Phys 402

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Purposes of Course

- Generalize 1-d formalism of 401 to multi-dimensional problems, more than on particle, spin degrees of freedom etc
- Application of QM mostly in atomic physics but also condensed matter + possibly particles
- build a tool kit of approximation methods (recall even in 1-D few problems we could solve exactly)

- Assume you are familiar with Dirac notation

How do we generalize Q.M. to more than 1 degree of freedom

one D.O.F / for particle motion in one direction

Start Formally:

Q.M. <u>is</u> the theory of Hermitian operators in a complex Hilbert space (with physical interpretations for eigenvalues and expectation values)

for operator $\hat{A}$ — $\langle\Psi|\hat{A}|\Psi\rangle$ average value of $\hat{A}$ in state $|\Psi\rangle$ (many measurements)

— $\hat{A}|i\rangle = A_i\,|i\rangle$

A_i are possible results of measurements

— $|\Psi\rangle = \sum_i c_i|i\rangle \quad P_i = |c_i|^2$

Suppose I have two quantum systems with different Hilbert spaces (e.g. motion in x and motion in y)

system 1: basis states $\{|i\rangle^{(1)}\}$
operators $\hat{A}^{(1)}$
matrix elements
${}^{(1)}\langle j|\hat{A}^{(1)}|i\rangle^{(1)}$

system 2: basis states $\{|i\rangle^{2}\}$
operators $\hat{A}^{(2)}$
ME's ${}^{(2)}\langle j|\hat{A}^{(2)}|i\rangle^{(2)}$

Claim: we can form a new Hilbert space with Hermitian operators by taking outer productors

different notation

basis states : $|i,j\rangle = |i\rangle^{(1)}|j\rangle^{(2)} = |i\rangle^{(1)} \otimes |j\rangle^{(2)}$
simple product of unconnected spaces

operators : $\hat{C} = \hat{A}^{(1)}\hat{B}^{(2)}$ or sum of operators of this form
note either $\hat{A}^{(1)}$ or $\hat{B}^{(2)}$ could be $\mathbb{1}$

$\hat{H}$ is sum of operators of this form

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

M.E's consider M.E's of $\hat{C} = \hat{A}^{(1)} \hat{B}^{(2)}$

$$\langle i', j' | \hat{C} | i j \rangle = \langle i', j' | \hat{A}^{(1)} \hat{B}^{(2)} | i j \rangle$$

$$\equiv {}^{(1)}\langle i' | \hat{A}^{(1)} | i \rangle^{(1)} \; {}^{(2)}\langle j' | \hat{B}^{2} | j \rangle$$

Note "Matrix" is of form $C_{(i' j'),(i j)}$
each label of state has two numbers

generally $\hat{C} | \Psi \rangle^{(1)} | \phi \rangle^{2} = (\hat{A}^{(1)} | \Psi \rangle^{(1)}) (\hat{B}^{(2)} | \Psi \rangle^{2})$

Easy to prove:

1. this construction forms a vector space

2. if $\hat{A}^{(1)}$ and $\hat{B}^{(2)}$ are Hermitian in their spaces then $\hat{C} = \hat{A}^{(1)} \hat{B}^{(2)}$ is Hermitian in the combined space

$\therefore$ We now have Q.M. for a combined system a few simple facts

— although basis states are simple products general states are not i.e in general

$$|\psi\rangle \neq |\psi\rangle^{(1)} |\psi\rangle^{(2)}$$

why not consider

$$|\psi\rangle = |i, j\rangle + |k, l\rangle$$
$$= |i\rangle^{(1)} |j\rangle^{(2)} + |k\rangle^{(1)} |l\rangle^{(2)}$$

entanglement (key to quantum information theory, quantum computing)

— suppose $\hat{C} = \hat{A}^{(1)} = \hat{A}^{(1)} \otimes \mathbb{1}^{(2)}$

suppose $\hat{A}^{(1)} |j\rangle^{(1)} = a_j |j\rangle^{(1)}$

then eigenstates of $\hat{C}$ are of form

$$\hat{C} |j\rangle^{(1)} |\phi\rangle^{(2)} = \left(\hat{A}^{(1)} |j\rangle^{(1)}\right) |\phi\rangle^{(2)} = a_j |j\rangle^{(1)} |\phi\rangle^{(2)}$$

↑ arbitrary

Highly degenerate

- combine any number of systems this way
- standard quantum interpretation
  $\langle\Psi|\Psi\rangle = 1$

eg $\quad |\Psi\rangle = \sum_{ij} c_{ij}\, |i,j\rangle \qquad P_{ij} = |c_{ij}|^2$

- analogous results using continuous basis

Concrete example Q.M. of 1 particle in three dimension (next several weeks)

- basis states $\{|x,y,z\rangle\}$
- $\hat{H} = \dfrac{P_x^2 + P_y^2 + P_z^2}{2m} + \underbrace{V(\hat{x},\hat{y},\hat{z})}_{\hat{V}}$ (classical Energy function in 3-d)
- $|\Psi\rangle = \underbrace{\int dx\, dy\, dz}_{\text{analog of } \sum_{i,j,k}}\ \underbrace{\Psi(x,y,z)}_{c_{ijk}}\ |x,y,z\rangle$
- $\langle x'y'z'|x,y,z\rangle = \delta(x-x')\delta(y-y')\delta(z-z') \equiv \delta^{(3)}(\vec{r}-\vec{r}\,')$
- $\langle x',y',z'|\hat{V}|x,y,z\rangle = V(x,y,z)\,\delta(x-x')\delta(y-y')\delta(z-z')$
- $\langle x',y',z'|P_x|x,y,z\rangle = -i\hbar\dfrac{\partial}{\partial x}\delta(x-x')\delta(y-y')\delta(z-z')$

$\Psi(x,y,z) = \langle x,y,z|\Psi\rangle$

time dep Schrödinger eq

$$\hat{H}|\psi\rangle = i\hbar \frac{\partial}{\partial t}|\psi\rangle$$

in $|x,y,z\rangle$ basis

$$\langle x,y,z|\hat{H}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\underbrace{\langle x,y,z|\psi(t)\rangle}_{\psi(x,y,z)}$$

insert

$\mathbb{1} = \int dx'dy'dz' |x',y',z'\rangle\langle x,y,z|$

get after simple algebra H.W

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\psi(x,y,z,t) = i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}$$

$$\boxed{\left[\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\psi = i\hbar\frac{\partial\psi}{\partial t}}$$

time ind Schrödinger equation

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad \text{(same steps)}$$

$$\boxed{\left[\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)\right]\psi = E\psi}$$

simple example particle in 3-d box
of sides L_x, L_y, L_z

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0<x<L_x, \text{ and } 0<y<L_y \text{ and } 0<z<L_z \\ \infty & \text{otherwise} \end{cases}$$

free Schrödinger equation with b.c.
find energy eigenstates

problem is <u>separable</u> in cartesian coordinates

$$\Psi(x,y,z) = \psi_x(x)\,\psi_y(y)\,\psi_z(z)$$

b.c. ~~$\psi_x(x)$~~ $\psi_x(0) = \psi_x(L_x) = \psi_y(0) = \psi_y(L_y) = \psi_z(0) = \psi_z(L_z) = 0$

in box $0<x<L_x$ $\quad 0<y<L_y$ $\quad 0<z<L_z$

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

divide both sides by ψ_x

$$-\frac{\hbar^2}{2m}\left[\frac{\psi_x''}{\psi_x}\underbrace{\psi_y\,\psi_z}_{\text{ind of } x} + \underbrace{\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_y\,\psi_z}_{\text{ind of } x}\right] = \underbrace{E\,\psi_y\,\psi_z}_{\text{ind. of } x}$$

$$\therefore \quad \frac{\psi_x''}{\psi_x} \text{ is ind. of } x \quad \text{so} \quad \frac{\psi_x''}{\psi_x} = \overset{\text{const}}{-k_x^2}$$

divide eq by $\psi_x\psi_y\psi_z$

similarly $\frac{\psi_y''}{\psi_y} = -k_y^2$ $\quad \frac{\psi_z''}{\psi_z} = -k_z^2$; $\frac{-\hbar^2}{2m}\left[\frac{\psi_x''}{\psi_x}+\frac{\psi_y''}{\psi_y}+\frac{\psi_z''}{\psi_z}\right] = E$

$$\boxed{\frac{-\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) = E}$$

$\psi_x = \sin(k_x x)$ for $0<x<L_x$

$\psi_y = \sin(k_y y)$ $\quad 0<y<L_y$

$\psi_z = \sin(k_z z)$ $\quad 0<z<L_z$

now $\psi_x(L_x)=0$ $\quad k_x L_x = n_x \pi$

$k_y L_y = n_y \pi$

$k_z L_z = n_z \pi$

Energy Eigenstates normalization

$$\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sqrt{\frac{2}{L_z}}\sin\left(\frac{n_x x}{\pi}\right)\sin\left(\frac{n_y y}{\pi}\right)\sin\left(\frac{n_z z}{\pi}\right)$$

in box

$= 0$ out of box

$$|n_x\ n_y\ n_z\rangle = \int dx\,dy\,dz\ \psi_{n_x n_y n_z}\ |x,y,z\rangle$$

$$\hat{H}\,|n_x\ n_y\ n_z\rangle = \frac{+\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right) = E_{n_x,n_y,n_z}$$

time depent solutions via superposition

$$|\Psi(t)\rangle = \sum e^{-iE_{n_x,n_y,n_z}t/\hbar}\,|n_x,n_y,n_z\rangle\langle n_x,n_y,n_z|\Psi(0)\rangle$$

Problems which are seperable in Cartesian coordinates ~~are~~ rare (and mostly man-made)

- Seperablity related to symmetry

- **Many** problems have rotational symmetry

happens if $V(x, y, z) = V(r)$ $\quad r = \sqrt{x^2+y^2+z^2}$

eg. electrostatic force
gravity

these problems have simple seperation of variables in spherical coordinates

r, θ, ϕ

θ: polar angle

ϕ: azimuthal angle

t.i. Schrödinger equation $|\vec{r}\rangle$ basis

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi$$

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{d}{d\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

(check your vec calc. book

Assume S.E. separates

$$\Psi = \underset{\text{radial}}{R(r)}\ \underset{\text{angular}}{Y(\theta,\phi)}$$

plug Ψ into S.E. in spherical coordinates

$$\frac{-\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}r^2\frac{dR}{dr} + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{d^2Y}{d\phi^2}\right]$$

$$+ VRY = ERY$$

divide both sides by $R\,Y$ and mult by $-\frac{2mr^2}{\hbar^2}$

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)\right]$$

$$+\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{dY}{d\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0$$

note first bracket is ind of θ, ϕ
and second is ind of r

thus $\left[\frac{1}{R}\frac{d}{dr}r^2\frac{dR}{dr} - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)\right] = \text{const} = \ell(\ell+1)$

$$\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{dY}{d\theta} + \frac{1}{\sin^2\theta}\frac{d^2Y}{d\phi^2}\right] = -\text{const} = -\ell(\ell+1)$$

We will show in a bit ℓ is an integer which characterizes the angular momentum

Note only works if V only depends on r
for general case fails

lets do radial part first
its easy

trick   let : $\boxed{R = u/r}$

simple algebra

$$\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R = \frac{\partial}{\partial r} r^2 \frac{d}{dr} u/r = \frac{d}{dr} r^2 \left[\frac{u'}{r} - \frac{u}{r^2}\right]$$

$$= \frac{d}{dr}\left[ru' - u\right] = u' + ru'' - u' = ru''$$

so

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

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

$$ru'' - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]\frac{u}{r} = l(l+1) R$$

$$r\left[u'' - \frac{2m}{\hbar^2}\left(V(r) - E\right] u\right] = l(l+1)\frac{u}{r}$$

or

$$u'' - \frac{2m}{\hbar} V(r) u = \frac{2m}{\hbar^2} E\, u/r + l(l+1)\frac{2m\hbar^2}{r^2} u$$

$$-\frac{\hbar^2 u''}{2m} + \left(V(r) + \frac{2m(l)(l+1)\hbar^2}{r^2}\right) u = E u$$

$$-\frac{\hbar^2}{2m} u'' + V_{eff}(r)\, u = E\, u$$

with $V_{eff} = V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$ ← centrifugal barrier

Same <u>form</u> as 1-d S.E.

but different b.c.

here: $r > 0$ in 1-d $-\infty < x < \infty$

$u(0) = 0$

since $R = \frac{u}{r}$

Angular Equation

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{dY}{d\theta}\right) + \frac{d^2 Y}{d\phi^2} = -l(l+1)\sin^2\theta\, Y$$

Note this independent of

E, V

Solutions are universal; good for all ~~s~~ rotationally invariant problems

solutions

$Y = Y_l^m(\theta, \phi)$ spherical Harmonic

(derived via separation of variables)

~~see book for details~~

solid angle

properties of $Y_l^m(\theta,\phi) = Y_l^m(\Omega)$

1. l is a positive integer
2. $-l \le m \le l$ with m integer

} single valuedness condition

3. $Y_{l,m}$ for an orthonormal set

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \; Y_l^{m*}(\theta,\phi)\, Y_{l'}^{m'} = \delta_{m,m'}\,\delta_{l,l'}$$

or defining $\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta$

$$\boxed{\int d\Omega \; Y_l^{m*}(\Omega)\, Y_{l'}^{m'} = \delta_{l,l'}\,\delta_{m,m'}}$$

Form derived in book, solved via separation of variables related to Legendre Polynomials in $\cos\theta$; go like $e^{im\phi}$

$Y_0^0 = \frac{1}{\sqrt{4\pi}}$

$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\phi}$ $\quad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$ $\quad Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{-i\phi}$

$Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{2i\phi}$ $\quad Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \, e^{i\phi}$ $\quad Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$

$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \, e^{-i\phi}$ $\quad Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{-2i\phi}$

Note $e^{im\phi}$ factors

Return to general solution to Schrodinger equation

state labeled by three numbers

labels radial solut → n, l, m ← angular

$-l \le m \le l$

Key thing radial equation depends on l (thru centrifugal barrier) but **not** on m

thus solutions are $(2l+1)$-fold degenerate

$$\hat{H}\,|n, l, m\rangle = E_{n,l}\,|n, l, m\rangle$$

$l = 0$ states singlets
$l = 1$ states triplets $m = -1, 0, 1$

Note we can take any linear combo and it is still degenerate

$$\hat{H}\,\frac{1}{\sqrt{2}}\left(|n, l=1, m=1\rangle + |n, l=1, m=-1\rangle\right)$$

$$= E_{n,l}\,\frac{1}{\sqrt{2}}\left(|n, l=1\ m=1\rangle + |n, l=1, m=-1\rangle\right)$$

Simple example — infinite spherical square well

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

b.c. ~~[illegible]~~ $\psi(r=a,\theta,\phi) = 0$

for $r<a$ radial eq becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \frac{\hbar^2 \ell(\ell+1)}{2m\, r^2} u = E u$$

or

$$\frac{\partial^2 u}{\partial r^2} = \frac{\ell(\ell+1)}{r^2} u - \frac{2mE}{\hbar^2} u$$

$$\frac{2mE}{\hbar^2} u = k^2 u$$

separately consider each ℓ

$\underline{\ell = 0}$

$$\frac{\partial^2 u}{\partial r^2} = -k^2 u \qquad \text{looks like 1-d problem}$$

$u = A\sin(kr) + B\cos(kr)$

b.c. $u(r=0) = 0$ general

$\boxed{0 = B}$

$u(r=a) = 0 = A \sin(ka)$

so $ka = n\pi$ $\quad k = \frac{n\pi}{a}$

thus for $\underline{l=0}$

$$\boxed{E_{n,l=0} = \frac{\hbar^2 n^2 \pi^2}{2m\, a^2}}$$

but this is $\underline{\text{not}}$ the energy for a 1-d well from $-a$ to a

from 401

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2m(2a)^2}$$ why the difference

b.c. requires $u=0$ at $r=0$ so only odd solution of 1-d problem (odd solutions are even n

what about $l=1$

$$\frac{d^2u}{dr^2} = \frac{(1)(1+1)}{r^2}u - k^2 u \qquad k^2 = \frac{2mE}{\hbar^2}$$

solutions : $u = A\left[\frac{\sin(kr)}{kr} - \cos(kr)\right]$

$$B\left[-\frac{\cos(kr)}{(kr)} - \sin(kr)\right]$$

you can check this

the A term is zero at $r=0$
B term is ∞ at $r=0$

$\therefore$ $B=0$

Higher ℓ's in terms of spherical Bessel functions : sin's & cos divided by r?

b.c. for $l=1$

$$\frac{\sin(ka)}{ka} - \cos(ka) = 0$$

Trancendental equation

I called the $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ term a centrifugal barrier.

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

Why?

Consider classical Mechanics in 3-d with central potential $V(\vec{r}) = V(|r|)$
use spherical coordinates r, θ, ϕ
& note motion stays in plane $\theta = \frac{\pi}{2}$

Now what is kinetic Energy

$$T = \frac{1}{2} m(\dot{x}^2 + \dot{y}^2 + \overset{=0 \text{ in plane}}{\dot{z}^2}) = \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\phi}^2)$$

so

$$E = \frac{1}{2} m\dot{r}^2 + \frac{1}{2} m r^2 \dot{\phi}^2 + V(r)$$

now $m\dot{r} = p_r$ radial momenta (canonical momentum)
and $mr^2\dot{\phi} = L$ orbital angular momentum (conserved)

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$$

so far as r motion is concerned
1-d problem in r

with $V_{eff}(r) = V(r) + \dfrac{L^2}{2mr^2}$

compare with Q.M $V_{eff} = V(r) + \dfrac{\hbar^2 \, l(l+1)}{2m\, r^2}$

same! if $L^2 = \hbar^2 l(l+1)$

so the l in Y_l^m is related to angular momentum

to understand what they are we need to understand angular momentum in Q.M. (Do angular momentum before we do Hydrogen

$$\vec{L} = \vec{r} \times \vec{p} \qquad \text{classical}$$

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} \qquad \text{Q.M.}$$

or by components

$\hat{L}_i = \sum_{jk} \varepsilon_{ijk} \hat{r}_j \hat{p}_k$ where ε_{ijk} is completely anti symmetric tensor

$\varepsilon_{ijk} = -\varepsilon_{jik} = +\varepsilon_{jki} = -\varepsilon_{kji} = +\varepsilon_{kij} = -\varepsilon_{ikj}$

+ even permutation
- odd "

$\varepsilon_{ijk} = 0$ if any two indices the same explicitly

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

Now let us look at commutators of L's (for math majors this is a Lie algebra; it's generators of a Lie group)

eg $[L_x, L_y]$

trick in computation

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

proof:

$$\hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} = (\hat{A}\hat{B}\hat{C} - \cancel{\hat{B}\hat{A}\hat{C}}) + (\cancel{\hat{B}\hat{A}\hat{C}} - \hat{B}\hat{C}\hat{A})$$

Q.E.D.

so

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

or

$$[\hat{A}\hat{B}, \hat{C}\hat{D}] = \hat{A}[\hat{B},\hat{C}\hat{D}] + [\hat{A},\hat{C}\hat{D}]\hat{B}$$
$$= \hat{A}[\hat{B},\hat{C}]\hat{D} + \hat{A}\hat{C}[\hat{B},\hat{D}] + \hat{C}[\hat{A},\hat{D}]\hat{B} + [\hat{A},\hat{C}]\hat{D}\hat{B}$$

Now what are commutators of x's, p's

$$[\hat{x},\hat{y}] = [\hat{x},\hat{z}] = [\hat{y},\hat{z}] = [\hat{x},\hat{p}_y] = [\hat{x},\hat{p}_z] =$$
$$[\hat{y},\hat{p}_x] = [\hat{y},\hat{p}_z] = [\hat{z},\hat{p}_x] = [\hat{z},\hat{p}_y] = [\hat{p}_x,\hat{p}_y] =$$
$$[\hat{p}_x,\hat{p}_z] = [\hat{p}_y,\hat{p}_z] = 0$$

$$[\hat{x},\hat{p}_x] = i\hbar$$

$$[\hat{y},\hat{p}_y] = i\hbar$$

$$[\hat{z},\hat{p}_z] = i\hbar$$

so look at

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

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

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

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

$$\boxed{\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_z \end{aligned}}$$

simlar calculation yield

(Lie Algebra)

$$[\hat{L}_j, \hat{L}_k] = i\hbar \, \varepsilon_{jkl} \hat{L}_l$$

Nasty feature; we canot simultaneously measure all componets of $\vec{L}$ (unless they are all zero)

$$\hat{\sigma}_{L_x}^2 \hat{\sigma}_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle\right)^2$$

How can I characterize what I can simlutaneously measure?

Clearly I can measure one component. Conventionally one usally chooses to measure $\hat{L}_z$

what else: — $\hat{L}^2 = \hat{\vec{L}} \cdot \hat{\vec{L}} = \hat{L}_x\hat{L}_x + \hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z$

cool fact:

$$[\hat{L}_x, \hat{L}^2] = [\hat{L}_x, \hat{L}_x\hat{L}_x + \hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z]$$

$$= \cancel{\hat{L}_x[\hat{L}_x,\hat{L}_x] + [\hat{L}_x,\hat{L}_x]\hat{L}_x}$$

$$+ \hat{L}_y[\hat{L}_x,\hat{L}_y] + [\hat{L}_x,\hat{L}_y]\hat{L}_y$$

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

$$= i\hbar \cancel{\hat{L}_y\hat{L}_z} + i\hbar \cancel{\hat{L}_z\hat{L}_y} - i\hbar \cancel{\hat{L}_z\hat{L}_y} - i\hbar \cancel{\hat{L}_y\hat{L}_z} = 0$$

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

$\therefore$ You can simultaneously measure $\hat{L}^2$ and any component of $\vec{L}$ (say $\hat{L}_z$)

What are the eigenstates of $\hat{L}^2$ and $\hat{L}_z$

Formal properties:

$$\left.\begin{aligned} \hat{L}^2 |l,m\rangle &= l(l+1)\hbar^2|l,m\rangle \\ \hat{L}_z|l,m\rangle &= m\hbar|l,m\rangle \end{aligned}\right\}$$ eigenstates (I will prove l, m integer in a bit)

Language $l=0$ s-wave
$l=1$ p-wave
$l=2$ d-wave

properties of $|l,m\rangle$ using ladder operators

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \qquad \hat{L}_\pm^\dagger = \hat{L}_\mp$$

$$[\hat{L}_\pm, \hat{L}^2] = 0 \quad \text{trivial}$$

$$[\hat{L}_\pm, \hat{L}_z] = \mp\hbar L_\pm$$

Proof $[L_x \pm iL_y, \hat{L}_z] = i\hbar[-\hat{L}_y \pm iL_x]$

$$= \mp\hbar[L_x \pm \hat{L}_y] = \mp\hbar L_\pm$$

Cool fact.

$$(\hat{L}_\pm)|l,m\rangle = \underbrace{\eta}_{\text{some normalization constant}}|l, m\pm1\rangle$$

$\hat{L}_\pm$ is a ladder operator analogous to $a^\dagger$ & a for H.O.

Proof

$$L_z(L_\pm|l,m\rangle) = \hat{L}_z\hat{L}_\pm|l,m\rangle = (\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z) + \hat{L}_\pm\hat{L}_z)|l,m\rangle$$

$$= [\hat{L}_z, \hat{L}_\pm]|l,m\rangle + \hat{L}_\pm\hat{L}_z|l,m\rangle$$

$$= \pm(\hat{L}_\pm)|l,m\rangle + (L_\pm)m|l,m\rangle$$

$$= (m\pm 1)(\hat{L}_\pm)|l,m\rangle$$

so $(\hat{L}_\pm)|l,m\rangle$ is an eigenstate of L_z with eigenvalue $m\pm 1$

of course not necessarily normalized so

$$(\hat{L}_\pm)|l,m\rangle = \eta\,|l, m\pm 1\rangle$$

Now we need to find η

$$\langle l,m|(\hat{L}_\mp)(\hat{L}_\pm)|l,m\rangle = \eta^2\langle l\ m\pm 1\,|\,l, m\pm 1\rangle = \eta^2$$

$$\hat{L}_\mp \hat{L}_\pm = (\hat{L}_x \mp i\hat{L}_y)(\hat{L}_x \pm iL_y) = \hat{L}_x^2 + \hat{L}_y^2 \pm i[L_x, L_y]$$

$$= \hat{L}_x^2 + L_y^2 \pm i(iL_z\hbar) = L_x^2 + L_y^2 \mp L_z\hbar = L_x^2 + L_y^2 + L_z^2 - L_z^2 \mp L_z\hbar$$

$$= \hat{L}^2 - \hat{L}_z^2 \mp \hat{L}_z\hbar$$

so

$$\eta^2 = \langle l,m|(\hat{L}_\mp)(\hat{L}_\pm)|l,m\rangle = \langle l,m|\hat{L}^2 - \hat{L}_z^2 \mp \hat{L}_z|l,m\rangle = \hbar^2(l(l+1) - m^2 \mp m)$$

$$= \hbar^2(\,l(l+1) - m(m\pm 1)\,)$$

so $\eta = \hbar\sqrt{l(l+1) - m(m\pm 1)}$

$$(\hat{L}_\pm)|l,m\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}\;|l, m\pm 1\rangle$$

Now under what circumstances are these states normalized $\eta^2 \geq 0$

only if $\ell(\ell+1) - m(m\pm1) \geq 0$
clearly since m keeps increasing and decreasing we need to hit zero to stop chain

$L_+ |\ell, m_{max}\rangle = 0$

$\hbar \underbrace{\sqrt{\ell(\ell+1) - m(m+1)}}_{=0} \; |\ell, m_{max}+1\rangle$

or $\boxed{m_{max} = \ell}$ or negative m

similarly

$L_- |\ell, m_{min}\rangle = 0$

$\hbar \underbrace{\sqrt{\ell(\ell+1) - m_{min}(m_{min}-1)}}_{=0} \; |\ell, m_{min}-1\rangle$

or $\boxed{m_{min} = -\ell}$ or positive

Note also $m_{max} = m_{min} = n$ which is an integer since we took ~~~~ n steps of 1 from top to bottom

so ~~~~ $m_{max} - m_{min} = 2\ell$ is an integer

so ℓ is either an integer or $\frac{1}{2}$ integer

Now I will prove only integer l, m make sense for orbital motion

— connect Y_l^m with $|l, m\rangle$

claim. $Y_l^m(\theta, \phi) = \langle \theta, \phi | l, m \rangle$

consider $L_z = \hat{x}\hat{p}_y - \hat{y}p_x$

$$\langle r, \theta, \phi | \hat{L}_z | \psi \rangle = \Big[\underbrace{x(-i\hbar \tfrac{\partial}{\partial y}) - y(-i\hbar \tfrac{\partial}{\partial x})}_{\text{by calc. 3}} \Big] \langle r, \theta, \phi | \psi \rangle$$

$$= -i\hbar \frac{\partial}{\partial \phi} \langle r, \theta, \phi | \psi \rangle$$

similarly $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + L_z^2$

$\Big\downarrow$ boring! by calc. 3

$$\langle r, \theta, \phi | \hat{L}^2 | \psi \rangle$$

$$= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \langle r, \theta, \phi | \psi \rangle$$

to find eigenstates of $\hat{L}^2, \hat{L}_z$ note ind of r so I'll drop $\hat{r}$

$$-i\hbar \frac{\partial}{\partial \phi} \langle \theta, \phi | \psi \rangle = \hbar m \langle \theta, \phi | \psi \rangle$$

$$-\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \langle \theta, \phi | l\, m \rangle = \hbar^2\, l(l+1) \langle \theta, \phi | l, m \rangle$$

but that is equation for Y_{lm}

so $\langle \theta, \phi | l, m \rangle = Y_l^m(\theta, \phi)$

Now let us look at ϕ dependence

recall $Y_l^m \sim e^{im\phi}$

Now $Y_l^m(\theta, \phi + 2\pi) = Y_l^m(\theta, \phi)\, e^{im 2\pi}$

Now if wavefunction is single valued
$Y_l^m(\theta, \phi + 2\pi) = Y_l^m(\theta, \phi)$ $\quad e^{im 2\pi} = 1$

m is an integer

$\frac{1}{2}$ integer is <u>not</u> possible
(for orbital motion)

summary:

$$\boxed{\begin{aligned}
&Y_l^m(\theta, \phi) = \langle \theta, \phi | l, m \rangle \qquad l, m \text{ integer}; -l \le m \le l,\ l \ge 0 \\
&\hat{L}_z | l, m \rangle = \hbar m | l, m \rangle \\
&\hat{L}^2 | l, m \rangle = \hbar^2 l(l+1) | l, m \rangle \\
&\hat{L}_\pm | l, m \rangle = \hbar \sqrt{l(l+1) - m(m\pm1)}\, | l, m \pm 1 \rangle \qquad L_\pm = L_x \pm i L_y
\end{aligned}}$$

A few comments

$\langle\Psi|\hat{L}^2|\Psi\rangle > \langle\Psi|L_z^2|\Psi\rangle$ unless both are zero

note in eigenstates

$\langle\hat{L}^2\rangle = \ell(\ell+1)$ $\quad\langle L_z^2\rangle = m^2$ $\quad m^2_{max} = \ell^2$

but $\ell^2+\ell \geq \ell^2$ for all nonzero ℓ

You can't determine direction for $\vec{L}$ exactly!

what is

$\langle \ell, m | L_x | \ell', m'\rangle$ $\quad L_x = \frac{1}{2}(L_+ + L_-)$

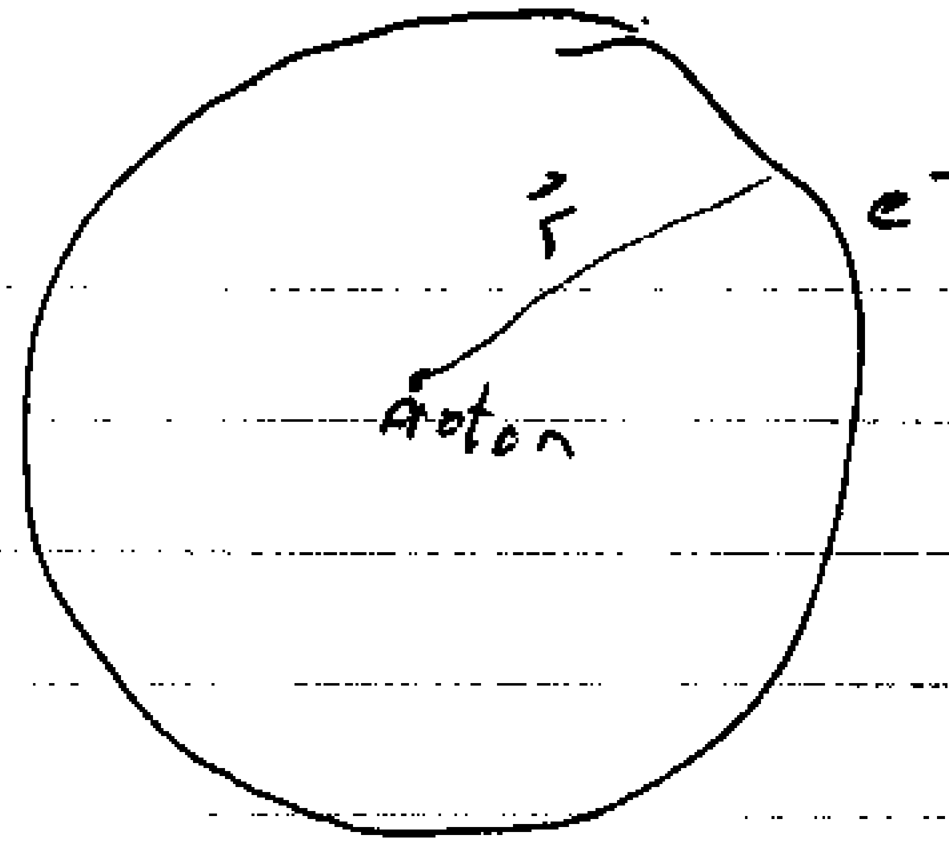
$= \langle \ell, m | \frac{1}{2}(L_+ + L_-) | \ell, m'\rangle$

$= \frac{1}{2}\langle \ell, m | \left(\sqrt{\ell'(\ell'+1) - m(m+1)}\,|\ell', m'+1\rangle\right)$
$+ \frac{1}{2}\langle \ell, m | \left(\sqrt{\ell'(\ell'+1) - m(m-1)}\,|\ell', m'-1\rangle\right)$

$= \frac{1}{2}\sqrt{\ell(\ell+1) - m(m+1)}\;\delta_{\ell,\ell'}\,\delta_{m,m'+1}$

$+ \frac{1}{2}\sqrt{\ell(\ell+1) - m(m-1)}\;\delta_{\ell,\ell'}\,\delta_{m,m'-1}$

Hydrogen atom —



baby version:

- ignore proton motion (assume it is so heavy it is "nailed down")
- ignore spin of electron
- ignore spin of proton
- ignore relativistic effects
- ignore vacuum polarization
- ignore scattering states (look only at bound states)

Force law is inverse square so potential is $\frac{1}{r}$

$$V(r) = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} \qquad \text{(SI units)}$$

$$\psi_{nlm}(r) = \frac{u(r)}{r}\,Y_{lm}(\theta,\phi)$$

$E<0$ bound states

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Easier to use dimensionless units

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \qquad \text{divide by } E = \frac{\hbar^2\kappa^2}{2m}$$

$$-\frac{1}{\kappa^2}\frac{d^2u}{dr^2} - \left(\frac{e^2 m}{2\pi\epsilon_0 \kappa\hbar^2}\frac{1}{\kappa r} + \frac{l(l+1)}{\kappa^2}\right)u = u$$

introduce $\rho = \kappa r \qquad \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$

$$\boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]}$$

Now before solving key issues are solutions at $r \to \infty$ and $r \to 0$ since quantization comes from these (wave function can't blow up)

first look at u as $r \to 0$
clearly the centrifugal term dominates

$$\frac{d^2u}{d\rho^2} \approx \frac{l(l+1)}{\rho^2}u$$

Solutions are trivially $u = C\rho^{l+1} + D\rho^{-l}$

$$u' = C(l+1)\rho^{l} + D(-l)\rho^{-l-1}$$

$$u'' = C\,l(l+1)\rho^{l-1} + D(l+1)l\,\rho^{-l-2} = \frac{l(l+1)}{\rho^2}(D\rho^{l+1} + C\rho^{-l})$$

form is familiar from solution of Laplace eq. in E & M!

Clearly on physical grounds $D = 0$ as [scribbled out] ψ blows up otherwise

so as $\rho \to 0$ $\quad u \simeq c\rho^{l+1}$

what about as $\rho \to \infty$

clearly both $\frac{\rho_0}{\rho}$ and $\frac{l(l+1)}{\rho^2}$ get as small as we want

so

$$\frac{d^2u}{d\rho^2} \approx u$$

or $\quad u \simeq A e^{-\rho} + B e^{+\rho}$

actually this is a bit of swindle

on physical grounds $B = 0$

so solutions smoothly match from

$c\rho^{l+1}$ at small ρ

to $Ae^{-\rho}$ at large ρ (strictly all we know is it is an exponential)

Now let us encode this info

correct power law as $\rho \to 0$

exponential decay as $\rho \to \infty$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$$

hopefully simple

plug into

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

slightly
ugly algebra

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

Next write $v(\rho)$ as a series

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j = \sum_{k=0}^{\infty} a_k \rho^k \qquad v'(\rho) = \sum_{j=0} a_j\, j\, \rho^{j-1} = \sum_{k=0}^{\infty} a_{k+1}(k+1)\rho^k$$

$$v''(\rho) = \sum_{j=0}^{\infty} a_j\, j(j-1)\, \rho^{j-2} = \sum_{k=0}^{\infty} a_{k+1} k(k+1)\rho^{k-1}$$

we need to find the a_j

plug into d.f. eq.

$$\sum_{k=0}^{\infty}\left[k(k+1)\, a_{k+1}\rho^k + 2(\ell+1)(k+1)\, a_{k+1}\rho^k - 2k a_k \rho^k + [\rho_0 - 2(\ell+1)]a_k \rho^k\right]$$

$= 0$

only way it can vanish for all ρ

is if each term vanishes i.e. each power of ρ^k

so

$$a_{k+1}\left[k(k+1) + 2(l+1)(k+1)\right] - a_k\left(2k + 2(l+1) - \rho_0\right) = 0$$

or

$$a_{k+1} = \frac{\left(2k + 2(l+1) - \rho_0\right)}{k(k+1) + 2(l+1)(k+1)}\, a_k$$

$$= \left(\frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)}\right) a_k$$

two possibilities series truncates or not

if not at large k ($k \gg l, \rho_0$

$a_{k+1} \approx \frac{2}{k+1} a_k$ solution is easy

$a_k = \frac{2^k}{k!}$ const check this

so $v = \sum_k a_k \rho^k \approx \text{const} \sum_k \frac{2^k \rho^k}{k!} = \text{const}\; e^{2\rho}$

but this has wrong Assymptotic form
$u \sim \rho^{l+1} e^{-\rho} \;\; \cancel{\vee} \;\; \rho^{l+1} e^{\rho} \rightarrow$ diverges
at large ρ and not allowed

so series must stop

i.e. there exists a k_{max} such that

$$a_{k_{max}+1} = 0 = \frac{2(k_{max}+l+1) - \rho_0}{(k_{max}+1)(k_{max}+2l+2)} a_{k_{max}}$$

or $\boxed{2(k_{max}+l+1) = \rho_0}$

but $k_{max}+l+1$ must be a non-negative integer
call it n;

$n = k_{max}+l+1$

or

$\rho_0 = 2n$

but from definition

$$\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2 k} \quad \text{or}$$

with $\frac{\hbar^2 k^2}{2m} = -E$

$\rightarrow$

so $E = \frac{-\hbar^2 \kappa^2}{2m}$ $\kappa = \frac{m e^2}{4\pi\epsilon_0 \hbar^2 n}$

or $E = \frac{m e^4}{8\pi\epsilon_0 \hbar^2 m^2} \frac{1}{n^2} = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$

this is the Bohr formula!
Real Q.M. reproduces it

$E_1 \simeq 13.6$ eV

some comments

allowed n's

$n = l+1, l+2, l+3, \ldots$

degeneracy of levels

					Energy
$n=1$	only	$l=0$	1	state	E_1
$n=2$		$l=0,1$	4	states	$E_1/4$
$n=3$		$l=0,1,2$	9	states	$E_1/9$

generally n^2 state.

Note states with different l's are degenerate!

- in general one has $E_{n,l}$ so only states which are degenerate have same (2l+1-fold degeneracy)

$\therefore \frac{1}{r}$ potential has extra symmetries!!

recall $\lambda = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} \equiv \frac{1}{an}$

$a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ Bohr radius

typical size of hydrogen atom

Now what are the actual wave functions

a's give us them

$u \sim \rho^l e^{-\rho} \sum_k a_k \rho^k$ with a_k given by a recursion formula

$$\boxed{a_{k-1} = \frac{(k)(k+2l+1)}{2(k+l)-2n}\, a_k}$$

with $k_{max} = n-l-1$