Postulate 1:

The State of a quantum mechanical system, including all the info you can know it, is represented mathmatically by a normalized ket $|\psi\rangle$

$\Rightarrow$ Vector space of $|\psi\rangle \longrightarrow$ Hilbert space

↳ dimension depends on the observable

intrinsic spin ↑ + z direction; spin up; spin down

ex: For S_z : $|+\rangle$ & $|-\rangle$ $\Rightarrow$ 2D Hilbert space $\Rightarrow$ basis = $\{|+\rangle, |-\rangle\}$

- Complete $\boxed{|\psi\rangle = a|+\rangle + b|-\rangle}$, $\underbrace{a = \langle +|\psi\rangle \ \& \ b = \langle -|\psi\rangle}_{\text{probability amplitude}}$

- orthogonal $\langle +|-\rangle = \langle -|+\rangle = 0$
- normalized $\langle +|+\rangle = \langle -|-\rangle = 1$

} orthonormal: $\langle e_i | e_j \rangle = \delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}$

- dual vector: $\langle \psi | = a^* \langle + | + b^* \langle - |$

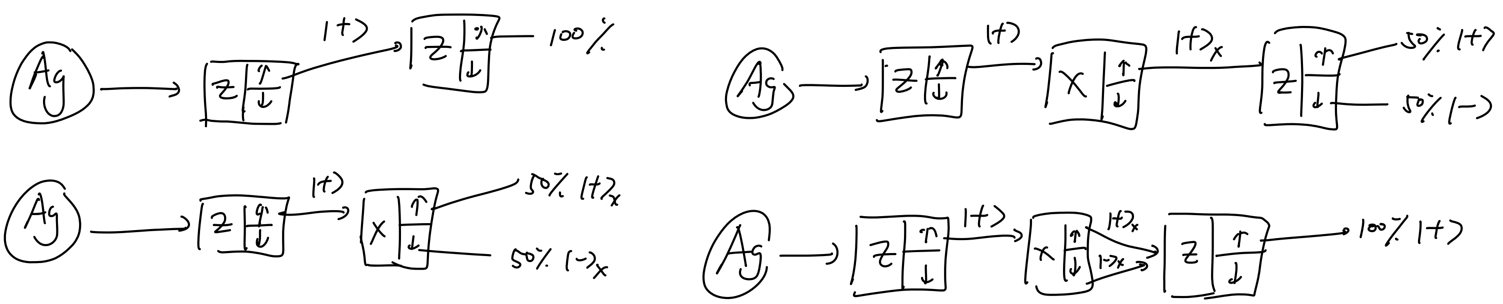
Postulate 4

$\boxed{P_{out} = |\langle out | \psi \rangle|^2}$ $\Rightarrow P_\pm = |\langle \pm | \psi \rangle|^2$

↳ probability of measuring out from $|\psi\rangle$

$\Rightarrow |\langle out | in \rangle|^2 = \langle out | in \rangle \langle in | out \rangle$

SG Experiment



Quantum Topology

$|\psi\rangle = a|+\rangle + b|-\rangle \longrightarrow$ we only care about <u>relative</u> <u>phase</u>

$\therefore$ Let $\underbrace{a = r_1}_{\text{real}}$, $\underbrace{b = r_2 e^{i(\beta-\alpha)}}_{\text{complex.}}$

Quantum Ket in the z-basis

$|+\rangle \qquad |+\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle) \qquad |+\rangle_y = \frac{1}{\sqrt{2}}(|+\rangle + i|-\rangle)$

$|-\rangle \qquad |-\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle) \qquad |-\rangle_y = \frac{1}{\sqrt{2}}(|+\rangle - i|-\rangle)$

Coordinate Representation

$|\psi\rangle = a|+\rangle + b|-\rangle \xrightarrow{z\text{-basis}} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \langle +|\psi\rangle \\ \langle -|\psi\rangle \end{pmatrix}$ column of probability amplitude.

$\langle\psi| = a^*\langle +| + b^*\langle -| \xrightarrow{z\text{-basis}} (a^* \;\; b^*) = (\langle\psi|+\rangle \;\; \langle\psi|-\rangle)$

$\therefore \langle\psi|\psi\rangle = (a^* \;\; b^*)\begin{pmatrix} a \\ b \end{pmatrix} = a^*a + b^*b$

Postulate 2

A <u>physical observable</u> is represented mathematically by <u>operator A</u> that act on kets:

$$\underset{\text{operator}}{A}\, |\psi\rangle \xrightarrow{\text{transform}} = |\phi\rangle$$

Postulate 3

The only possible result of a measurement of an observable is one of the the eigenvalues a_n of the corresponding operator A.

$$\boxed{A\,|\psi\rangle = a_n\,|\psi\rangle}$$

operator eigenvalue eigenstate

$$\Rightarrow S_z|+\rangle = +\tfrac{\hbar}{2}\,|+\rangle$$
$$S_z\,|-\rangle = -\tfrac{\hbar}{2}\,|-\rangle$$

eigenstates: $|+\rangle, |-\rangle$
eigenvalues: $+\tfrac{\hbar}{2}, -\tfrac{\hbar}{2}$

Hermitian Operators

$$A = A^{\dagger}$$

QM operators must be Hermitian because:

- eigenvalues are real $\Rightarrow$ outcomes are real
- eigenvectors form a complete set of basis vectors
- Same operator for dual space vector

$$A\,|\alpha\rangle = |\beta\rangle \quad \& \quad A\,\langle\alpha| = \langle\beta|$$

Completeness

$$\sum_{i=1}^{n} |e_i\rangle\langle e_i| = \mathbb{1} \longrightarrow \text{identity operator}$$

Spectral Decomposition

eigenvalue

$$\text{Operator } A = \sum_i a_i\,|a_i\rangle\langle a_i|$$

Coordinate Representation of Operators

If $|\psi\rangle$ is a n-component column vector, A must be $n \times n$ matrix

$$A \xrightarrow[\text{basis}]{\text{orthonormal}} \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix}, \quad A_{ij} = \langle e_i | A | e_j \rangle$$

ex: $$S_z \xrightarrow{z\text{-basis}} \begin{pmatrix} \langle + | S_z | + \rangle & \langle + | S_z | - \rangle \\ \langle - | S_z | + \rangle & \langle - | S_z | - \rangle \end{pmatrix} = \begin{pmatrix} \langle + | +\frac{\hbar}{2} | + \rangle & \langle + | -\frac{\hbar}{2} | - \rangle \\ \langle - | +\frac{\hbar}{2} | + \rangle & \langle - | -\frac{\hbar}{2} | - \rangle \end{pmatrix} = \begin{pmatrix} +\frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix}$$

$$\therefore \quad S_z \xrightarrow{z\text{-basis}} \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad S_x \xrightarrow{z\text{-basis}} \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y \xrightarrow{z\text{-basis}} \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Some Math

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} e \\ f \end{pmatrix} = \begin{pmatrix} ae + bf \\ ce + df \end{pmatrix}$$

$$\begin{pmatrix} a & c \\ b & d \end{pmatrix}\begin{pmatrix} e & g \\ f & h \end{pmatrix} = \begin{pmatrix} ae + cf & ac + ch \\ be + df & bg + dh \end{pmatrix}$$

$$\begin{pmatrix} a \\ b \end{pmatrix}\begin{pmatrix} c & d \end{pmatrix} = \begin{pmatrix} ac & ad \\ bc & bd \end{pmatrix}$$

Expectation Value

- Mean average of all measurements

For observable x with i eigenvalues of $\underline{x_i}$ (outcomes), with ket $|\psi\rangle$:

$$\langle x \rangle = \sum_i x_i \, \text{prob}(x_i) = \sum_i x_i |\langle x_i | \psi \rangle|^2$$

or: $\langle x \rangle = \langle \psi | X | \psi \rangle$

$\Rightarrow$ Not the most common value or the eigenvalue

↳ unless you are measuring the $\underline{\underline{\text{eigenstate}}}$ $\Rightarrow$ 100% prob. of outcome.

- Projection Operators

$P_+ = |+\rangle\langle+|$ $P_- = |-\rangle\langle-|$ $\Rightarrow$ component of $|\psi\rangle$ in each direction

- Postulate 5

After the measurment of A, you get a_n, the QM system is in the new state :

$$|\psi'\rangle = \frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}}$$

$\longrightarrow$ projection of $|\psi\rangle$ onto P_n

$\longrightarrow$ normalization

$\Rightarrow \langle P_n \rangle = \langle n|\psi\rangle$

$\downarrow$ expectation of projection

$\leftarrow$ probability of the outcome on the direction

- Commutator

A & B operators commute if: $\boxed{[A,B] = AB - BA = 0}$

↳ If they commute, they share the same eigenvector, but with different eigenvalues:

$A|a\rangle = a|a\rangle$
$B|a\rangle = b|a\rangle$

↳ Commuting operators share state information & eigenvalues can be known <u>simultaneously</u>

↳ Otherwise you lose state information during measurment

- Uncertainty

root mean square deviation : $\boxed{\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}, \quad A^2 = AA}$

- Uncertainty Principle

$\Delta A \Delta B \geq \frac{1}{2} |\langle[A,B]\rangle| \Rightarrow \begin{cases} \text{If } [A,B] = 0 \Rightarrow \text{we can have } \Delta A = 0 \text{ \& } \Delta B = 0 \\ \text{If } [A,B] \neq 0 \Rightarrow \text{we must have } \Delta A \neq 0 \text{ \& } \Delta B \neq 0 \end{cases}$

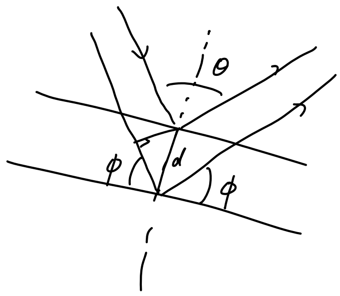
De Broglie's Proposal

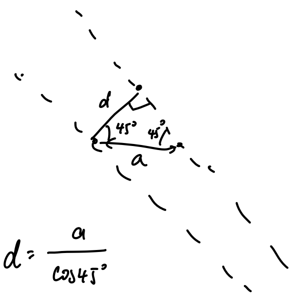
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}}$$

Bragg Scattering

$$n\lambda = 2d\sin\phi$$

$$\theta + 2\phi = 180°$$





$$d = \frac{a}{\cos 45°}$$

$$d = \frac{a}{\sqrt{2}}$$

Postulate

$$\Psi = \psi_0 e^{i(kx - \omega t)} \quad , \quad k = \frac{2\pi}{\lambda} , \; p = \hbar k , \; \omega = \frac{E}{\hbar}$$

$$\Rightarrow \Psi = \psi_0 e^{i/k\,(xp - Et)}$$

$$P(x,t) = |\Psi(x,t)|^2 \qquad \int_{-\infty}^{\infty} P(x,t)\,dx = 1$$

Interference

$$\Psi_T(x,t) = \Psi_1(x,t) + \Psi_2(x,t)$$

Postulate 6

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H(t)\,|\psi(t)\rangle$$

Hamiltonian Operator

$$H(t) = E_k + E_p \qquad \Rightarrow \text{Hermitian}$$

$\Rightarrow$ Eigenvalue: allowed energy

Eigenfunction: energy eigenstate of the system.

- Time - Independent Schroedinger Equation

$$H(t)\underbrace{|E_n\rangle}_{\text{Energy Eigenfunction}} = E_n|E_n\rangle$$

$$|\psi\rangle = \sum_n C_n|E_n\rangle \quad , \quad C_n = \langle E_i|\psi\rangle$$

$$\langle E_n|E_m\rangle = \delta_{nm} = \begin{cases} 1 & \text{if } n=m \\ 0 & \text{if } n\neq m \end{cases} \Rightarrow \text{orthonormality}$$

$$\Rightarrow \langle E_n|E_m\rangle = \int_{-\infty}^{\infty} E_n^*(x)\, E_m(x)\, dx$$

- Continuous vs. descrete

	Continuous	descrete
Basis	$\|x\rangle \equiv$ position of atom at x $\Rightarrow$ continuous set of basis	$\|+\rangle \equiv$ spin up in z-component $\|-\rangle \equiv$ spin down in z-component or generally, $\|a_k\rangle \equiv k^{th}$ measured outcome.
Wave function	$\|\psi\rangle = \int_{-\infty}^{\infty} \|x\rangle \overbrace{\psi(x)}^{\text{probability amplitude}} dx$	$\|\psi\rangle = \sum_k \|a_k\rangle \overbrace{\langle a_k\|\psi\rangle}^{\text{probability amplitude}}$
normalization	$\int_{-\infty}^{\infty} \|\psi(x)\|^2 = 1$	$\langle\psi\|\psi\rangle = 1$
probability	around a region: $\int_a^b \|\psi(x)\|^2 dx$ $(a\leq x\leq b)$ $P(out) = \left(\int_{-\infty}^{\infty} out^*(x)\psi(x)\, dx\right)^2$	$P(out) = \|\langle out\|\psi\rangle\|^2$
Completeness	$\int_{-\infty}^{\infty} \|x\rangle\langle x\|\, dx = 1$	$\sum_k \|a_k\rangle\langle a_k\| = 1$
Expectation	$\langle \hat{A}\rangle = \int_{-\infty}^{\infty} \psi^*(x)(A(x)\psi(x))\, dx$	$\langle\hat{A}\rangle = \langle\psi\|\hat{A}\|\psi\rangle$
uncertainty	$\Delta A = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$	$\Delta A = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$

- **Operators**

(i) Position operator ($\hat{x}$)

$$\hat{x} \xrightarrow{\text{position basis}} x \qquad \hat{x}|x\rangle = x|x\rangle$$

(ii) Momentum Operator ($\hat{p}$)

$$\hat{p} \xrightarrow{\text{position basis}} -i\hbar\frac{d}{dx}$$

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

(iii) Hamiltonian ($\hat{H}$)

$$\hat{H} = V(\hat{x}) + \frac{\hat{p}^2}{2m} \xrightarrow{\text{position basis}} \hat{H} = V(x) + \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2$$

- **Time Independent Schroedinger Equation**

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_i + V(x)\psi_i(x) = E_i\psi_i(x)$$

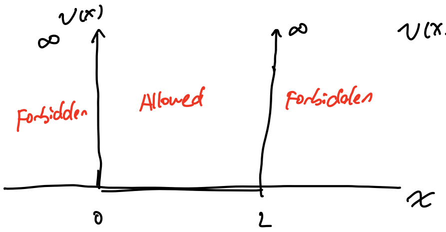
- **TISE for piecewise PE function**

- Classically allowed: $V(x) < E_T \Rightarrow$ complex exponential ($\psi(x) = Ae^{\pm ikx}$)
- Classically forbidden: $V(x) > E_T \Rightarrow$ real exponential ($\psi(x) = Be^{kx}$)

- Boundary Condition

  - $\psi(x)$ must be normalized
  - eigenfunction must be continuous
  - $\frac{d}{dx}$ eigenfunction must be continuous (unless $V(x)$ infinite)

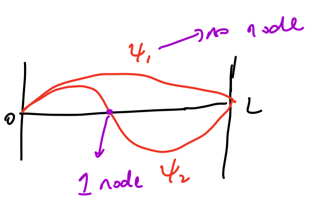
- Infinite Square Well



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

$$\Longrightarrow \begin{cases} u_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) & \text{for } 0 \leq x \leq L \\ \psi_n = 0 & \text{otherwise} \end{cases}$$ eigenfunctions

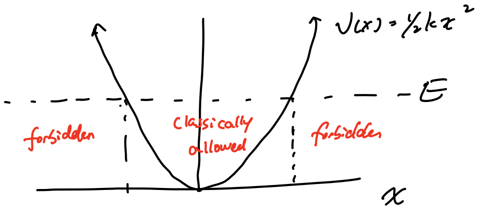
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \Rightarrow E_n \propto n^2$$ eigenvalue.



#node = n − 1

For n = 1, 2, 3, ...

- Simple Harmonic Oscillator (SHO)



$$E_n = (n+\tfrac{1}{2})\hbar\omega \quad , \; n = 0, 1, 2, \ldots$$

- Ladder Operator

$$\hat{a}_\pm = \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega\hat{x}) \quad \Rightarrow \quad [\hat{a}_-, \hat{a}_+] = \hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = \tfrac{1}{2} - (-\tfrac{1}{2}) = 1$$

$$[\hat{x}, \hat{p}] = i\hbar \qquad \hat{H} = \hbar\omega(\hat{a}_-\hat{a}_+ - \tfrac{1}{2}) = \hbar\omega(\hat{a}_+\hat{a}_- + \tfrac{1}{2})$$

For $\quad \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

we have:

$$\hat{H}(\hat{a}_+|\psi_n\rangle) = E_{n+1}|\psi_{n+1}\rangle \quad , \; E_{n+1} = E_n + \hbar\omega$$

$$\hat{H}(\hat{a}_-|\psi_n\rangle) = E_{n-1}|\psi_{n-1}\rangle \quad , \; E_{n-1} = E_n - \hbar\omega$$

AND:

Ladder Termination: $\hat{a}_-|\psi_0\rangle = 0$

H-Atom phenomenon

- **Emission / Absorption Spectrum:**

$$1/\lambda = R_H\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right), \quad R_H = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2 hc} = 1.097\times10^7\ m^{-1}$$

$$\boxed{E_n = E_1\frac{1}{n^2} = \frac{-13.6\,eV}{n^2}}$$

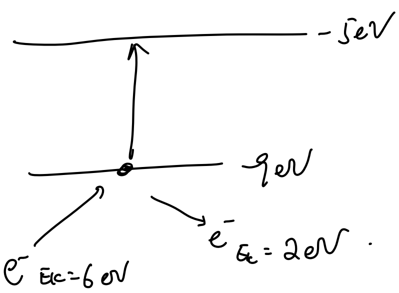
$\Rightarrow$ Paschen series: $n_f \rightarrow n_i = 3$

Balmer Series: $n_f \rightarrow n_i = 2$

Lyman Series: $n_f \rightarrow n_i = 1$

$\Rightarrow$ has to absorb exactly the energy difference to jump

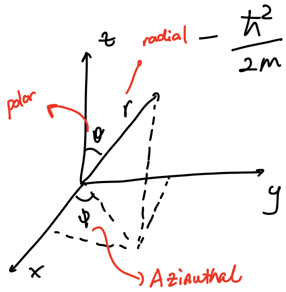
↳ otherwise, jump + remaining energy in the incident electron.



- **TISE in 3D** $\quad \hat{H}|\psi\rangle = E|\psi\rangle$

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

in polar coordinate (r,θ,ϕ)

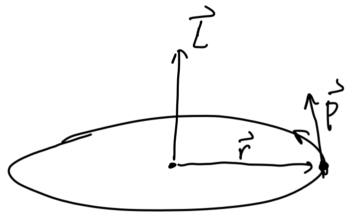


$$\underbrace{-\frac{\hbar^2}{2m}\Big[\underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{radial part}} + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{L^2 \text{ Angular part}}\Big]\psi(r,\theta,\phi)}_{KE}$$

energy eigenstate.

$$+\underbrace{V(r)}_{P.E}\psi(r,\theta,\phi) = \underbrace{E}_{\text{Energy eigenvalue}}\psi(r,\theta,\phi)$$

- **Angular momentum**



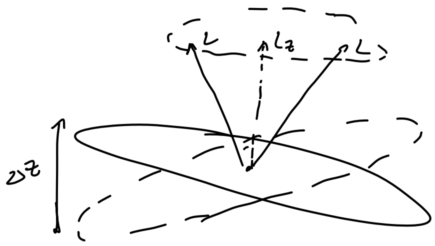
$\vec{L} = \vec{r} \times \vec{p}$

$\Rightarrow \hat{L} = \hat{r} \times \hat{p}$

- **Measure $\vec{L}$ in QM**

① $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \neq 0$ $\Rightarrow$ Cannot know 2 components at the same time

② $[\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = 0$ $\Rightarrow$ Can know total $\vec{L}$ and a component simultaneously



② $\begin{cases} \bullet\ \Delta z \neq 0 \longrightarrow \text{Cannot orbit in one plane} \rightarrow \text{in all 3 dir.} \\ \bullet\ \Delta p_z \neq 0 \longrightarrow \Delta z \Delta p_z \geq \hbar/2 \rightarrow \text{both have uncertainty} \end{cases}$

③ • $L \neq L_z \longrightarrow$ Cannot be all in one component
[ie: NOT ($L_x = 0$ AND $L_y = 0$)]

$\Rightarrow$ Similar to $[S_x, S_y] \neq 0$ but $[S^2, S_x] = 0$

- **Eigenstates & Eigenvalues**

- Assume $\psi(r, \theta, \phi) = R_l^n(r)\, Y_l^m(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$
- $[H, L^2] = 0$ & $[H, L_z] = 0$ $\Rightarrow$ H & L^2 & L_z share the same eigenstate

$$\Rightarrow \boxed{\begin{aligned} \hat{L}_z |\psi\rangle &= m\hbar |\psi\rangle \\ \hat{L}^2 |\psi\rangle &= l(l+1)\hbar^2 |\psi\rangle \\ H |\psi\rangle &= E_n |\psi\rangle = -\frac{13.6\,eV}{n^2} |\psi\rangle \end{aligned}}$$

$\Rightarrow$ possible $L_z = m\hbar$

$\Rightarrow$ possible $|\hat{L}| = \sqrt{l(l+1)}\,\hbar$

note that for a l, $m\hbar < \sqrt{l(l+1)}\,\hbar$

$$\begin{cases} n = 1, 2, \ldots \infty \\ l = 0, 1, \ldots, n-1 \\ m = -l, -l+1, \ldots, 0, \ldots, l-1, l \end{cases}$$

- Energy Degeneracy

  - For H, for the same n, you get same E_n

    ↳ it is just about how much is radial & how much is angular.

  - # of eigenstates with the same E_n for an n:

    - with spin (intrinsic angular momentum) : $2n^2$
    - with orbital angular momentum only : n^2

  - degeneracy in l is accidental → due to $1/r$ in $V(r)$

    degeneracy in m is due to many possible choice of z-axis

- Spectroscopic Notation (n, l)

  $n = 1, 2, 3, \ldots \infty$

  $l = 0, 1, 2, 3, 4, 5, \ldots, n-1$

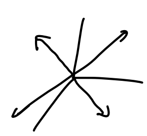
  $\downarrow$ s, $\downarrow$ p, $\downarrow$ d, $\downarrow$ f, $\downarrow$ g, $\downarrow$ h

- Angular & Radial Probability distribution

  - Angular (spherical harmonics) ⇒ n independent

    ↳ s state $(l=0)$ has $L = 0$ ⇒ all motion is in radial → can cross origin

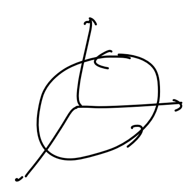
    $P(r=0)$ is at max

    ↳ All other states, $L \neq 0$ ⇒ Some angular motion around $r=0$

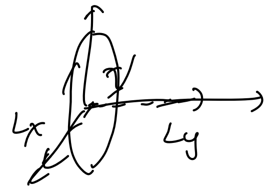
    → cannot cross origin

    $P(r=0) = 0$

↳ for $\underset{(L_z=0)}{\underline{m=0}}$ & $\underset{(L\neq0)}{l\neq0}$

↳ no L_z $\Rightarrow$ all motion must be in $\underline{z \text{ direction}}$



$\Rightarrow P(x=0, y=0, z) \neq 0$

- $\underline{\text{Radial (n dependent)}}$

↳ high n = more nodes on $R(r)$ vs. r

↳ due to higher frequency.

- $\underline{\text{Probability}}$

↳ Radial probability density: $|R(r)|^2 r^2 \, dr$

↳ angular probability density: $|Y(\theta,\phi)|^2 \sin\theta \, d\theta \, d\phi$.

↳ Normalization: $\int_{r=0}^{r=\infty} \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} |R(r)|^2 \, |Y(\theta,\phi)|^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi = 1$