAL QUANTUM NUMBER"

AND ② m IS AN INTEGER SATISFYING

$$\boxed{|m| \leq \ell}$$

IE, $-\ell, -\ell+1, -\ell+2, \ldots, \ell-2, \ell-1, \ell$

m = "THE z-CPT OF THE ANGULAR MOMENTUM" OR "THE MAGNETIC QUANTUM NUMBER"

> ORBITAL ANGULAR MOMENTUM IS INTEGER $\times\,\hbar$ QUANTIZED
>
> $$L^2 Y_{\ell m}(\theta,\varphi) = \hbar^2\,\ell(\ell+1)\,Y_{\ell m}(\theta,\varphi)$$
>
> $$L_z Y_{\ell m}(\theta,\varphi) = \hbar m\, Y_{\ell m}(\theta,\varphi)$$

$$Y_{\ell m}(\theta, \varphi) = P_{\ell m}(\theta)\, e^{im\varphi}$$

QUANTUM NUMBERS

$Y_{\ell m}(\theta, \varphi)$ = "<u>SPHERICAL HARMONICS</u>"

NOTE: • $|Y_{\ell m}(\theta, \varphi)|^2$ IS INDEP'T OF φ (SUPERPOSITIONS MAY NOT BE!)

• $|Y_{\ell m}|^2$ MATCH THE "ORBITALS" OF A-LEVEL CHEMISTRY

The Spherical Harmonics

The spherical harmonics $Y_{\ell,m}(\theta,\phi)$ are eigenfunctions of angular momentum and satisfy the equations

$$\begin{aligned} L^2 Y_{\ell,m} &= \hbar^2 \ell(\ell+1) Y_{\ell,m} \\ L_z Y_{\ell,m} &= \hbar m Y_{\ell,m} \end{aligned}$$

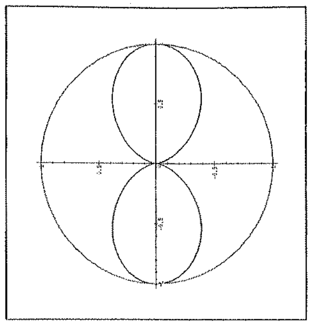
where $\ell = 0, 1, 2, \ldots$ and, for a fixed ℓ, $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$. They are normalized so that

$$\int Y^*_{\ell,m}(\theta,\phi) Y_{\ell',m'}(\theta,\phi)\, d\Omega = \delta_{\ell\ell'}\delta_{mm'} \tag{1}$$

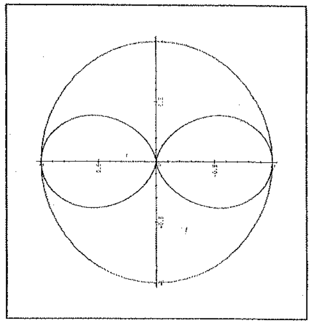
The first few spherical harmonics are

$$\begin{aligned} Y_{0,0}(\theta,\phi) &= \sqrt{\frac{1}{4\pi}} \\ Y_{1,0}(\theta,\phi) &= \sqrt{\frac{3}{4\pi}}\cos\theta \\ Y_{1,\pm1}(\theta,\phi) &= \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi} \\ Y_{2,0}(\theta,\phi) &= \sqrt{\frac{5}{4\pi}}\frac{1}{2}(3\cos^2\theta - 1) \\ Y_{2,\pm1}(\theta,\phi) &= \sqrt{\frac{5}{24\pi}}\, 3\sin\theta\cos\theta\, e^{\pm i\phi} \\ Y_{2,\pm2}(\theta,\phi) &= \sqrt{\frac{5}{96\pi}}\, 3\sin^2\theta\, e^{\pm 2i\phi} \end{aligned}$$

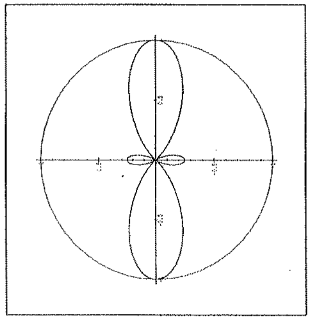
$\ell = 1,\ m = 0$



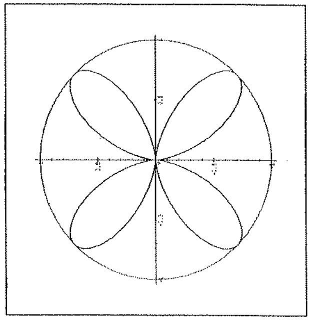
$\ell = 1,\ m = \pm 1$



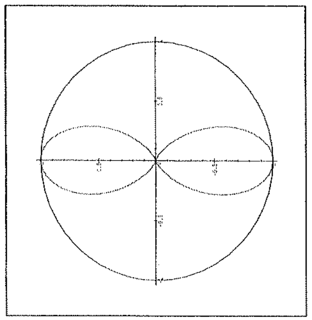
$\ell = 2,\ m = 0$

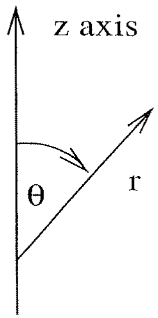


$\ell = 2,\ m = \pm 1$



$\ell = 2,\ m = \pm 2$





$r \simeq |Y_{\ell,m}(\theta,\phi)|^2$

ANGULAR MOMENTUM: A BETTER METHOD

RECALL THAT FOR S.H.O. HAD TWO WAYS OF GETTING EIGENVALUES/EIGENVECTORS

- DIFFERENTIAL EQNS
- 'ALGEBRAIC' USING a_+, a_- OPS

SIMILARLY FOR ANGULAR MOMENTUM THERE ARE 2 WAYS OF GETTING ANG. MOM'M QUANTIZATION CONDITIONS

1) REPRESENT L_x, L_y, L_z, L^2 AS DIFFERENTIAL OPERATORS AND SOLVE FOR EIGENFUNCTIONS $Y_{\ell m}(\theta, \varphi)$ AND EIGENVALUES

$$\boxed{\begin{aligned} L^2 Y_{\ell m}(\theta,\varphi) &= \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\varphi) \\ L_z Y_{\ell m}(\theta,\varphi) &= \hbar m Y_{\ell m}(\theta,\varphi) \\ \ell &= \text{INTEGER} \\ m &= \text{INTEGER}, \quad |m| \leq \ell \end{aligned}}$$

THIS IS WHAT WE DID LAST TIME...

2) ALTERNATIVELY, JUST LIKE IN SHO CASE WE CAN INTRODUCE 'STEP' OR 'LADDER' OPERATORS AND SOLVE FOR EIGENVALUES OF L^2 AND L_z ALGEBRAICALLY

BIG DIFFERENCE THOUGH

THE ALGEBRAIC METHOD SHOWS THAT THERE ARE MORE POSSIBLE EIGENVALUES OF L^2 AND L_z THAN WERE FOUND BY USING DIFFERENTIAL OPS. (AND FUNCTIONS OF θ, φ)!

- LET'S SEE HOW THIS CAN HAPPEN...

BECAUSE $[L_x, L_y] = i\hbar L_z$ ETC. THE MAXIMAL SET OF COMMUTING OPS. IS

$$L^2 \;,\quad L_z$$

AND WE'RE INTERESTED IN EIGENVALUE EQNS

$$\boxed{\begin{aligned} L^2\psi &= \hbar^2 K^2 \psi \\ L_z \psi &= \hbar k \psi \end{aligned}}$$ ANG. MOM'M EIGENVALUE EQNS

- TO FIND OUT WHAT K^2 AND k ARE CONSIDER

$$\boxed{\begin{aligned} L_+ &= L_x + iL_y \\ L_- &= L_x - iL_y \end{aligned}}$$ ANG. MOM'M 'STEP' OPERATORS

AND NOTE THAT

$$\underline{[L_\pm, L_z]} = [L_x \pm iL_y, L_z]$$
$$= -i\hbar L_y \pm i(i\hbar L_x)$$
$$= \mp \hbar L_x - i\hbar L_y$$
$$\underline{= \mp \hbar L_\pm}$$

- NOW <u>CONSIDER A ψ_k WHICH SATISFIES</u>

$$L_z \psi_k = \hbar k \psi_k$$

AND DEFINE A NEW $\underline{\psi' = L_+ \psi_k}$ (IF IT EXISTS – IT MIGHT BE ZERO, $\psi' = 0$ – COME BACK TO THIS...)

WHAT L_z VALUE DOES $\psi' = L_+\psi_k$ HAVE?

IE, $L_z(L_+\psi_k) = ?$

USE COMMUTATION RELATION

$$[L_z, L_+] = +\hbar L_+$$

$$\Rightarrow L_z L_+ = \hbar L_+ + L_+ L_z$$

THUS

$$L_z(L_+\psi_k) = (\hbar L_+ + L_+ L_z)\psi_k$$
$$= \hbar\psi' + L_+ \hbar k \psi_k$$
$$= (\hbar + \hbar k)\psi'$$

SO THE <u>STATE ψ' MUST BE PROPORTIONAL TO ONE WITH L_z EIGENVALUE $\hbar(k+1)$</u>

$$L_+\psi_k = \underbrace{C_+(k)}_{\text{NORMALIZATION}} \psi_{k+1}$$

SIMILARLY EASY TO SHOW THAT $L_-\psi_k$ SATISFIES

$$L_z(L_-\psi_k) = \hbar(k-1)\, L_-\psi_k$$

SO <u>$L_-\psi_k$ MUST BE PROPORTIONAL TO STATE WITH L_z VALUE $\hbar(k-1)$</u>

$$L_-\psi_k = C_-(k)\,\psi_{k-1}$$

$$\boxed{\text{L_+ AND L_- STEP UP AND DOWN TOWER OF L_z EIGENVALUES BY ONE $\hbar$ UNIT}}$$

- WHAT DO L_+, L_- DO TO L^2 EIGENVALUES?

  WELL, SINCE L^2 COMMUTES WITH L_x AND L_y, AND $L_\pm = L_x \pm i L_y$ OBVIOUS THAT

$$\underline{[L^2, L_\pm] = 0}$$

THIS MEANS THAT IF ψ_k SATISFIES $L^2\psi_k = \overset{\hbar^2}{\vee}K^2\psi_k$ (SO REALLY SHOULD DENOTE STATE AS ψ_{k,K^2}) THEN

$$\begin{aligned} L^2 L_+ \psi_{k,K^2} &= L_+ L^2 \psi_{k,K^2} \\ &= L_+ \hbar^2 K^2 \psi_{k,K^2} \\ &= \hbar^2 K^2 (L_+ \psi_{k,K^2}) \end{aligned}$$

AND SIMILARLY FOR $L_-\psi_{k,K^2}$

$$\boxed{\text{THUS L_+, L_- DO NOT CHANGE L^2 EIGENVALUE}}$$

- BUT THIS IMPLIES THAT TOWER OF L_z EIGENSTATES WITH EIGENVALUES

$$\ldots \hbar(k-2),\ \hbar(k-1),\ \hbar k,\ \hbar(k+1), \ldots$$

GENERATED BY L_+ OR L_- REPEATEDLY ACTING ON ψ_k <u>MUST TERMINATE AT BOTH ENDS</u>

TO SEE THIS NOTE THAT

$$\begin{aligned} L^2 - L_z^2 &= L_x^2 + L_y^2 + L_z^2 - L_z^2 \\ &= L_x^2 + L_y^2 \end{aligned}$$

NOW CONSIDER AN ARBITRARY MEMBER OF THE TOWER (SAY ψ_{k',K^2}) AND TAKE EXPECTATION VALUE OF BOTH SIDES OF $L^2 - L_z^2 = L_x^2 + L_y^2$ IN THIS STATE

$$\text{LHS} = \int \psi^*_{k',K^2} (L^2 - L_z^2)\, \psi_{k',K^2}\, d\Omega$$

(S)WITCH TO EASIER DIRAC NOTATION

$$= \langle k', K^2 | (L^2 - L_z^2) | k', K^2 \rangle$$

$$= \left(\hbar^2 K^2 - (k'\hbar)^2\right) \langle k', K^2 | k', K^2 \rangle$$

$$= \hbar^2 (K^2 - k'^2)$$

BUT $\text{RHS} = \langle k', K^2 | (L_x^2 + L_y^2) | k', K^2 \rangle$

≥ 0 SINCE SUM OF EXPECTATION VALUES OF SQUARES OF HERMITIAN OPERATORS

$$\Rightarrow \hbar^2 (K^2 - k'^2) \geq 0$$

$$\Rightarrow \underline{k'^2 \leq K^2}$$ IE, $\underline{L_z}$ EIGENVALUE IS BOUNDED

SINCE k'^2 IS BOUNDED BY K^2 THERE MUST EXIST BOTH A STATE WITH HIGHEST L_z

$$\underline{\psi_{k_{max}, K^2}}$$

AND A STATE WITH LOWEST L_z

$$\underline{\psi_{k_{min}, K^2}}$$

- THE ONLY WAY THIS CAN BE CONSISTENT WITH ACTION OF L_+ AND L_- IS IF

① $\underline{L_+ \psi_{k_{max}, K^2} = 0}$ (ie, $C_+(k_{max}) = 0$)

AND

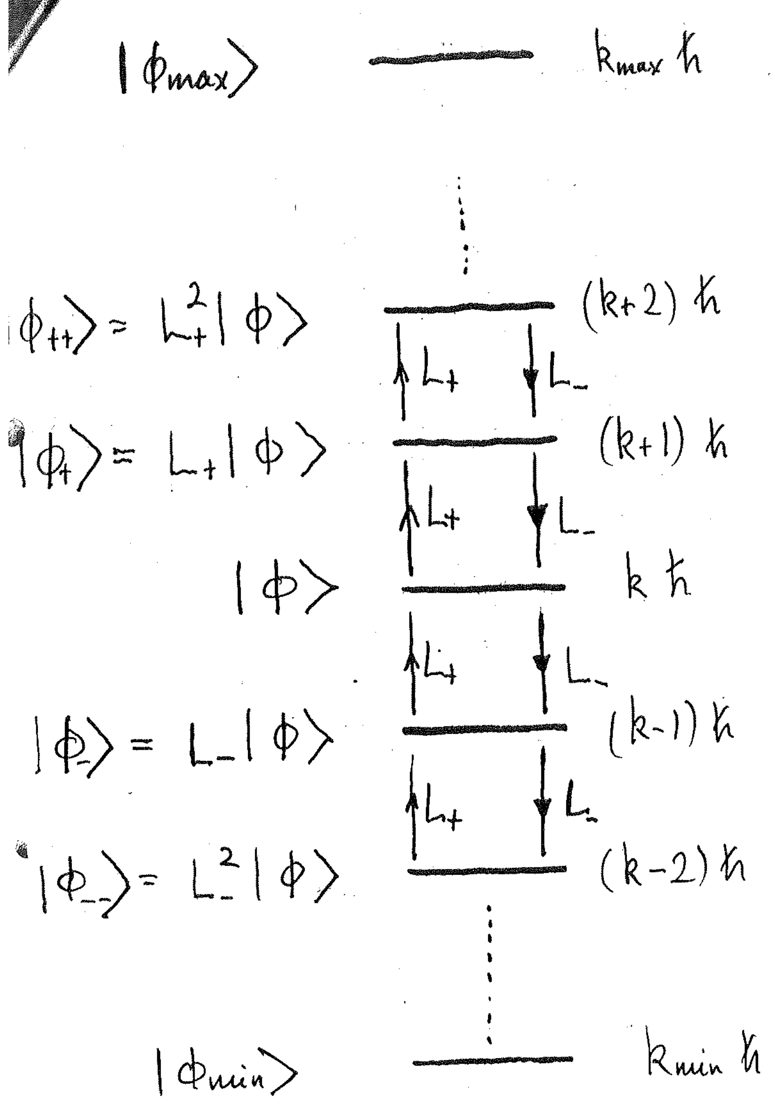
② $\underline{L_- \psi_{k_{min}, K^2} = 0}$ (ie, $C_-(k_{min}) = 0$)

- IN FACT THERE IS A CONNECTION BETWEEN VALUES k_{max} AND K^2 (OR k_{min} AND K^2)

TO SEE THIS NEED TO MANIPULATE OPERATORS

$L_- L_+$

$L_+ L_-$



- $$L_-L_+ = (L_x - iL_y)(L_x + iL_y)$$
$$= L_x^2 + L_y^2 + i[L_x, L_y]$$
$$= L_x^2 + L_y^2 + i(i\hbar L_z)$$
$$= L^2 - L_z^2 - \hbar L_z \quad (A)$$

- SIMILARLY
$$L_+L_- = L^2 - L_z^2 + \hbar L_z \quad (B)$$

- NOW ACT ON EQN 1 WITH L_-, AND USE (A) TO GIVE
$$(L^2 - L_z^2 - \hbar L_z)\psi_{k_{max},K^2} = 0$$

$$\Rightarrow \hbar^2(K^2 - k_{max}^2 - k_{max})\psi_{k_{max},K^2} = 0$$

$$\Rightarrow \underline{K^2 = k_{max}(k_{max}+1)} \quad (3)$$

- IMAGINE <u>STARTING FROM TOP OF TOWER</u> <u>ψ_{k_{max},K^2}</u> <u>AND ACTING</u> q <u>TIMES WITH L_-</u> <u>TILL WE REACH</u> ψ_{k_{min},K^2}

BUT ψ_{k_{min},K^2} SATISFIES $L_- \psi_{k_{min},K^2} = 0$

AND ACTING WITH L_+ ON THIS EQN (EQN ②)

AND USING (B) GIVES

$$(L^2 - L_z^2 + \hbar L_z)\,\psi_{k_{min},K^2} = 0$$

$$\Rightarrow \hbar^2 (K^2 - k_{min}^2 + k_{min})\,\psi_{k_{min},K^2} = 0$$

$$\Rightarrow \quad \underline{K^2 = k_{min}(k_{min} - 1)} \quad ④$$

BUT COMPARING EQNS ③ AND ④ WE SEE

$$k_{max}(k_{max}+1) = k_{min}(k_{min}-1)$$

$$\Rightarrow \underline{-k_{max} = k_{min}}$$

MOREOVER, AS WE GOT FROM k_{max} TO k_{min} IN q STEPS (USING L_-) MUST HAVE

$$k_{max} - k_{min} = 2k_{max} = q$$

$$\Rightarrow \underline{k_{max} = \frac{q}{2}} \qquad q = 0, 1, 2, 3, \ldots$$

CONVENTIONAL TO REFER TO $q/2 = j$

WHERE $j = 0, 1/2, 1, 3/2, \ldots$

AS THE ANGULAR MOMENTUM OF STATE.

$(j = k_{max})$

FINALLY HAD EQN ③

$$K^2 = k_{max}(k_{max}+1)$$
$$= j(j+1)$$

THUS LEARNT

$$\boxed{\begin{aligned} L^2 \psi_{jm} &= \hbar^2 j(j+1)\,\psi_{jm} \\ L_z \psi_{jm} &= \hbar m\,\psi_{jm} \\ j &= 0, 1/2, 1, 3/2, \ldots \\ m &= -j, -j+1, -j+2, \ldots, j-1, j \end{aligned}}$$

MEANING OF ANG. MOM'M OPERATOR RESULTS

LAST LECTURE SHOWED THAT OPERATOR ANALYSIS OF ANG. MOM. ALGEBRA ALLOWED

$$L^2 \psi_{jm} = \hbar^2 j(j+1)\psi_{jm}$$

$$L_z \psi_{jm} = \hbar m \psi_{jm} \qquad (m = -j, -j+1, \ldots, j-1, j)$$

WITH BOTH

I) $j = 0, 1, 2, \ldots$ INTEGER

AND

II) $j = 1/2, 3/2, 5/2, \ldots$ ODD HALF INTEGER

BUT DIDN'T WE SHOW EARLIER THAT $L_z = -i\hbar\, \partial/\partial\varphi$ (AND SIMILAR DIFFERENTIAL REPRESENTATION FOR L^2) ONLY HAD INTEGER EIGENVALUES ?

YES! AND THAT RESULT IS QUITE CORRECT, BUT EXISTENCE OF $j = 1/2, 3/2, 5/2, \ldots$ IS ALSO CORRECT

WHAT'S GOING ON ?

THE EXTRA HALF-INTEGRAL EIGENVALUES AROSE BECAUSE WE HAVE IN FACT SOLVED A MORE GENERAL PROBLEM THAN THAT OF L_x, L_y, L_z, L^2 (ALTHOUGH WE DIDN'T KNOW WE WERE !...)

- NOWHERE DID WE USE EXPLICIT DIFFERENTIAL REPRESENTATIONS FOR L_z, L^2, ETC

- WE JUST USED COMMUTATION RELATIONS

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

WHICH REFLECT THE LAW OF THE COMBINATION OF ROTATIONS IN 3-DIMS AND WHICH MUST BE SATISFIED WHATEVER BE THE NATURE OF THE 'WAVE FUNCTIONS' THEY ROTATE

- WHAT WE HAVE DISCOVERED IS 'SPIN' WHICH CAN TAKE ON BOTH INTEGRAL AND ODD-HALF-INTEGRAL VALUES

E.G. PHOTON $j=1$ (BUT AS MASSLESS IN FACT MORE COMPLICATED)

PION $j=0$

HIGGS (IF IT EXISTS!) $j=0$

MANY NUCLEI... $j=0,1,\ldots$

ELECTRON $j=1/2$

PROTON $j=1/2$

MANY NUCLEI $j=1/2, 3/2, \ldots$

- SPIN 'WAVEFUNCTIONS' ARE NOT FUNCTIONS OF ANGULAR COORDS θ, φ, BUT MUST INSTEAD BE REPRESENTED AS

2-STATE VECTORS $\begin{pmatrix} \cdot \\ \cdot \end{pmatrix}$ FOR $j=1/2$

3-STATE VECTORS $\begin{pmatrix} \cdot \\ \cdot \\ \cdot \end{pmatrix}$ FOR $j=1$

4-STATE VECTORS $\begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$ FOR $j=3/2$

ETC...

THEN THE L_x, L_y, L_z, L^2 ACT AS MATRICES ON THESE VECTORS AND RE-SHUFFLE THEIR COMPONENTS

SIDE NOTE: SPIN HAS FORCED US TO HEISENBERG'S FORMULATION OF QM ('MATRIX MECHANICS') WHICH IS MORE GENERAL, THOUGH MORE ABSTRACT THAN SCHRÖDINGER'S. HEISENBERG THOUGHT OF ALL OPERATORS AS BEING MATRICES (IN WHICH CASE DIFFERENTIAL OPS LIKE $p_x = -i\hbar\partial_x$ REQUIRE INFINITE-DIMENSIONAL MATRICES!)

- ON THE OTHER HAND NORMAL 'ORBITAL' ANGULAR MOMENTUM IS ALWAYS INTEGRAL AND THEREFORE CAN ALWAYS BE REPRESENTED BY $Y_{\ell m}(\theta,\varphi)$ AND DIFFERENTIAL OPS.

- IT IS HELPFUL TO HAVE A NOTATION WHICH DISTINGUISHES 'ORBITAL' FROM 'SPIN' (OR 'INTRINSIC') ANGULAR MOM'M

LET'S WRITE

$$\boxed{J_i = L_i + S_i} \qquad i = x, y, z$$

TOTAL ANG. MOM'M ($j = 0, 1/2, 1, 3/2, \dots$)

ORBITAL ANG. MOM'M ($\ell = 0, 1, 2, \dots$ ONLY)

SPIN ANG. MOM'M ($s = 0, 1/2, 1, 3/2, 2, \dots$)

SINCE ROTATIONS IN 3-DIMENSIONS ALWAYS OBEY THE SAME COMPOSITION RULES <u>THE OPERATORS</u> S_i <u>OBEY THE SAME COMMUTATION RELATIONS</u>

$$[S_x, S_y] = i\hbar S_z \quad \text{AND CYCLIC}$$

THUS SO DOES J (AS THEY MUST!)

$$[J_x, J_y] = i\hbar J_z \quad \text{AND CYCLIC}$$

- SO EIGENVALUE EQNS ARE

TOTAL
$$\begin{cases} J^2 \psi_{jj_z} = \hbar^2 j(j+1)\psi_{jj_z} & j = 0, 1/2, 1, \dots \\ J_z \psi_{jj_z} = \hbar j_z \psi_{jj_z} & = -j, -j+1, \dots, j \end{cases}$$

ORBITAL
$$\begin{cases} L^2 \psi_{\ell m} = \hbar^2 \ell(\ell+1)\psi_{\ell m} & \ell = 0, 1, 2, \dots \\ L_z \psi_{\ell m} = \hbar m \psi_{\ell m} & m = -\ell, \dots, \ell \end{cases}$$

SPIN
$$\begin{cases} S^2 \psi_{ss_z} = \hbar^2 s(s+1)\psi_{ss_z} & s = 0, 1/2, 1, \dots \\ S_z \psi_{ss_z} = \hbar s_z \psi_{ss_z} & s_z = -s, -s+1, \dots, +s \end{cases}$$

AND AS $J_i = L_i + S_i$ HAVE

$$J_z = L_z + S_z \quad \text{SO}$$

$$\underline{j_z = m + s_z}$$

NOTE: ALSO IMPORTANT IN ATOMIC PHYSICS IS

EQN $J^2 = \sum_{i=x,y,z} (L_i + S_i)^2 = L^2 + S^2 + 2\vec{L}.\vec{S}$

$$\Longrightarrow \vec{L}.\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

MORE SPIN LATER.... FOR MOMENT **IGNORE**

NOW, RADIAL WAVE EQUATIONS

- YOU RECALL (I HOPE!) THAT WE WERE CONSIDERING 3-DIM PROBLEMS OF FORM

$$H = \frac{p^2}{2m} + V(r)$$

WHICH WE WERE ABLE TO TURN INTO THE TISE

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r\psi) + \frac{L^2}{2mr^2}\psi + V(r)\psi = E\psi$$

- WE THEN WROTE

$$\psi(r,\theta,\varphi) = R(r)\,Y_{\ell m}(\theta,\varphi)$$

WHERE

$$L^2 Y_{\ell m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\,Y(\theta,\varphi)$$

- SINCE $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$ THERE ARE

$$\boxed{2\ell+1 \text{ STATES OF SAME } \ell \text{ BUT VARYING } m}$$

- THE $\psi = Y(\theta,\varphi)R(r)$ SEPARATION OF VARIABLES LEAVES US WITH THE RADIAL WAVE EQN.

$$\boxed{\frac{-\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r R) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}R + VR = ER}$$

- ONE IMMEDIATE CONSEQUENCE OF THIS IS THAT

$$\boxed{\text{ENERGY EIGENVALUES } E \text{ CANNOT DEPEND ON THE QUANTUM NUMBER } m}$$

WHEN $V = V(r)$ AS ABOVE EQN INDEP'T OF m

$\Rightarrow$ $(2\ell+1)$ DEGENERATE STATES WHEN TOTAL ORBITAL ANG. MOM'M $= \ell$

$$\boxed{\text{THIS DEGENERACY IS A CONSEQUENCE OF ROTATIONAL SYMMETRY}}$$

∞'ly DEEP SPHERICAL WELL

LET'S FIRST TRY TO SOLVE RADIAL EQN FOR

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}$$

THIS $\Longrightarrow$ $\psi(r \geq a) = 0 \Rightarrow \underline{R(r \geq a) = 0}$
<u>AS A BOUNDARY CONDITION</u>

- FOR $r < a$ $R(r)$ SATISFIES

$$-R'' - \frac{2}{r} R' + \frac{\ell(\ell+1)R}{r^2} = \epsilon R$$

$$\epsilon \equiv \frac{2mE}{\hbar^2}$$

NOW LET $r = \rho / \sqrt{\epsilon}$ AND FIND

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2}\right)R = 0$$

THIS IS THE 'SPHERICAL BESSEL EQUATION':
IF WE MAKE FURTHER SUBSTITUTION

$$R = \frac{1}{\sqrt{\rho}} Q$$

NOTE

WE FIND

$$\frac{d^2Q}{d\rho^2} + \frac{1}{\rho}\frac{dQ}{d\rho} + \left(1 - \frac{(\ell+\frac{1}{2})^2}{\rho^2}\right)Q = 0$$

WHICH IS ORDINARY BESSEL EQN BUT FOR
$\frac{1}{2}$ - INTEGER ORDER

THUS SOLUTIONS $J_{\pm(\ell+\frac{1}{2})}(\rho)$. AND EQUIV

$$R_{\pm}(\rho) = \frac{1}{\sqrt{\rho}} J_{\pm(\ell+\frac{1}{2})}(\rho)$$

- <u>ARE BOTH THESE FORMS ALLOWABLE?</u>

RECALL FROM MATHS METHODS THAT

$$J_\nu(x) \sim x^\nu \quad \text{AS } x \to 0$$

THUS $R_+(r) \sim r^{-1/2}\, r^{(\ell+1/2)} \sim r^{\ell}$

$$R_-(r) \sim r^{-1/2}\, r^{-\ell-1/2} \sim r^{-\ell-1}$$

SINCE R_- BLOWS UP AS $r \to 0$ IT MAY SEEM AS THOUGH IT CANNOT BE NORMALIZABLE (AND THUS ALLOWABLE)

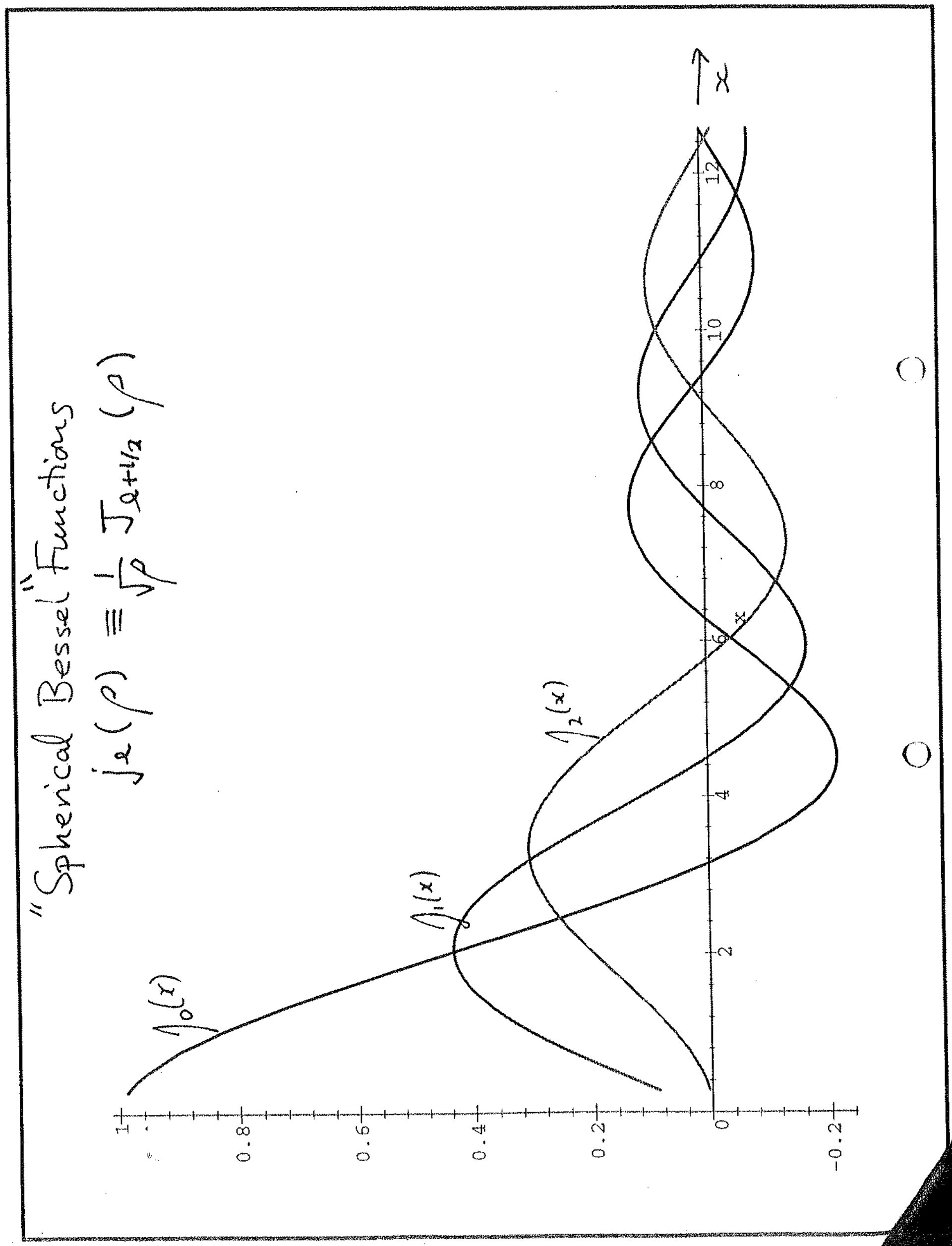
BUT NORMALIZATION INTEGRAL HAS FORM

$$\int_0^\infty r^2 |R|^2 dr$$ SO BEHAVIOR AT 0 IS

$$\int_0 r^2 |R_+|^2 dr \sim \int_0 r^{2+2\ell} dr \sim \underline{\text{FINITE}}\checkmark$$

FROM $d(\mathrm{Vol})$
$= r^2 \sin\theta \, d\theta \, d\phi \, dr$
IN 3-DIM

$$\int_0 r^2 |R_-|^2 dr \sim \int_0 r^{-2\ell} dr \sim \begin{cases} \underline{\infty \text{ IF } \ell \geq 1} \\ \underline{\text{FINITE IF } \ell = 0} \end{cases}$$



THUS THE $R_-(r)$ SOL'NS WITH $\ell = 0$, ie

$R(r) \sim \frac{1}{\sqrt{r}} J_{-1/2}(r)$ **ARE** ALLOWED **BY** **NORMALIZABILITY** (ALL $J_{-(1/2+\ell)}$ FOR $\ell \geq 1$ NOT ALLOWED)

- HOWEVER $R_-^{\ell=0}(r) \sim \frac{1}{r}$ AS $r \to 0$

  AND THIS IS DISALLOWED BECAUSE IT IN FACT DOES **NOT** SOLVE OUR EQN EVERYWHERE

- TO SEE THIS RECALL FROM ELEC + MAG. THAT THE POTENTIAL $1/4\pi r$ OF A POINT CHARGE SATISFIES

$$\nabla^2 \left(1/4\pi r \right) = -\delta^{(3)}(\vec{r})$$

BUT WE ARE SOLVING EXACTLY A RADIAL EQN OF THIS FORM

$$\nabla^2 R_- = (E - V(r)) R_-$$

SO UNLESS $V(r)$ CONTAINS A δ-FUNCTION CHARGE AT ORIGIN (OR SIMILAR LEADING TO $V \sim \delta^{(3)}(r)$) $R_-^{\ell=0}$ NOT IN FACT ALLOWED

THUS ALLOWED SOL'NS OF SPHERICAL WELL ARE OF FORM $R(\rho) = \frac{1}{\sqrt{\rho}} J_{\ell+1/2}(\rho)$

$\Rightarrow$ GENERAL SOL'N OF FORM

$$\boxed{\psi(r,\theta,\varphi) = \sum_{\substack{\ell=0 \\ |m|\leq \ell}}^{\infty} c_\ell^m \frac{1}{\sqrt{\rho}} J_{\ell+1/2}(\rho)\, Y_{\ell m}(\theta,\varphi)}$$

BUT MUST IMPOSE B.C.'n $R(r=a)=0$

LET'S LOOK AT SOME SPECIFIC CASES

1) $\ell=0$: $R = \frac{1}{r\sqrt{\epsilon}} \sin(r\sqrt{\epsilon})$

$R(a)=0 \Rightarrow \sin(a\sqrt{\epsilon}) = 0$

$\Rightarrow a\sqrt{\epsilon} = n\pi \quad n=1,2,3,\ldots$

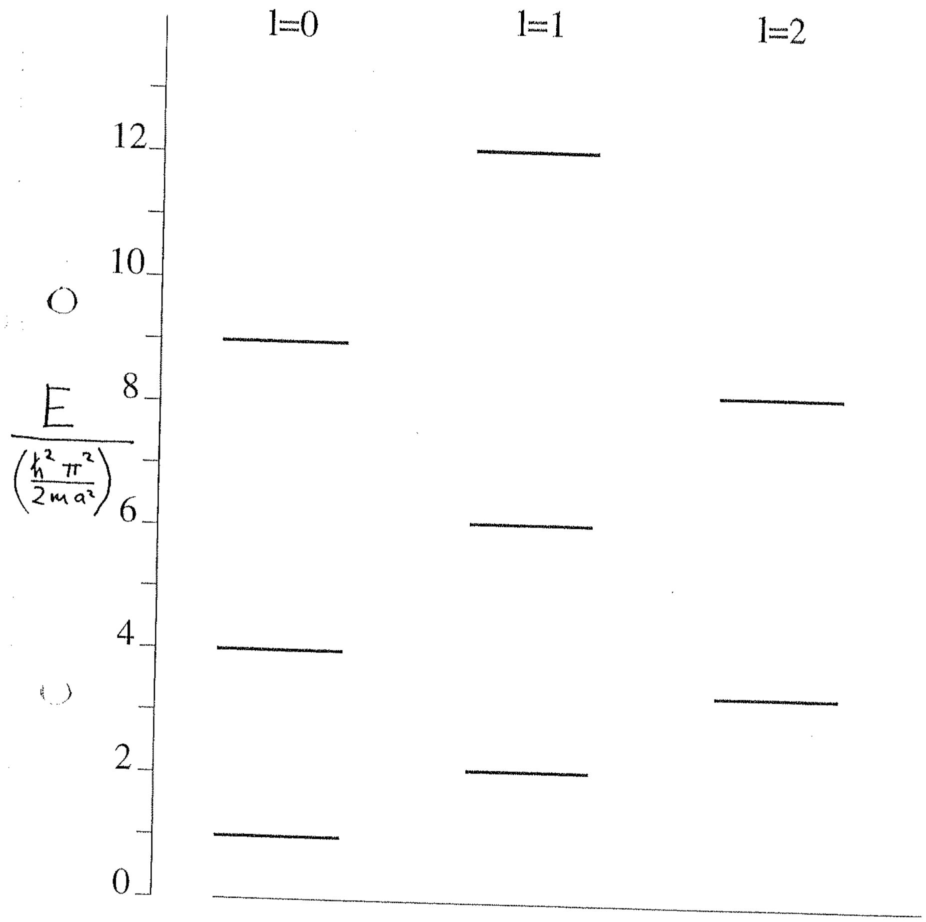
$\Rightarrow E = \frac{\hbar^2\pi^2 n^2}{2ma^2}$ (SAME AS 1d SQUARE WELL. WHY?)

2) $\ell=1$: $R = \frac{1}{(r\sqrt{\epsilon})^2}\sin(r\sqrt{\epsilon}) - \frac{\cos(r\sqrt{\epsilon})}{r\sqrt{\epsilon}}$

ZEROES NOW MORE COMPLICATED

$a\sqrt{\epsilon} = 4.49, 7.72, 10.90, \ldots$

3) $\ell=2$: SEE PICTURES...



Spectrum of spherical well potential

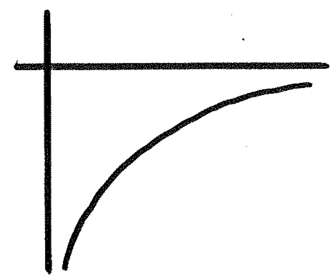
WHAT DO WE SEE?

- ① FOR **EACH** ℓ VALUE (ORB. ANG. MOM'M.) THERE IS A **TOWER OF STATES** (**RADIAL EXCITATIONS**) LABELLED BY A '**PRINCIPAL QUANTUM NUMBER**' WHICH COUNTS NUMBER OF NODES IN $R(r)$
- ② STATES WITH **HIGHER ℓ HAVE HIGHER ENERGIES FOR A GIVEN PRINCIPAL QUANT. #**
- ③ FOR EACH **ℓ THERE ARE $(2\ell+1)$** STATES OF VARYING L_z, SO EACH OF PLOTTED LEVELS IS **DEGENERATE** (APART FROM $\ell=0$)
- ④ DON'T FORGET WE HAVE TO **NORMALIZE** THE RADIAL $R(r)$.

THE HYDROGEN ATOM

- NOW WE START THE STUDY OF A SYSTEM OF GREAT PHYSICAL IMPORTANCE. FOR THE TIME BEING WE'LL STUDY ONLY THE SIMPLEST LEADING APPROXIMATION TO THE REAL HYDROGEN ATOM
  - WE'LL IGNORE RELATIVISTIC EFFECTS, ELECTRON SPIN, NUCLEAR (PROTON) SPIN, FINITE MASS OF THE NUCLEUS, FINITE SIZE OF NUCLEUS, ...
  - EVEN SO WE'LL FIND A GOOD AND VERY USEFUL DESCRIPTION
- IN THIS CASE WE HAVE

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



THIS MEANS THAT WE EXPECT BOUND STATES TO HAVE NEGATIVE ENERGY (JUST A CONSEQUENCE OF TAKING THE ZERO OF ENERGY TO BE AT $V(r\to\infty)$)

THE RADIAL WAVE EQN IS NOW

$$\boxed{-\frac{1}{r^2}\partial_r(r^2\partial_r R) + \frac{\ell(\ell+1)}{r^2}R - \frac{2me^2}{4\pi\epsilon_0\hbar^2}\frac{R}{r} = \frac{2mE}{\hbar^2}R}$$

INTRODUCE $\quad a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{me^2}$ (THIS LENGTH IS IN FACT THE <u>BOHR RADIUS</u>)

AND LET $r = a_0\rho$ GIVING

$$\boxed{\begin{gathered} -R'' - \frac{2}{\rho}R' + \left(\frac{\ell(\ell+1)}{\rho^2} - \frac{2}{\rho}\right)R = \epsilon R \qquad (*) \\ \text{WITH } \epsilon = \frac{2mEa_0^2}{\hbar^2} \end{gathered}}$$

LET'S START OUR ANALYSIS OF THIS EQN BY FINDING BEHAVIOUR AT LARGE r ($\rho \gg 1$)

EQN $\Rightarrow \quad -R'' = \epsilon R$

SOL'N $\quad R \sim \exp(-\sqrt{-\epsilon}\,\rho)$

FOR BOUND STATES WITH $\epsilon < 0$

OTHER SIGN NOT NORMALIZABLE

NOW WHAT HAPPENS FOR SMALL $\rho \ll 1$

$$\underbrace{-R'' - \frac{2}{\rho}R'}_{-\frac{1}{\rho^2}\partial_\rho(\rho^2\partial_\rho R)} + \frac{\ell(\ell+1)}{\rho^2}R = 0$$

MUST KEEP ALL OF THIS

CAN IGNORE COULOMB + ENERGY TERMS

TRY POWER-LAW SOL'N $R \sim \rho^{\nu}$: FIND

$$-\nu(\nu+1)\rho^{\nu-2} + \ell(\ell+1)\rho^{\nu-2} = 0$$

$$\Rightarrow \quad \nu = \begin{cases} \ell \\ -(\ell+1) \end{cases}$$

- NORMALIZABILITY DISALLOWS THE $\nu = -\ell-1$ SOL'NS FOR $\ell \geq 1$ BUT AS IN ∞ SPHERICAL WELL CASE COULD IN PRINCIPLE HAVE

  $\nu = -1$ WHICH IS NORMALIZABLE $\int_0 dr\, r^2 (r^{-1})^2 \sim$ FINITE

- HOWEVER JUST AS IN SPHERICAL WELL CASE A SOL'N OF FORM $R \sim r^{-1}$ WOULD IMPLY

  $V(r) \sim \delta^{(3)}(r)$ NEAR ORIGIN

UNLIKE ∞ SPHERICAL WELL CASE THERE <u>IS</u> NOW SOMETHING GOING ON AT ORIGIN – THE NUCLEUS SITS THERE! BUT FORTUNATELY IN REALITY (<u>AS EXPERIMENTS TELL US</u>) <u>THE INTERACTIONS OF THE (FINITE SIZED) PROTON WITH THE e^-</u> DO <u>NOT</u> LEAD TO A TERM IN THE POTENTIAL $V(r) = V_{coulomb} + \cancel{\delta^{(3)}(r)}$

$\Rightarrow$ $\nu = -1$ MODE ALSO DISALLOWED

- THUS <u>ALLOWED</u> MODES BEHAVE AS

$$\underline{R \sim \rho^{\ell}} \quad \text{FOR } \rho \ll 1$$

- NOTE THAT EQN (*) BEING WRITTEN IN TERMS OF DIMENSIONLESS QUANTITIES (ρ, ϵ, ℓ) MUST HAVE SOL'NS FOR ϵ WHICH ARE PURE NUMBERS, SO

$$E = \frac{\hbar^2}{2m} a_0^{-2} \epsilon = \frac{\hbar^2}{2m} \frac{m^2}{\hbar^4} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \epsilon$$

$$= \underline{\frac{m}{2\hbar} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \epsilon}$$

IF WE HAD A CENTRAL CHARGE Ze INSTEAD OF e WE'D GET

$$E = \frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \epsilon$$

$$= \frac{mc^2 Z^2}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^2 \epsilon$$

SO WE SEE THAT THE ENERGY OF THE STATES IN THE COULOMB POTENTIAL IS

- PROPORTIONAL TO THE MASS OF THE ORBITING PARTICLE
- PROPORTIONAL TO THE NUCLEAR CHARGE <u>SQUARED</u>
- OF ORDER (IN HYDROGEN-LIKE SYSTEMS)

$$\boxed{\frac{Z^2}{2} m_e c^2 \alpha^2}$$

USEFUL TO REMEMBER!

MASS-ENERGY OF ELECTRON $\simeq 0.5$ MeV

DIMENSIONLESS 'FINE STRUCTURE CONSTANT' $\alpha \simeq 1/137$

$$\Rightarrow E_H \sim \frac{m_e c^2 \alpha^2}{2} \sim \frac{0.5\times10^6}{2} \times \left(\frac{1}{140}\right)^2 \simeq 12\text{ eV}$$

<u>NOW LET'S SOLVE EQN (*) EXACTLY</u>

REASONABLE TO FACTOR OUT KNOWN LARGE ρ AND SMALL ρ BEHAVIOUR, SO DEFINE F VIA

$$R = \rho^{l} e^{-\lambda\rho} F(2\lambda\rho)$$

WHERE $\lambda = \sqrt{-\epsilon}$

SUBST THIS INTO (*) GIVES THAT $F(y)$ SATISFIES

$$y F''(y) + F'(y)\left(2(l+1) - y\right) - \left(l+1-1/\lambda\right)F(y) = 0$$

THIS IS YET ANOTHER DIFFERENTIAL EQN WHICH YOU CAN LOOK UP IN BOOKS.
IT IS THE '<u>GENERALIZED LAGUERRE EQN</u>'

THE SOL'NS ARE <u>POLYNOMIALS</u>

$$L_k^{(2l+1)}(y)$$

WHERE $\underline{\lambda = \frac{1}{k+l+1}}$ <u>AND $k = 0, 1, 2, \ldots$</u>

WE HAVE NOW FOUND SPECTRUM AS

$$\epsilon = -\lambda^2 \qquad \text{(BY DEF.'N OF } \lambda)$$

AND

$$E = \frac{\hbar^2}{2ma_0^2}\epsilon$$

$$\Rightarrow \boxed{E = -\frac{\hbar^2}{2ma_0^2}\frac{1}{(k+l+1)^2} \qquad k = 0, 1, 2, \ldots}$$

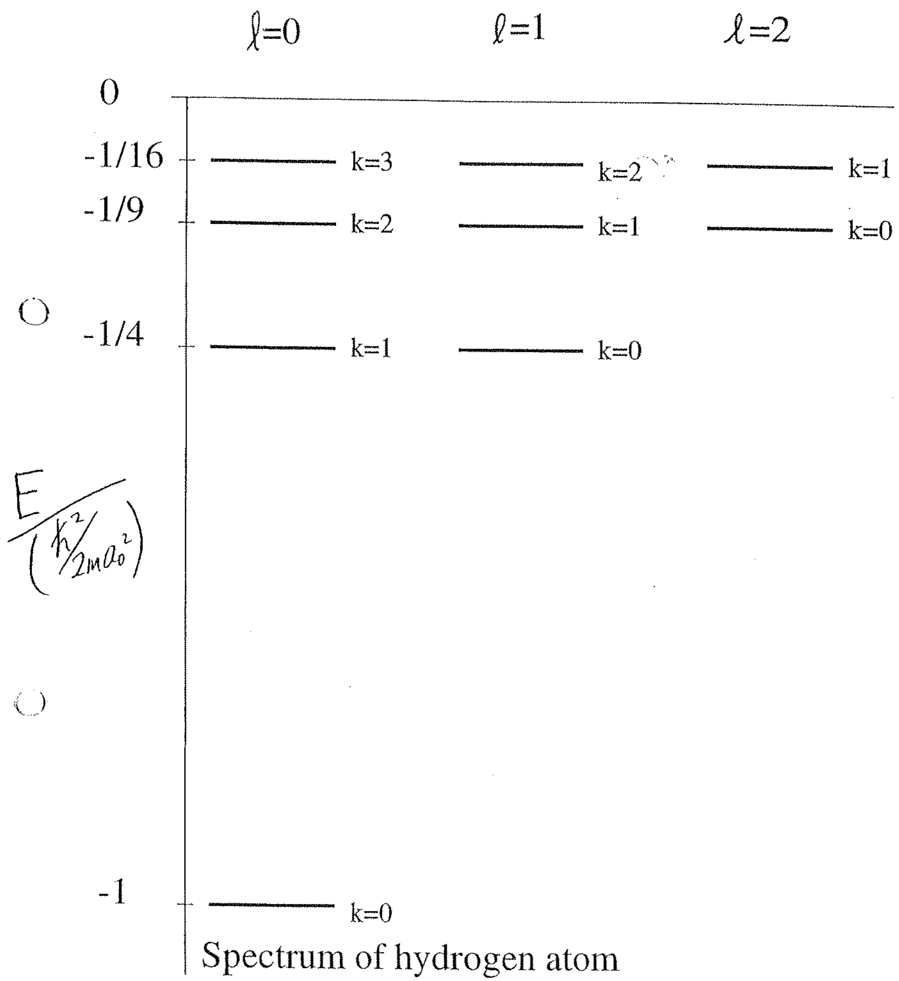
$\longrightarrow$ SEE SPECTRUM

<u>COMMENTS</u>

- THE ENERGY LEVELS OBEY THE RULE FIRST PROPOSED BY BALMER, AND ALSO 'PREDICTED' BY THE BOHR MODEL, IE,

$$(R \simeq 13.6\,\text{eV}) \qquad E = -\frac{R}{n^2} \qquad n = 1, 2, 3, \ldots$$

NOTE HOWEVER THAT THE ANG. MOM'M. QUANTUM NUMBERS ARE <u>DIFFERENT</u> FROM THE BOHR MODEL (WHICH ASSUMES $mr^2\omega = n\hbar$) <u>AND THAT ALL LEVELS EXCEPT $n=1$ ARE HIGHLY DEGENERATE</u>



Spectrum of hydrogen atom

- THE NOMENCLATURE IS CONFUSING. IN ATOMIC PHYSICS WE USE THE QUANTUM NUMBERS n, ℓ (AND m) TO LABEL THE STATES (HISTORICAL HANGOVER), WHEREAS IN NUCLEAR PHYSICS WE USE k, ℓ (AND m) WHICH MAKES MORE SENSE AS

$$\underline{k-1 = \#\text{ OF NODES OF } R(r)}$$

IN ANY CASE IT IS UNFORTUNATELY STANDARD TO CALL

$$\underline{n = k + \ell + 1} \qquad n = 1, 2, 3, \ldots$$

'THE PRINCIPAL QUANTUM NUMBER', SO AT EACH n THE ALLOWED VALUES OF ℓ ARE

$$\ell = n - k - 1 = \underline{0, 1, 2, \ldots, (n-1)}$$

MOREOVER FOR EACH ℓ WE HAVE $(2\ell+1)$ DEGENERATE m VALUES $-\ell, -\ell+1, \ldots, \ell$

SO TOTAL DEGENERACY AT EACH n IS

$$\sum_{\ell=0}^{n-1} (2\ell+1) = \underline{n^2}$$

- THE FACT THAT FOR A GIVEN n, DIFFERENT ℓ VALUES ARE DEGENERATE IS A SPECIAL FEATURE OF THE EXACT COULOMB POTENTIAL (THERE IS IN FACT A 'HIDDEN' SYMMETRY THAT LEADS TO THIS DEGENERACY).
- IN THE REAL HYDROGEN ATOM THIS DEGENERACY OF DIFFERENT ℓ's IS REMOVED BY ALL THE (SMALLER) INTERACTIONS AND EFFECTS WE HAVE IGNORED IN OUR IDEALIZED TREATMENT (SPIN ORBIT COUPLING, RELATIVISTIC CORRECTIONS, ETC...)
  - THESE ARE THE SUBJECT OF THE ATOMIC PHYSICS COURSE (APPLICATIONS OF Q.M.)
- AS EMPHASIZED BEFORE, THE DEGENERACY IN m VALUES AT A GIVEN ℓ

$$m = -\ell, -\ell+1, -\ell+2, \dots, \ell-1, \ell$$

IS DUE TO ROTATIONAL SYMMETRY

NORMALIZATION OF HYDROGEN WAVEFUNCTIONS

THIS REQUIRES

$$1 = \int d(\text{Vol})\, \psi^* \psi$$

$$= \int \sin\theta \, d\theta \, d\phi \int_0^\infty r^2 dr \, |R_{n,\ell} Y_{\ell,m}|^2$$

$$= \underbrace{\int d\Omega \, |Y_{\ell m}|^2}_{1} \int_0^\infty \underset{\substack{\uparrow \\ \text{NOTE}}}{r^2} |R_{n,\ell}|^2 dr$$

THIS MEANS PROBABILITY OF FINDING e^- BETWEEN r AND $r+dr$ IS

$$r^2 |R_{n,\ell}|^2 \quad \textbf{NOT} \quad |R_{n,\ell}|^2 !$$

LOOK AT IMPLICATIONS OF THIS FOR GROUND STATE

$$\psi = Y_{00} \, C \, e^{-r/a_0}$$

$$\Rightarrow 1 = C^2 \int_0^\infty r^2 e^{-2r/a_0} dr = 2C^2 \left(\frac{a_0}{2}\right)^3$$

$$\Rightarrow C = \frac{2}{a_0^{3/2}}$$

NOW LET'S CALCULATE (FOR **GROUND** STATE)

$$\langle r \rangle = \int dV\, \psi^* r\, \psi$$

$$= \int d\Omega\, |Y_{00}|^2 \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0}\, dr$$

$$= \frac{4}{a_0^3} \left(\frac{a_0}{2}\right)^4 \cdot 6$$

$$= \frac{3}{2} a_0$$

ON OTHER HAND THE <u>SINGLE MOST PROBABLE VALUE OF r</u> IS AT THE MAXIMUM OF $r^2 e^{-2r/a_0}$

$$\Rightarrow \quad 0 = 2r e^{-2r/a_0} - \frac{2}{a_0} r^2 e^{-2r/a_0}$$

$$\Rightarrow \quad \underline{r = a_0} \; ! \qquad \text{BOHR RADIUS}$$

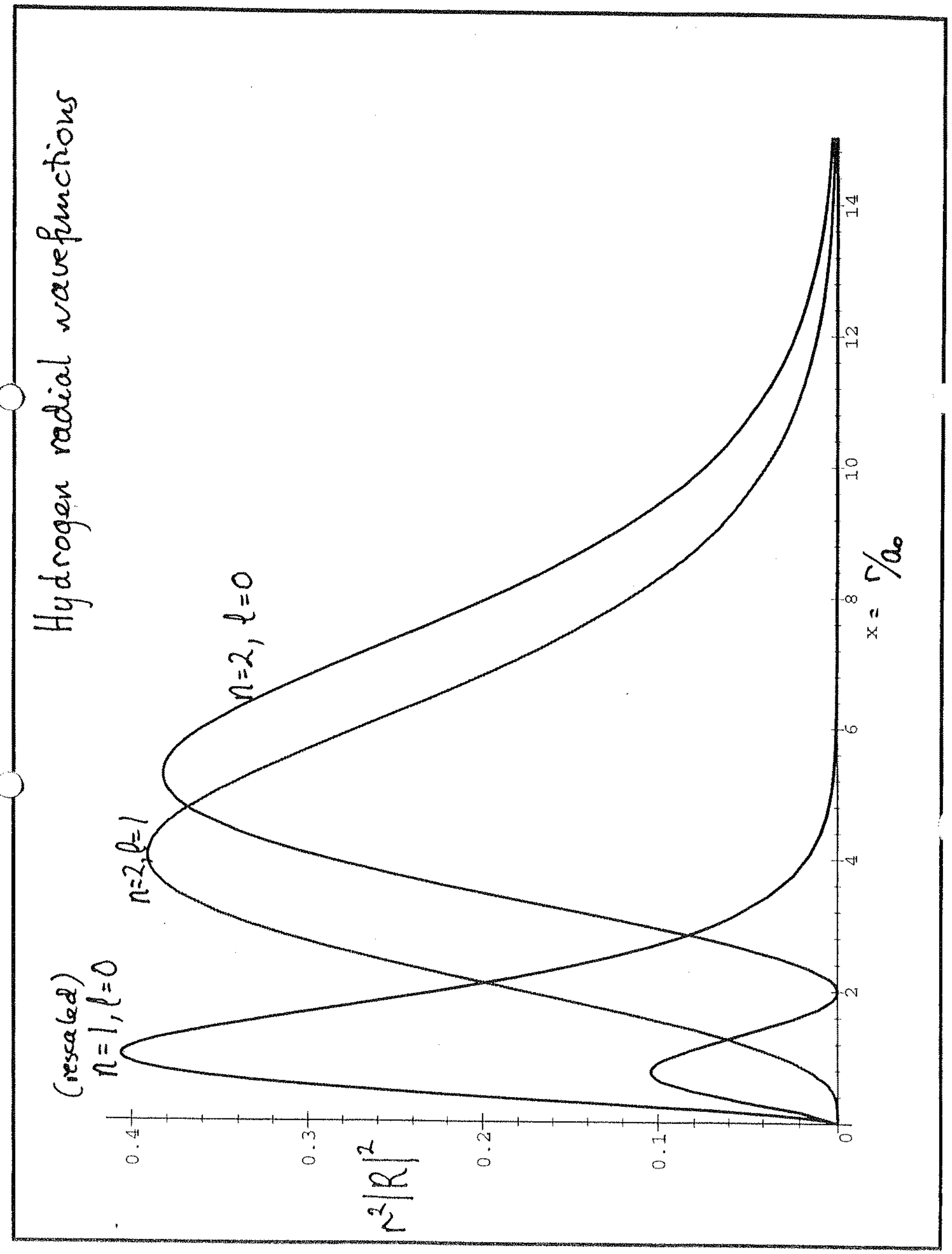
<u>GENERAL FEATURES OF RADIAL WAVEFUNCTIONS</u> (PICTURES)

$$R_{n,\ell} = \text{CONST.}\; e^{-r/na_0}\, r^{\ell}\, (1 + O(r))$$

AS n GETS LARGER PROB DENSITY SPREADS OUT. BUT ALWAYS EXPONENTIALLY SMALL AT LARGE DISTANCES

NOTE

F IS ALWAYS POLYNOMIAL IN r, STARTING WITH 1



SPIN ½

WE SHOWED PREVIOUSLY THAT POSSIBLE TO HAVE STATES SATISFYING

$$J^2 \left|\tfrac{1}{2}, \pm\tfrac{1}{2}\right\rangle = \hbar^2 j(j+1) \left|\tfrac{1}{2}, \pm\tfrac{1}{2}\right\rangle$$

$j = 1/2$

$$J_z \left|\tfrac{1}{2}, \pm\tfrac{1}{2}\right\rangle = \pm\hbar\tfrac{1}{2} \left|\tfrac{1}{2}, \pm\tfrac{1}{2}\right\rangle$$

j_z

THESE DO NOT TURN UP WHEN WE SOLVE THE SCHRODINGER EQN., BUT REQUIRE USE OF THE <u>MATRIX</u> FORMULATION OF Q.M. THE SPIN ½ CASE IS PARTICULARLY IMPORTANT AS ELECTRONS, PROTONS, NEUTRONS, QUARKS,... ALL HAVE SPIN ½.

SINCE FOR $j = 1/2$ IT IS NOT POSSIBLE TO REPRESENT ANGULAR MOMENTUM OPERATORS AS DIFFERENTIAL OPS.

CONSIDER THE MATRICES

$$S_x = \frac{\hbar}{2}\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hookrightarrow \sigma_x} \qquad S_y = \frac{\hbar}{2}\underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\hookrightarrow \sigma_y}$$

$$S_z = \frac{\hbar}{2}\underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\hookrightarrow \sigma_z}$$

$\sigma_x, \sigma_y, \sigma_z$ ARE "PAULI SPIN MATRICES"

THESE ARE HERMITIAN

$$S_x^\dagger = S_x \quad , \quad S_y^\dagger = S_y \quad , \quad S_z^\dagger = S_z$$

SO HAVE REAL EIGENVALUES

NOW CALCULATE

$$[S_x, S_y] = \left(\frac{\hbar}{2}\right)^2 \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right)$$

$$= \frac{\hbar^2}{4}\left(\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right)$$

$$= \frac{\hbar^2}{4} \cdot 2i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= i\hbar S_z$$

EXACTLY THE ANGULAR MOMENTUM COMMUTATION RELATION.

IT'S A SIMPLE EXERCISE TO CHECK (DO IT!) THAT

$$[S_y, S_z] = i\hbar S_x \,, \quad [S_z, S_x] = i\hbar S_y$$

- WE CAN ALSO CALCULATE THE MATRIX FOR S^2

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

$$= \frac{\hbar^2}{4}\left\{\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}^2 + \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}^2 + \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}^2\right\}$$

$$= \frac{\hbar^2}{4}\left\{\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\right\}$$

$$= \frac{\hbar^2}{4} \cdot 3 \cdot \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$= \hbar^2 \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) I$$ UNIT MATRIX

EXACTLY WHAT WE WANT FOR S^2 <u>SINCE THEN ANY TWO COMPONENT VECTOR</u> $\begin{pmatrix}a\\ b\end{pmatrix}$ <u>IS AN EIGENVECTOR OF S^2 WITH EIGENVALUE $\hbar^2 \frac{1}{2}(\frac{1}{2}+1)$</u>

THUS $\begin{pmatrix}a\\ b\end{pmatrix}$ FOR ANY a, b (a, <u>b NOT BOTH $= 0$</u>) REPRESENTS A STATE WITH TOTAL ANG. MOM'M $j = \frac{1}{2}$

- LET'S ALSO LOOK AT $S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$

WHAT ARE IT'S EIGENVALUES?

SINCE S_z DIAGONAL, OBVIOUS THAT

$$S_z\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}1\\ 0\end{pmatrix}$$

$\Rightarrow \begin{pmatrix}1\\ 0\end{pmatrix}$ IS STATE WITH $S_z = +\hbar/2$

SIMILARLY

$\begin{pmatrix}0\\ 1\end{pmatrix}$ IS STATE WITH $S_z = -\hbar/2$

- IT'S NOT MUCH MORE DIFFICULT TO FIND EIGENVALUES AND EIGENVECTORS OF S_x AS WELL

$$\det\begin{pmatrix}-\lambda & \hbar/2\\ \hbar/2 & -\lambda\end{pmatrix} = 0 \Rightarrow \lambda^2 - (\hbar/2)^2 = 0$$

$$\Rightarrow \lambda = \pm\hbar/2 \quad \text{AGAIN}$$

THIS TIME THE EIGENVECTORS ARE

$$\left.\begin{array}{ll}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ 1\end{pmatrix} & \text{FOR } \lambda = +\hbar/2 \\ \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -1\end{pmatrix} & \text{FOR } \lambda = -\hbar/2\end{array}\right\} S_x$$

• SIMILARLY FOR S_y

$$\det\begin{pmatrix} -\lambda & -i\hbar/2 \\ i\hbar/2 & -\lambda \end{pmatrix} = 0 \Rightarrow \lambda^2 - \hbar^2/4 = 0$$

$$\Rightarrow \lambda = \pm \hbar/2 \text{ AGAIN}$$

WITH EIGENVECTORS

$$\boxed{\begin{array}{ll} \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} & \text{FOR } \lambda = +\hbar/2 \\ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix} & \text{FOR } \lambda = -\hbar/2 \end{array}}$$

<u>IMPORTANT</u>: EIGENVALUES FOR S_x, S_y, S_z ARE THE SAME BUT THE EIGENVECTORS ARE DIFFERENT, AND THIS IMPLIES THAT MEASUREMENT OF S_x, S_y, S_z HAVE SOME INTERESTING PROPERTIES

- E.G. SUPPOSE WE START WITH $S_x = +\hbar/2$ STATE $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ AND THEN MEASURE S_z. SO MUST DECOMPOSE INTO S_z EIGENVECTORS

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

THUS UPON MEASUREMENT OF S_z COULD FIND EITHER $\pm\hbar/2$ EACH WITH PROB $= 1/2$

SUPPOSE FIND $S_z = +\hbar/2$

$\Rightarrow$ AFTER MEASUREMENT STATE $= \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

NOW MEASURE S_x. SO MUST DECOMPOSE STATE INTO S_x EIGENVECTORS

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}\right)$$

THUS MEASUREMENT OF S_x CAN GIVE

$S_x = +\hbar/2$ WITH PROB. $= 1/2$

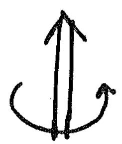
OR $\underbrace{S_x = -\hbar/2}$ WITH PROB. $= 1/2$

SO S_z MEASUREMENT HAS 'GENERATED' THIS POSSIBILITY OF FINDING $S_x = -\hbar/2$ EVEN THOUGH INITIALLY HAD <u>ONLY</u> $S_x = +\hbar/2$

STERN-GERLACH EXPERIMENT

HOW DO WE KNOW THE ELECTRON HAS SPIN = 1/2 ?

WELL, CLASSICALLY A CHARGED OBJECT WITH ANGULAR MOMENTUM HAS A MAGNETIC DIPOLE MOMENT. QUANTUM MECHANICS ALSO LEADS TO THIS CONCLUSION (STRICTLY SPEAKING RELATIVISTIC QM, EQUIVALENTLY QUANTUM FIELD THEORY IS NEEDED TO GIVE A TRULY CONSISTENT AND PRECISE UNDERSTANDING OF e^- MAGNETIC DIPOLE MOMENT)



$$\vec{\mu} \sim \vec{S}$$

BECAUSE e^- CHARGE IS NEGATIVE

$$\vec{\mu} = -g_s \frac{e}{2m_e} \vec{S}$$

g_s: CORRECTION DUE TO QUANTUM EFFECTS (NEEDS DIRAC EQN. AND QFT TO CALCULATE)

$\frac{e}{2m_e}$: CLASSICAL COEFFICIENT OF PROPORTIONALITY BETWEEN $\vec{\mu}$ AND $\vec{S}$

NOW IF HAVE MAGNETIC FIELD IN Z-DIR'N B_z THERE ARE TWO POSSIBLE VALUES FOR INTERACTION ENERGY $-\vec{B}.\vec{\mu}$

DUE TO QUANTIZATION OF S_z
IF $S_z = +\hbar/2$ $\quad -\vec{B}.\vec{\mu} = +\frac{g_s e}{2m_e}.\frac{\hbar}{2}.B_z$
IF $S_z = -\hbar/2$ $\quad -\vec{B}.\vec{\mu} = -\frac{g_s e}{2m_e}.\frac{\hbar}{2}.B_z$
$\Longleftrightarrow$ TWO DISCRETE POSSIBLE VALUES OF MAGNETIC DIPOLE MOMENT

COMBINATION

$$\frac{e\hbar}{2m_e} \equiv \mu_B \quad \text{"BOHR MAGNETON"}$$

OF COURSE, TYPICALLY THE POTENTIAL ENERGY OF A SYSTEM WILL BE A COMBINATION OF A SPIN-INDEPENDENT $V(r)$, AND A SPIN-DEPENDENT TERM (ARISING, SAY, FROM A $\vec{B}.\vec{\mu}$ INTERACTION)

THUS TYPICALLY THE FORM OF THE ENERGY (HAMILTONIAN) FOR A SPIN ½ SYSTEM (E.G. AN ELECTRON IN AN ATOM) WILL BE

$$H = H_0 I + \frac{g_s e}{2m_e} \vec{B}.\vec{S}$$

IDENTITY MATRIX, SO ENERGY FROM H_0 TERM INDEP'T OF SPIN STATE

COULD BE, E.G., COULOMB POTENTIAL + K.E.

MEANS $B_x S_x + B_y S_y + B_z S_z$

THUS WE CAN CONSIDER A MODIFIED FORM OF TDSE

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

H IS NOW A 2x2 MATRIX AS WELL AS A DIFFERENTIAL OPERATOR

Ψ IS A TWO COMPONENT VECTOR, WITH EACH COMPONENT BEING A FUNCTION OF (t, r, θ, φ)

I.E., $\begin{pmatrix} \psi_1(t,r,\theta,\varphi) \\ \psi_2(t,r,\theta,\varphi) \end{pmatrix} = \Psi$

IF B-FIELD IS A CONSTANT THEN THIS EQN (MODIFIED TDSE) IS SIMPLE TO ANALYSE.

WRITE

$$\Psi = \Phi(t, r, \theta, \varphi)\,\vec{u}$$

A CONSTANT TWO COMPONENT VECTOR

THIS GIVES

$$(H_0 \Phi)\vec{u} + \Phi \frac{g_s e}{2m_e}(\vec{B}.\vec{S})\vec{u} = i\hbar \frac{\partial \Phi}{\partial t}\vec{u} \quad (*)$$

THIS CAN ONLY BE SATISFIED IF

$$(\vec{B}.\vec{S})\,\vec{u} = \lambda \vec{u}$$

MOREOVER, IF REST OF PROBLEM (IE APART FROM $\vec{B}$) IS SPHERICALLY SYMMETRIC, THEN WE CAN ALWAYS CHOOSE DIRECTION OF x, y, z AXES SUCH THAT z-AXIS IS IN $\vec{B}$ DIRECTION. WITH THIS COORDINATE CHOICE

$$\vec{B} = (0, 0, B_z)$$

THEN

$$B S_z \vec{u} = \lambda \vec{u}$$

$$\lambda = \pm \frac{\hbar B}{2} \quad \text{FOR } \vec{u} = \begin{pmatrix}1\\0\end{pmatrix}, \begin{pmatrix}0\\1\end{pmatrix}$$

PUTTING THIS BACK INTO (✱) WE GET 2 EQNS

$$\left(H_0 + \frac{g_s e}{2m_e}\frac{\hbar B}{2}\right)\phi_1(t,r,\theta,\varphi) = i\hbar\frac{\partial \phi_1}{\partial t} \quad (1)$$

$$\left(H_0 - \frac{g_s e}{2m_e}\frac{\hbar B}{2}\right)\phi_2(t,r,\theta,\varphi) = i\hbar\frac{\partial \phi_2}{\partial t} \quad (2)$$

ϕ_1 AND ϕ_2 ARE TOP AND BOTTOM COMPONENTS OF $\underline{\Phi} = \begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix}$

NOW CAN SEPARATE VARIABLES AS USUAL FOR (1) AND (2), E.G.

$$\phi_1(t,r,\theta,\varphi) = e^{-iE_1 t/\hbar}\,\tilde{\varphi}_1(r,\theta,\varphi)$$

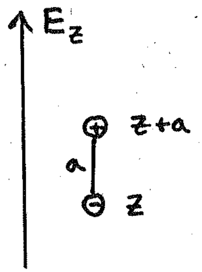
$$\phi_2(t,r,\theta,\varphi) = e^{-iE_2 t/\hbar}\,\tilde{\varphi}_2(r,\theta,\varphi)$$

GIVING TISE'S FOR $\tilde{\varphi}_1$ AND $\tilde{\varphi}_2$.

INTERPRETATION IS SIMPLY THAT e^- CAN EITHER HAVE SPIN ALIGNED WITH $\vec{B}$, OR ANTI-ALIGNED, AND ENERGIES ARE SHIFTED BY $\pm g_s \mu_B B/2$ RESPECTIVELY.

- NOW CONSIDER DIPOLE IN **NON-UNIFORM** B-FIELD

TO GET ORIENTED WITH THE PHYSICS CONSIDER ELECTRIC DIPOLE IN NON UNIFORM $\vec{E}$



NET FORCE

$$= qE(z+a) - qE(z)$$

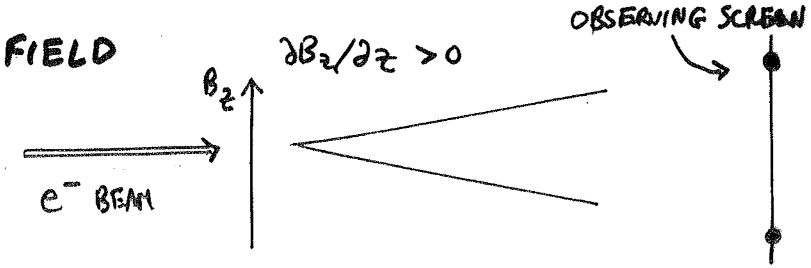
$$\simeq q\left(E(z) + a\left.\frac{\partial E}{\partial z}\right|_z - E(z)\right)$$

$$\simeq qa\frac{\partial E}{\partial z} = p\frac{\partial E}{\partial z}$$

SIMILARLY IF WE HAVE A MAGNETIC DIPOLE IN A NON-UNIFORM FIELD

$$F = \mu \frac{\partial B}{\partial z}$$

NOW SUPPOSE WE HAVE A BEAM OF ELECTRONS GOING THROUGH A REGION OF NON-UNIFORM B_z FIELD



UP OR DOWN DEPENDING ON WHICH WAY THEIR $\vec{\mu}$ (IE S_z) IS POINTING.

THIS IS THE ESSENCE OF THE STERN-GERLACH EXPERIMENT (SEE FRENCH + TAYLOR, SECTION 10.3 FOR MORE INFORMATION, AS WELL AS HT PROBLEM SET)

- IMPORTANT POINTS TO NOTE:

  1. CLASSICALLY ONE WOULD EXPECT TO SEE A CONTINUOUS DISTRIBUTION OF e^- DEFLECTIONS ON OBSERVING SCREEN (AS CLASSICALLY S_z, AND THUS μ_z, CAN TAKE ON ANY VALUE – NOT QUANTIZED)
  2. THE EXPERIMENT INSTEAD SHOWS JUST <u>TWO</u> SPOTS (FOR SPIN ½ SYSTEM) ON SCREEN $\rightarrow$ <u>S_z IS QUANTIZED</u> (AND SIMILARLY FOR ANY OTHER AXIS) <u>WITH 2 VALUE</u>
  3. IN DETAIL WHEN ONE CALCULATES POSITIONS OF SPOTS ONE FINDS THEY ARE TWICE AS FAR APART AS EXPECTED BASED UPON

$$\vec{\mu} = -\frac{e}{2m_e}\vec{S}$$

THIS IS (ONE OF MANY) REASON(S) WHY FORCED TO INTRODUCE

$$g_s \simeq 2 = \text{"GYROMAGNETIC RATIO"}$$

SO

$$\vec{\mu} = -\frac{g_s e}{2m_e}\vec{S}$$

AROUND ANY AXIS GIVES $\pm\hbar/2$ EIGENVALUES

$$= -g_s \mu_B \left(\pm\tfrac{1}{2}\right)$$

$$\mu_B = \frac{e\hbar}{2m_e}$$

TWO OR MORE PARTICLES

- SO FAR HAVE ONLY STUDIED THE QM OF 1 PARTICLE IN AN EXTERNAL STATIC POTENTIAL.
- HOWEVER MOST OF THE WORLD IS NOT LIKE THIS : USUALLY WE HAVE SYSTEM OF TWO OR MORE PARTICLES INTERACTING WITH EACH OTHER
- SIMPLEST CASE

  2 PARTICLES INTERACTING VIA A POTENTIAL WHICH DEPENDS ON <u>THEIR SEPARATION</u>

  E.G. ELECTRON AND PROTON IN H

  THEN

$$H = \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(\vec{r}_1 - \vec{r}_2)$$

AND $\psi(\vec{r}_1, \vec{r}_2, t)$

THE TDSE IS NOW

$$\left\{ -\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 + V(\vec{r}_1 - \vec{r}_2) \right\} \psi(\vec{r}_1, \vec{r}_2, t)$$

$$= i\hbar \frac{\partial \psi(\vec{r}_1, \vec{r}_2, t)}{\partial t}$$

NOTE THAT THE TIME DEPENDENCE IS STILL SEPERABLE

$$\psi(\vec{r}_1, \vec{r}_2, t) = e^{-iEt/\hbar}\,\Phi(\vec{r}_1, \vec{r}_2)$$

LEADING TO

$$\left\{ -\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 + V(\vec{r}_1 - \vec{r}_2) \right\} \Phi(\vec{r}_1, \vec{r}_2)$$

$$= E\,\Phi(\vec{r}_1, \vec{r}_2)$$

THIS CAN ALWAYS BE SIMPLIFIED BY <u>INTRODUCING A CENTER OF MASS COORD</u>. LET

$$\vec{X} = \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$$

$$\vec{x} = \vec{r} = \vec{r}_1 - \vec{r}_2$$

THEN

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} = \frac{m_1}{m_1+m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_2} = \frac{\partial X}{\partial x_2}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} = \frac{m_2}{m_1+m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

AND THEREFORE

$$\frac{-\hbar^2}{2}\left\{\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2}\right\}$$

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

SO WE GET

$$\left\{\frac{-\hbar^2}{2M}\vec{\nabla}_R^2 - \frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})\right\}\Phi = E\,\Phi$$

TOTAL MASS
$M = m_1 + m_2$

"REDUCED" MASS
$\mu = \frac{m_1 m_2}{m_1 + m_2}$

NOW WE SEE THAT THE <u>X AND x PARTS ARE SEPARABLE</u>

$$\Phi(\vec{r}_1,\vec{r}_2) = e^{\cdots}\,\underbrace{\phi(\vec{x})}_{\text{ALL } \vec{x} \text{ DEP. IN HERE}}$$

CENTER-OF-MASS MOMENTUM

$$\text{SO}\quad E = \underbrace{\frac{\hbar^2}{2M}\left(\frac{\vec{p}_{CM}}{\hbar}\right)^2}_{\text{KE OF C.O.M. MOTION}} + E_{INT}$$

INTERACTION ENERGY

WHERE

$$\left\{\frac{-\hbar^2}{2\mu}\vec{\nabla}_x^2 + V(\vec{x})\right\}\phi(\vec{x}) = E_{INT}\,\phi(\vec{x})$$

- NOTE THAT THIS IS OF THE <u>FORM OF A SINGLE-PARTICLE TISE WITH EXTERNAL POTENTIAL $V(\vec{x})$</u>, WHICH WE KNOW HOW TO SOLVE

  PROBLEM THUS SPLITS INTO

  A CENTER OF MASS MOTION CONTRIBUTION

  \+ INTERNAL EXCITATION CONTRIBUTION

- ALSO EXPLAINS WHY WE COULD SOLVE HYDROGEN ATOM PROBLEM (WHICH INVOLVES 2 PARTICLES) USING JUST SINGLE-PARTICLE TISE

• DIFFERENCE IS THAT THE INTERNAL EXCITATION PROBLEM INVOLVES <u>REDUCED MASS μ</u>

FOR H THIS MEANS THAT REALLY SHOULD NOT USE m_e IN COMPUTING SPECTRUM BUT

$$\mu_H = \frac{m_e m_p}{m_e + m_p} \simeq m_e\left(1 - \frac{m_e}{m_p} + \dots\right)$$

SMALL CORRECTION AS $m_e/m_p \simeq 1800$

HOWEVER IN SOME SYSTEMS THE REDUCED MASS EFFECT IS NOT SMALL AT ALL

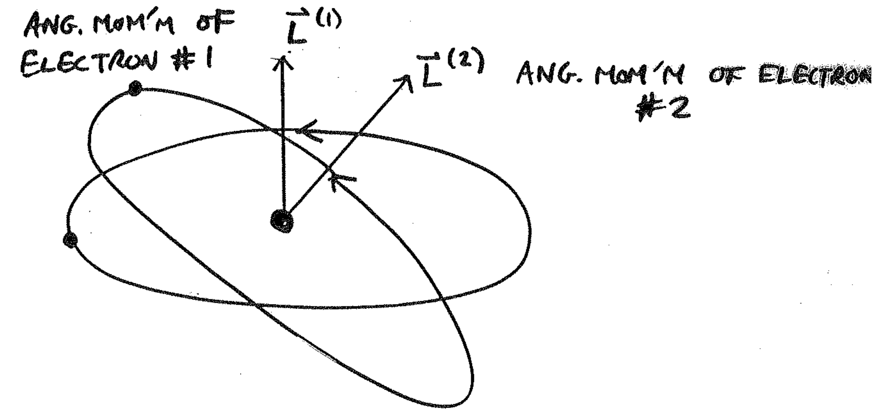
E.G. 'POSITRONIUM' – BOUND e^+e^- SYSTEM

$$\mu = \frac{m_e^2}{2m_e} = \frac{m_e}{2}$$

SO FAR IN 2-PARTICLE SYSTEMS HAVE NOT LOOKED AT ANGULAR MOMENTUM

AS AN EXAMPLE OF THE USEFULNESS OF CONSIDERING ANG. MOM.'M FOR MULTI-PARTICLE SYSTEMS LET'S CONSIDER THE HELIUM ATOM IN LIMIT THAT NUCLEUS IS TAKEN INFINITELY HEAVY (ONLY CONSIDERING MOTION OF 2 e^-'s)

THE CLASSICAL PICTURE IS LIKE A STAR WITH TWO PLANETS



• FIRST SUPPOSE THAT THE ELECTRONS FEEL <u>ONLY</u> THE CENTRAL POTENTIAL (WE SWITCH OFF THEIR REPULSION)

THEN CLASSICALLY

$\vec{L}^{(1)}$ IS CONSERVED, IE. A CONSTANT VECTOR

$\vec{L}^{(2)}$ " " " " "

TOTAL ANG. MOM.'M IS

$$\vec{L} = \vec{L}^{(1)} + \vec{L}^{(2)}$$

AND $\vec{L}$ IS CONSERVED TOO (JUST VECTOR SUM OF $\vec{L}^{(1)}$ AND $\vec{L}^{(2)}$)

- WHAT HAPPENS (STILL CLASSICALLY) WHEN SWITCH BACK ON REPULSION

   $\Rightarrow$ ELECTRON #1 <u>NO LONGER</u> IN A CENTRAL POTENTIAL, SO

   <u>$\vec{L}^{(1)}$ IS NOT CONSERVED</u>. IT IS A TIME-DEP'T VECTOR

<u>SIMILARLY FOR $\vec{L}^{(2)}$</u>.

- HOWEVER, THERE IS NO EXTERNAL COUPLE ON THE ENTIRE SYSTEM AND THEREFORE

   <u>$\vec{L} = \vec{L}^{(1)} + \vec{L}^{(2)}$ IS STILL CONSERVED</u>

WHAT HAPPENS IN QM?

THE TISE TAKES FORM

$$H\,\Phi(\vec{r}_1,\vec{r}_2) = E\,\Phi(\vec{r}_1,\vec{r}_2)$$

POSITION OF ELECTRON 1 WRT NUCLEUS

POSITION OF #2 WRT NUCLEUS

WITH

$$H = -\frac{\hbar^2}{2m_e}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_e}\vec{\nabla}_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}$$

$$= H_1 + H_2 + H_{INT}$$

THIS IS NASTY: BECAUSE $\vec{r}_1$, $\vec{r}_2$ <u>AND</u> $|\vec{r}_1-\vec{r}_2|$ APPEAR IN POTENTIAL THIS EQN. IS <u>NOT SEPARABLE</u>

IN FACT IT CANNOT BE SOLVED EXACTLY

- HOWEVER OUR CLASSICAL DISCUSSION SUGGESTS THAT WE MIGHT BE ABLE TO SAY SOMETHING ABOUT THE ANG. MOM'M OF THE SYSTEM.

   - WE KNOW THAT, E.G., $L_z^{(1)} = -i\hbar\left(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1}\right)$ COMMUTES WITH H_1 (AS JUST LIKE HYDROGEN)

ALSO $L_z^{(2)} = -i\hbar\left(x_2 \frac{\partial}{\partial y_2} - y_2 \frac{\partial}{\partial x_2}\right)$

COMMUTES WITH $L_z^{(1)}$, ($L_x^{(1)}$, $L_y^{(1)}$, $\vec{L}^{(1)2}$ TOO)

> THIS IS AN EXAMPLE OF FACT THAT OPERATORS ASSOCIATED PURELY WITH SYSTEM #1 (EG. $\vec{X}_1$, $\vec{P}_1 = -i\hbar\vec{\nabla}_1$, ETC) COMMUTE WITH THOSE ASSOCIATED PURELY WITH SYSTEM #2 (EG. $\vec{X}_2$, $\vec{P}_2$, $\vec{L}_2$, ...)

- THE PROBLEM IS THAT $L_z^{(1)}$ DOES NOT COMMUTE WITH THE $H_{INT} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}$ PART OF H

LET'S CALCULATE

$$[L_z^{(1)}, H_{INT}] = \frac{-i\hbar e^2}{4\pi\epsilon_0}\left(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1}\right)\left((x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2\right)^{-1/2}$$

$$= \frac{i\hbar e^2}{4\pi\epsilon_0}(y_1x_2 - x_1y_2)/|\vec{r}_1 - \vec{r}_2|^3$$

(CHECK THIS!)

$$\neq 0$$

BUT WE EXPECT (BASED ON CLASSICAL PHYSICS) THAT IT SHOULD BE $L_z^{(1)} + L_z^{(2)}$ THAT IS SIMPLE

SO ALSO CALCULATE

$$[L_z^{(2)}, H_{INT}] = \frac{-i\hbar e^2}{4\pi\epsilon_0}\left(x_2\frac{\partial}{\partial y_2} - y_2\frac{\partial}{\partial x_2}\right)\left[(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2\right]^{-1/2}$$

$$= \frac{-i\hbar e^2}{4\pi\epsilon_0}(y_1x_2 - x_1y_2)/|\vec{r}_1 - \vec{r}_2|^3$$

$$\neq 0$$

BUT <u>SUM</u> $L_z = L_z^{(1)} + L_z^{(2)}$ SATISFIES

$$\underline{[L_z, H_{INT}] = 0}$$

SIMILARLY $L_x = L_x^{(1)} + L_x^{(2)}$ AND $L_y = L_y^{(1)} + L_y^{(2)}$ COMMUTE WITH H_{INT}, AND THUS $H_{TOTAL} = H_1 + H_2 + H_{INT}$ TOO.

$$\Rightarrow \boxed{\begin{array}{l}\vec{L} = \vec{L}^{(1)} + \vec{L}^{(2)} \\ \text{COMMUTES WITH HAMILTONIAN}\end{array}}$$

ALSO BE EIGENSTATES OF L

$\boxed{\text{(TOT.) ANG. MOM'M QUANTUM NUMBERS ARE GOOD QUANTUM \#'s}}$

• <u>BUT WHAT ARE THEY ?</u>

CONSIDER AGAIN He ATOM WITH REPULSION TURNED OFF. TISE IS THEN

$$(H_1 + H_2)\,\Phi(\vec{r}_1,\vec{r}_2) = E\,\Phi(\vec{r}_1,\vec{r}_2)$$

THIS <u>IS SEPARABLE</u> : SUBSTITUTE

$$\Phi(\vec{r}_1,\vec{r}_2) = \phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)$$

THEN WE GET

$$\underbrace{\frac{1}{\phi_1}\left\{\frac{-\hbar^2}{2m}\vec{\nabla}_1^{\,2} + V(r_1)\right\}\phi_1}_{\substack{=E_1 \\ \text{HYDROGEN-LIKE } Z=2}} + \underbrace{\frac{1}{\phi_2}\left\{\frac{-\hbar^2}{2m}\vec{\nabla}_2^{\,2} + V(r_2)\right\}\phi_2}_{\substack{=E_2 \\ \text{HYDROGEN-LIKE } Z=2}} = E$$

SO $\quad \Phi = \phi_{n_1 \ell_1 m_1}(\vec{r}_1)\,\phi_{n_2 \ell_2 m_2}(\vec{r}_2)$

IS AN <u>EIGENSTATE</u>.

• ELECTRON #1 HAS $L^{(1)2}$ ... $\ell_1(\ell_1+1)\hbar^2$
$L_z^{(1)}$ $\quad m_1\hbar$

ELECTRON #2 " $L^{(2)2}$ $\quad \ell_2(\ell_2+1)\hbar^2$
$L_z^{(2)}$ $\quad m_2\hbar$

• WHAT ABOUT WHOLE ATOM?

LET'S LOOK AT COMMUTATORS OF $\vec{L}$

$$[L_x, L_y] = [L_x^{(1)} + L_x^{(2)},\ L_y^{(1)} + L_y^{(2)}]$$
$$= [L_x^{(1)}, L_y^{(1)}] + [L_x^{(2)}, L_y^{(2)}]$$
$$= i\hbar L_z^{(1)} + i\hbar L_z^{(2)}$$
$$= i\hbar L_z$$

AS EXPECTED. (SIMILARLY FOR OTHERS)

THUS WE KNOW THAT EIGENSTATES Ψ MUST SATISFY

TOTAL ANG. MOM'M OPERATORS

$$\vec{L}^2\,\Psi = \hbar^2 L(L+1)\,\Psi \qquad \underbrace{L = 0,1,2,\ldots}$$
$$L_z\,\Psi = \hbar M\,\Psi$$
$$|M| \leq L$$

WE'VE BEEN DOING ORBITAL ANG. MOM'M – SIMILAR WOULD BE TRUE FOR SPIN CA...

THUS THE STATES OF THE HELIUM ATOM HAVE ORBITAL ANG. MOM'M QUANTUM #'s L, M JUST LIKE H ATOM HAS ℓ, m

(THIS ARGUMENT WORKS FOR ALL ATOMS)

THERE IS A CORRESPONDENCE BETWEEN $(\ell_1, m_1), (\ell_2, m_2)$ AND (L, M)

$$L_z \Phi = M\hbar \Phi$$

$$L_z \Phi = (L_z^{(1)} + L_z^{(2)})\Phi$$

$$= (L_z^{(1)} + L_z^{(2)})\phi_{n_1 \ell_1 m_1}(r_1)\phi_{n_2 \ell_2 m_2}(r_2)$$

$$= \hbar(m_1 + m_2)\phi_{n_1 \ell_1 m_1}\phi_{n_2 \ell_2 m_2}$$

$$= \hbar(m_1 + m_2)\Phi$$

$$\Rightarrow \boxed{M = m_1 + m_2}$$

ADDITION RULE FOR Z-CPT OF ANG. MOM'M OF TWO SYSTEMS

<u>BUT</u> NOT SO SIMPLE FOR $\vec{L}^2$

$$\vec{L}^2\Phi = (\vec{L}^{(1)} + \vec{L}^{(2)})^2\Phi$$

$$= (\vec{L}^{(1)2} + \vec{L}^{(2)2} + 2\vec{L}^{(1)}\cdot\vec{L}^{(2)})\Phi$$

$$= \left(\vec{L}^{(1)2} + \vec{L}^{(2)2} + 2\left[L_x^{(1)}L_x^{(2)} + L_y^{(1)}L_y^{(2)} + L_z^{(1)}L_z^{(2)}\right]\right)\phi_{n_1 \ell_1 m_1}\phi_{n_2 \ell_2 m_2}$$

$\phi_{n_1 \ell_1 m_1}\phi_{n_2 \ell_2 m_2}$ IS AN EIGENSTATE OF THESE

$\phi_{n_1 \ell_1 m_1}\phi_{n_2 \ell_2 m_2}$ IS NOT AN EIGENSTATE OF THESE

BECAUSE $\phi_{n_1 \ell_1 m_1}\phi_{n_2 \ell_2 m_2}$ IS NOT AN EIGENSTATE OF ALL OF $\vec{L}^2$ OPERATOR, WHEN WE MEASURE $\vec{L}^2$ THERE IS IN GENERAL A SUPERPOSITION OF DIFFERENT VALUES WE CAN GET

Φ IS A LINEAR SUPERPOSITION OF EIGENSTATES OF $\vec{L}^2$ WITH DIFFERENT VALUES OF QUANT. #L

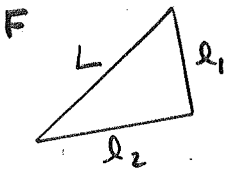
IN THIS COURSE WE WON'T PROVE FOLLOWING RESULT

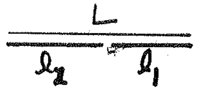
IF TWO ANG. MOM'M (WITH QUANTUM #'s ℓ_1 AND ℓ_2) ARE COMBINED THEN POSSIBLE OUTCOMES FOR L ARE

$$L = \ell_1 + \ell_2,\ \ell_1 + \ell_2 - 1,\ \dots,\ |\ell_1 - \ell_2|$$

THIS RESULT (WHICH YOU NEED TO KNOW!) HAS A GEOMETRICAL INTERPRETATION (MUCH LOVED BY CHEMISTS)

TRIANGLE RULE

IF  IS A POSSIBLE TRIANGLE

(INCLUDING ) THEN L IS A POSSIBLE OUTCOME WHEN THE TOTAL ANG. MOM'M QUANTUM NUMBER IS MEASURED

EXAMPLE (1)

SUPPOSE $\ell_1 = 1$, $\ell_2 = 2$

POSSIBLE L VALUES ARE $1+2 = 3$

$1+2-1 = 2$

$2-1 = 1$

NOTE TOTAL NUMBER OF STATES MATCHES

$\ell_1 = 1$ $\quad m_1 = 1, 0, -1$ $\quad$ 3 STATES

$\ell_2 = 2$ $\quad m_2 = 2, 1, 0, -1, -2$ $\quad$ 5 STATES

POSSIBLE COMBINATIONS $3 \times 5 = 15$

$L = 3$ $\quad M = 3, 2, 1, 0, -1, -2, -3$ $\quad$ 7 STATES

$L = 2$ $\quad M = 2, 1, 0, -1, -2$ $\quad$ 5 STATES

$L = 1$ $\quad M = 1, 0, -1$ $\quad$ 3 STATES

$\underline{\overline{15}}$ ✓

EXAMPLE (2)

ALSO WORKS FOR ANG. MOM'M <u>INCLUDING</u> <u>SPIN</u>, EG.

$j_1 = 1/2 \qquad j_2 = 1$

POSSIBLE J VALUES ARE $1 + 1/2 = 3/2$

$1 - 1/2 = 1/2$

TOTAL # OF STATES

$j_1 = 1/2 \quad j_z = +1/2, -1/2$ $\quad$ 2 STATES

$j_2 = 1 \quad j_z = 1, 0, -1$ $\quad$ 3 STATES

$\Rightarrow$ 6 POSSIBLE COMBINATIONS

$J = 3/2 \quad J_z = 3/2, 1/2, -1/2, -3/2$ $\quad$ 4 STATES

$J = 1/2 \quad J_z = 1/2, -1/2$ $\quad$ 2 STATES

$\underline{\overline{6}}$ ✓

LET'S NOW TURN BACK ON REPULSION H_{INT} BETWEEN ELECTRONS.

AS WE'VE SEEN $(L^{(1)})^2$ ETC... DO NOT COMMUTE WITH H_{INT}, BUT L^2 DOES

$\Rightarrow$ IF MEASURE L^2 GET $L(L+1)$

" " L_z " M

<u>BUT</u> BECAUSE OF H_{INT} $L^{(1)}$ AND $L^{(2)}$ ARE NOT INDIVIDUALLY MEANINGFUL (TIME INDEP'T)

<u>ONLY</u> COUNTING OF POSSIBLE L, M VALUES GIVEN BY ANG. MOM'M ADDITION RULES

$$M = m_1 + m_2$$

$$L = l_1 + l_2,\ l_1 + l_2 - 1,\ \dots,\ |l_1 - l_2|$$

IS SENSIBLE

(OF COURSE SOMETIMES H_{INT} IS RELATIVELY WEAK SO CLASSIFICATION VIA l_1, l_2, m_1, m_2 IS APPROXIMATELY VALID. SEE FURTHER Q.M. COURSE...)