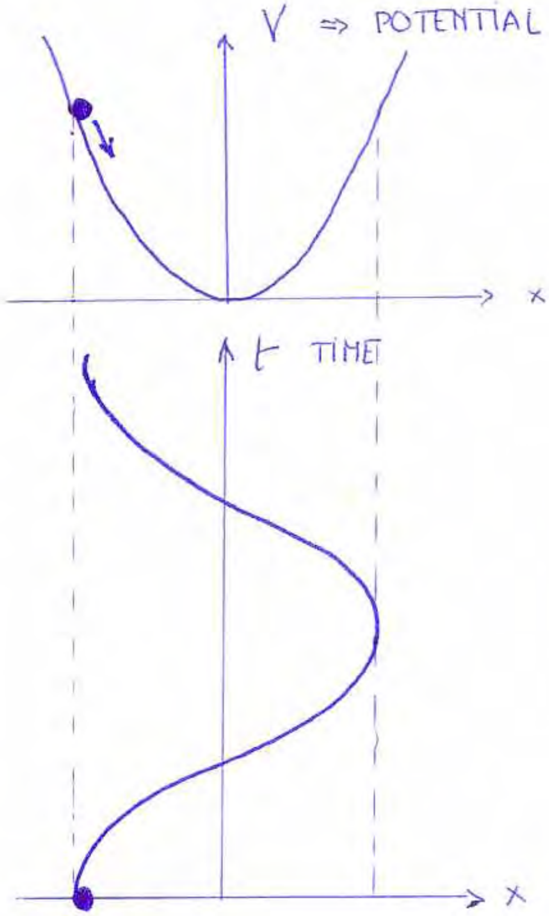
CHAPTER 1 : WAVE FUNCTION

1.1 SCHRÖDINGER EQUATION

- CLASSICAL MECHANICS

e.g. (HARMONIC OSCILLATOR)



$x(t)$ SOLUTION OF NEWTON'S EQ.

$$\underset{\text{MASS}}{m} \cdot \frac{d^2x}{dt^2} = \underset{\text{FORCE}}{F} = -\frac{\partial V}{\partial x}$$

POTENTIAL

SOLVE NEWTON'S EQ. , INITIAL CONDITIONS $x(0)$, $v(0)$

$\Downarrow$

POSITION $x(t)$

$\downarrow$

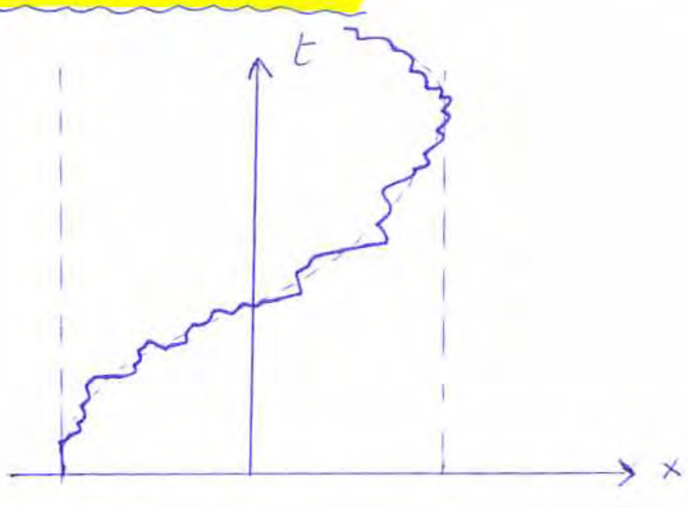
VELOCITY $v(t) = \frac{dx}{dt}$

$\Downarrow$

MOMENTUM $p = mv$

KINETIC ENERGY $T = \frac{1}{2} m v^2 = \frac{p^2}{2m}$

- QUANTUM MECHANICS



→ POSITION CAN NOT BE DETERMINED TO ARBITRARY ACCURACY

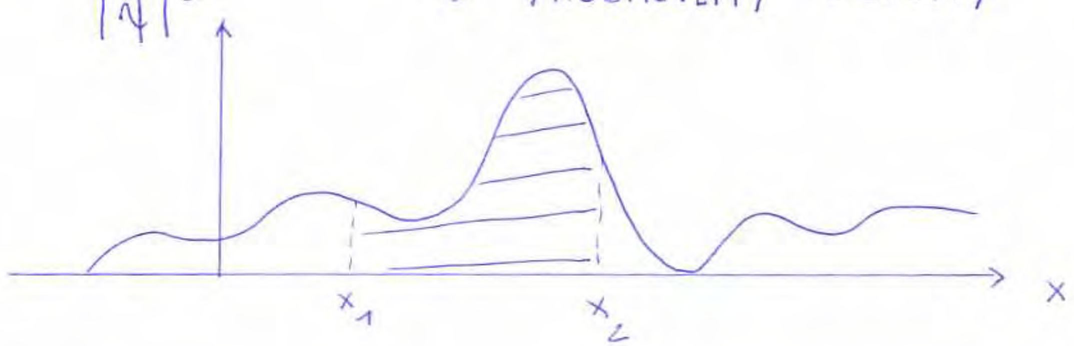
→ FLUCTUATIONS (ON MICROSCOPIC SCALE) AROUND CLASSICAL PATH / TRAJECTORY

→ WE CAN ONLY SPEAK OF PROBABILITY TO FIND $\left\{\begin{array}{l}\text{PARTICLE}\\ \text{OBJECT}\end{array}\right.$ AT A GIVEN TIME t AT A GIVEN POSITION x

→ BASIC CONCEPT : WAVE FUNCTION $\psi(x,t)$

INTERPRETATION . $|\psi(x,t)|^2 = \psi^*(x,t) \cdot \psi(x,t)$

↳ PROBABILITY DENSITY



$$\int_{x_1}^{x_2} dx \; |\psi(x,t)|^2$$ IS PROBABILITY TO FIND $\left|\begin{array}{l}\text{PARTICLE}\\ \text{OBJECT}\end{array}\right.$ AT TIME t

BETWEEN x_1 AND x_2.

→ WAVE FUNCTION SATISFIES SCHRÖDINGER EQ.

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = i\hbar\frac{\partial\psi}{\partial t}}$$

KINETIC ENERGY — POTENTIAL ENERGY — TOTAL ENERGY

SOLUTION $\left[+ \left\{ \begin{array}{l}\text{BOUNDARY}\\ \text{INITIAL}\end{array}\right. \text{CONDITIONS} \quad \psi(x,0) \right]$

↳ $\psi(x,t)$

$$\hbar = \frac{h}{2\pi} = 1.054572 \; 10^{-34} \; J.s$$

h : PLANCK's CONSTANT $\left\{ \begin{array}{l} \text{RECALL: LIGHT OF FREQUENCY } \nu \\ \downarrow \\ \text{ENERGY PACKETS } E = h\nu \text{ (PHOTON)} \end{array}\right.$

→ SMALLNESS OF h : FOR MACROSCOPIC OBJECTS

FLUCTUATIONS AROUND CLASSICAL TRAJECTORY

VERY TINY ⇒ TO GOOD APPROXIMATION :

WE CAN APPLY NEWTON's EQ.

1.3 PROBABILITY

- **DISCRETE VARIABLES**

GROUP OF PEOPLE N = TOTAL # PERSONS

$j = 0, 1, 2, \ldots$ AGE OF PERSON IN GROUP

$N(j)$ = # PERSONS WITH AGE j

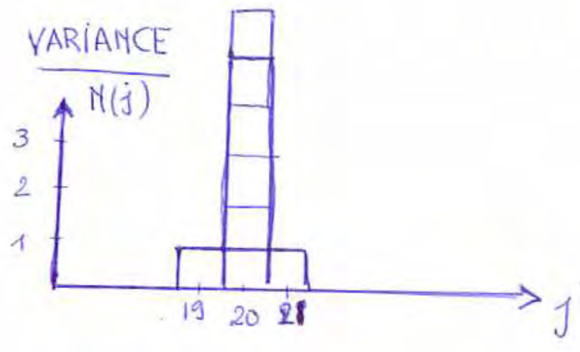
→ PROBABILITY TO FIND PERSON WITH AGE j

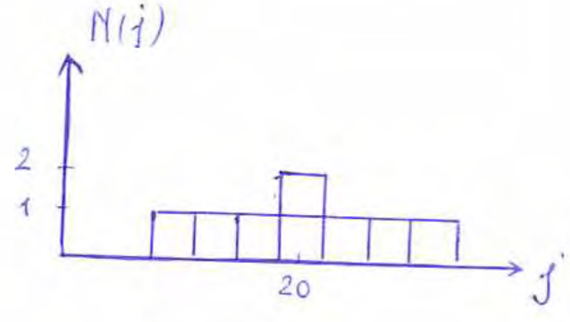
$$P(j) = \frac{N(j)}{N}$$

→ AVERAGE AGE

$$\langle j \rangle = \sum_{j=0}^{\infty} j \, P(j) = \frac{1}{N} \sum_{j=0}^{\infty} j \, N(j)$$

→ VARIANCE





2 DISTRIBUTIONS HAVE SAME AVERAGE BUT DIFFERENT SPREAD

⇓

MEASURE OF SPREAD : VARIANCE σ^2

$$\sigma^2 \equiv \langle (j - \langle j \rangle)^2 \rangle$$

$$= \langle j^2 - 2j\langle j \rangle + \langle j \rangle^2 \rangle$$

$$= \langle j^2 \rangle - 2\langle j \rangle^2 + \langle j \rangle^2$$

$$= \langle j^2 \rangle - \langle j \rangle^2$$

→ STANDARD DEVIATION

$$\sigma = \sqrt{\sigma^2} = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$$

- CONTINUOUS VARIABLES

e.g. HEIGHT OF PERSON x

→ PROBABILITY DENSITY $\rho(x)$

* INFINITESIMAL INTERVAL

PROBABILITY TO FIND SOMEONE WITH HEIGHT BETWEEN x AND $x + dx$

$$\hookrightarrow \rho(x)\, dx$$

* FINITE INTERVAL

PROBABILITY TO FIND SOMEONE WITH HEIGHT BETWEEN a AND b

$$\hookrightarrow P_{ab} = \int_a^b dx\ \rho(x)$$

* NORMALIZATION

$$1 = \int_{-\infty}^{+\infty} dx\ \rho(x)$$

→ AVERAGE

$$\langle x \rangle = \int_{-\infty}^{+\infty} dx\ x\ \rho(x)$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} dx\ f(x)\ \rho(x).$$

→ VARIANCE

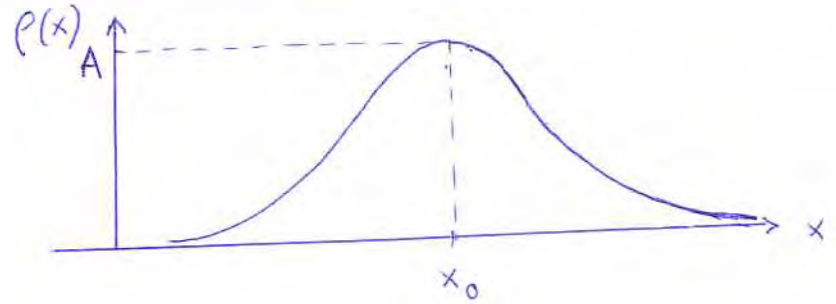
$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$$

$$= \int_{-\infty}^{+\infty} dx \, (x - \langle x \rangle)^2 \rho(x)$$

$$= \langle x^2 \rangle - \langle x \rangle^2$$

→ EXAMPLE : GAUSSIAN DISTRIBUTION.

* $\rho(x) = A \, e^{-\lambda (x - x_0)^2}$



* NORMALIZATION

$$\int_{-\infty}^{+\infty} dx \, \rho(x) = 1$$

$$1 = A \int_{-\infty}^{+\infty} dx \, e^{-\lambda (x - x_0)^2} = A \underbrace{\int_{-\infty}^{+\infty} dx' \, e^{-\lambda x'^2}}_{= \sqrt{\frac{\pi}{\lambda}}}$$

GAUSSIAN INTEGRAL

$x' = x - x_0$

$dx' = dx$

$$1 = A \cdot \sqrt{\frac{\pi}{\lambda}}$$

$$\Downarrow$$

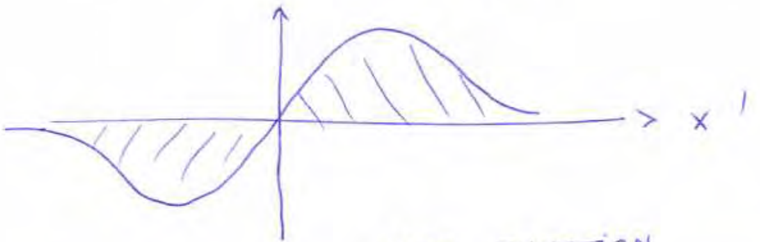
$$A = \sqrt{\frac{\lambda}{\pi}}$$

* AVERAGE

$$\langle x \rangle = A \int_{-\infty}^{+\infty} dx \quad x \quad e^{-\lambda (x - x_0)^2}$$

$$\underset{x' = x - x_0}{=} A \int_{-\infty}^{+\infty} dx' \, (x' + x_0) \, e^{-\lambda x'^2}$$

$$= A \left\{ \underbrace{\int_{-\infty}^{+\infty} dx' \, x' \, e^{-\lambda x'^2}}_{0} + x_0 \underbrace{\int_{-\infty}^{+\infty} dx' \, e^{-\lambda x'^2}}_{\sqrt{\frac{\pi}{\lambda}}} \right\}$$



ODD FUNCTION
INTEGRATED BETWEEN
SYMMETRIC INTEGRATION BOUNDS

$$= A \, x_0 \sqrt{\frac{\pi}{\lambda}}$$

$$\langle x \rangle = x_0$$

* VARIANCE

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$= \langle (x - \langle x \rangle)^2 \rangle$$

$$= \langle (x - x_0)^2 \rangle$$

$$= A \int_{-\infty}^{+\infty} dx \; (x - x_0)^2 \; e^{-\lambda (x - x_0)^2}$$

$$x' = x - x_0$$

$$= A \int_{-\infty}^{+\infty} dx' \; x'^2 \; e^{-\lambda x'^2}$$

$$= A \; \frac{1}{2} \sqrt{\frac{\pi}{\lambda}} \; \frac{1}{\lambda}$$

$$\boxed{\sigma^2 = \frac{1}{2\lambda}}$$

$$\sigma = \frac{1}{\sqrt{2\lambda}} \quad , \quad \lambda = \frac{1}{2\sigma^2}$$

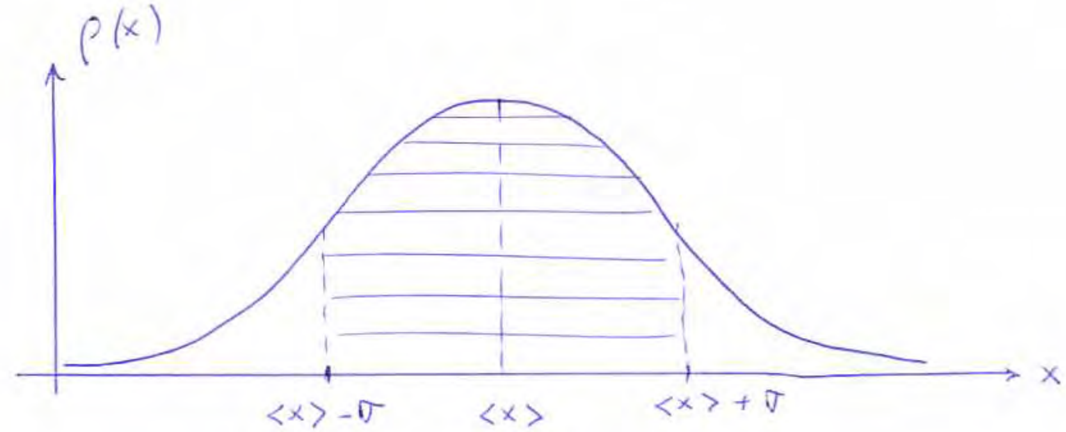
MATH HELP:

$$\int_{-\infty}^{+\infty} dx \; e^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}}$$

$$\int_{-\infty}^{+\infty} dx \; x^2 \, e^{-\lambda x^2} = -\frac{d}{d\lambda} \int_{-\infty}^{+\infty} dx \; e^{-\lambda x^2}$$

$$= -\frac{d}{d\lambda} \sqrt{\frac{\pi}{\lambda}}$$

$$= \frac{1}{2} \sqrt{\frac{\pi}{\lambda}} \; \frac{1}{\lambda}$$



$$\underline{\underline{\rho(x) = \frac{1}{\sqrt{2\pi}}\frac{1}{\sigma} e^{-\frac{1}{2\sigma^2}\left(x - \langle x\rangle\right)^2}}}$$

PROBABILITY $x \in \left[\langle x\rangle - \sigma, \ \langle x\rangle + \sigma\right]$

$P_{1\sigma}$ "1σ" DEVIATION FROM AVERAGE

$$P_{1\sigma} = A \int_{\langle x\rangle - \sigma}^{\langle x\rangle + \sigma} dx \cdot e^{-\frac{1}{2\sigma^2}\left(x - \langle x\rangle\right)^2}$$

$$\downarrow \quad x' = x - \langle x\rangle$$

$$= A \int_{-\sigma}^{+\sigma} dx' \ e^{-\frac{1}{2\sigma^2} x'^2}$$

$$\downarrow \quad A = \sqrt{\frac{\lambda}{\pi}} = \frac{1}{\sqrt{2\pi}\,\sigma}$$

$P_{1\sigma} = 0.68 \quad (68\%)$

$$\boxed{\begin{aligned} P_{1\sigma} &= 68\% \\ P_{2\sigma} &= 95\% \\ P_{3\sigma} &= 99.7\% \end{aligned}}$$

1.4 NORMALIZATION

→ WAVE FUNCTION $\Psi(x,t)$: INTERPRET AS "PROBABILITY AMPLITUDE"

SOLUTION OF SCHRÖDINGER EQUATION

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar\frac{\partial \Psi}{\partial t}$$

→ PROBABILITY DENSITY

$$\rho(x,t) = |\Psi(x,t)|^2 = \Psi^*\Psi$$

↳ PROBABILITY TO FIND PARTICLE AT POINT x AT TIME t

Ψ is COMPLEX

$\Psi = |\Psi|\, e^{i\phi}$ $\qquad |\Psi|$: AMPLITUDE

$\phantom{\Psi = |\Psi|\, e^{i\phi}} \qquad \phi$: PHASE

$\mathrm{Re}\,\Psi = |\Psi| \cos\phi$

$\mathrm{Im}\,\Psi = |\Psi| \sin\phi$

→ NORMALIZATION

$|\Psi(x,t)|^2\, dx$: PROB. TO FIND PARTICLE BETWEEN x & $x + dx$

PROB. TO FIND PARTICLE BETWEEN $-\infty$ & $+\infty$ $= 1$.

$$1 = \int_{-\infty}^{+\infty} dx \; |\Psi(x,t)|^2.$$

IF Ψ IS SOLUTION OF SCHRÖDINGER EQ.

$A\Psi$ IS ALSO SOLUTION OF SCHRÖDINGER EQ.

- NON-NORMALIZABLE SOLUTION $\int_{-\infty}^{+\infty} dx \; |\Psi(x,t)|^2 \neq 1$

  ↳ DOES NOT DESCRIBE A PHYSICAL STATE

- NORMALIZABLE SOLUTION $\int_{-\infty}^{+\infty} dx \; |\Psi(x,t)|^2 = 1.$

SQUARE, INTEGRABLE SOLUTION

↳ DESCRIBES PHYSICAL STATES, PARTICLES

→ NORMALIZATION IS TIME - INDEPENDENT

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

$$\frac{d}{dt} \int_{-\infty}^{+\infty} dx \; |\Psi(x,t)|^2 = 0$$

$$\int_{-\infty}^{+\infty} dx \; \frac{\partial}{\partial t} |\Psi(x,t)|^2 = 0.$$

PROOF THAT A SOLUTION OF SCHRÖDINGER EQ. PRESERVES THE NORMALIZATION

$$\hookrightarrow \frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial t}\left(\Psi^*\Psi\right)$$

$$= \left(\frac{\partial \Psi^*}{\partial t}\right)\Psi + \Psi^*\left(\frac{\partial \Psi}{\partial t}\right)$$

$$\hookrightarrow i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

POTENTIAL V IS REAL

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + V\Psi^*$$

$$\hookrightarrow \Psi^*\left(\frac{\partial \Psi}{\partial t}\right) = \frac{i\hbar}{2m}\Psi^*\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V|\Psi|^2$$

$$\left(\frac{\partial \Psi^*}{\partial t}\right)\Psi = -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2}\Psi + \frac{i}{\hbar}V|\Psi|^2$$

$+$

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi\right)$$

$$= \frac{i\hbar}{2m}\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right)$$

$$\hookrightarrow \int_{-\infty}^{+\infty} dx \; \frac{\partial}{\partial t} |\Psi(x,t)|^2$$

$$= \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} dx \; \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right)$$

$$\downarrow \qquad \int_a^b dx \; \frac{\partial F(x)}{\partial x} = F(b) - F(a)$$

$$= \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right]_{-\infty}^{+\infty}$$

$\downarrow$ FOR A NORMALIZABLE WAVE FUNCTION

$$\Psi(x = +\infty, t) = \Psi(x = -\infty, t) = 0.$$

$= 0$

■ QED

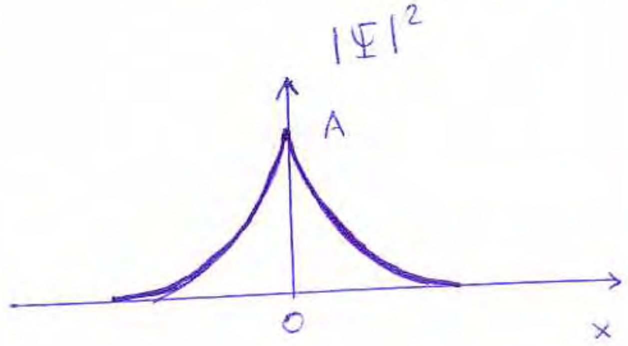
$\therefore$ IF $\Psi(x,t)$ IS NORMALIZED AT $t = 0$

IT STAYS NORMALIZED AT ALL TIMES.

→ EXAMPLE : PROBLEM 1.5

$$\Psi(x,t) = A\, e^{-\lambda|x|}\, e^{-i\omega t}$$

$$|\Psi(x,t)|^2 = A^2\, e^{-2\lambda|x|}$$



- NORMALIZATION

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

$$\Downarrow$$

$$A^2 \int_{-\infty}^{+\infty} dx\, e^{-2\lambda|x|} = 1.$$

$$2A^2 \underbrace{\int_{0}^{+\infty} dx\, e^{-2\lambda x}}_{\left[-\frac{1}{2\lambda} e^{-2\lambda x}\right]_0^{+\infty}} = 1$$

$$\frac{2A^2}{2\lambda} = 1 \implies \underline{\underline{A = \sqrt{\lambda}}}$$

- $\langle x \rangle = 0$

- $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

$$= \langle x^2 \rangle = A^2 \int_{-\infty}^{+\infty} dx\, x^2\, e^{-2\lambda|x|}$$

$$= 2A^2 \int_{0}^{+\infty} dx\, x^2\, e^{-2\lambda x}$$

MATH HELP

$$\int_0^{+\infty} dx \; x^2 \, e^{-2\lambda x}$$

$$= \frac{1}{4} \frac{d^2}{d\lambda^2} \int_0^{+\infty} dx \; e^{-2\lambda x}$$

$$= \frac{1}{4} \frac{d^2}{d\lambda^2} \left(\frac{1}{2\lambda} \right)$$

$$= \frac{1}{4} \cdot \frac{2}{2\lambda^3}$$

$$\sigma^2 = 2A^2 \cdot \frac{1}{4\lambda^3} = \frac{1}{2\lambda^2}$$

$$\underline{\underline{\sigma = \frac{1}{\sqrt{2}\lambda}}}$$

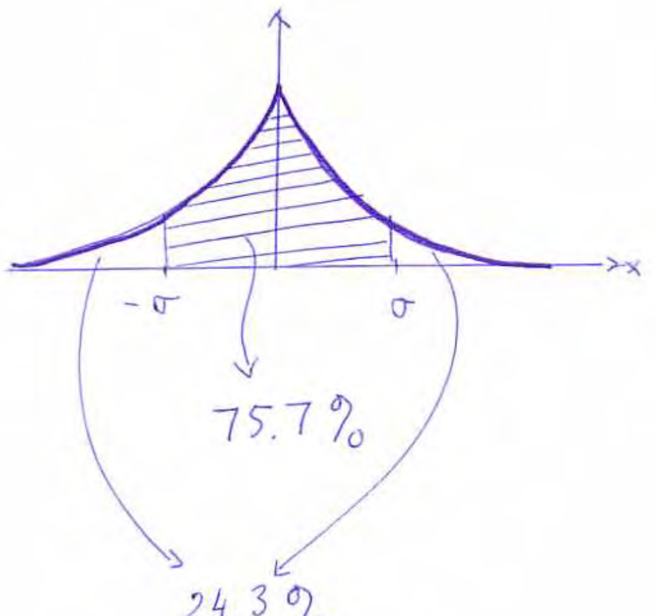
- $P\left(x \in [-\sigma, \sigma] \right)$

$$= \int_{-\sigma}^{\sigma} dx \; |\Psi(x,t)|^2$$

$$= 2A^2 \int_0^{\sigma} dx \; e^{-2\lambda x}$$

$$= -\frac{2A^2}{2\lambda} e^{-2\lambda x} \Big|_0^{\sigma}$$

$$= 1 - \underbrace{e^{-\sqrt{2}}}_{0.243} = \underset{\sim\sim}{0.757} \quad (75.7\,\%)$$



1.5 MOMENTUM

→ EXPECTATION VALUE

$\Psi(x,t)$ DESCRIBES STATE OF SYSTEM

IMAGINE AN ENSEMBLE OF SYSTEMS

↳ AVERAGE POSITION $\langle x \rangle$ OVER THIS ENSEMBLE

$$\langle x \rangle = \int_{-\infty}^{+\infty} dx \; x \; |\Psi(x,t)|^2$$

↳ TIME EVOLUTION OF $\langle x \rangle$

$$\frac{d}{dt}\langle x \rangle = \int_{-\infty}^{+\infty} dx \; x \; \frac{\partial}{\partial t}|\Psi(x,t)|^2$$

SEE P. 1.14

$$= \frac{i\hbar}{2m}\int_{-\infty}^{+\infty} dx \; x \; \frac{\partial}{\partial x}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right)$$

↓ INTEGRATION BY PARTS

$$= -\frac{i\hbar}{2m}\int dx \left(\Psi^* \frac{\partial \Psi}{\partial x} - \underbrace{\frac{\partial \Psi^*}{\partial x}\Psi}_{\text{INTEGRATION BY PARTS}}\right) + \cancel{\text{BOUNDARY TERM @ } -\infty \text{ AND } +\infty}$$

0

$\Psi(x=\pm\infty, t) = 0$

$$= -\frac{i\hbar}{m}\int dx \; \Psi^* \frac{\partial \Psi}{\partial x}$$

$\langle v \rangle$ EXPECTATION VALUE OF VELOCITY

$$\langle v \rangle = \frac{d}{dt} \langle x \rangle$$

↳ $\langle p \rangle$ EXPECTATION VALUE OF MOMENTUM

$$\langle p \rangle = m \langle v \rangle = -i\hbar \int dx\, \Psi^* \frac{\partial \Psi}{\partial x}$$

↳ 'OPERATORS'

$$\langle x \rangle = \int dx\, \Psi^* \, \underset{\substack{\uparrow \\ \text{POSITION 'OPERATOR'}}}{x} \, \Psi$$

$$\langle p \rangle = \int dx\, \Psi^* \underset{\substack{\uparrow \\ \text{MOMENTUM 'OPERATOR'}}}{\left(-i\hbar \frac{\partial}{\partial x} \right)} \Psi$$

$\langle T \rangle$ KINETIC ENERGY

$$T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

$$\langle T \rangle = \int dx\, \Psi^* \underset{\substack{\uparrow \\ \text{KINETIC ENERGY 'OPERATOR'}}}{\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right)} \Psi$$

$$\langle V \rangle = \int dx\, \Psi^* \, V \, \Psi$$

↳ POTENTIAL ENERGY 'OPERATOR'

↳ SCHRÖDINGER EQ

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

↓ MULTIPLY ON LEFT BY Ψ^* AND $\int dx$

$$\underbrace{\int dx\ \Psi^*\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\Psi}_{\langle T\rangle} + \underbrace{\int dx\ \Psi^* V\Psi}_{\langle V\rangle} = \underbrace{\int dx\ \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi}_{\langle E\rangle}$$

EXPECTATION VALUE
OF TOTAL ENERGY

↳ TIME EVOLUTION OF $\langle p\rangle$

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

$$= -i\hbar\int dx\left(\frac{\partial\Psi^*}{\partial t}\cdot\frac{\partial\Psi}{\partial x} + \Psi^*\frac{\partial}{\partial x}\cdot\frac{\partial\Psi}{\partial t}\right)$$

- $i\hbar\dfrac{\partial\Psi}{\partial t} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi}{\partial x^2} + V\Psi$

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + V\Psi^*$$

$$\frac{d}{dt}\langle p\rangle = \int dx \left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\cdot\frac{\partial\Psi}{\partial x} + V\Psi^*\frac{\partial\Psi}{\partial x} + \frac{\hbar^2}{2m}\Psi^*\frac{\partial}{\partial x}\frac{\partial^2\Psi}{\partial x^2} - \Psi^*\frac{\partial}{\partial x}(V\Psi)\right)$$

$\downarrow$ INTEGRATION BY PARTS TWICE ON FIRST TERM

$$\int_{-\infty}^{+\infty} dx \, \frac{\partial^2\Psi^*}{\partial x^2}\cdot\frac{\partial\Psi}{\partial x} = -\int_{-\infty}^{+\infty} dx \, \frac{\partial\Psi^*}{\partial x}\frac{\partial^2\Psi}{\partial x^2}$$

$$= +\int_{-\infty}^{+\infty} dx \, \Psi^* \frac{\partial^3\Psi}{\partial x^3}$$

$$\frac{d}{dt}\langle p\rangle = \int dx \left(\cancel{-\frac{\hbar^2}{2m}\Psi^*\frac{\partial^3\Psi}{\partial x^3}} + \cancel{V\Psi^*\frac{\partial\Psi}{\partial x}} + \cancel{\frac{\hbar^2}{2m}\Psi^*\frac{\partial^3\Psi}{\partial x^3}} - \Psi^*\frac{\partial V}{\partial x}\Psi - \cancel{V\Psi^*\frac{\partial\Psi}{\partial x}}\right)$$

$$\frac{d}{dt}\langle p\rangle = \int dx \, \Psi^*\left(-\frac{\partial V}{\partial x}\right)\Psi$$

$$= \left\langle -\frac{\partial V}{\partial x}\right\rangle$$

EHRENFEST's THEOREM

↳ EXPECTATION VALUES OBEY CLASSICAL LAWS (e.g. NEWTON's LAWS)

1.6 UNCERTAINTY PRINCIPLE

→ WAVE FUNCTION Ψ

WAVELENGTH λ

$\updownarrow$

PARTICLE MOMENTUM p

PARTICLE - WAVE DUALITY IN Q.M.

DE BROGLIE FORMULA : $\boxed{p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}}$ $\quad \hbar = \frac{h}{2\pi}$

→ HEISENBERG 's UNCERTAINTY PRINCIPLE

THE MORE PRECISE WE KNOW POSITION,
THE LESS PRECISE WE KNOW ITS MOMENTUM
AND VICE VERSA

$$\boxed{\sigma_x \cdot \sigma_p \geqslant \frac{\hbar}{2}}$$

SOMETIMES ONE ALSO DENOTES $\sigma_x = \Delta x$

$\sigma_p = \Delta p$

$$\Delta x . \Delta p \geqslant \frac{\hbar}{2}$$

CHAPTER 2 : TIME - INDEPENDENT SCHRÖDINGER EQUATION

⇒ 2.1 STATIONARY STATES

- SOLVE SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\,\Psi = i\hbar\frac{\partial \Psi}{\partial t}$$

FOR TIME-INDEPENDENT POTENTIAL $V(x,t) = V(x)$

- METHOD OF SEPARATION OF VARIABLES. TO SOLVE PARTIAL DIFFERENTIAL EQ.

TRY SOLUTION OF FORM

$$\Psi(x,t) = \psi(x) \cdot \varphi(t)$$

$$\hookrightarrow \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2} \cdot \varphi$$

$$\hookrightarrow \frac{\partial \Psi}{\partial t} = \psi \cdot \frac{d\varphi}{dt}$$

↳ SCHRÖDINGER EQ.

$$i\hbar\, \psi \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\varphi + V(x)\,\psi\varphi$$

↓ DIVIDE BY $\psi \cdot \varphi$

$$\underbrace{i\hbar \frac{1}{\varphi}\frac{d\varphi}{dt}}_{\text{ONLY FUNCTION OF } t} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x)}_{\text{ONLY FUNCTION OF } x}$$

ONLY POSSIBLE IF BOTH ARE CONSTANT

DENOTING CONSTANT BY E

$$\begin{cases} i\hbar \dfrac{1}{\varphi}\dfrac{d\varphi}{dt} = E \\[2ex] -\dfrac{\hbar^2}{2m}\dfrac{1}{\psi}\dfrac{d^2\psi}{dx^2} + V(x) = E \end{cases}$$

∴ USING METHOD OF SEPARATION OF VARIABLES.
TO TURN PARTIAL DIFFERENTIAL EQUATION
INTO 2 ORDINARY DIFFERENTIAL EQUATIONS

↳ ONE FOR $\varphi(t)$

↳ ONE FOR $\psi(x)$

$$\boxed{i\hbar \frac{\partial \varphi}{\partial t} = E \varphi}$$

GENERAL SOLUTION

$$\varphi(t) = \underset{\substack{\uparrow \\ \text{CONSTANT}}}{C} \cdot e^{-\frac{i}{\hbar} E t}$$

BECAUSE WE WILL NORMALIZE $\Psi = \psi(x) \cdot \varphi(t)$,

WE CAN SET (WITHOUT LOSS OF GENERALITY) $C = 1$

$$\varphi(t) = e^{-\frac{i}{\hbar} E t}$$

$\psi(x)$ SATISFIES

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi}$$

TIME INDEPENDENT SCHRÖDINGER EQUATION

GENERAL SOLUTION OF FORM

$$\boxed{\Psi(x,t) = \psi(x)\, e^{-\frac{i}{\hbar} E t}}$$

- SOLUTION $\Psi(x,t) = \psi(x)\, e^{-\frac{i}{\hbar}Et}$

IS A STATIONARY STATE

↳ PROBABILITY DENSITY IS TIME INDEPENDENT

$$|\Psi(x,t)|^2 = |\psi(x)|^2$$

ALSO EXPECTATION VALUES ARE TIME INDEPENDENT

$$\text{e.g.} \quad \langle x \rangle = \int dx\, x\, |\Psi(x,t)|^2$$

$$= \int dx\, x\, |\psi(x)|^2$$

$$m \frac{d}{dt} \langle x \rangle = \langle p \rangle = 0$$

↳ AVERAGE MOMENTUM IN STATIONARY STATE = 0.

↳ STATIONARY STATE IS STATE OF DEFINITE TOTAL ENERGY E

HAMILTONIAN: CLASSICAL MECH $\quad H(x,p) = \frac{p^2}{2m} + V(x)$

↓

QUANTUM MECH $\quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

$p \to -i\hbar \frac{\partial}{\partial x}$

TIME INDEPENDENT SCHRÖDINGER EQ.

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

$$\hat{H}\,\psi(x) = E\,\psi(x)$$

EXPECTATION VALUE OF TOTAL ENERGY

$$\langle H \rangle = \int dx \;\; \psi^*(x)\;\hat{H}\;\psi(x)$$

$$= E\int dx \;\; \psi^*\psi$$

$$= E\,\underbrace{\int dx \;\; |\Psi|^2}_{1}$$

$$\underline{\underline{\langle H \rangle = E}}$$

↳ GENERAL SOLUTION : LINEAR COMBINATION OF SEPARABLE SOLUTIONS

$$\Psi_1(x,t) = \psi_1(x)\, e^{-\frac{i}{\hbar}E_1 t}$$
$$\Psi_2(x,t) = \psi_2(x)\, e^{-\frac{i}{\hbar}E_2 t}$$

....

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \underbrace{\psi_n(x)\, e^{-\frac{i}{\hbar}E_n t}}_{\Psi_n(x,t)}}$$

⇑
EACH SEPARABLE SOLUTION IS A STATIONARY STATE

↳ EXAMPLE : SUM OF 2 STATIONARY STATES

REAL

INITIAL STATE $(t=0)$ $\quad \Psi(x,0) = c_1\psi_1(x) + c_2\psi_2(x)$

↓

GENERAL STATE $\quad \Psi(x,t) = c_1\psi_1(x)\, e^{-\frac{i}{\hbar}E_1 t} + c_2\psi_2(x)\, e^{-\frac{i}{\hbar}E_2 t}$

PROBABILITY DENSITY $\quad |\Psi(x,t)|^2 = c_1^2\psi_1^2 + c_2^2\psi_2^2$

$$+ 2c_1c_2\psi_1\psi_2 \cos\left[(E_1 - E_2)\frac{t}{\hbar}\right]$$

OSCILLATION IN TIME OF $|\Psi|^2$ WITH FREQUENCY $(E_1 - E_2)/\hbar$

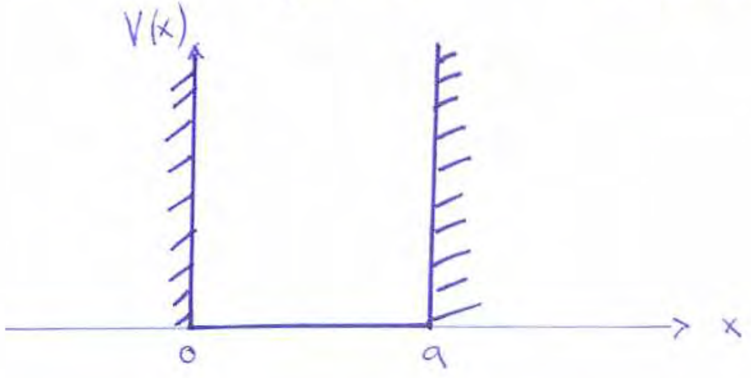
VISUALIZATION:
↳ SEE
WEBPHYSICS.DAVIDSON.EDU/MJB/NCS_AAPT_QM_2002/WELCOME.HTML

MAX $\quad |\Psi|^2_{MAX} = (c_1\psi_1 + c_2\psi_2)^2$

MIN $\quad |\Psi|^2_{MIN} = (c_1\psi_1 - c_2\psi_2)^2$

⇒ 2.2 INFINITE SQUARE WELL

- $$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{OTHERWISE} \end{cases}$$



- FOR $x < 0$ OR $x > a$ $\quad \psi(x) = 0$

FOR $0 \leq x \leq a$

↳ $\psi(x)$ IS SOLUTION OF $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

$$\downarrow \quad k = \frac{\sqrt{2mE}}{\hbar}$$

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2\psi}$$

GENERAL SOLUTION :

$$\psi(x) = A \sin kx + B \cos kx.$$

A, B: REAL CONSTANTS.

- A & B DETERMINED BY <u>BOUNDARY CONDITIONS</u>

$$\psi(0) = \psi(a) = 0$$

ψ MUST BE A CONTINUOUS FUNCTION (IS ZERO OUTSIDE THE WELL)

$$\psi(0) = 0 \quad \Rightarrow \quad B = 0$$

$$\psi(a) = 0 \quad \Rightarrow \quad A \sin ka = 0$$

$$\Downarrow$$

$$ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \ldots$$

↳ $A = 0$ SOLUTION IS NOT ACCEPTABLE BECAUSE IT IS NOT NORMALIZABLE

↳ SAME APPLIES TO $k = 0$

↳ SOLUTIONS FOR $ka = -n\pi$

ARE EQUIVALENT TO THOSE FOR $ka = +n\pi$

BECAUSE $\sin(-x) = -\sin x$

& MINUS SIGN CAN BE ABSORBED IN A

↳ DISTINCT SOLUTIONS:

$$\boxed{k_n = n\frac{\pi}{a}} \quad , \quad n = 1, 2, 3, \ldots$$

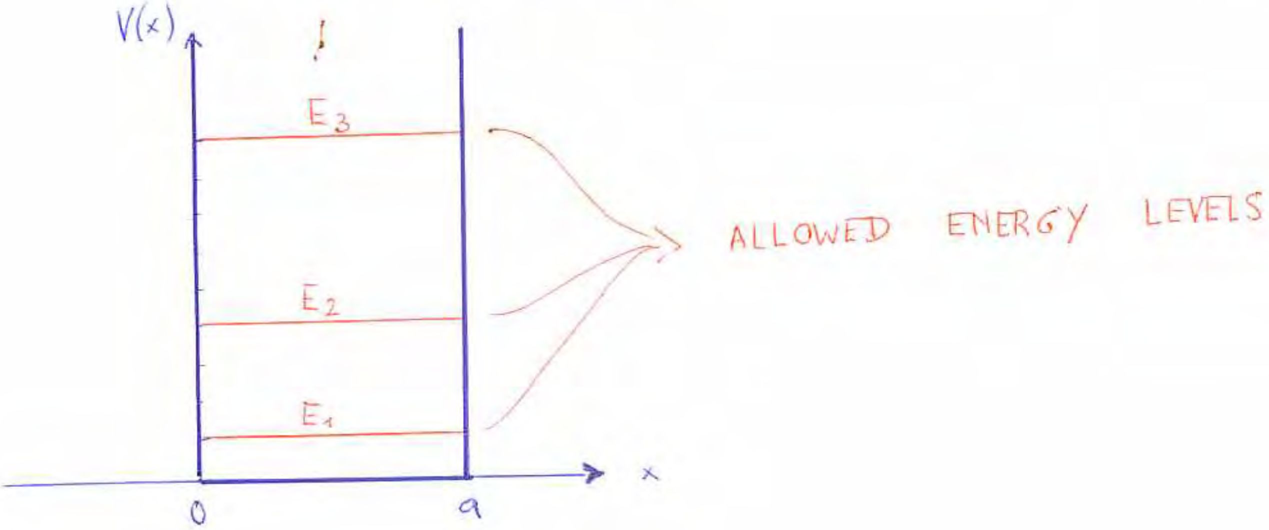
↳ BOUNDARY CONDITIONS DETERMINE

ALLOWED VALUES FOR k

" " " E

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2ma^2}} = n^2 E_1$$

ENERGY IS QUANTIZED



- NORMALIZATION

$$\int_{-\infty}^{+\infty} dx \; |\psi(x)|^2 = 1$$

$$\Downarrow$$

$$|A|^2 \int_0^a dx \; \sin^2\left(n \frac{\pi}{a} x\right) = 1$$

MATH HELP :

$$\sin^2 x = \frac{1}{2}\left(1 - \cos 2x\right)$$

PROOF : SECOND TERM GIVES 0 UPON INTEGRATION

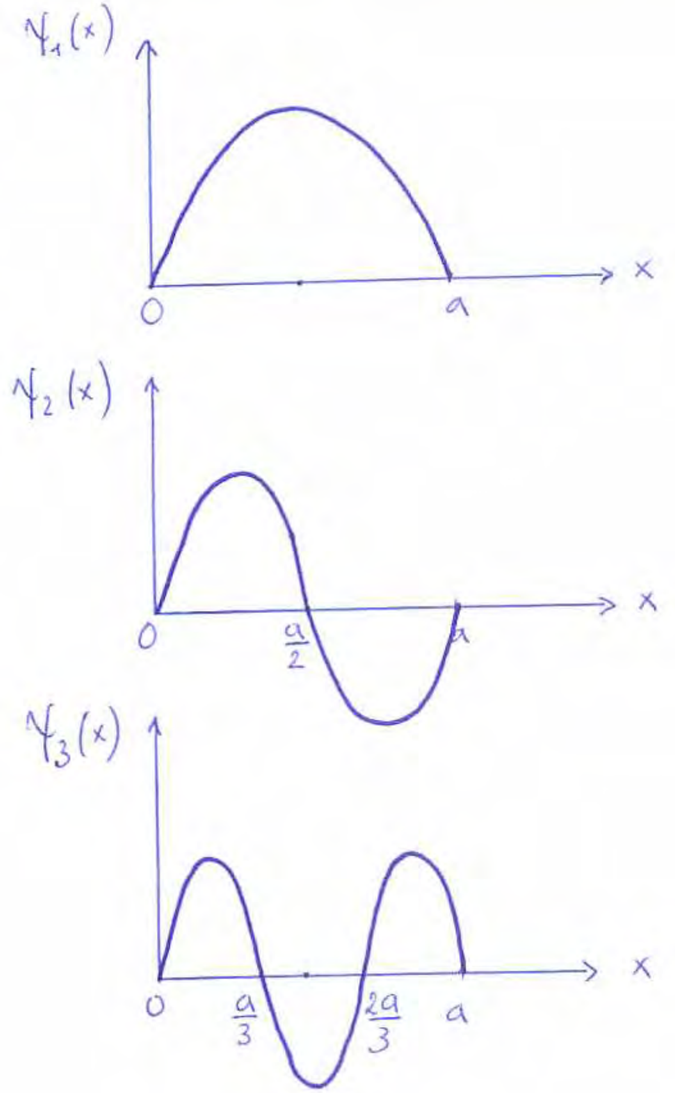
$$|A|^2 \cdot \frac{a}{2} = 1$$

$$\boxed{A = \sqrt{\frac{2}{a}}}$$

(ABSOLUTE PHASE HAS NO PHYSICAL SIGNIFICANCE)

∴ SOLUTIONS

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{n\pi}{a}x\right)}$$



$$\psi_1(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{\pi}{a}x\right)$$

GROUND STATE
(STATE OF LOWEST ENERGY)

$$\psi_2(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{2\pi}{a}x\right)$$

1 NODE (ZERO) AT $x = \frac{a}{2}$

$$\psi_3(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{3\pi}{a}x\right)$$

2 NODES AT $x = \frac{a}{3}, \frac{2a}{3}$

$\psi_2, \psi_3, \ldots$ ARE CALLED EXCITED STATES

SOLUTIONS ARE STANDING WAVES

• PROPERTIES OF SOLUTIONS

↳ EVEN OR ODD w.r.t CENTER OF WELL

$n = 1, 3, 5, \ldots \Rightarrow$ EVEN (SYMMETRY PROPERTY)

$n = 2, 4, 6, \ldots \Rightarrow$ ODD

↳ EXCITED STATES HAVE NODES (ZEROS)

ψ_n HAS $n-1$ NODES.

THE HIGHER THE ENERGY, THE MORE NODES

↳ SOLUTIONS ARE ORTHOGONAL TO EACH OTHER

$\int dx \; \psi_m^*(x) \cdot \psi_n(x) = 0$	$n \neq m$

PROOF: $\int dx \; \psi_m^*(x)\, \psi_n(x)$

$$= \frac{2}{a} \int_0^a dx \; \sin\left(\frac{m\pi}{a} x\right) \sin\left(\frac{n\pi}{a} x\right)$$

MATH HELP

$$\sin x \cdot \sin y = -\frac{1}{2}\left[\cos(x+y) - \cos(x-y)\right]$$

$$= -\frac{1}{a} \int_0^a dx \left[\cos\left(\frac{(m+n)\pi}{a} x\right) - \cos\left(\frac{(m-n)\pi}{a} x\right)\right]$$

↳ SOLUTIONS ARE COMPLETE

i.e. ANY OTHER FUNCTION CAN BE WRITTEN AS A LINEAR COMBINATION OF THEM

$$\boxed{f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)}$$

$$f(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right)$$

(FOURIER SERIES)

COEFFICIENTS c_n DETERMINED FROM ORTHONORMALITY:

$$\int dx\, \psi_m^*(x) f(x) = \sum_{n=1}^{\infty} c_n \underbrace{\int dx\, \psi_m^*(x) \psi_n(x)}_{\delta_{nm}}$$

$$= c_m$$

$$\boxed{c_n = \int dx\, \psi_n^*(x) f(x)}$$

$$= -\frac{1}{a}\left[\frac{a}{\pi(m+n)}\sin\left(\frac{(m+n)\pi}{a}x\right)\right.$$

$$\left.-\frac{a}{\pi(m-n)}\sin\left(\frac{(m-n)\pi}{a}x\right)\right]_0^a$$

ONLY VALID FOR $m \neq n$!

$$= -\frac{1}{\pi}\left\{\sin\left((m+n)\pi\right) - \sin\left((m-n)\pi\right)\right\}$$

$$\overset{!}{=} 0$$

FOR $m = n$: NORMALIZATION CONDITION

∴ COMBINE ORTHOGONALITY & NORMALIZATION

INTO:

$$\boxed{\int dx\ \psi_m^*(x)\ \psi_n(x) = \delta_{nm}}$$

$$\delta_{nm} = \begin{cases} 1 & , \ n = m \\ 0 & , \ n \neq m \end{cases}$$

ψ_n's ARE CALLED <u>ORTHONORMAL</u>

↳ STATIONARY STATE

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{i}{\hbar}E_n t}$$

WITH $E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$

↳ MOST GENERAL SOLUTION OF TIME DEPENDENT SCHRÖDINGER EQ. IN INFINITE SQUARE WELL POTENTIAL:

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{i}{\hbar}E_n t}}$$

IF WE KNOW THE INITIAL $\Psi(x, t=0)$

WE CAN DETERMINE c_n

⇓

WE ALSO KNOW SOLUTION AT ALL TIMES t

$$c_n = \int dx \; \psi_n^*(x) \; \Psi(x,0)$$

$$= \sqrt{\frac{2}{a}} \int_0^a dx \; \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)$$

∴ KNOWING $\Psi(x,t)$ ⇒ CALCULATE ALL OBSERVABLES

$\langle x \rangle$, $\langle p \rangle$, ...

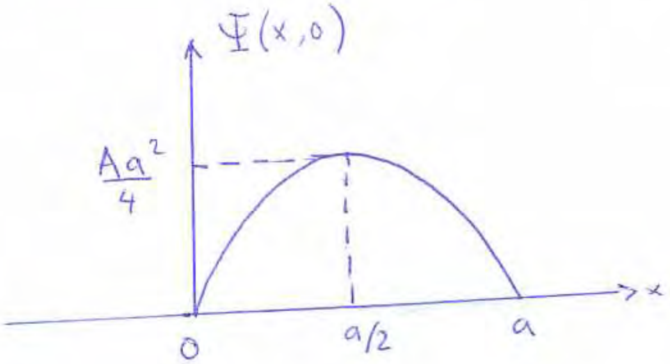
σ_x, σ_y, ...

- EXAMPLE

PARTICLE IN INFINITE SQUARE WELL

INITIAL W.F. $\Psi(x,0) = A\,x\,(a-x) \quad , \quad 0 \leq x \leq a$

$= 0 \quad , \quad$ ELSEWHERE



DETERMINE W.F. AT ANY TIME

↳ NORMALIZATION

$$1 = \int dx \; |\Psi(x,0)|^2$$

$$= A^2 \int_0^a dx \; x^2 (a-x)^2 = A^2 \int_0^a dx \; x^2 (a^2 - 2ax + x^2)$$

$$= A^2 \left(\frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5} \right)$$

$$= A^2 \frac{a^5}{30}$$

$$\boxed{A = \sqrt{\frac{30}{a^5}}}$$

$$\hookrightarrow \quad \Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{i}{\hbar}E_n t}$$

$$c_n = \sqrt{\frac{2}{a}} \int_0^a dx \ \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)$$

$$c_n = \sqrt{\frac{2}{a}} \underset{\substack{\uparrow \\ \sqrt{\frac{30}{a^5}}}}{A} \int_0^a dx \ \sin\left(\frac{n\pi}{a}x\right) \ x(a-x)$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ a\int_0^a dx \ x \sin\left(\frac{n\pi}{a}x\right) - \int_0^a dx \ x^2 \sin\left(\frac{n\pi}{a}x\right) \right\}$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ -\frac{a^2}{n\pi} \ x \cos\left(\frac{n\pi}{a}x\right) \Big|_0^a \right.$$

$$+ \cancel{\frac{a^2}{n\pi} \int_0^a dx \ \cos\left(\frac{n\pi}{a}x\right)}$$

$$+ \frac{a}{n\pi} \ x^2 \cos\left(\frac{n\pi}{a}x\right) \Big|_0^a$$

$$\left. - \frac{2a}{n\pi} \int_0^a dx \ x \ \cos\left(\frac{n\pi}{a}x\right) \right\}$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ \cancel{-\frac{a^3}{n\pi} \cos(n\pi) + \frac{a^3}{n\pi} \cos(n\pi)} \right.$$

$$\left. - \frac{2a^2}{(n\pi)^2} \ \cancel{x \sin\frac{n\pi}{a}x \Big|_0^a} + \frac{2a^2}{(n\pi)^2} \int_0^a dx \sin\left(\frac{n\pi}{a}x\right) \right\}$$

$$c_n = \frac{2\sqrt{15}}{a^3} \cdot (-1) \frac{2a^2}{(n\pi)^2} \cdot \frac{a}{n\pi} \cos\left(\frac{n\pi}{a}x\right)\Big|_0^a$$

$$c_n = \frac{4\sqrt{15}}{(n\pi)^3} \left[1 - \cos(n\pi)\right]$$

$$\boxed{c_n = \begin{cases} 0 & , \quad n \text{ EVEN} \\ \dfrac{8\sqrt{15}}{(n\pi)^3} & , \quad n \text{ ODD} \end{cases}}$$

$$\boxed{\Psi(x,t) = \sqrt{\frac{30}{a}} \left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^3} \sin\left(\frac{n\pi}{a}x\right) e^{-\frac{i}{\hbar}E_n t}}$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$$

c_n : OVERLAP OF WAVEFUNCTION WITH n-th STATIONARY STATE

LARGEST OVERLAP WITH c_1 $\qquad |c_1|^2 = \left(\dfrac{8\sqrt{15}}{\pi^3}\right)^2$

$c_n \sim \dfrac{1}{n^3}$

$= 0.99855\ldots$

$(99.9\,\%)$

↳ $|c_n|^2$ PROBABILITY TO FIND Ψ IN STATE n

$$\boxed{\sum_{n=1}^{\infty} |c_n|^2 = 1}$$

PROOF: $1 = \int dx \, |\Psi(x,0)|^2$

$$= \int dx \left(\sum_{m=1}^{\infty} c_m \psi_m(x) \right)^* \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right)$$

$$= \sum_n \sum_m c_n c_m^* \underbrace{\int dx \, \psi_m^*(x) \psi_n(x)}_{\delta_{nm}}$$ ORTHONORMAL

$$= \sum_{n=1}^{\infty} |c_n|^2$$

■ QED

↳ EXPECTATION VALUE OF ENERGY

$$\langle H \rangle = \int dx \, \Psi \hat{H} \Psi \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$= \sum_n \sum_m c_m^* c_n \int dx \, \psi_m^*(x) \underbrace{\hat{H} \psi_n(x)}_{E_n \psi_n(x)}$$

$$= \sum_n \sum_m c_m^* c_n E_n \int dx \, \psi_m^*(x) \psi_n(x)$$

$$\boxed{\langle H \rangle = \sum_{n=1}^{\infty} E_n |c_n|^2}$$

• CHECK OF UNCERTAINTY PRINCIPLE FOR INFINITE SQUARE WELL

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$$

FOR STATIONARY STATE $\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$.

$$\hookrightarrow \langle x \rangle = \int_0^a dx \; \psi_n^*(x) \; x \; \psi_n(x)$$

$$= \frac{2}{a} \int_0^a dx \; x \; \underbrace{\sin^2\left(\frac{n\pi}{a} x\right)}_{\frac{1}{2}\left(1 - \cos\left(\frac{2n\pi}{a} x\right)\right)}$$

$$= \frac{2}{a} \int_0^a dx \; \frac{x}{2}$$

$$\underline{\underline{\langle x \rangle = \frac{1}{2} a}} \qquad \text{INDEPENDENT OF } n$$

$$\hookrightarrow \langle p \rangle = m \frac{d}{dt} \langle x \rangle = 0$$

$$\underset{\text{CHECK}}{=} m \int_0^a dx \; \psi_n^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi_n(x)$$

$$= -i\hbar \, m \, \frac{2}{a} \cdot \frac{2n\pi}{a} \underbrace{\int_0^a dx \; \sin\left(\frac{n\pi}{a} x\right) . \cos\left(\frac{n\pi}{a} x\right)}_{0}$$

$$\underline{\underline{\langle p \rangle = 0}}$$

$$\hookrightarrow \langle x^2 \rangle = \frac{2}{a}\int_0^a dx \; x^2 \underbrace{\sin^2\left(\frac{n\pi}{a}x\right)}_{\frac{1}{2}\left(1-\cos\left(\frac{2n\pi}{a}x\right)\right)}$$

$$= \frac{1}{a}\left\{ \frac{a^3}{3} - \frac{a}{2n\pi}\underbrace{\cancel{x^2 \sin\left(\frac{2n\pi}{a}x\right)}\Big|_0^a}_{0} + \frac{a}{2n\pi}\cdot 2\int_0^a dx \; x \sin\left(\frac{2n\pi}{a}x\right)\right\}$$

$$= \frac{1}{a}\left\{ \frac{a^3}{3} - \frac{a}{n\pi}\cdot\frac{a}{2n\pi}\, x\cos\left(\frac{2n\pi}{a}x\right)\Big|_0^a + \frac{a}{n\pi}\cdot\frac{a}{2n\pi}\underbrace{\cancel{\int_0^a dx \cos\left(\frac{2n\pi}{a}x\right)}}_{0}\right\}$$

$$= \frac{1}{a}\left\{ \frac{a^3}{3} - \frac{a^3}{2(n\pi)^2}\cdot\underbrace{\cos(2n\pi)}_{1}\right\}$$

$$\langle x^2 \rangle = a^2\left[\frac{1}{3} - \frac{1}{2(n\pi)^2}\right]$$

$$\hookrightarrow \langle p^2 \rangle = \int dx \; \psi_n^*(x) \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi_n(x)$$

$$= \int_0^a dx \; \psi_n^*(x) \left(2m E_n \right) \psi_n(x)$$

$$= 2m E_n$$

$$\underline{\underline{\langle p^2 \rangle = \hbar^2 \left(\frac{n\pi}{a} \right)^2}}$$

$$\hookrightarrow \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$= \frac{a^2}{4} \left[\frac{1}{3} - \frac{2}{(n\pi)^2} \right]$$

$$\sigma_x = \frac{a}{2} \sqrt{\frac{1}{3} - \frac{2}{(n\pi)^2}}$$

$$\hookrightarrow \sigma_y^2 = \langle p^2 \rangle - \underbrace{\cancel{\langle p \rangle^2}}_{0}$$

$$\sigma_y = \hbar \; \frac{n\pi}{a}$$

$$\hookrightarrow \boxed{\sigma_x \cdot \sigma_p = \frac{\hbar}{2} \cdot \underbrace{\sqrt{\frac{(n\pi)^2}{3} - 2}}_{\text{SMALLEST FOR } n = \underline{1} \,:\, \sqrt{\frac{\pi^2}{3} - 2} = 1.136} \geqslant \frac{\hbar}{2}}$$

⇒ 2.3 HARMONIC OSCILLATOR

- CLASSICAL H.O.

$$F = -\underset{\substack{\uparrow \\ \text{SPRING CONSTANT}}}{k}\;\underset{\substack{\uparrow \\ \text{DISPLACEMENT}}}{x}$$

$$m \frac{d^2 x}{dt^2} = -kx$$

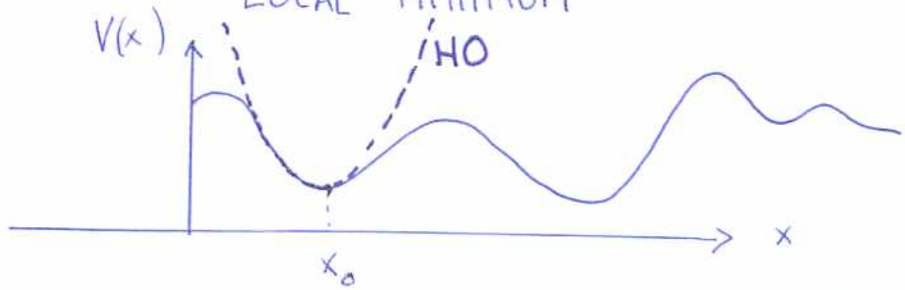
↳ SOLUTION: $x(t) = A \sin(\omega t) + B \cos(\omega t)$

$\omega = \sqrt{\frac{k}{m}}$ ANGULAR FREQUENCY

↳ POTENTIAL ENERGY $F = -\frac{dV}{dx}$

$$\underline{\underline{V(x) = \frac{1}{2} k x^2}}$$ PERFECT H.O.

↳ IN REALITY: H.O. IS GOOD APPROX. AROUND LOCAL MINIMUM



FOR x AROUND x_0: TAYLOR SERIES

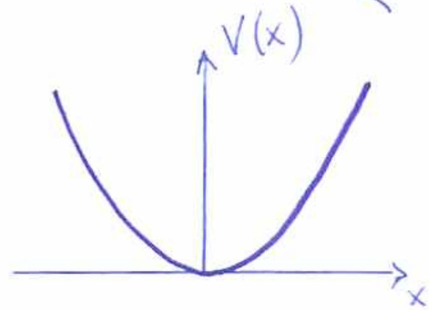
$$V(x) = V(x_0) + \underbrace{\cancel{V'(x_0)}}_{\substack{0 \\ \text{LOCAL MIN.}}}(x-x_0) + V''(x_0)\frac{1}{2}(x-x_0)^2 + \dots$$

H.O. $$\boxed{V(x) - V(x_0) \simeq \frac{1}{2} V''(x_0)\,(x-x_0)^2} \rightarrow k \equiv V''(x_0).$$

2.23

- QUANTUM H.O.

$$\boxed{V(x) = \frac{1}{2} m \omega^2 x^2}$$



TIME INDEPENDENT SCHRÖDINGER EQ.

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2} m \omega^2 x^2 \psi(x) = E\,\psi(x)}$$

2 METHODS TO SOLVE ↗ ALGEBRAIC METHOD
↘ POWER SERIES METHOD

(1) ALGEBRAIC METHOD TO QUANTUM H.O.

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

$$= \int dx\, \psi^*(x)\underbrace{\left(-i\hbar\frac{d}{dx}\right)}_{\hat{p}\,:\ \text{MOMENTUM OPERATOR}}\psi(x)$$

SCHRÖDINGER EQ.

$$\frac{\hat{p}^2}{2m}\psi + \frac{1}{2} m\omega^2 x^2 \psi = E\psi$$

$$\hat{H}\psi = E\psi$$

↳ HAMILTONIAN

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 x^2}$$

↳ IDEA TRY TO FACTOR $\hat{H}$

CONSIDER $\left(i\hat{p} + m\omega x\right)\cdot\left(-i\hat{p} + m\omega x\right)$

$$= \hat{p}^2 + i m\omega\left(\hat{p}\,x - x\,\hat{p}\right) + m^2\omega^2 x^2$$

$$= 2m\hat{H} + \underbrace{i m\omega\left(\hat{p}\,x - x\,\hat{p}\right)}_{\text{EXTRA TERM}}$$

ATTENTION $\hat{p}$ AND x DO NOT COMMUTE

COMMUTATOR $\boxed{[x, \hat{p}] \equiv x\hat{p} - \hat{p}x}$

$$[x, \hat{p}]f(x) = \left(-i\hbar\, x\frac{d}{dx} + i\hbar\frac{d}{dx}\, x\right) f(x)$$

$$= \cancel{-i\hbar\, x\frac{df}{dx}} + i\hbar f + \cancel{i\hbar\, x\frac{df}{dx}}$$

$$= i\hbar\, f(x)$$

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

CANONICAL COMMUTATION RELATION

↳ DEFINE OPERATORS WHICH CORRESPOND WITH THE ABOVE FACTORS

i.e.

$$\boxed{\begin{aligned} a_+ &\equiv \frac{1}{\sqrt{\hbar\omega\, 2m}}\left(-i\hat{p} + m\omega x\right) \\ a_- &\equiv \frac{1}{\sqrt{\hbar\omega\, 2m}}\left(+i\hat{p} + m\omega x\right) \end{aligned}}$$

⇑

NORMALIZATION FACTOR
TO GIVE SIMPLE PHYSICAL INTERPRETATION
TO a_+ & a_- (SEE FURTHER ON)

↳ $$a_- a_+ = \frac{1}{\hbar\omega\, 2m}\left\{ 2m\hat{H} + i m\omega(-i\hbar)\right\}$$

⇓

$$\hat{H} = \hbar\omega\left(a_- a_+ - \frac{1}{2}\right)$$

↳ ANALOGOUSLY WE CAN CALCULATE $a_+ a_-$

$$a_+ a_- = \frac{1}{\hbar\omega\, 2m}\left(-i\hat{p} + m\omega x\right)\left(+i\hat{p} + m\omega x\right)$$

$$= \frac{1}{\hbar\omega\, 2m}\left(2m\hat{H} + i m\omega \underbrace{[x, \hat{p}]}_{i\hbar}\right)$$

$$\hat{H} = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)$$

$$a_- a_+ - \frac{1}{2} = a_+ a_- + \frac{1}{2}$$

$$\downarrow$$

$$\boxed{[a_-, a_+] = 1.}$$

↳ SCHRÖDINGER EQ.

$$\hat{H} \psi = E \psi$$

$$\boxed{\begin{aligned} \hat{H} &= \hbar\omega \left(a_+ a_- + \frac{1}{2}\right) \\ &= \hbar\omega \left(a_- a_+ - \frac{1}{2}\right) \end{aligned}}$$

$$\hbar\omega \left(a_+ a_- + \frac{1}{2}\right) \psi = E \psi$$

OR EQUIVALENTLY

$$\hbar\omega \left(a_- a_+ - \frac{1}{2}\right) \psi = E \psi$$

CRUCIAL STEP IF ψ IS SOLUTION OF SCHRÖDINGER EQ. WITH ENERGY E

$$\Downarrow$$

$a_+ \psi$ IS SOLUTION WITH ENERGY $E + \hbar\omega$

$a_- \psi$ IS SOLUTION WITH ENERGY $E - \hbar\omega$

PROOF $\hat{H} \psi = E \psi$

(1) $$\hat{H}(a_+ \psi) = \hbar\omega \left(a_+ a_- + \frac{1}{2}\right)(a_+ \psi)$$

$$= \hbar\omega \left(a_+ \underbrace{a_- a_+}_{\downarrow\, a_- a_+ = 1 + a_+ a_-} + \frac{1}{2} a_+\right) \psi$$

$$\downarrow$$

2.27

$$\hat{H}(a_+\psi) = \hbar\omega\left(a_+ + a_+a_+a_- + \tfrac{1}{2}a_+\right)\psi$$

$$= a_+ \; \hbar\omega\left(a_+a_- + \tfrac{1}{2} + 1\right)\psi$$

$$\downarrow \quad \hat{H} = \hbar\omega\left(a_+a_- + \tfrac{1}{2}\right)$$

$$= a_+\left(\hat{H} + \hbar\omega\right)\psi$$

$$= a_+\left(E + \hbar\omega\right)\psi$$

$$= \left(E + \hbar\omega\right)\left(a_+\psi\right).$$

$\therefore$ $(a_+\psi)$ IS SOLUTION WITH ENERGY $E + \hbar\omega$

② $$\hat{H}(a_-\psi) = \hbar\omega\left(a_-a_+ - \tfrac{1}{2}\right)(a_-\psi)$$

$$= \hbar\omega\left(a_-a_+a_- - \tfrac{1}{2}a_-\right)\psi$$

$$= a_- \; \underbrace{\hbar\omega\left(a_+a_- - \tfrac{1}{2}\right)}_{\hat{H} - \hbar\omega}\psi$$

$$= a_-\left(\hat{H} - \hbar\omega\right)\psi$$

$$= a_-\left(E - \hbar\omega\right)\psi$$

$$= \left(E - \hbar\omega\right)\left(a_-\psi\right)$$

$\therefore$ $(a_-\psi)$ IS SOLUTION WITH ENERGY $E - \hbar\omega$

↳ BY APPLYING $a_\pm$ OPERATOR ON

A GIVEN SOLUTION WITH ENERGY E

ONE GENERATES A NEW SOLUTION WITH ENERGY $E \pm \hbar\omega$

$$a_+ \leftrightarrow E + \hbar\omega$$
$$a_- \leftrightarrow E - \hbar\omega$$

a_+ CALLED 'RAISING' OPERATOR

↳ RAISES ENERGY BY 'QUANTUM' $\hbar\omega$

a_- CALLED 'LOWERING' OPERATOR

↳ LOWERS ENERGY BY 'QUANTUM' $\hbar\omega$

- ONE CAN APPLY a_+ SUCCESSIVELY TO GET STATES OF HIGHER ENERGY

e.g. $$\hat{H}\left(a_+^2 \psi\right) = \left(E + 2\hbar\omega\right)\left(a_+^2 \psi\right)$$
$$\vdots$$
$$\hat{H}\left(a_+^n \psi\right) = \left(E + n\hbar\omega\right)\left(a_+^n \psi\right)$$

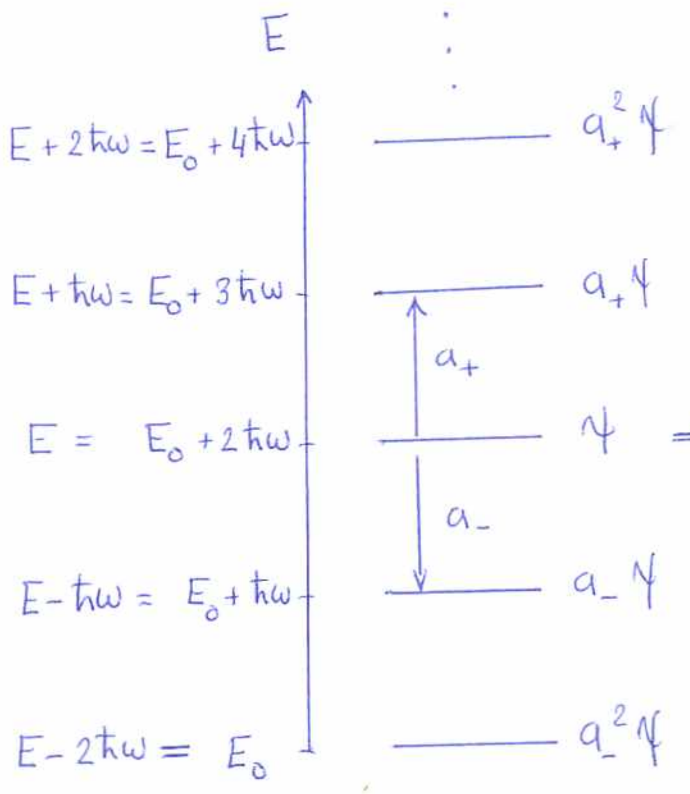
- ONE CAN APPLY a_- SUCCESSIVELY TO GET STATES OF LOWER ENERGY

e.g. $$\hat{H}\left(a_-^2 \psi\right) = \left(E - 2\hbar\omega\right)\left(a_-^2 \psi\right)$$
$$\vdots$$

BUT PAY ATTENTION !

BY REPEATED APPLICATION OF a_-
ONE WOULD EVENTUALLY REACH A STATE WITH NEGATIVE ENERGY $\downarrow$ UNPHYSICAL

$\therefore$ THERE MUST BE A STATE OF LOWEST ENERGY E_0
$\hookrightarrow$ GROUND STATE



$\psi \implies$ LET'S SAY WE KNOW THIS SOLUTION

$a_-^2 \psi \equiv \underbrace{\psi_0}$

GROUND STATE
= STATE WITH LOWEST ENERGY

FOR GROUND STATE

$$a_- \psi_0 = 0$$

i.e. ONE CANNOT GET A STATE OF LOWER ENERGY THAN ψ_0

$\hat{H}(a_- \psi_0) = 0$ NOT NORMALIZABLE SOLUTION OF SCHRÖDINGER EQ.

↳ USE CONDITION $\underline{\underline{a_- \psi_0 = 0}}$ TO DETERMINE

GROUND STATE ψ_0

$$a_- \psi_0 = 0$$

$$\Updownarrow$$

$$\frac{1}{\sqrt{\hbar\omega 2m}} \left(i\hat{p} + m\omega x \right) \psi_0 = 0$$

$$\left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0$$

$$\boxed{\frac{d\psi_0}{dx} = - \frac{m\omega}{\hbar} x \, \psi_0}$$

SOLUTION : $\psi_0(x) = A \, e^{-\frac{m\omega}{2\hbar} x^2}$

USE NORMALIZATION TO DETERMINE A :

$$1 = \int_{-\infty}^{+\infty} dx \, |\psi_0(x)|^2 = |A|^2 \underbrace{\int_{-\infty}^{+\infty} dx \, e^{-\frac{m\omega}{\hbar} x^2}}$$

GAUSSIAN (MATH HELP) INTEGRAL

$$\int_{-\infty}^{+\infty} dx \, e^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}}$$

$$= |A|^2 . \sqrt{\frac{\pi\hbar}{m\omega}}$$

$$A = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4}$$

∴ GROUND STATE OF QUANTUM H.O.

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}}$$

↳ GROUND STATE ENERGY E_0

$$E_0 = \langle \hat{H} \rangle = \int_{-\infty}^{+\infty} dx \; \psi_0^*(x) \; \underset{\displaystyle -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2}{\underset{\downarrow}{\hat{H}}} \; \psi_0(x)$$

EVALUATE ....

BUT THERE IS A SHORTER WAY TO DETERMINE E_0

$$\hat{H} = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)$$

$$\hat{H}\psi_0 = E_0\psi_0 = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right)\psi_0$$

$\downarrow$ $\quad a_-\psi_0 = 0$

THIS DEFINES THE GROUND STATE ψ_0.

$$= \frac{1}{2}\hbar\omega \; \psi_0$$

$$\boxed{E_0 = \frac{1}{2}\hbar\omega}$$

GROUND STATE ENERGY OF QUANTUM H.O. is NOT ZERO ! (IN CLASSICAL LIMIT $\hbar \to 0$, $E_0 \to 0$)

↳ ANY OTHER SOLUTION

BY REPEATED APPLICATION OF a_+ ON ψ_0.

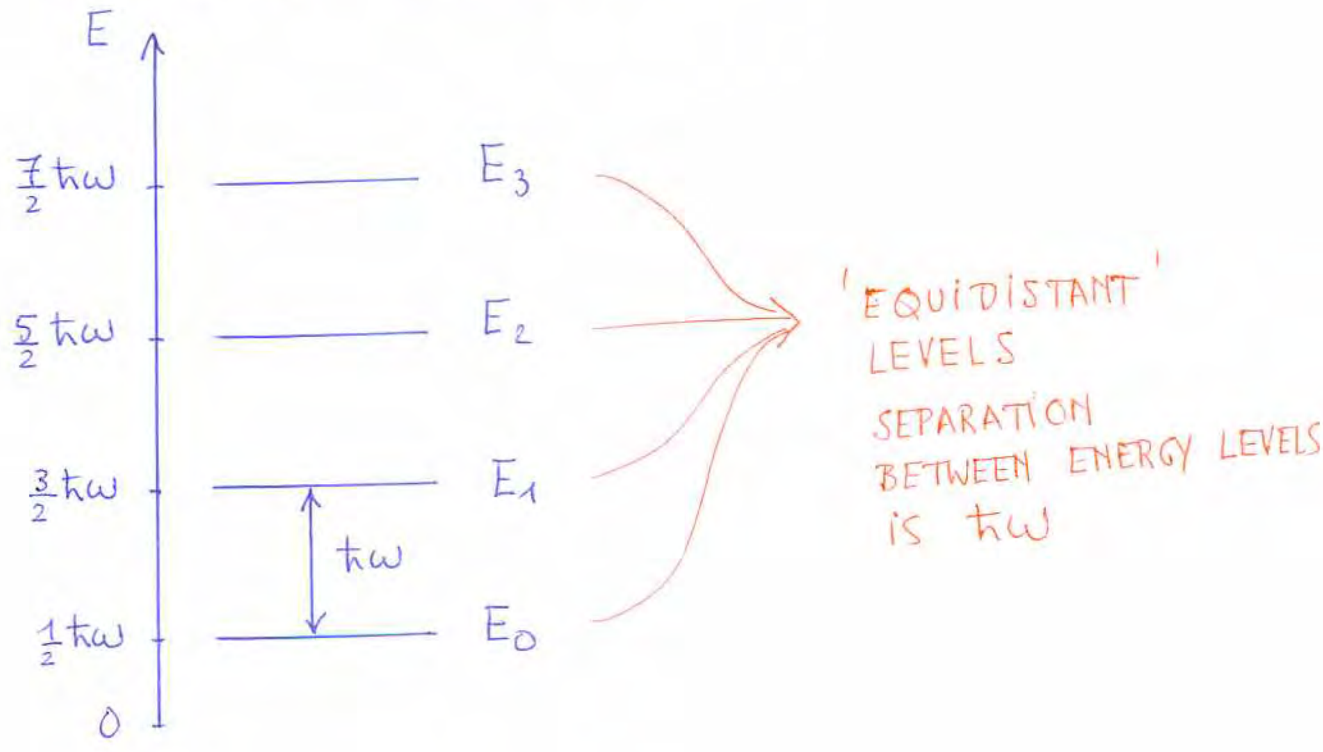
$$\boxed{\psi_n(x) = A_n \, a_+^n \, \psi_0}$$

↑ NORMALIZATION CONSTANT

ψ_n HAS ENERGY $E_n = E_0 + n\hbar\omega$

$$\boxed{E_n = \hbar\omega\left(\frac{1}{2} + n\right)}$$

SPECTRUM OF QUANTUM H.O.



e.g. FIRST EXCITED STATE

$$\psi_1(x) = A_1 \; a_+ \psi_0(x)$$

$$= A_1 \frac{1}{\sqrt{\hbar\omega 2m}} \left(-i\hat{p} + m\omega x\right) \underbrace{\psi_0(x)}_{\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}}$$

$$= A_1 \frac{1}{\sqrt{\hbar\omega 2m}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(-\hbar\frac{d}{dx} + m\omega x\right) e^{-\frac{m\omega}{2\hbar}x^2}$$

$$= A_1 \frac{1}{\sqrt{\hbar\omega 2m}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} 2m\omega x \; e^{-\frac{m\omega}{2\hbar}x^2}$$

$$\boxed{\psi_1(x) = A_1 \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} \; x \; e^{-\frac{m\omega}{2\hbar}x^2}}$$

NORMALIZATION $1 = \int_{-\infty}^{+\infty} dx \; |\psi_1(x)|^2$

$$= |A_1|^2 \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \cdot \frac{2m\omega}{\hbar} \cdot \underbrace{\int_{-\infty}^{+\infty} dx \; x^2 e^{-\frac{m\omega}{\hbar}x^2}}$$

MATH HELP: $\int_{-\infty}^{+\infty} dx \; x^2 e^{-\lambda x^2} = \frac{1}{2}\sqrt{\frac{\pi}{\lambda}}$ ...

$\downarrow$

$$= |A_1|^2 \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \cdot \frac{2m\omega}{\hbar} \; \frac{1}{2} \left(\frac{\pi\hbar}{m\omega}\right)^{1/2} \frac{\hbar}{m\omega}$$

$$= |A_1|^2$$

$A_1 = 1$

$$\boxed{A_n = \frac{1}{\sqrt{n!}}}$$

PROOF

$$a_+ \psi_n = c_n \psi_{n+1}$$
$$a_- \psi_n = d_n \psi_{n-1}.$$

$$a_+ a_- \psi_n = d'_n \psi_n$$

WE KNOW
$$\begin{cases} \hat{H} \psi_n = E_n \psi_n = \hbar\omega \left(\frac{1}{2} + n\right) \psi_n \\ \hat{H} = \hbar\omega \left(a_+ a_- + \frac{1}{2}\right) \end{cases}$$

$$\boxed{a_+ a_- \psi_n = n \psi_n}$$

"NUMBER" OPERATOR COUNTS THE STATE n

$$\boxed{a_- a_+ \psi_n = \left(1 + a_+ a_-\right) \psi_n = (n+1) \psi_n}$$

NORMALIZATION:
$$\int_{-\infty}^{+\infty} dx \, \underbrace{\left(a_+ \psi_n\right)^*}_{\frac{1}{\sqrt{\hbar\omega 2m}} \left(-\hbar\frac{d}{dx} + m\omega x\right) \psi_n^*} \left(a_+ \psi_n\right) = |c_n|^2 \underbrace{\int_{-\infty}^{+\infty} dx \, |\psi_{n+1}|^2}_{1}$$

$\downarrow$ INTEGRATION BY PARTS.

$$|c_n|^2 = \int_{-\infty}^{+\infty} dx \; \psi_n^* \frac{1}{\sqrt{\hbar\omega 2m}} \left(+\hbar \frac{d}{dx} + m\omega x \right) a_+ \psi_n$$

$$= \int_{-\infty}^{+\infty} dx \; \psi_n^* \; a_- a_+ \psi_n$$

$$= (n+1)$$

$$\therefore \quad \boxed{a_+ \psi_n = \sqrt{n+1} \; \psi_{n+1}}$$

ANALOGOUSLY $\quad |d_n|^2 = n$

$$\boxed{a_- \psi_n = \sqrt{n} \; \psi_{n-1}}$$

$$\rightsquigarrow \quad \psi_1 = a_+ \psi_0$$

$$\psi_2 = \frac{1}{\sqrt{2}} a_+ \psi_1 = \frac{1}{\sqrt{2}} a_+^2 \psi_0$$

$$\psi_3 = \frac{1}{\sqrt{3}} a_+ \psi_2 = \frac{1}{\sqrt{3.2}} a_+^3 \psi_0 = \frac{1}{\sqrt{3!}} a_+^3 \psi_0$$

$$\vdots$$

$$\psi_n = \frac{1}{\sqrt{n}} a_+ \psi_{n-1} = \frac{1}{\sqrt{n(n-1)}} a_+^2 \psi_{n-2} = \frac{1}{\sqrt{n!}} a_+^n \psi_0$$

$$\Uparrow$$

$$A_n = \frac{1}{\sqrt{n!}} \quad \blacksquare \text{ QED}$$

↳ SOLUTIONS OF H.O. ARE ORTHONORMAL

$$\boxed{\int_{-\infty}^{+\infty} dx \; \psi_m^*(x)\, \psi_n(x) = \delta_{nm}}$$

PROOF

$$\int_{-\infty}^{+\infty} dx \; \psi_m^*(x)\, a_+ a_- \psi_n(x)$$

BY PARTIAL INTEGRATION TWICE

$$= n \int_{-\infty}^{+\infty} dx \; \psi_m^*(x)\, \psi_n(x)$$

$$= \int_{-\infty}^{+\infty} dx \; \underbrace{\left(a_+ a_- \psi_m \right)^*}_{m \psi_m^*} \psi_n$$

$$= m \int_{-\infty}^{+\infty} dx \; \psi_m^* \psi_n$$

FOR $n \neq m \Rightarrow \int_{-\infty}^{+\infty} dx \; \psi_m^* \psi_n = 0.$

$n = m \Rightarrow \int_{-\infty}^{+\infty} dx \; |\psi_n|^2 = 1$ NORMALIZATION

∎ QED

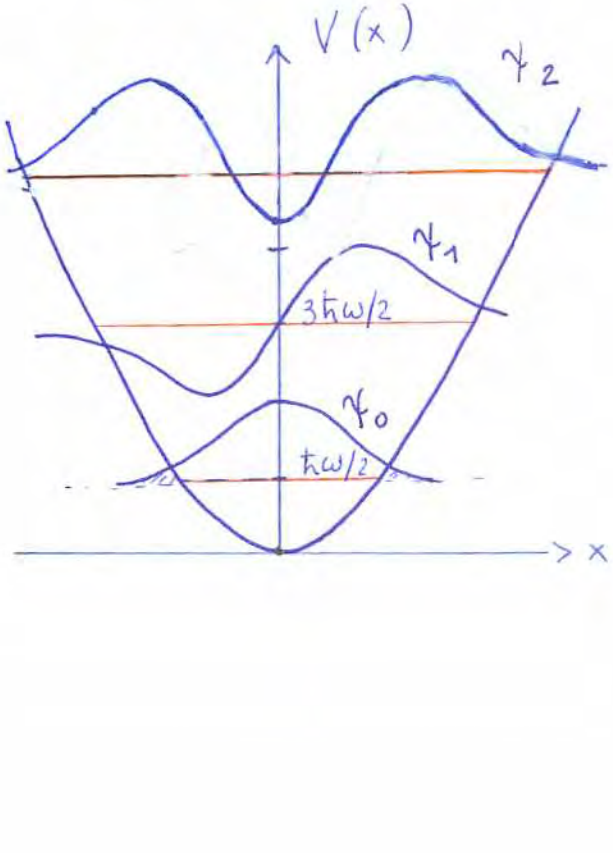
↳ PLOT OF LOWEST FEW WAVE FUNCTIONS.

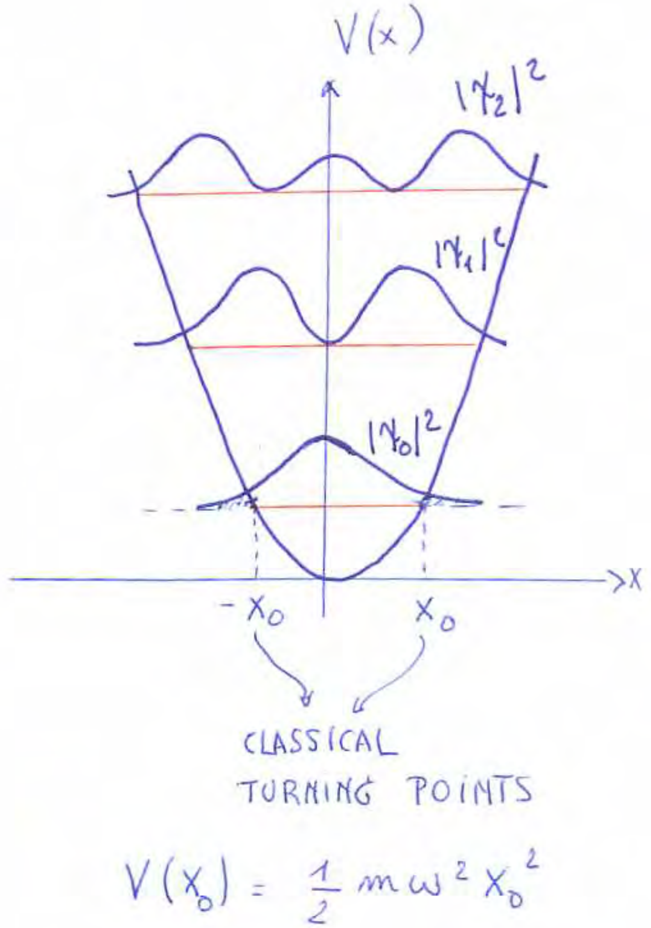
- $\psi_0(x) \sim e^{-\frac{m\omega}{2\hbar}x^2}$ EVEN IN x

$|\psi_0|^2 \sim e^{-\frac{m\omega}{\hbar}x^2}$

- $\psi_1 \sim x\, e^{-\frac{m\omega}{2\hbar}x^2}$ ODD IN x

$|\psi_1|^2 \sim x^2\, e^{-\frac{m\omega}{2\hbar}x^2}$





CLASSICAL TURNING POINTS

$$V(x_0) = \frac{1}{2} m\omega^2 x_0^2$$

$$= E_0 = \frac{1}{2}\hbar\omega$$

$$\Downarrow$$

$$x_0 = \sqrt{\frac{\hbar}{m\omega}}$$

- FOR ENERGY LEVEL E_n

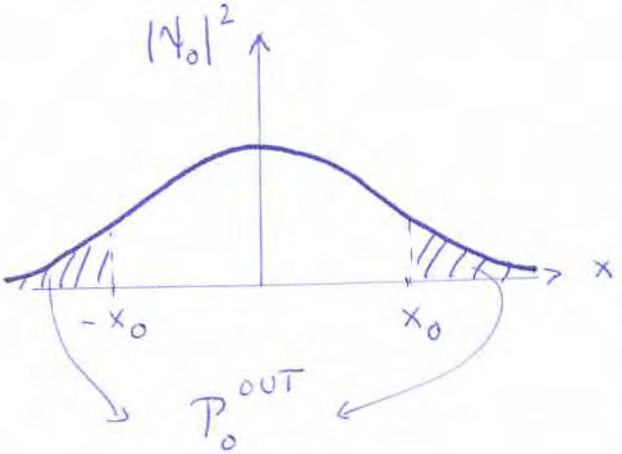
THE CLASSICAL TURNING POINTS x_n ARE

$$V(x_n) = \frac{1}{2} m \omega^2 x_n^2 = E_n$$

$$x_n = \sqrt{\frac{2E_n}{m\omega^2}}$$

- IN Q.M. THERE IS A NON-ZERO PROBABILITY TO FIND PARTICLE OUTSIDE THE CLASSICALLY ALLOWED REGION

FOR ψ_0 :



$$P_0^{OUT} = 2 \int_{x_0}^{\infty} dx \quad |\psi_0(x)|^2$$

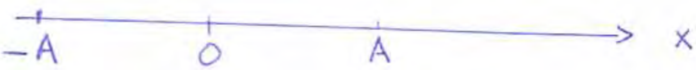
$$= 2 \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{\sqrt{\frac{\hbar}{m\omega}}}^{\infty} dx \quad e^{-\frac{m\omega}{\hbar}x^2}$$

$\downarrow$ DIMENSIONLESS VAR $\xi \equiv x \Big/ \left(\frac{\hbar}{m\omega}\right)^{1/2}$

$$= \frac{2}{\sqrt{\pi}} \int_{1}^{\infty} d\xi \; e^{-\xi^2} = 0.1573 \quad 15.7\,\% \; !$$

CLASSICAL $\leftrightarrow$ QUANTUM PROBABILITY DENSITIES FOR H.O.

- CLASSICAL



$$x(t) = A \cos(\omega t) \qquad \omega = \sqrt{\frac{k}{m}}$$

$$\downarrow$$

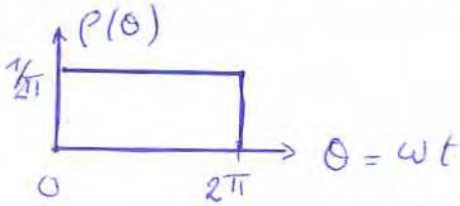
PERIOD $T = \dfrac{2\pi}{\omega}$

FOR $t \gg T$: H.O. GOES BACK & FORTH MANY, MANY TIMES

$P_{cl}(x)\, dx$: PROBABILITY TO FIND PARTICLE (▨ IN FIGURE) BETWEEN x & $x + dx$

$\hookrightarrow$ FOR $t \gg T$: EACH VALUE OF $\theta = \omega t$ WILL HAVE SAME PROBABILITY

$$\rho(\theta) = \frac{1}{2\pi}$$



θ & $-\theta$ CORR. WITH SAME X-VALUE

$$P_{cl}(x)\, dx = 2\, \rho(\theta)\, d\theta$$

$$\left| \frac{dx}{d\theta} \right| = A \sin(\omega t) = A \sqrt{1 - \frac{x^2}{A^2}}$$

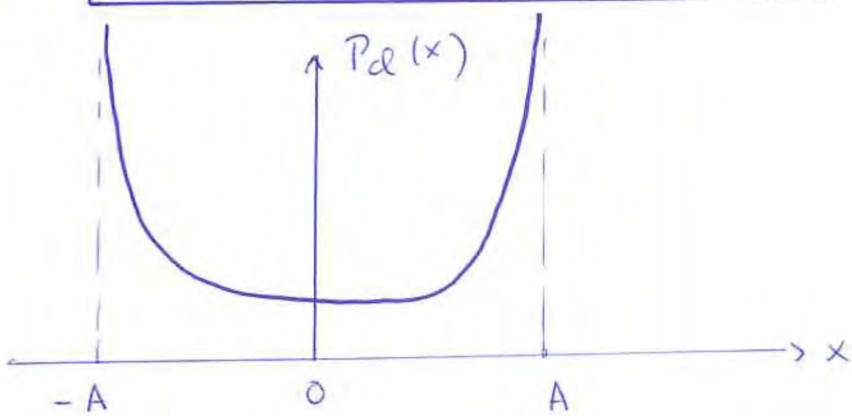
$$P_{cl}(x) = \frac{2}{2\pi}\left|\frac{d\Theta}{dx}\right|$$

$$= \frac{2\omega}{2\pi}\cdot\left|\frac{dt}{dx}\right|$$

$$= \frac{2}{T}\cdot\frac{1}{|v|}$$

↳ VELOCITY

$$\boxed{P_{cl}(x) = \frac{1}{\pi}\,\frac{1}{A}\,\frac{1}{\sqrt{1-\frac{x^2}{A^2}}}}$$



- QUANTUM

HOW DOES THIS PROBABILITY DENSITY COMPARE WITH QUANTUM?

$$P_{QM}(x) = |\psi(x,t)|^2$$

IF H.O. IS IN STATIONARY STATE ψ_n

WITH ENERGY $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$

$$\boxed{P_{QM} = |\psi_n(x)|^2}$$

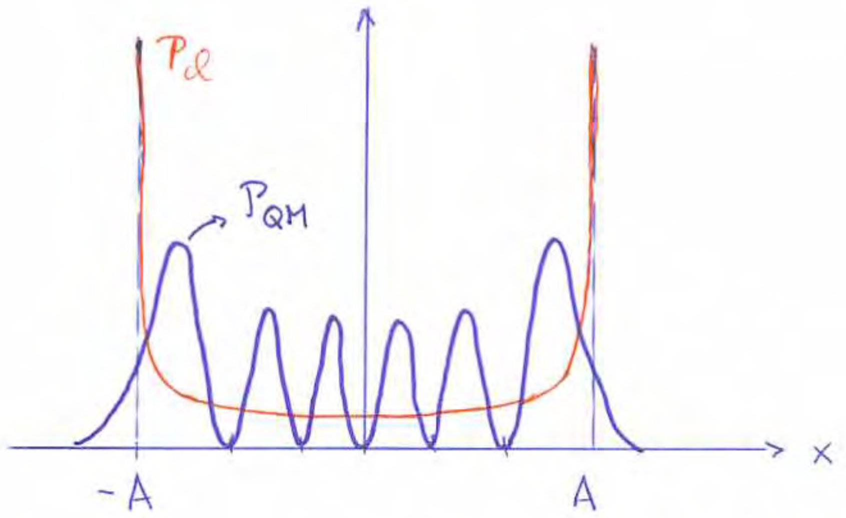
FOR ENERGY E_n: CLASSICAL TURNING POINTS A:

$$\frac{1}{2} m\omega^2 A^2 = \frac{\hbar\omega}{2}(2n+1)$$

$$A = \sqrt{\frac{\hbar}{m\omega}}\sqrt{2n+1}$$

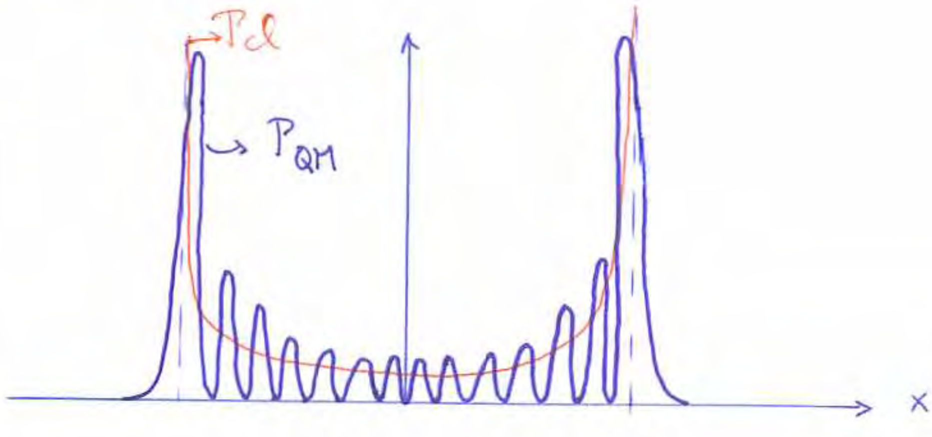
$$\boxed{P_{CL}(x) = \frac{1}{2\pi}\frac{1}{\sqrt{\hbar/m\omega}}\frac{1}{\sqrt{2n+1}}\cdot\frac{1}{\sqrt{1-\frac{x^2}{(\hbar/m\omega)}\frac{1}{2n+1}}}}$$

GRAPHICAL e.g. $n = 5$ (5 NODES)



$$n = 5: \qquad A = \sqrt{\frac{\hbar}{m\omega}} \underbrace{\sqrt{11}}_{3.32}$$

FOR $n \gg$



! QUANTUM PROBABILITY OSCILLATES AROUND CLASSICAL PROBABILITY

↳ CORRESPONDENCE PRINCIPLE

- VISUALIZATION

SEE WEBPHYSICS.DAVIDSON.EDU/MJB/NCS_AAPT_QM_2002/WELCOME.HTML

⇒ 2.4 THE FREE PARTICLE

- $V(x) = 0$ EVERY WHERE

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\Downarrow$$

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2\psi}$$

$$\boxed{E \equiv \frac{\hbar^2 k^2}{2m}}$$ k : WAVEVECTOR

↳ GENERAL SOLUTION $\psi(x) = A e^{ikx} + B e^{-ikx}$

SIMILAR AS INSIDE REGION OF INFINITE SQUARE WELL

DIFFERENCE : NO BOUNDARY CONDITIONS TO CONSTRAIN k

↓

FREE PARTICLE CAN MOVE WITH ANY VALUE OF E

↳ TIME DEPENDENCE

$$\Psi_k(x,t) = A\, e^{-\frac{i}{\hbar}Et}\, e^{ikx} + B\, e^{-\frac{i}{\hbar}Et}\, e^{-ikx}$$

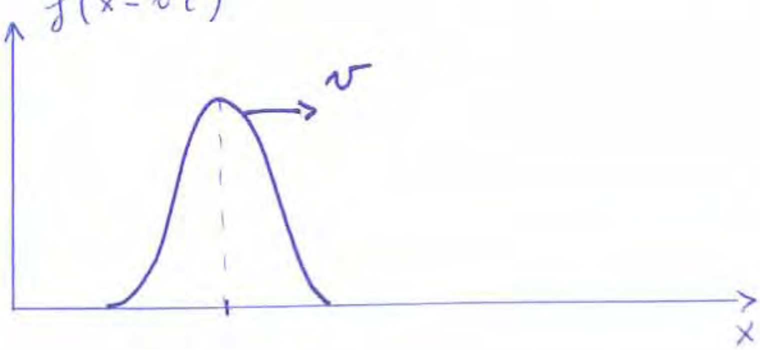
$$= A\, e^{+ik\left(x - \frac{\hbar k}{2m}t\right)} + B\, e^{-ik\left(x + \frac{\hbar k}{2m}t\right)}$$

↳ SOLUTION DEPENDS ON CONTINUOUS VARIABLE k

STATIONARY STATE

$f(x \mp v t)$ CORRESPONDS WITH WAVE

TRAVELLING WITH VELOCITY v IN $\pm$ X-DIRECTION



$$k = \pm \frac{\sqrt{2mE}}{\hbar}$$

$k > 0$: WAVE TRAVELING TO RIGHT

$k < 0$: WAVE TRAVELING TO LEFT

↳ MOMENTUM CARRIED BY WAVE

$$p = \hbar k \qquad k = \frac{2\pi}{\lambda} \Rightarrow p = \frac{h}{\lambda}$$

DE BROGLIE FORMULA

↳ SPEED OF WAVE

QUANTUM :
$$v_{QM} = \frac{\hbar k}{2m} = \sqrt{\frac{E}{2m}}$$

CLASSICAL PARTICLE WITH KIN. ENERGY E

$$E = \frac{1}{2} m v^2 \Rightarrow v_{CL} = \sqrt{\frac{2E}{m}} = 2 v_{QM}$$

! QUANTUM WAVE TRAVELS AT HALF THE SPEED OF CLASSICAL PARTICLE ? (SEE LATER)

↳ NORMALIZATION

$$\Psi_k(x,t) = A\, e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)}$$

$$\int_{-\infty}^{+\infty} dx\, |\Psi(x,t)|^2 = |A|^2 \underbrace{\int_{-\infty}^{+\infty} dx\; 1}_{\infty}$$

NOT NORMALIZABLE !

UNPHYSICAL ⇒ A FREE PARTICLE CANNOT EXIST IN A STATIONARY STATE

BUT : WE CAN CONSTRUCT NORMALIZABLE SOLUTIONS AS LINEAR COMBINATIONS OF STATIONARY STATES

BECAUSE STATIONARY STATE DEPENDS ON CONTINUOUS VARIABLE k

GENERAL SOLUTION IS INTEGRAL OVER k. (INSTEAD OF A SUM OVER A DISCRETE INDEX n)

$$\boxed{\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk\; \phi(k)\; e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)}}$$

⇒ WAVE PACKET

CONVENIENT NORMALIZATION FACTOR

ROLE OF C_n BEFORE $\longleftrightarrow$ $\frac{1}{\sqrt{2\pi}}\, \phi(k)$

↳ HOW TO DETERMINE $\phi(k)$

USUALLY ONE IS GIVEN AN INITIAL WAVEFUNCTION

$\Psi(x, t=0)$ => FROM WHICH ONE DETERMINES $\phi(k)$

$$\boxed{\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \ \phi(k)\, e^{ikx}}$$

NORMALIZED

⇓

$\phi(k)$ DETERMINED BY FOURIER TRANSFORM

$$\boxed{\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \ e^{-ikx} \ \Psi(x,0)}$$

↓

GENERAL SOLUTION OBTAINED BY PLUGGING $\phi(k)$ INTO $\Psi(x,t)$

FOURIER TRANSFORM

PROOF OF :

$$\boxed{\begin{gathered} f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; e^{ikx} \; F(k) \\ \Updownarrow \\ F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \; e^{-ikx} \; f(x) \end{gathered}}$$

↳ CONSIDER FIRST FINITE INTERVAL $x \in [-a, a]$

AND LET $a \to \infty$ AT END

GENERAL SOLUTION $(t=0)$

$$f(x) = \sum_{n=0}^{\infty} \left\{ a_n \sin\left(\frac{n\pi}{a} x\right) + b_n \cos\left(\frac{n\pi}{a} x\right) \right\}$$

PERIODIC BOUNDARY CONDITION $f(a) = f(-a)$

$$\cos(kx) = \cos(k(x+2a))$$

$$\sin(kx) = \sin(k(x+2a))$$

$$2ka = n \cdot 2\pi$$

$$\underline{\underline{k = \frac{n}{a}\pi}}$$

USING $e^{\pm ikx} = \cos kx \pm i \sin kx$

$$\cos\left(\frac{n\pi}{a}x\right) = \frac{1}{2}\left(e^{i\frac{n\pi}{a}x} + e^{-i\frac{n\pi}{a}x}\right)$$

$$\sin\left(\frac{n\pi}{a}x\right) = \frac{1}{2i}\left(e^{i\frac{n\pi}{a}x} - e^{-i\frac{n\pi}{a}x}\right)$$

$$f(x) = \sum_{n=0}^{\infty}\left\{\frac{1}{2}\left(-ia_n + b_n\right)e^{i\frac{n\pi}{a}x} + \frac{1}{2}\left(+ia_n + b_n\right)e^{-i\frac{n\pi}{a}x}\right\}$$

DEFINE
$$c_n \equiv \begin{cases} b_0 \,, & n = 0 \\ \frac{1}{2}\left(-ia_n + b_n\right), & n = 1, 2, 3, \ldots \\ \frac{1}{2}\left(ia_n + b_{-n}\right), & n = -1, -2, -3, \ldots \end{cases}$$

$$\boxed{f(x) = \sum_{n=-\infty}^{+\infty} c_n \, e^{i\frac{n\pi}{a}x}}$$

$$\hookrightarrow \quad \boxed{C_n = \frac{1}{2a}\int_{-a}^{a} dx \quad e^{-i\frac{n\pi}{a}x} \; f(x)}$$

PROOF:

$$\int_{-a}^{a} dx \quad e^{-i\frac{n\pi}{a}x} \; f(x)$$

$$= \sum_{m=-\infty}^{+\infty} C_m \int_{-a}^{a} dx \; e^{-i\frac{n\pi}{a}x} \; e^{i\frac{m\pi}{a}x}$$

$$= \sum_{m=-\infty}^{+\infty} C_m \underbrace{\int_{-a}^{a} dx \quad e^{-i\frac{\pi}{a}(n-m)x}}$$

FOR $n = m \implies +2a$.

FOR $n \neq m$ $\quad -\frac{a}{i\pi}\frac{1}{(n-m)} \; e^{-i\frac{\pi}{a}(n-m)x}\Big|_{-a}^{a}$

$$= \frac{ia}{\pi}\frac{1}{(n-m)} \underbrace{\left\{ e^{-i\pi(n-m)} - e^{i\pi(n-m)} \right\}}_{-2i\sin((n-m)\pi)}$$

$$\| \quad \quad$$

$$0$$

FOR $n \neq m$

$$= \sum_{m=-\infty}^{+\infty} c_m \cdot \delta_{nm}\,(2a)$$

$$= 2a\, C_n$$ ■ QED

↳ EXTEND INTERVAL TO $[-\infty, +\infty]$

$a \to \infty$

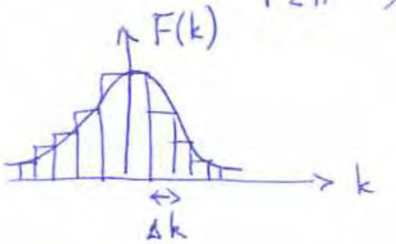
DEFINE $\underbrace{k_n = \frac{n\pi}{a}}$

$\Delta k = \frac{\pi}{a}$ INCREMENT IN k

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n \, e^{i k_n x}$$

$$= \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{+\infty} \frac{\sqrt{2\pi}\, a}{\pi} \, c_n \, . \, \Delta k \, . \, e^{i k_n x}$$

$$= \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{+\infty} \underbrace{\left(\sqrt{\frac{2}{\pi}}\, a \, c_n \right)}_{\equiv \, F(k_n)} . \, \Delta k \; e^{i k_n x}$$



$$\xrightarrow[\Delta k \to 0]{} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; F(k) \; e^{ikx}$$

$a \to \infty$

DEFINITION OF INTEGRAL.

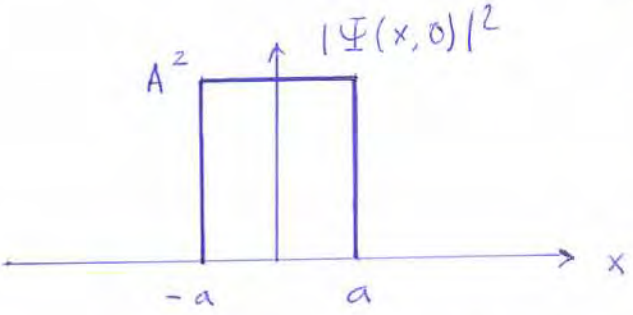
$$\therefore \quad F(k) = \sqrt{\frac{2}{\pi}}\, a \, c_n = \sqrt{\frac{2}{\pi}} \, a \, . \, \frac{1}{2a} \int_{-a}^{a} dx \; f(x) \, e^{-ikx}$$

$$\xrightarrow[a \to \infty]{} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \; e^{-ikx} \; f(x) \quad \blacksquare \text{ QED}$$

- EXAMPLE

FREE PARTICLE INITIALLY LOCALIZED IN INTERVAL $x \in [-a, a]$
$(t=0)$

$$\Psi(x,0) = \begin{cases} A & -a < x < a \\ 0 & \text{otherwise} \end{cases}$$



WHAT IS $\Psi(x,t)$?

↳ NORMALIZATION $\int_{-\infty}^{+\infty} dx \; |\Psi(x,0)|^2 = 1$

$$\downarrow$$

$$2a\,A^2 = 1 \Rightarrow \boxed{A = \frac{1}{\sqrt{2a}}}$$

↳ $$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; \phi(k)\, e^{ikx}\, e^{-i\frac{\hbar k^2}{2m}t}$$

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \; e^{-ikx}\, \Psi(x,0)$$

2.52

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-a}^{a} dx \, \frac{1}{\sqrt{2a}} e^{-ikx}$$

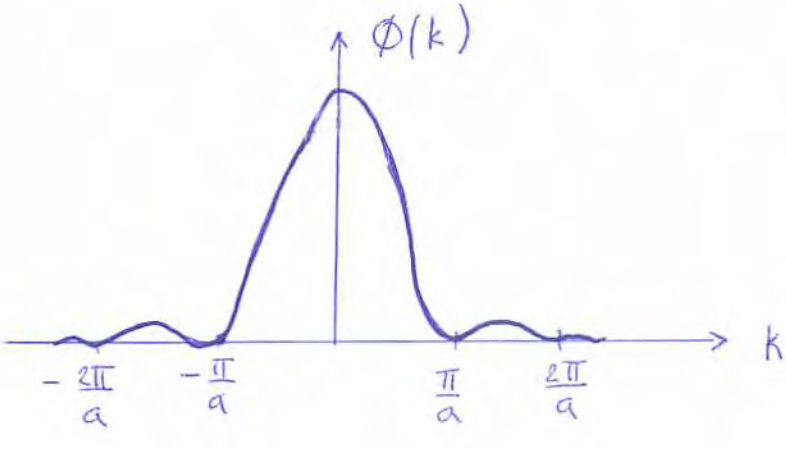
$$= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \frac{1}{(-ik)} e^{-ikx} \Big|_{-a}^{a}$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \frac{1}{k} \underbrace{\frac{e^{ika} - e^{-ika}}{i}}_{2 \sin ka}$$

$$\boxed{\phi(k) = \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k}}$$

$\frac{\sin z}{z}$ HAS MAXIMUM AT $z = 0$

HAS ZEROS AT $z = \pm\pi, \pm 2\pi, \ldots \Rightarrow$ $k = \pm \frac{\pi}{a}, \pm\frac{2\pi}{a}, \ldots$

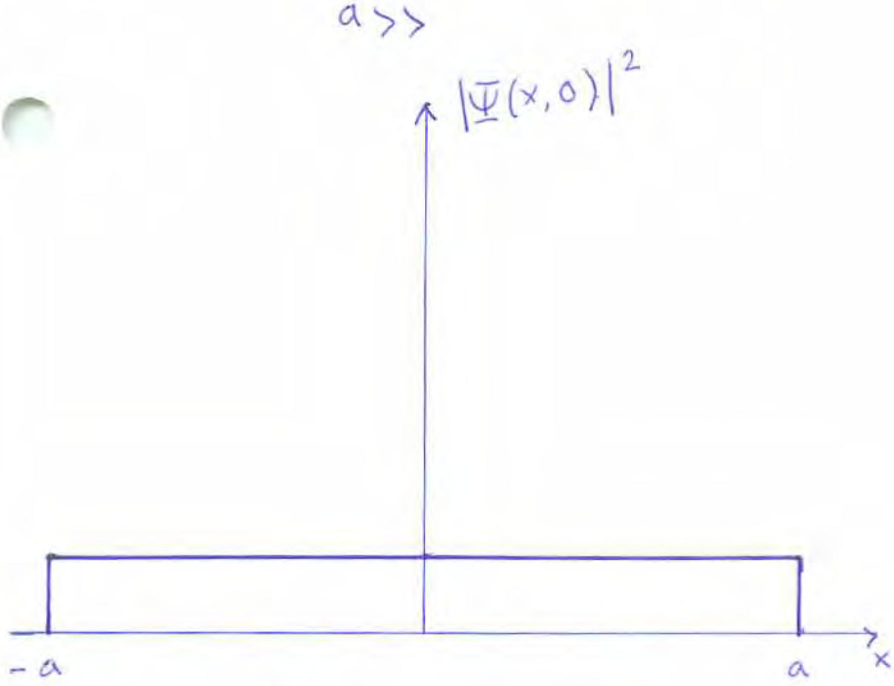


FOR $z \to 0$

$\frac{\sin z}{z} \to 1$

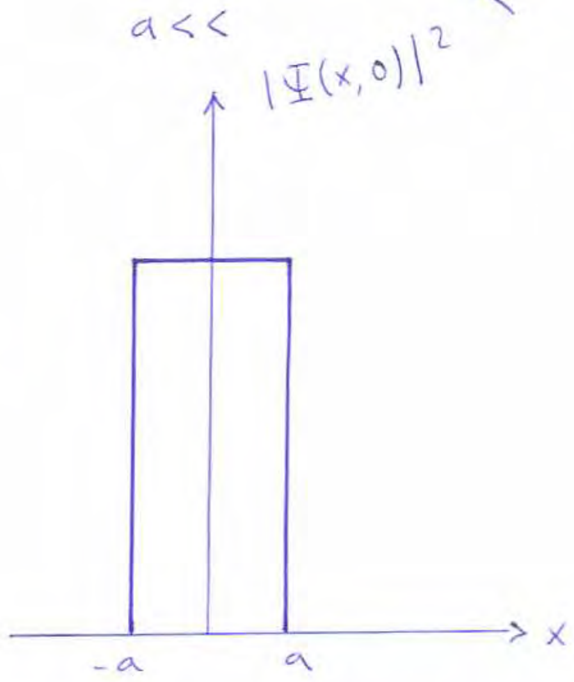
$\Downarrow$

$$\phi(k=0) = \sqrt{\frac{a}{\pi}}$$



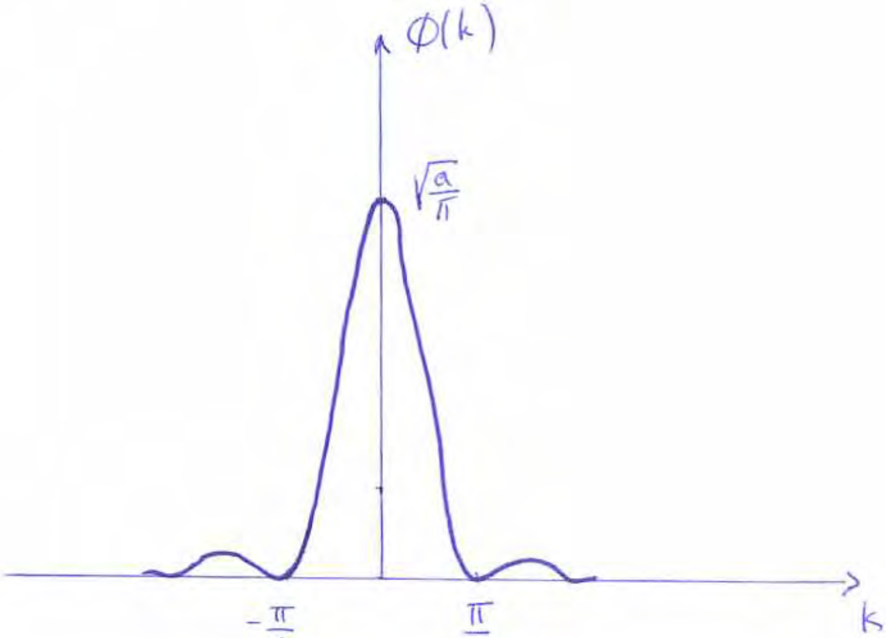
NOT WELL LOCALIZED
IN POSITION

$\Downarrow$

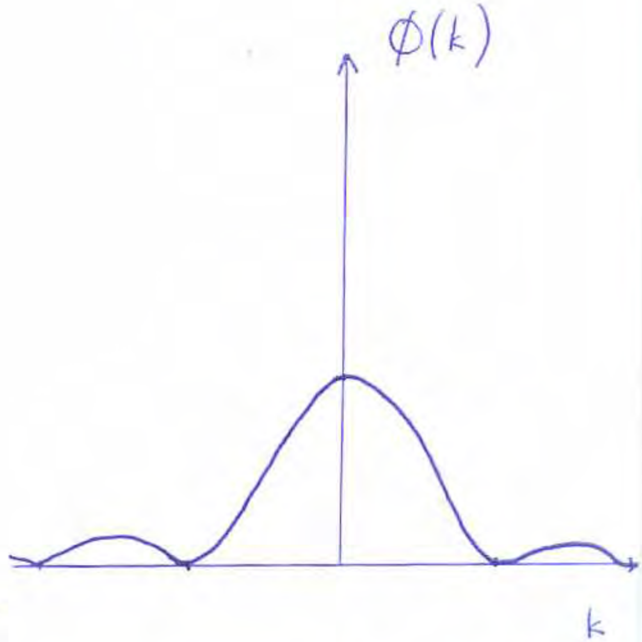


WELL LOCALIZED
IN POSITION

$\Downarrow$



WELL LOCALIZED
IN MOMENTUM



<u>NOT</u> WELL LOCALIZED
IN MOMENTUM

$\therefore$ HEISENBERG'S UNCERTAINTY PRINCIPLE

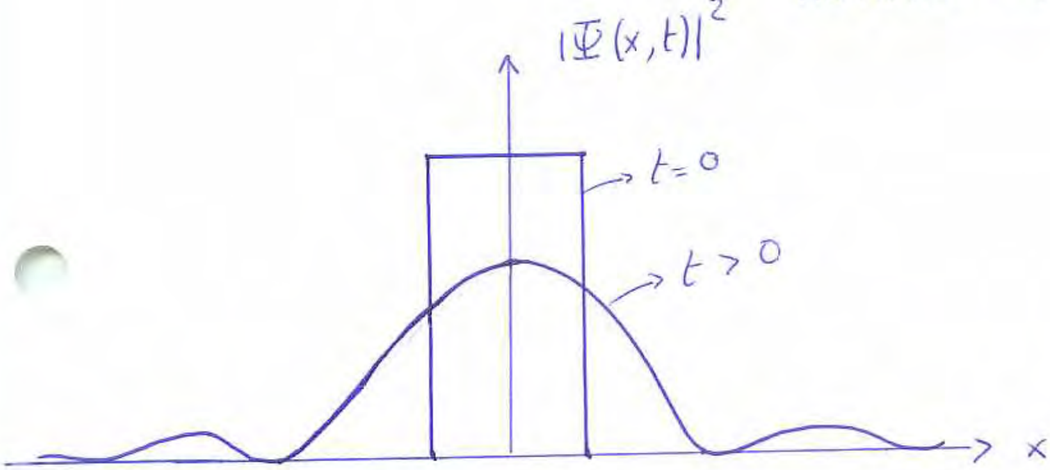
↳ PLUG $\phi(k)$ INTO $\Psi(x,t)$

$$\boxed{\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; \phi(k) \; e^{ikx} \; e^{-i\frac{\hbar k^2}{2m}t}}$$

$$= \frac{1}{\sqrt{2a}} \cdot \frac{1}{\pi} \int_{-\infty}^{+\infty} dk \; \frac{\sin(ka)}{k} \; e^{ikx} \; e^{-i\frac{\hbar k^2}{2m}t}$$

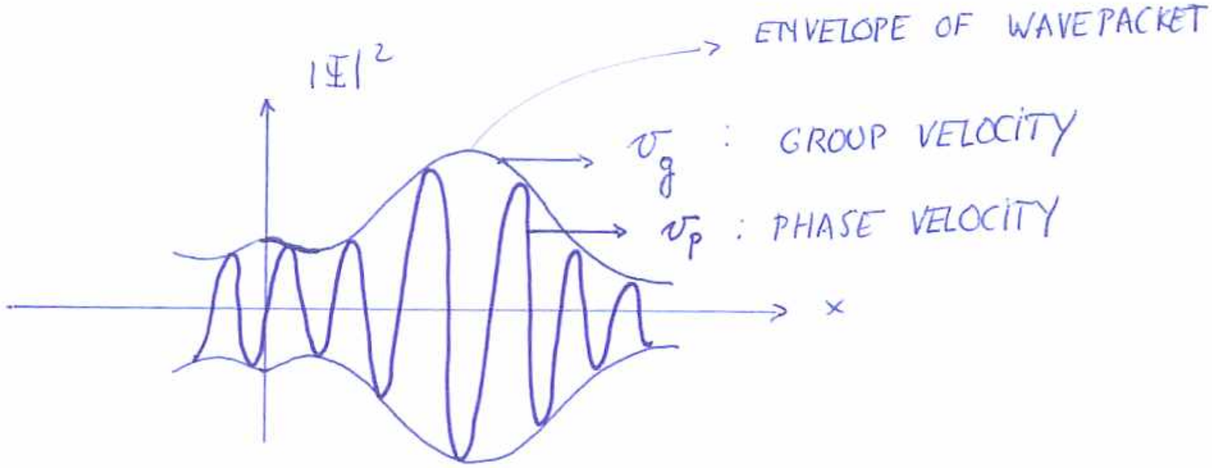
↓

INTEGRAL CAN ONLY BE SOLVED NUMERICALLY



FOR $t > 0$: WAVE PACKET SPREADS OUT

GROUP VELOCITY <-> PHASE VELOCITY



$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; \phi(k) \, e^{i(kx - \omega t)}$$

FOR FREE PARTICLE $\omega(k) = \frac{\hbar k^2}{2m}$

ASSUME $\phi(k)$ NARROWLY DISTRIBUTED AROUND k_0

TAYLOR EXPAND $\omega(k) \simeq \overbrace{\omega(k_0)}^{\omega_0} + \omega_0'(k - k_0)$

+ CHANGE OF VARIABLES $\underline{k' = k - k_0}$

$$\Psi(x,t) \simeq \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk' \; \phi(k' + k_0) \, e^{i\left[(k_0 + k')x - (\omega_0 + \omega_0' k')t\right]}$$

$$= e^{i(-\omega_0 t + \omega_0' k_0 t)} \cdot \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk' \; \phi(k' + k_0) \, e^{i(k_0 + k')(x - \omega_0' t)}$$

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk' \, \phi(k' + k_0) \, e^{i(k_0 + k')x}$$

SHIFT FROM $x \rightarrow x - \omega_0' t$

$$\boxed{\Psi(x,t) = e^{-i(\omega_0 - \omega_0' k_0)t} \, \Psi(x - \omega_0' t, 0)}$$

↳ WAVE PACKET MOVES AT SPEED

$$v_g = \frac{d\omega}{dk} = \omega_0' \quad : \text{GROUP VELOCITY}$$

↳ PHASE VELOCITY

$$v_p = \frac{\omega}{k}$$

FOR Q.M FREE PARTICLE $v_g = 2 v_p$

↑

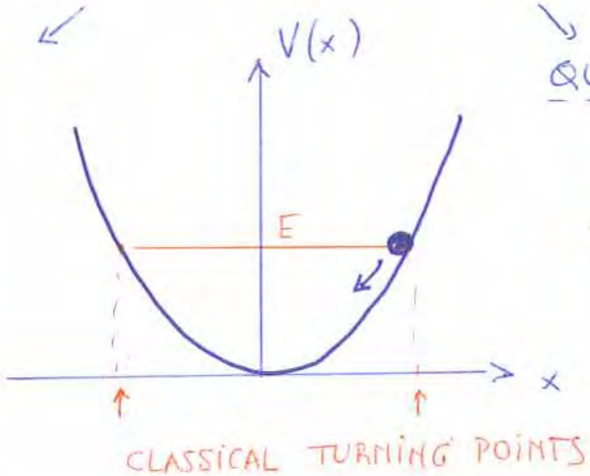
CLASSICAL VELOCITY

⇒ 2.5 DELTA - FUNCTION POTENTIAL

- **BOUND STATES VS SCATTERING STATES**

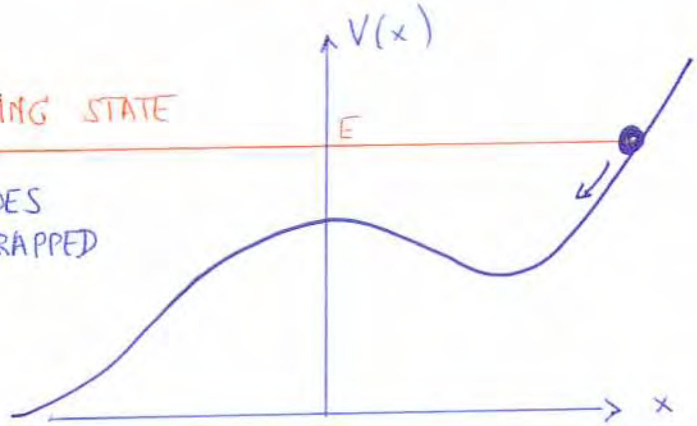
↳ CLASSICAL ↙ ↘ QUANTUM

BOUND STATE
↓
PARTICLE "TRAPPED"



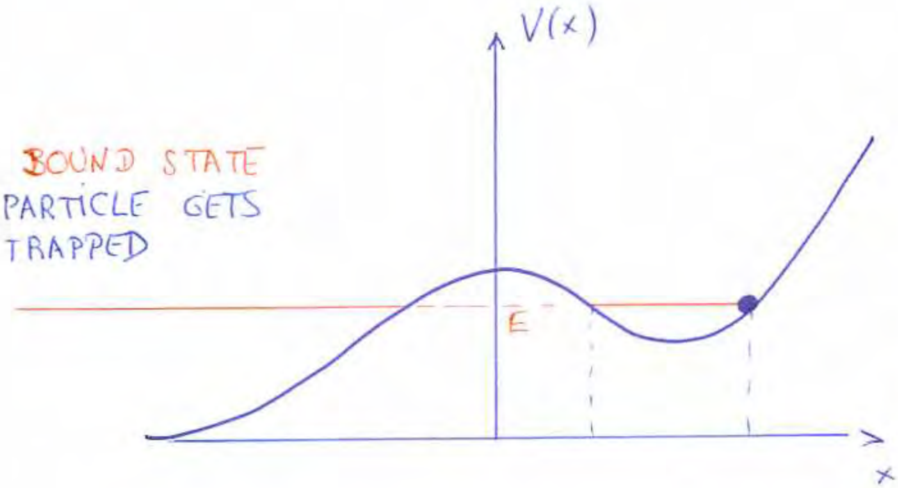
BOUND STATE

SCATTERING STATE
↓
PARTICLE DOES NOT GET TRAPPED



SCATTERING STATE

BOUND STATE
PARTICLE GETS TRAPPED



SCATTERING STATE
↓
PARTICLE CAN 'TUNNEL' THROUGH FINITE BARRIER AND ESCAPE

↳ QUANTUM :

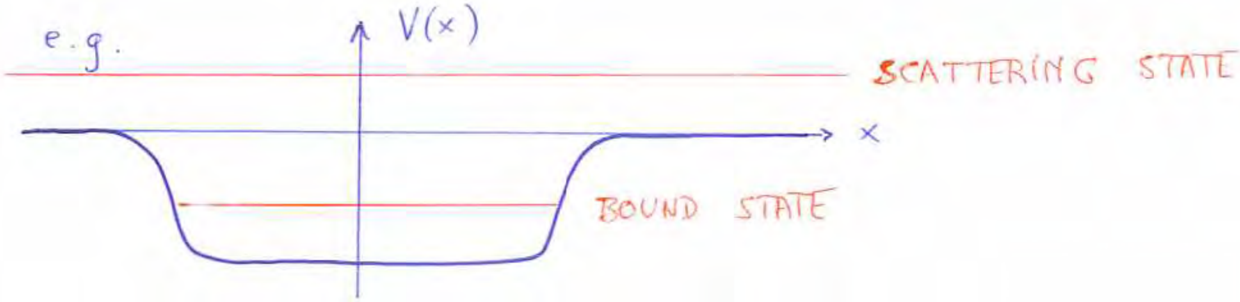
BOUND STATE $E < \left[V(x=+\infty) \ \& \ V(x=-\infty) \right]$

SCATTERING STATE $E > \left[V(x=+\infty) \text{ OR } V(x=-\infty) \right]$

IN PHYSICAL APPLICATIONS :

OFTEN $V(x = \pm\infty) = 0$

e.g.



POTENTIAL FELT BY NUCLEON (PROTON OR NEUTRON) IN THE ATOMIC NUCLEUS.

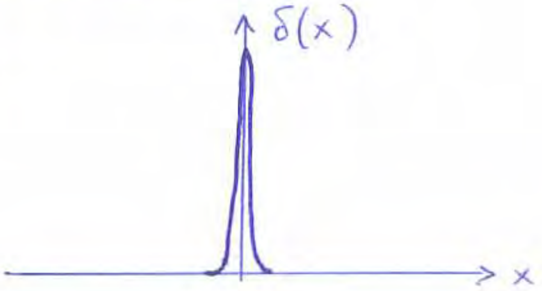
CHARACTERIZED BY

$E < 0$: BOUND STATE $\Rightarrow$ DISCRETE INDEX n

$E > 0$: SCATTERING STATE $\Rightarrow$ CONTINUOUS VARIABLE k

δ - FUNCTION WELL

↳ SPIKE



$$\delta(x) = \begin{cases} 0 & , \; x \neq 0 \\ \infty & , \; x = 0 \end{cases}$$

WITH SURFACE = 1

$$\int_{-\infty}^{+\infty} dx \; \delta(x) = 1.$$

↳ IN MATHEMATICS :

$\delta(x)$ IS NOT A FUNCTION

BUT A 'DISTRIBUTION'

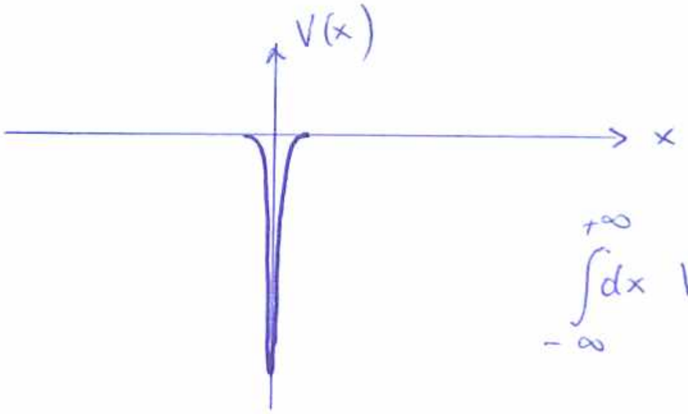
↳ $\delta(x-a)$ SPIKE POSITIONED AT $x = a$

↳ PROPERTIES

$$f(x) \cdot \delta(x-a) = f(a)\, \delta(x-a)$$

$$\int_{-\infty}^{+\infty} dx \; f(x)\, \delta(x-a) = f(a) \int_{-\infty}^{+\infty} dx \; \delta(x-a) = f(a)$$

- $V(x) = -\alpha\,\delta(x)$ WITH $\alpha > 0$



$$\int_{-\infty}^{+\infty} dx\; V(x) = -\alpha.$$

↳ TIME - INDEPENDENT SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\,\delta(x)\,\psi = E\,\psi$$

SOLUTIONS WITH $E < 0$: BOUND STATES

SOLUTIONS WITH $E > 0$: SCATTERING STATES.

- BOUND STATE SOLUTIONS : $E < 0$

↳ INTRODUCE $E \equiv -\dfrac{\hbar^2 K^2}{2m}$ $\Rightarrow$ $\boxed{K \equiv \dfrac{\sqrt{-2mE}}{\hbar}}$

$K > 0$

$$\frac{d^2\psi}{dx^2} + \frac{2m\alpha}{\hbar^2}\,\delta(x)\,\psi = K^2\,\psi$$

↳ FOR $x < 0$: $\dfrac{d^2\psi}{dx^2} = K^2\psi$

↳ SOLUTION $\psi(x) = A e^{-Kx} + B e^{+Kx}$

$\psi(x = -\infty) = 0 \Rightarrow A = 0$

$\therefore$ $\boxed{\psi(x) = B e^{Kx}, \quad x < 0}$

↳ FOR $x > 0$: $\dfrac{d^2\psi}{dx^2} = K^2 \psi$

↳ SOLUTION $\psi(x) = F e^{-Kx} + G e^{+Kx}$

$\psi(x = +\infty) = 0 \Rightarrow G = 0$

$$\therefore \boxed{\psi(x) = F e^{-Kx} \,, \quad x > 0}$$

↳ FOR ANY x : ① ψ SHOULD BE CONTINUOUS

② $\dfrac{d\psi}{dx}$ IS CONTINUOUS EXCEPT WHERE $V = \infty$

$$\psi(x \to 0^-) = \psi(x \to 0^+)$$

APPROACHING ZERO FROM BELOW

APPROACHING ZERO FROM ABOVE

$\psi(x \to 0^-) = B$

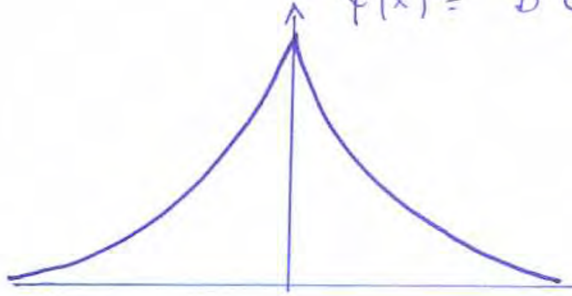
$\psi(x \to 0^+) = F$

$\therefore$ CONTINUITY IMPLIES $\underline{\underline{B = F}}$

$$\boxed{\psi(x) = \begin{cases} B e^{Kx} \,, & x \leq 0 \\ B e^{-Kx} \,, & x \geq 0 \end{cases}}$$

2.62

$\psi(x) = B e^{-K|x|}$



↳ NORMALIZATION $\displaystyle\int_{-\infty}^{+\infty} dx \; B^2 e^{-2K|x|} = 1$

$$2B^2 \int_0^{\infty} dx \; e^{-2Kx} = 1$$

$$\frac{2B^2}{(-2K)} \; e^{-2Kx} \Big|_0^{\infty} = 1$$

$$B^2 = K \quad \Rightarrow \quad \boxed{B = \sqrt{K}}$$

↳ $\dfrac{d\psi}{dx}$ IS DISCONTINUOUS AT $x = 0$ WHERE $V(x) = -\infty$

INTEGRATE SCHRODINGER EQ. FROM $-\varepsilon$ TO $+\varepsilon$ $(\varepsilon > 0)$
AND LET $\varepsilon \to 0$

$$-\frac{\hbar^2}{2m} \int_{-\varepsilon}^{\varepsilon} dx \; \frac{d^2\psi}{dx^2} + \int_{-\varepsilon}^{+\varepsilon} dx \; V(x)\,\psi(x) = E \int_{-\varepsilon}^{+\varepsilon} dx \; \psi(x)$$

$$-\frac{\hbar^2}{2m} \left(\frac{d\psi}{dx}\Big|_{x=+\varepsilon} - \frac{d\psi}{dx}\Big|_{x=-\varepsilon} \right) + \int_{-\varepsilon}^{+\varepsilon} dx \; V(x)\,\psi(x)$$

$$= E\,\psi(0) \cdot 2\varepsilon \xrightarrow[\varepsilon \to 0]{} 0$$

JUMP (DISCONTINUITY) IN DERIVATIVE

$$\Delta\left(\frac{d\psi}{dx}\right)_{x=0} \equiv \left.\frac{d\psi}{dx}\right|_{x=+\varepsilon} - \left.\frac{d\psi}{dx}\right|_{x=-\varepsilon} \quad (\varepsilon \to 0)$$

$$-\frac{\hbar^2}{2m}\,\Delta\left(\frac{d\psi}{dx}\right)_{x=0} = -\int_{-\varepsilon}^{+\varepsilon} dx\; V(x)\,\psi(x)$$

CASE 1 : $V(x)$ IS FINITE AT $x=0$

RHS $\displaystyle\int_{-\varepsilon}^{+\varepsilon} dx\; V(x)\,\psi(x) = 2\varepsilon\, V(0)\,\psi(0) \xrightarrow[\varepsilon\to 0]{} 0$

$\Downarrow$

$\Delta\left(\frac{d\psi}{dx}\right)_{x=0} = 0$: $\frac{d\psi}{dx}$ IS CONTINUOUS

CASE 2 : $V(x)$ IS INFINITE AT $x=0$

e.g. $V(x) = -\alpha\,\delta(x)$

RHS $\displaystyle\int_{-\varepsilon}^{+\varepsilon} dx\; V(x)\,\psi(x) = -\alpha\int_{-\varepsilon}^{+\varepsilon} dx\;\delta(x)\,\psi(x)$

$\Downarrow$ $\qquad = -\alpha\,\psi(0)$

$$\boxed{\Delta\left(\frac{d\psi}{dx}\right)_{x=0} = -\frac{2m\alpha}{\hbar^2}\,\psi(0)}$$

↳ APPLY TO OUR SOLUTION

$$\psi(x) = \begin{cases} \sqrt{K}\, e^{Kx}, & x \leqslant 0 \\ \sqrt{K}\, e^{-Kx}, & x \geqslant 0 \end{cases}$$

$$\left.\frac{d\psi}{dx}\right|_{x=-\varepsilon} = K\sqrt{K}\, e^{-K\varepsilon} \xrightarrow[\varepsilon \to 0]{} K^{3/2}$$

$$\left.\frac{d\psi}{dx}\right|_{x=+\varepsilon} = -K\sqrt{K}\, e^{-K\varepsilon} \xrightarrow[\varepsilon \to 0]{} -K^{3/2}$$

$$\Delta\left(\frac{d\psi}{dx}\right)_{x=0} = -2K^{3/2}$$

$$\therefore \quad -2K^{3/2} = -\frac{2m\alpha}{\hbar^2} \cdot \underbrace{\sqrt{K}}_{\psi(0)}$$

$$\Downarrow$$

$$\boxed{K = \frac{m\alpha}{\hbar^2}}$$

BOUND STATE ENERGY

$$\boxed{E = -\frac{\hbar^2 K^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}}$$

δ - FUNCTION POTENTIAL HAS 1 BOUND STATE

$$\psi(x) = \sqrt{K}\, e^{-K|x|}$$

• SCATTERING SOLUTIONS : $E > 0$

↳ INTRODUCE $E = \frac{\hbar^2 k^2}{2m}$ $\Rightarrow$ $\boxed{k \equiv \frac{\sqrt{2mE}}{\hbar}}$

$$\frac{d^2\psi}{dx^2} + \frac{2m\alpha}{\hbar^2}\delta(x)\psi = -k^2\psi$$

↳ FOR $x < 0$: $\frac{d^2\psi}{dx^2} = -k^2\psi$

↳ SOLUTION $\psi(x) = A e^{ikx} + B e^{-ikx}$

NONE OF THE TERMS BLOWS UP FOR $x \to -\infty$

↳ FOR $x > 0$: $\psi(x) = F e^{ikx} + G e^{-ikx}$

↳ CONTINUITY AT $x = 0$

$$\psi(0^-) = A + B = \psi(0^+) = F + G$$

↳ JUMP IN DERIVATIVE

$$\left.\frac{d\psi}{dx}\right|_{x=0^-} = ik(A - B)$$

$$\left.\frac{d\psi}{dx}\right|_{x=0^+} = ik(F - G)$$

$$\Delta \left(\frac{d\psi}{dx}\right)_{x=0} = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

$$\Downarrow$$

$$ik\,(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A+B)$$

↳ $$F - G = A(1 + 2i\beta) - B(1 - 2i\beta)$$

$$\boxed{\beta \equiv \frac{m\alpha}{\hbar^2 k}}$$

↳ PROBLEM : 4 UNKNOWNS A, B, F, G

ONLY 2 EQUATIONS.

(FOR BOUND STATES 2 UNKNOWNS WERE ELIMINATED FROM ASYMPTOTIC CONDITIONS)

↳

$e^{ikx} \cdot e^{-\frac{i}{\hbar}Et}$: WAVE TRAVELING $\longrightarrow$

$e^{-ikx} \cdot e^{-\frac{i}{\hbar}Et}$: WAVE TRAVELING $\longleftarrow$

IN AN EXPERIMENT A WAVE IS TRAVELING FROM ONE SIDE TO THE OTHER.

SAY WE CONSIDER WAVE TRAVELING $\longrightarrow$ STARTING FROM $x = -\infty$

$\therefore$ $\underbrace{G = 0}_{\text{NO WAVE IS COMING IN FROM } x = +\infty}$ (BOUNDARY CONDITIONS)

$$\begin{cases} F = A + B \\ F = A(1+2i\beta) - B(1-2i\beta). \end{cases}$$

$$\hookrightarrow \quad A + B = A(1+2i\beta) - B(1-2i\beta)$$

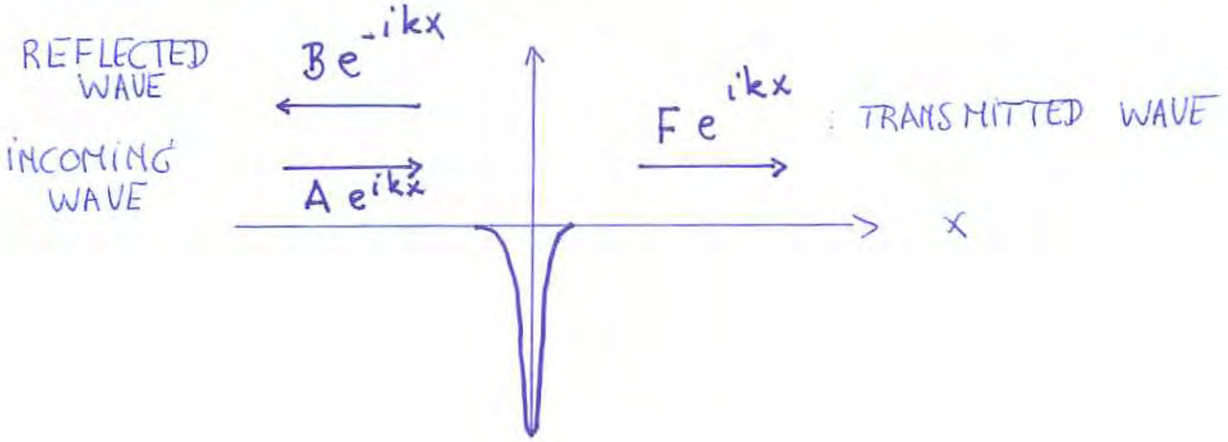
$$\Downarrow$$

$$(1 - i\beta)\, 2B = 2i\beta\, A$$

$$\boxed{B = \frac{i\beta}{1-i\beta}\, A}$$

$$\hookrightarrow \quad F = A + B = \frac{1-i\beta+i\beta}{1-i\beta}\, A$$

$$\boxed{F = \frac{1}{1-i\beta}\, A}$$



↳ PROBABILITY OF REFLECTION $|\Psi|^2$

$$\boxed{R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1+\beta^2}}$$

↳ PROBABILITY OF TRANSMISSION

$$\boxed{T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1+\beta^2}}$$

↳ $\underline{\underline{R + T = 1}}$

↳ IN TERMS OF α :

$$R = \frac{1}{1+1/\beta^2} = \frac{1}{1+\frac{\hbar^4 k^2}{m^2\alpha^2}} = \frac{1}{1+\frac{2\hbar^2 E}{m\alpha^2}}$$

$$T = \frac{1}{1+\beta^2} = \frac{1}{1+\frac{m\alpha^2}{2\hbar^2 E}}$$

$E \gg$ (VERY LARGE) $\quad R \to 0 \,, \; T \to 1 \quad$ PERFECT TRANSMISSION

$E \ll$ (VERY LOW) $\quad R \to 1 \,, \; T \to 0 \quad$ PERFECT REFLECTION

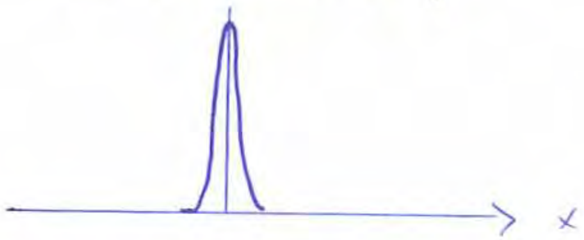
↳ NORMALIZATION

SCATTERING STATES OF DEFINITE k (PLANE WAVES) ARE NOT NORMALIZABLE.

↳ PHYSICAL PARTICLES ARE DESCRIBED BY LINEAR SUPERPOSITIONS OF PLANE WAVES ⇒ WAVE PACKETS

- δ - FUNCTION BARRIER

$$V(x) = +\alpha\,\delta(x)$$



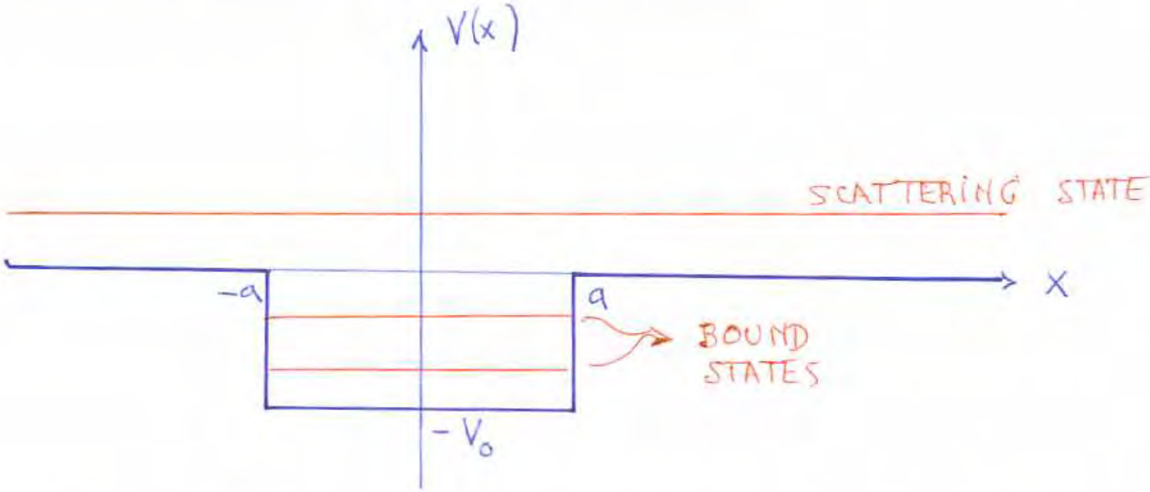
PUT $\alpha \to -\alpha$ IN PREVIOUS

↳ NO BOUND STATE

↳ EXACTLY SAME SCATTERING STATES.

R & T ONLY DEPEND ON α^2 !

⇒ FINITE SQUARE WELL

- 

$$V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & |x| > a \end{cases} \qquad (V_0 > 0)$$

↳ POTENTIAL ALLOWS FOR BOTH ↗ BOUND STATES $(E<0)$ ↘ SCATTERING STATES $(E>0)$

- BOUND STATES $(E<0)$

↳ $x < -a$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\downarrow \qquad E \equiv -\frac{\hbar^2 \kappa^2}{2m}, \quad \boxed{\kappa = \frac{\sqrt{-2mE}}{\hbar}}$$

$$\psi(x) = \cancel{Ae^{-\kappa x}} + Be^{\kappa x}$$

$$\psi(x \to -\infty) = 0$$

↳ $x > a$ ANALOGOUSLY

$$\psi(x) = Fe^{-\kappa x} + \cancel{Ge^{\kappa x}} \qquad \psi(x \to +\infty) = 0$$

↳ $-a < x < a$: $V(x) = -V_0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi$$

$$\Downarrow \quad \boxed{\ell \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar}}$$

$$\frac{d^2\psi}{dx^2} = -\ell^2\psi$$

$E < 0$
BUT $V_0 + E > 0$
$(E > -V_0)$

$$\Downarrow$$

$$\psi(x) = C\sin(\ell x) + D\cos(\ell x)$$

↳ BOUNDARY CONDITIONS

ψ & $\dfrac{d\psi}{dx}$ CONTINUOUS AT BOUNDARIES $x = \pm a$

SYMMETRIC POTENTIAL : SOLUTIONS EITHER EVEN OR ODD
$$\psi(-x) = \pm\psi(x)$$

- **EVEN SOLUTIONS** $\psi(-x) = \psi(x)$

BOUNDARY CONDITION AT $x = +a$

$$\psi(x) = \begin{cases} D\cos(\ell x), & 0 < x < a \\ Fe^{-\kappa x}, & x > a \end{cases}$$

$\Rightarrow$ CONTINUITY OF ψ AT $x = a$

$$\Downarrow$$

$$Fe^{-\kappa a} = D\cos(\ell a) \qquad (*)$$

$\Rightarrow$ CONTINUITY OF $\frac{d\psi}{dx}$ AT $x = a$.

$$\Downarrow$$

$$-F K e^{-Kx} = -D\ell \sin(\ell a) \qquad (**)$$

$$\frac{(**)}{(*)} \Rightarrow \boxed{+\ \ell \tan(\ell a) = K}$$

↳ TRANSCENDENTAL EQ.
TO BE SOLVED TO DETERMINE E

DEFINE

$$z \equiv \ell a = \frac{a}{\hbar}\sqrt{2m(E+V_0)}$$

$$z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}$$

$$z_0^2 - z^2 = \frac{a^2}{\hbar^2}(-2mE) = a^2 K^2$$

$$aK = \sqrt{z_0^2 - z^2}$$

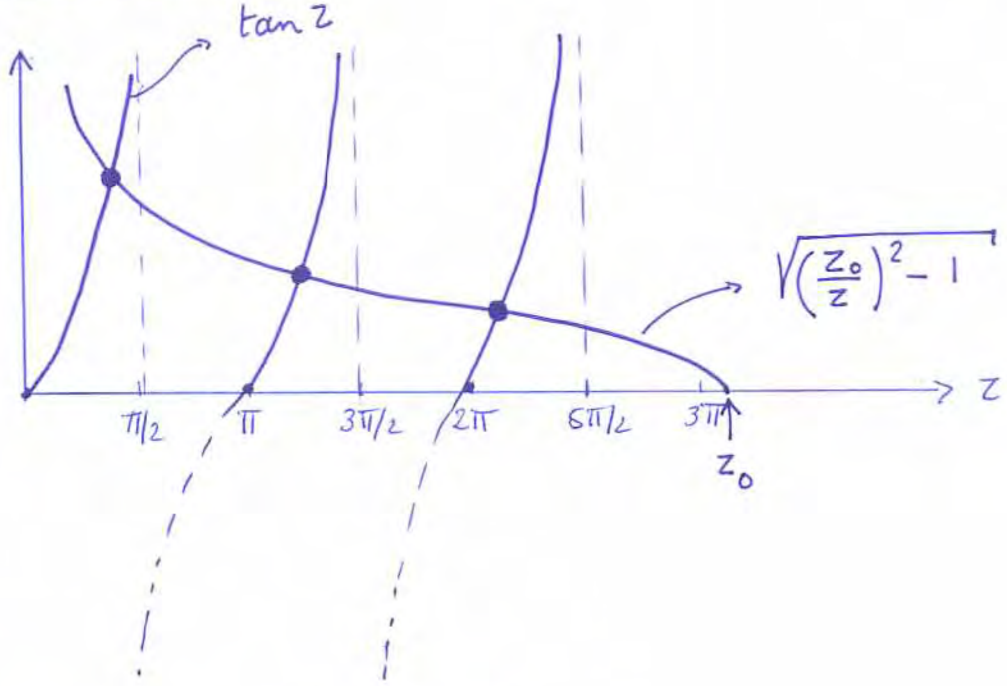
$$\therefore \quad a\ell \tan(\ell a) = aK$$

$$\Updownarrow$$

$$z \tan z = \sqrt{z_0^2 - z^2}$$

$$\boxed{\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}}$$

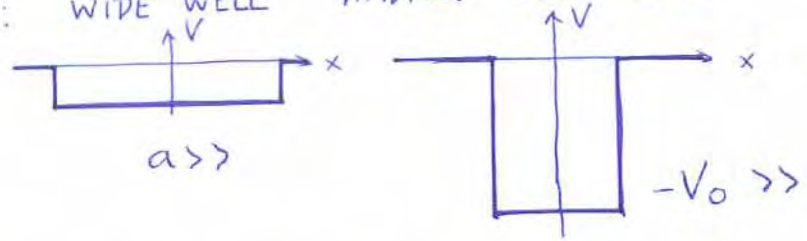
⇒ GRAPHICAL SOLUTION



INTERSECTIONS ARE SOLUTIONS.

⇒ SPECIAL LIMITING CASES.

- $z_0 \gg$: WIDE WELL AND/OR DEEP WELL



SOLUTIONS $\quad z \simeq z_n = n\frac{\pi}{2} \quad (n \text{ ODD})$

$$\underbrace{E_n + V_0}_{} \simeq \frac{\hbar^2}{2m}\frac{1}{a^2}\cdot\left(n\frac{\pi}{2}\right)^2$$

ENERGY ABOVE BOTTOM OF WELL

$$\boxed{E_n = -V_0 + \frac{\hbar^2\pi^2}{2m\,(2a)^2}\, n^2}$$

$(n \text{ ODD})$

FOR V_0 FINITE $\Rightarrow$ ONLY FINITE # BOUND STATES

FOR $V_0 \rightarrow +\infty$ $\Rightarrow$ ∞ # BOUND STATES

THIS IS INFINITE SQUARE WELL
OF WIDTH $(2a)$ FOR n ODD

$$E_1, E_3, E_5, \ldots$$

(EVEN n CORRESPOND WITH
ODD WAVE FUNCTIONS $\psi(-x) = -\psi(x)$)

- $z_0 \ll$ NARROW WELL AND/OR SHALLOW WELL
  $a \ll$ $-V_0 \ll$

$z_0 \downarrow$ LESS & LESS BOUND STATES.

FOR $z_0 < \frac{\pi}{2}$ $\Rightarrow$ ONLY 1 BOUND STATE REMAINS

$\therefore$ THERE IS ALWAYS 1 BOUND STATE
EVEN FOR SUPERWEAK POTENTIAL
OR VERY NARROW WELL

- **ODD SOLUTIONS** $\psi(-x) = -\psi(x)$

BOUNDARY CONDITION AT $x = +a$

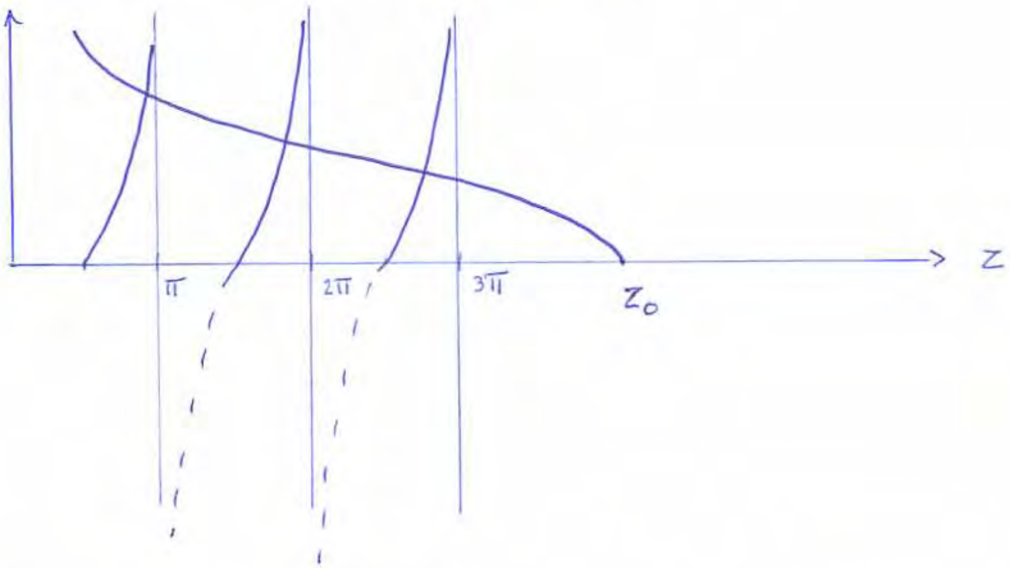
$$\psi(x) = \begin{cases} C \sin \ell x & , \quad 0 < x < a \\ F e^{-Kx} & , \quad x > a \end{cases}$$

$$\Rightarrow \quad F e^{-Ka} = C \sin \ell x$$

$$\Rightarrow \quad -F K e^{-Ka} = C \ell \cos \ell x$$

$$\therefore \quad \boxed{\ell \cot(\ell a) = -K}$$

$$\boxed{-\cot z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}}$$



SOLUTIONS $z_n \simeq n\pi \qquad n = 1, 2, 3 \dots$

$$= (2n)\frac{\pi}{2}$$

NO BOUND STATE IF $\boxed{z_0 < \frac{\pi}{2} \iff V_0 < \frac{\pi^2 \hbar^2}{8 m a^2}}$

- SCATTERING STATES $(E > 0)$

* ASSUMING: INCIDENT WAVE MOVING FROM $x = -\infty$ TO RIGHT

↳ $x < -a$ $\quad V(x) = 0$

$$\boxed{k \equiv \frac{\sqrt{2mE}}{\hbar}}$$

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

↳ INCIDENT AMPLITUDE

↳ $-a < x < a$ $\quad V(x) = -V_0$

$$\psi(x) = C \sin(\ell x) + D \cos(\ell x)$$

$$\boxed{\ell = \frac{1}{\hbar}\sqrt{2m(E+V_0)}}$$ AS BEFORE

↳ $x > a$ $\quad V(x) = 0$

$$\psi(x) = F e^{ikx}$$

(TERM $\sim e^{-ikx}$ ABSENT FOR INCIDENT WAVE MOVING FROM $x = -\infty$ TO RIGHT)

A: INCIDENT AMPLITUDE

B: REFLECTED AMPLITUDE

F: TRANSMITTED AMPLITUDE

↳ BOUNDARY CONDITIONS

CONTINUITY OF ψ AND $\frac{d\psi}{dx}$ AT $x=-a$ AND $x=+a$

(1) • $\psi(-a)$: $$A e^{-ika} + B e^{+ika} = -C \sin(la) + D \cos(la)$$

(2) • $\frac{d\psi}{dx}(-a)$: $$ik\left[A e^{-ika} - B e^{+ika}\right] = l\left[+C\cos(la) + D\sin(la)\right]$$

(3) • $\psi(+a)$: $$F e^{ika} = C\sin(la) + D\cos(la)$$

(4) • $\frac{d\psi}{dx}(+a)$: $$ik F e^{ika} = l\left[C\cos(la) - D\sin(la)\right]$$

(3)$\cdot l\sin(la)$ + (4) $\cos(la)$

↳ $$l C = F e^{ika}\left[l\sin(la) + ik\cos(la)\right]$$

$$\boxed{C = F e^{ika}\left[\sin(la) + i\frac{k}{l}\cos(la)\right]}$$

(3) $l\cos(la)$ − (4) $\sin(la)$

↳ $$\boxed{D = F e^{ika}\left[\cos(la) - i\frac{k}{l}\sin(la)\right]}$$

PLUG C, D INTO (1) & (2)

$$(*) \quad A e^{-ika} + B e^{ika}$$

$$= F e^{ika} \Big\{ - \sin^2(la) - i\frac{k}{l} \sin(la)\cos(la) + \cos^2(la) - i\frac{k}{l}\sin(la)\cos(la) \Big\}$$

$$= F e^{ika} \Big\{ \cos(2la) - i\frac{k}{l}\sin(2la) \Big\}$$

$$(**) \quad ik \left[A e^{-ika} - B e^{+ika} \right]$$

$$= F e^{ika}\, l \Big\{ + \sin(la)\cos(la) + i\frac{k}{l}\cos^2(la) + \sin(la)\cos(la) - i\frac{k}{l}\sin^2(la) \Big\}$$

$$= F e^{ika}\, l \Big\{ + \sin(2la) + i\frac{k}{l}\cos(2la) \Big\}$$

$\hookrightarrow \quad ik(*) - (**)$

$$B e^{ika} \cdot 2ik = F e^{ika} \Big\{ \cancel{ik\cos(2la)} + \frac{k^2}{l}\sin(2la) - l\sin(2la) - \cancel{ik\cos(2la)} \Big\}$$

$$= F e^{ika}\, \frac{k^2 - l^2}{l} \sin(2la)$$

$$\boxed{B = i\,\frac{\sin(2la)}{2kl}\,(l^2 - k^2)\, F}$$

↳ $ik(*) + (**)$

$$A e^{-ika} \cdot 2ik = F e^{ika} \left\{ ik \cos(2\ell a) + \frac{k^2}{\ell} \sin(2\ell a) + \ell \sin(2\ell a) + ik \cos(2\ell a) \right\}$$

$$= F e^{ika} \left\{ 2ik \cos(2\ell a) + \frac{k^2+\ell^2}{\ell} \sin(2\ell a) \right\}$$

$$\Downarrow$$

$$\boxed{F = A \cdot \frac{e^{-2ika}}{\cos(2\ell a) - i \frac{(k^2+\ell^2)}{2k\ell} \sin(2\ell a)}}$$

↳ R & T

$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|F|^2}{|A|^2}, \quad R + T = 1$$

$$T^{-1} = \cos^2(2\ell a) + \frac{(k^2+\ell^2)^2}{4k^2\ell^2} \sin^2(2\ell a)$$

$$= 1 + \frac{(k^2-\ell^2)^2}{4k^2\ell^2} \sin^2(2\ell a).$$

$$\ell^2 - k^2 = \frac{1}{\hbar^2} 2m V_0$$

$$\Downarrow$$

$$\boxed{T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)}$$

$T \leq 1$

$\Rightarrow$ REACHES 1 FOR ZEROES OF $\sin^2(\ )$

$$\Downarrow$$

$$T = 1 \Leftrightarrow \boxed{\frac{2a}{\hbar}\sqrt{2m(E_n+V_0)} = n\pi} \qquad n \text{ INTEGER}$$

↳ FOR THESE ENERGY : WELL BECOMES PERFECTLY TRANSPARANT

$$\Updownarrow$$

$$2\ell a = n\pi$$

$e^{i\ell a} \Longleftrightarrow$ WAVE WITH WAVELENGTH $\lambda = \frac{2\pi}{\ell}$

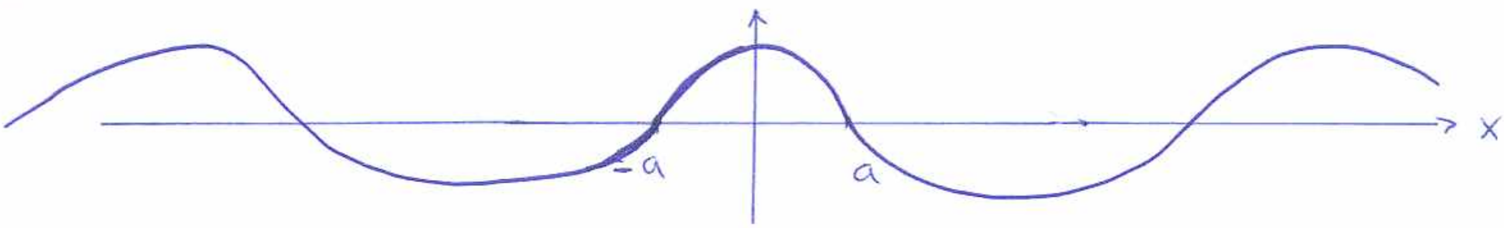
PERFECT TRANSPARANT FOR $2 \cdot \frac{2\pi}{\lambda} \cdot a = n\pi$

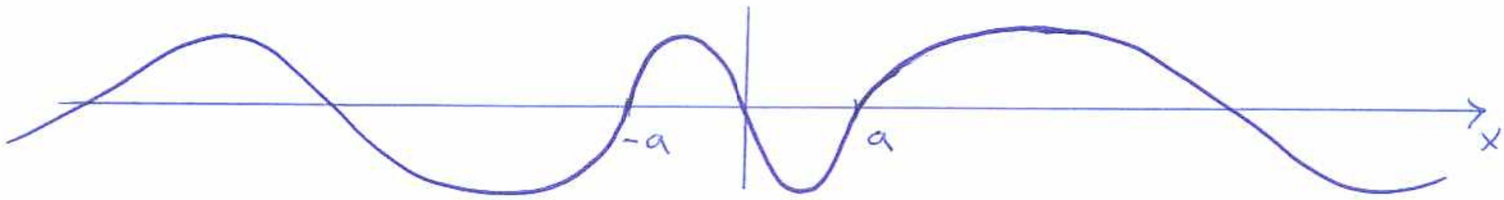
$$\Updownarrow$$

$$T = 1 \Leftrightarrow \boxed{(2a) = n\frac{\lambda}{2}}$$

∇ CONDITION FOR PERFECT TRANSPARANCY $(T=1)$

O WHEN WIDTH OF WELL FITS AN INTEGER TIMES $\lambda/2$



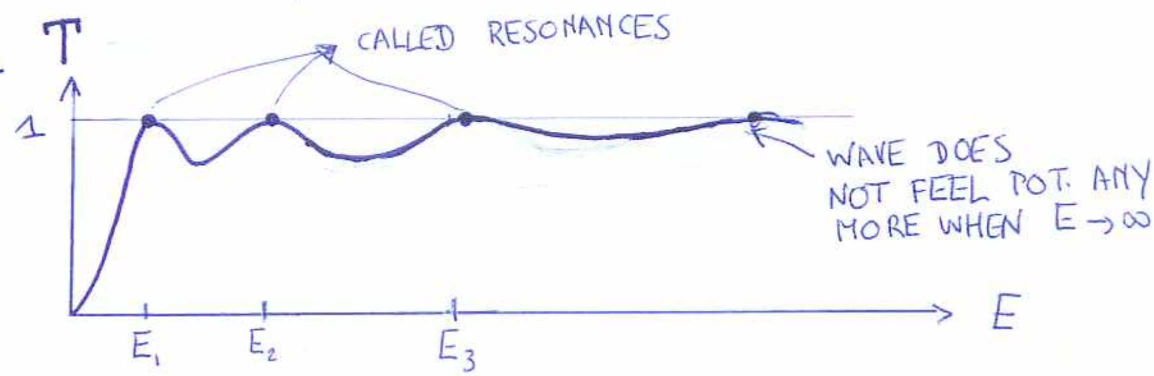


ENERGIES FOR PERFECT TRANSMISSION

$$E_n = -V_0 + \underbrace{n^2 \frac{\pi^2 \hbar^2}{2m\,(2a)^2}}, \qquad n \text{ INTEGER}, \; n = 1, 2, \ldots$$

(cf. ENERGIES OF INFINITE SQUARE WELL)

$\Rightarrow$ PLOT



T HAS MINIMA FOR $\sin(2a\ell) = 1$

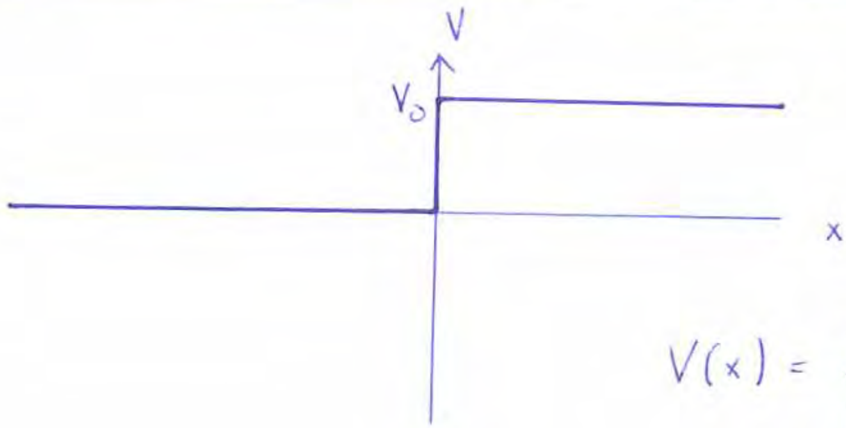
$$\Updownarrow$$

$$2a \cdot \frac{2\pi}{\lambda} = n' \frac{\pi}{2} \qquad (n' = 1, 3, 5, \ldots)$$

$$\downarrow$$

$$\boxed{2a = n' \cdot \frac{\lambda}{4}} \quad (n' = 1, 3, 5 \ldots)$$

⇒ FURTHER EXAMPLE : STEP POTENTIAL



$$V(x) = \begin{cases} 0, & x \leq 0 \\ V_0, & x > 0 \end{cases}$$

- $E < V_0$

↳ $x < 0$. SOLUTION $\psi(x) = Ae^{ikx} + Be^{-ikx}$

$$\boxed{k \equiv \frac{\sqrt{2mE}}{\hbar}}$$

↳ $x > 0$ $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi$

$$\downarrow$$

$$\frac{d^2\psi}{dx^2} = +\frac{2m}{\hbar^2}(V_0 - E)\psi$$

$$\downarrow \quad V_0 > E$$

$$\boxed{K \equiv \frac{\sqrt{2m(V_0 - E)}}{\hbar}}$$

$$\psi(x) = Ce^{-Kx}$$

↳ BOUNDARY CONDITION $x = 0$

ψ CONTINUOUS : $A + B = C$

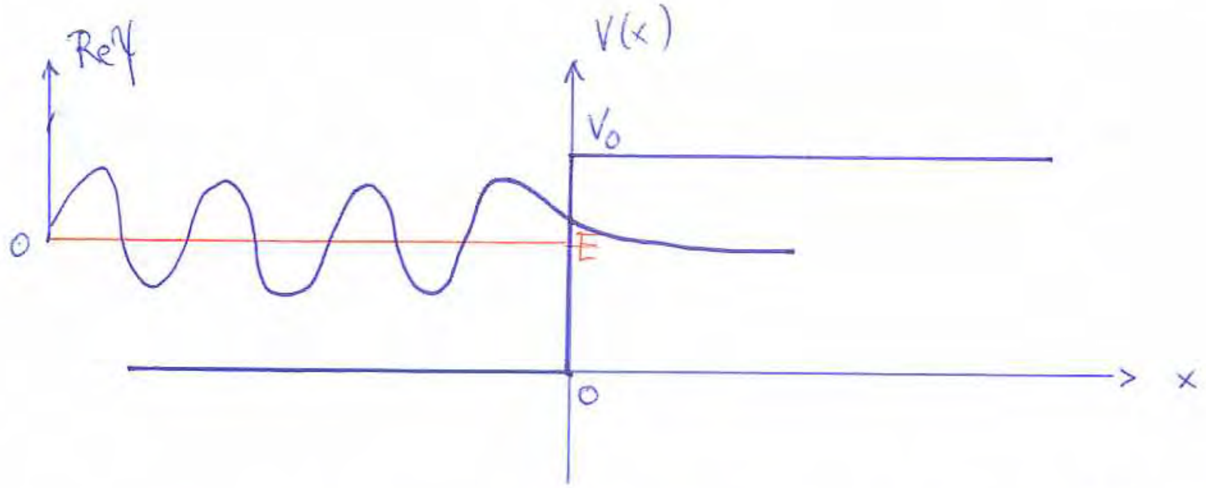
$\frac{d\psi}{dx}$ CONTINUOUS : $ik(A - B) = -CK$

$$\Downarrow$$

$$\frac{A - B}{A + B} = +\frac{i}{k}K$$

$$\boxed{B = A \cdot \frac{1 - \frac{i}{k}K}{1 + \frac{i}{k}K}}$$

REFLECTION COEFF. $R = \frac{|B|^2}{|A|^2} = 1$ TOTAL REFLECTION



$E = 0 \Rightarrow k = 0 \Rightarrow B = -A$

$E = V_0 \Rightarrow K = 0 \Rightarrow B = +A$

- $E > V_0$

↳ $\underline{x<0}$: $\psi(x) = A e^{ikx} + B e^{-ikx}$

↳ $\underline{x>0}$: $\psi(x) = D e^{ilx}$ FOR INCOMING WAVE FROM $x = -\infty$ ⟶

$$\boxed{l \equiv \frac{1}{\hbar}\sqrt{2m(E-V_0)}}$$

↳ BOUNDARY CONDITION $x = 0$

ψ : $A + B = D$

$\frac{d\psi}{dx}$: $ik(A-B) = il\,D$

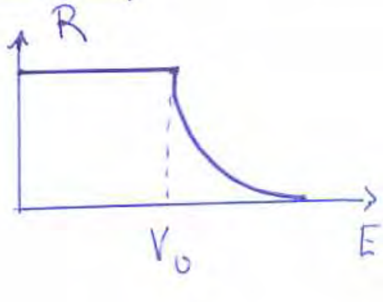
$$\Downarrow$$

$$k(A-B) = l(A+B)$$

$$\boxed{B = A \cdot \frac{(k-l)}{(k+l)}} \Rightarrow D = A + B = A\,\frac{2k}{(k+l)}$$

↳ REFLECTION COEFF. $\boxed{R = \frac{|B|^2}{|A|^2} = \frac{(k-l)^2}{(k+l)^2}}$

$$R = \frac{\left(\sqrt{E} - \sqrt{E-V_0}\right)^2}{\left(\sqrt{E} + \sqrt{E-V_0}\right)^2} = \frac{\left(\sqrt{E} - \sqrt{E-V_0}\right)^4}{V_0^{\,2}}$$



↳ TRANSMISSION COEFF. $T = 1 - R$

$$T = 1 - \frac{(k-\ell)^2}{(k+\ell)^2}$$

$$= \frac{(k^2 + 2k\ell + \ell^2 - k^2 + 2k\ell - \ell^2}{(k+\ell)^2}$$

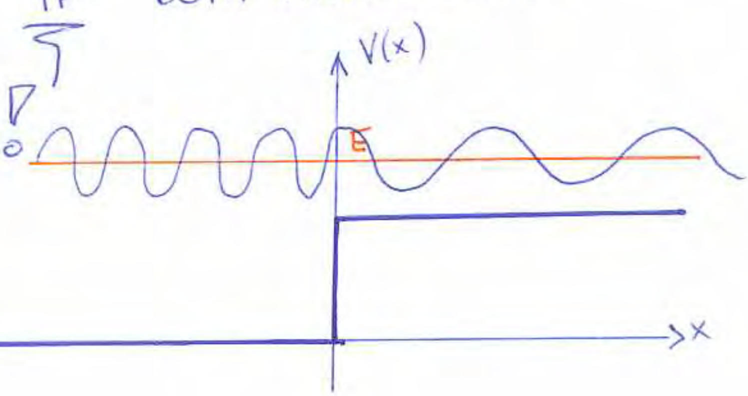
$$= \frac{4k\ell}{(k+\ell)^2}$$

$$= \frac{\ell}{k} \cdot \underbrace{\left(\frac{4k^2}{(k+\ell)^2} \right)}_{\frac{|D|^2}{|A|^2}}$$

$$\boxed{T = \frac{\ell}{k} \cdot \frac{|D|^2}{|A|^2}} = \frac{\sqrt{E - V_0}}{\sqrt{E}} \cdot \frac{|D|^2}{|A|^2}$$

↳ NOTE T COEFF. IS ONLY OBTAINED AS RATIO OF $|\ |^2$ IF BOTH WAVES TRAVEL AT SAME SPEED !

(SAME FOR R)



CHAPTER 3 : FORMALISM

⇒ 3.1 HILBERT SPACE

- QUANTUM THEORY ↗ WAVE FUNCTIONS ⇒ DESCRIBE STATE OF SYSTEM
  ↘ OPERATORS ⇒ DESCRIBE OBSERVABLES
  e.g. ENERGY, MOMENTUM, ...

- ↳ STATE VECTOR $|\alpha\rangle$ LIVES IN N-DIM SPACE

$$|\alpha\rangle \Leftrightarrow a = \begin{pmatrix} a_1 \\ \vdots \\ a_N \end{pmatrix}$$

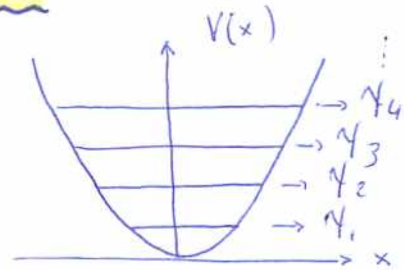
INNER PRODUCT $\langle\beta|\alpha\rangle = b^{+} a = \sum_{i=1}^{N} b_i^{*} a_i$

↳ OPERATORS ⇒ REPRESENTED BY MATRICES IN N-DIM SPACE

$$|\beta\rangle = \hat{T}\,|\alpha\rangle$$
$$\Updownarrow$$
$$b = T\,a \qquad T = \begin{pmatrix} T_{11} & \cdots & T_{1N} \\ \vdots & & \\ T_{N1} & \cdots & T_{NN} \end{pmatrix}$$

- HILBERT SPACE

↳ e.g. H.O.



VECTORS IN Q.M. ARE SQUARE INTEGRABLE FUNCTIONS $f(x)$

PHYSICAL STATE OF SYSTEM : $\int_{-\infty}^{+\infty} dx \; |\Psi(x,t)|^2 = 1$

↳ $f(x)$ IS SQUARE INTEGRABLE ON INTERVAL $[a,b]$

$$\Updownarrow$$

$$\int_a^b dx \; |f(x)|^2 < \infty$$

↳ SET OF ALL SQUARE INTEGRABLE FUNCTIONS
ON A SPECIFIED INTERVAL
IS CALLED A HILBERT SPACE (∞ DIMENSIONAL !)

- INNER PRODUCT OF 2 FUNCTIONS

↳ $$\boxed{\langle f | g \rangle \equiv \int_a^b dx \; f^*(x)\, g(x)}$$

IF BOTH f & g ARE SQUARE-INTEGRABLE

↳ INNER PRODUCT EXISTS

PROOF : SCHWARZ INEQUALITY

$$|\langle f|g\rangle|^2 \leq \langle f|f\rangle \langle g|g\rangle$$

↳ $\langle g | f \rangle = \langle f | g \rangle^*$ ✓ VERIFIED FROM DEFINITION

↳ $\langle f | f \rangle \geq 0$ & REAL

$\langle f | f \rangle = 0 \iff f(x) = 0$

$\therefore$ $\langle f | g \rangle$ SATISFIES ALL PROPERTIES OF AN INNER PRODUCT

- ORTHOGONALITY, NORMALIZATION

SET OF FUNCTIONS $\{f_n\}$ IS ORTHONORMAL

$$\Updownarrow$$

$$\langle f_n | f_m \rangle = \delta_{nm}$$

e.g. STATIONARY STATES $\{\psi_n\}$ OF H.O.

- COMPLETENESS

↳ SET OF FUNCTIONS IS COMPLETE

$$\Updownarrow$$

ANY OTHER FUNCTION IN HILBERT SPACE CAN BE EXPRESSED AS A LINEAR COMBINATION OF THEM

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$

e.g. STATIONARY STATES $\{\psi_n\}$ OF H.O

↳ IF $\{f_n\}$ ARE ORTHONORMAL

$$c_n = \langle f_n | f \rangle$$

⇒ 3.2 OBSERVABLES

• HERMITIAN OPERATORS

↳ EXPECTATION VALUE OF OBSERVABLE $Q(x, p)$

e.g. $H(x,p) = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$

$$\langle Q \rangle = \int dx \, \Psi^* \hat{Q} \Psi$$

$$= \langle \Psi | \hat{Q} \Psi \rangle$$

↳ MEASUREMENT ⇒ REAL OUTCOME

$\langle Q \rangle = \langle Q \rangle^*$ REAL EXPECTATION VALUES.

↳ $\langle \Psi | \hat{Q} \Psi \rangle^* = \langle \hat{Q} \Psi | \Psi \rangle$

$$= \langle \Psi | \hat{Q} \Psi \rangle$$

OPERATORS $\hat{Q}$ SATISFYING

$$\langle \hat{Q} \Psi | \Psi \rangle = \langle \Psi | \hat{Q} \Psi \rangle \quad \forall \, \Psi(x)$$

ARE HERMITIAN OPERATORS

∴ OBSERVABLES ARE REPRESENTED BY HERMITIAN OPERATORS

↳ $\langle \hat{Q} f | g \rangle = \langle f | \hat{Q} g \rangle \quad \forall \, f(x), g(x)$

SHOW THAT THIS IS EQUIVALENT TO ABOVE

↳ EXAMPLE : MOMENTUM OPERATOR $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

$$\langle f | \hat{p}\, g \rangle = \int_{-\infty}^{+\infty} dx \; f^*(x) \, (-i\hbar) \frac{d}{dx} g(x)$$

↓ INTEGRATION BY PARTS

$$= -i\hbar \cancel{f^* g \Big|_{-\infty}^{+\infty}} + i\hbar \int_{-\infty}^{+\infty} dx \left(\frac{d}{dx} f^*(x) \right) g(x)$$

f & g ARE
SQUARE-INTEGRABLE

$$= \int_{-\infty}^{+\infty} dx \left(-i\hbar \frac{d}{dx} f(x) \right)^* g(x)$$

$$= \langle \hat{p} f | g \rangle$$

■

$\left(-i\hbar \frac{d}{dx} \right)$ IS HERMITIAN

($\frac{d}{dx}$ is NOT !)

- DETERMINATE STATES

↳ IN DETERMINATE STATE: EVERY MEASUREMENT OF OBSERVABLE Q RETURNS THE SAME VALUE

e.g. STATIONARY STATES ARE DETERMINATE STATES OF HAMILTONIAN

$$\langle \psi_n | \hat{H} \psi_n \rangle = \underset{\substack{\uparrow \\ \text{ENERGY VALUE}}}{E_n}$$

↳ STANDARD DEVIATION σ OF Q IS ZERO IN A DETERMINATE STATE $|\hat{Q}\psi\rangle = q|\psi\rangle$

$$\langle \hat{Q} \rangle = \langle \psi | \hat{Q} \psi \rangle = q$$

$$\sigma^2 = \langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle$$

$$= \langle \psi | (\hat{Q} - q)^2 \psi \rangle$$

$$= \langle (\hat{Q} - q)\psi | (\hat{Q} - q)\psi \rangle$$

$$\supset \quad |\hat{Q}\psi\rangle = q|\psi\rangle$$

$$= 0$$

DETERMINATE STATE IS EIGENFUNCTION OF $\hat{Q}$

$$\hat{Q}|\psi\rangle = q|\psi\rangle$$

↳ EIGENVALUES OF HERMITIAN OPERATOR ARE <u>REAL</u>

COLLECTION OF ALL EIGENVALUES OF OPERATOR ⇒ <u>SPECTRUM</u>

IF 2 OR MORE LIN. INDEP EIGENFUNCTIONS SHARE SAME EIGENVALUE ⇒ SPECTRUM IS <u>DEGENERATE</u>

↳ e.g. ENERGY SPECTRUM

EIGENVALUES OF $\hat{H}$

$$\hat{H}\,|\psi_n\rangle = E_n\,|\psi_n\rangle$$

(TIME INDEP. SCHRÖDINGER EQ.)

↳ <u>EXAMPLE</u> $\quad \hat{Q} = i\dfrac{\partial}{\partial\phi}$

$$\phi \in [0, 2\pi] \quad \Rightarrow \quad f(\phi) = f(\phi + 2\pi) \qquad (*)$$

⇒ <u>HERMITIAN</u>

$$\langle f\,|\,\hat{Q} g\rangle = \int_0^{2\pi} d\phi\; f^*(\phi)\; i\frac{\partial}{\partial\phi}\, g(\phi)$$

$$= \underbrace{\cancel{i f^* g\Big|_0^{2\pi}}}_{(*)} - i\int_0^{2\pi} d\phi \left(\frac{\partial f}{\partial\phi}\right)^* g(\phi)$$

$$= \int_0^{2\pi} d\phi \left(i\frac{\partial}{\partial\phi} f\right)^* g$$

$$= \langle \hat{Q} f\,|\,g\rangle \quad \blacksquare \qquad \forall f, g$$

$\Rightarrow$ EIGENVALUES

$$i \frac{d}{d\phi} f(\phi) = q f(\phi)$$

$$f(\phi) = A e^{-iq\phi}$$

$$f(\phi) = f(\phi + 2\pi) \Rightarrow e^{-iq2\pi} = 1$$

$$\Downarrow$$

$$\underline{\underline{q = 0, \pm 1, \pm 2, \ldots}}$$

SPECTRUM OF $\hat{Q}$

⇒ 3.3 EIGENFUNCTIONS OF HERMITIAN OPERATOR

SPECTRUM

↗ DISCRETE e.g. H.O., INFINITE SQUARE WELL

↳ EIGENSTATES NORMALIZABLE

↘ CONTINUOUS e.g. $V(x) = 0$

↳ EIGENSTATES NOT NORMALIZABLE

- DISCRETE SPECTRUM OF HERMITIAN OPERATOR

↳ EIGENVALUES ARE REAL

$$\hat{Q}\,|f\rangle = q\,|f\rangle$$

$\hat{Q}$ is HERMITIAN $\quad \langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle$

$$q\,\langle f|f\rangle = q^*\,\langle f|f\rangle$$

$$q = q^* \;\blacksquare$$

↳ EIGENFUNCTIONS BELONGING TO DISTINCT EIGENVALUES ARE ORTHOGONAL $\quad (\hat{Q} = \hat{Q}^+)$

$$\hat{Q}\,|f\rangle = q\,|f\rangle$$

$$\hat{Q}\,|g\rangle = q'\,|g\rangle$$

$$\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$$

$$q'\langle f|g\rangle = q^*\langle f|g\rangle$$

$$= q\,\langle f|g\rangle$$

IF $q \neq q'$ ⇓ $\langle f|g\rangle = 0 \;\blacksquare$

IF NOT → USE GRAM SCHMIDT ORTHOGONALIZATION PROCEDURE TO CONSTRUCT ORTHOG. EIGENF.

↳ IN FINITE DIM. VECTOR SPACE

EIGENVECTORS OF HERMITIAN OPERATOR ARE COMPLETE

i.e. SPAN THE WHOLE SPACE

↳ FOR HILBERT SPACE (∞ DIM)

AXIOM : EIGENFUNCTIONS OF AN OBSERVABLE OPERATOR ARE COMPLETE :

ANY FUNCTION IN HILBERT SPACE CAN BE WRITTEN AS A LIN. COMBINATION OF THEM

- CONTINUOUS SPECTRUM

↳ EIGENFUNCTIONS NOT NORMALIZABLE

↳ HOW TO UNDERSTAND PROPERTIES SUCH AS REALITY (OF EIGENVALUES), ORTHOGONALITY, COMPLETENESS

↳ EXAMPLE : EIGENVALUES & EIGENFUNCTIONS OF MOMENTUM OPERATOR

$$\underbrace{-i\hbar \frac{d}{dx}}_{\hat{p}} f_p(x) = p\, f_p(x)$$

↳ EIGENFUNCTION

$$\Downarrow$$

$$f_p(x) = A\, e^{\frac{i}{\hbar} p x} \qquad \left(\Rightarrow \lambda = \frac{2\pi\hbar}{p} \right)$$

(NOT SQUARE INTEGRABLE)

$\Rightarrow f_p$ IS NOT A FUNCTION IN HILBERT SPACE

$\Rightarrow$ BUT, WE CAN UNDERSTAND ORTHONORMALITY IN FOLLOWING SENSE:

$$\langle f_{p'} | f_p \rangle = \int_{-\infty}^{+\infty} dx \; f_{p'}^*(x) \, f_p(x) = |A|^2 \int_{-\infty}^{+\infty} dx \; e^{-\frac{i}{\hbar}(p'-p)x}$$

$$= |A|^2 \, 2\pi\hbar \, \delta(p-p')$$

CHOOSE $\underline{\underline{A = \frac{1}{\sqrt{2\pi\hbar}}}}$

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \, e^{\frac{i}{\hbar} p x}$$

$$\langle f_{p'} | f_p \rangle = \delta(p-p')$$

REPLACES KRONECKER DELTA IN CONTINUOUS CASE

CALLED: DIRAC ORTHONORMALITY

$\Rightarrow$ EIGENFUNCTIONS ARE COMPLETE $\sum \longrightarrow \int$

$$f(x) = \int_{-\infty}^{+\infty} dp \; c(p) \, f_p(x)$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dp \; c(p) \, e^{\frac{i}{\hbar} p x} \qquad \text{(FOURIER TF.)}$$

$$\underline{\underline{\langle f_{p'} | f \rangle}} = \int_{-\infty}^{+\infty} dp \; c(p) \underbrace{\langle f_{p'} | f_p \rangle}_{\delta(p-p')} = \underline{\underline{c(p')}}$$

↳ EXAMPLE : EIGENVALUES & EIGENFUNCTIONS OF POSITION OPERATOR

$$\hat{x}\, g_y(x) = y\, g_y(x)$$

$$\underline{\underline{g_y(x) = A\,\delta(x-y)}}$$

$$\langle g_{y'} | g_y \rangle = \int dx\, g^*_{y'}(x)\, g_y(x)$$

$$= |A|^2 \int dx\, \delta(x-y')\,\delta(x-y)$$

$$= |A|^2\, \delta(y-y')$$

CHOOSE $A = 1$

$$g_y(x) = \delta(x-y)$$

$$\langle g_{y'} | g_y \rangle = \delta(y-y')$$

⇒ 'COMPLETENESS'

$$f(x) = \int_{-\infty}^{+\infty} dy\, c(y)\, g_y(x)$$

$$= \int_{-\infty}^{+\infty} dy\, c(y)\,\delta(x-y) = c(x)$$

$$c(y) = f(y)$$

⇒ 3.4 STATISTICAL INTERPRETATION

- OBSERVABLE $Q(x, p)$ HERMITIAN $Q^{+} = Q$

$\downarrow$

MEASUREMENT GIVES ONE OF THE REAL EIGENVALUES OF Q.

↳ DISCRETE SPECTRUM (q_n)

PROBABILITY TO FIND EIGENVALUE q_n

$$\hookrightarrow |c_n|^2 \Rightarrow \quad c_n = \langle f_n | \Psi \rangle$$

$$\Psi(x,t) = \sum_n c_n f_n(x)$$

↳ CONTINUOUS SPECTRUM $(q(z))$

PROBABILITY TO FIND EIGENVALUE IN RANGE dz

$$\hookrightarrow |c(z)|^2 dz \Rightarrow c(z) = \langle f_z | \Psi \rangle$$

$\therefore$ BY DOING THE MEASUREMENT $\rightsquigarrow$ MEASURING A PARTICULAR EIGENVALUE

$\Downarrow$

THE WAVE FUNCTION COLLAPSES TO THE CORRESPONDING EIGENSTATE

- TOTAL PROBABILITY / EXPECTATION VALUES

↳ $\sum_n |c_n|^2 = 1$ (TOTAL PROBABILITY)

↳ $\Psi = \sum_n c_n f_n$

$$\langle \Psi | \Psi \rangle = \sum_n \sum_{n'} c_n^* c_{n'} \underbrace{\langle f_n | f_{n'} \rangle}_{\delta_{nn'}}$$

$$= \sum_n |c_n|^2$$

$$= 1 \quad (\text{NORMALIZATION OF W.F.})$$

↳ $\langle Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle$

$$= \sum_n \sum_{n'} c_n^* c_{n'} \langle f_n | \underbrace{\hat{Q} f_{n'}}_{q_{n'} | f_{n'} \rangle} \rangle$$

$$= \sum_n \sum_{n'} c_n^* c_{n'} \, q_{n'} \, \delta_{nn'}$$

$$\langle Q \rangle = \sum_n q_n |c_n|^2$$

MOMENTUM SPACE WAVE FUNCTION

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar} p x}$$ EIGENFUNCTIONS OF $\hat{p}$

$$\hat{p}\, f_p(x) = p\, f_p(x)$$

$$C(p) = \langle f_p | \Psi \rangle$$ PROB. AMPL. TO FIND Ψ IS MOMENTUM EIGENSTATE

$$C(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx\, e^{-\frac{i}{\hbar} p x}\, \Psi(x,t)$$

$C(p) \equiv \Phi(p,t)$ IS CALLED MOMENTUM SPACE WAVE FUNCTION.

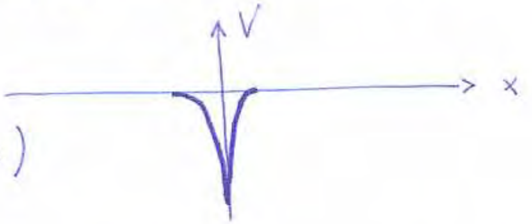
(FOURIER TF OF POSITION SPACE WF $\Psi(x,t)$)

$$\boxed{\begin{aligned} \Phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx\, e^{-\frac{i}{\hbar} p x}\, \Psi(x,t) \\ \Psi(x,t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dp\, e^{\frac{i}{\hbar} p x}\, \Phi(p,t) \end{aligned}}$$

$\therefore$ PROBABILITY THAT A MEASUREMENT OF MOMENTUM YIELDS A VALUE BETWEEN p AND $p + dp$

$$|\Phi(p,t)|^2\, dp$$

- EXAMPLE: MOM. SPACE W.F. OF PARTICLE OF MASS m IN δ - FUNCTION POT.



$$V(x) = -\alpha\,\delta(x)$$

↳ BEFORE $\quad E = -\dfrac{\hbar^2 K^2}{2m} \qquad K = \dfrac{m\alpha}{\hbar^2}$

↳ BOUND STATE ENERGY

$$\Psi(x,t) = \sqrt{K}\, e^{-K|x|}\, e^{-\frac{i}{\hbar}Et}$$

↳ $$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx\, e^{-\frac{i}{\hbar}px}\, \Psi(x,t)$$

$$= \frac{\sqrt{K}}{\sqrt{2\pi\hbar}}\, e^{-\frac{i}{\hbar}Et} \int_{-\infty}^{+\infty} dx\, e^{-\frac{i}{\hbar}px}\, e^{-K|x|}$$

$$= \frac{\sqrt{K}}{\sqrt{2\pi\hbar}}\, e^{-\frac{i}{\hbar}Et} \left\{ \int_{-\infty}^{0} dx\, e^{(K - \frac{i}{\hbar}p)x} + \int_{0}^{+\infty} dx\, e^{(-K - \frac{i}{\hbar}p)x} \right\}$$

$$\frac{1}{K - \frac{i}{\hbar}p}\, e^{(K - \frac{i}{\hbar}p)x}\Big|_{-\infty}^{0}$$

$$+ \frac{1}{-K - \frac{i}{\hbar}p}\, e^{-(K + \frac{i}{\hbar}p)x}\Big|_{0}^{+\infty}$$

$$= \frac{\sqrt{K}}{\sqrt{2\pi\hbar}}\, e^{-\frac{i}{\hbar}Et} \left\{ \frac{1}{K - \frac{i}{\hbar}p} + \frac{1}{K + \frac{i}{\hbar}p} \right\}.$$

$$\Phi(p,t) = \frac{\sqrt{K}}{\sqrt{2\pi\hbar}} \, e^{-\frac{i}{\hbar}Et} \, \frac{2K}{K^2 + \frac{p^2}{\hbar^2}}$$

$$\boxed{\Phi(p,t) = \sqrt{\frac{2}{\pi}} \, \frac{(\hbar K)^{3/2}}{p^2 + (\hbar K)^2} \, e^{-\frac{i}{\hbar}Et}}$$

↳ PROBABILITY TO FIND PARTICLE WITH MOMENTUM $> \hbar K$

$$P(p > \hbar K) = \int_{\hbar K}^{+\infty} dp \, |\Phi(p,t)|^2$$

$$= \frac{2}{\pi} (\hbar K)^3 \int_{\hbar K}^{+\infty} dp \, \frac{1}{\left(p^2 + (\hbar K)^2\right)^2}$$

HELP: $2p_0^3 \int dp \frac{1}{(p^2+p_0^2)^2} = \frac{p p_0}{p^2+p_0^2} + \mathrm{atan}\left(\frac{p}{p_0}\right)$

$$P(p > \hbar K) = \frac{1}{\pi} \left[\frac{p \, \hbar K}{p^2 + (\hbar K)^2} + \mathrm{atan}\left(\frac{p}{\hbar K}\right) \right]_{\hbar K}^{\infty}$$

$$= \frac{1}{\pi} \left[\frac{\pi}{2} - \frac{1}{2} - \frac{\pi}{4} \right]$$

$$= \frac{1}{4} - \frac{1}{2\pi} \simeq 0.09$$

⇒ 3.5 THE UNCERTAINTY PRINCIPLE

- PROOF OF UNCERTAINTY PRINCPLE

↳ OBSERVABLE A ($\hat{A}$ IS HERMITIAN)

$$\langle \hat{A} \rangle$$

$$\sigma_A^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle$$

$$= \langle \Psi | (\hat{A} - \langle \hat{A} \rangle)^2 \Psi \rangle \qquad \hat{A} \text{ HERMITIAN}$$

$$= \langle (\hat{A} - \langle \hat{A} \rangle) \Psi \mid (\hat{A} - \langle \hat{A} \rangle) \Psi \rangle$$

$$\equiv \langle f | f \rangle \quad \text{WITH } |f\rangle = |(\hat{A} - \langle \hat{A} \rangle)\Psi\rangle$$

↳ OBSERVABLE B ($\hat{B}$ IS HERMITIAN)

$$\langle \hat{B} \rangle$$

$$\sigma_B^2 \equiv \langle g | g \rangle \quad \text{WITH } |g\rangle = |(\hat{B} - \langle \hat{B} \rangle)\Psi\rangle$$

↳ SCHWARTZ INEQUALITY

$$\sigma_A^2 \sigma_B^2 = \langle f|f\rangle \langle g|g\rangle \geq |\langle f|g\rangle|^2$$

↳ $\forall z$: COMPLEX NUMBER

$$|z|^2 = (\mathrm{Re}\, z)^2 + (\mathrm{Im}\, z)^2 \geq (\mathrm{Im}\, z)^2 = \left[\frac{1}{2i}(z - z^*)\right]^2$$

LET $z = \langle f | g \rangle$

$$\frac{1}{2i}(z - z^*) = \frac{1}{2i}\left(\langle f|g\rangle - \langle f|g\rangle^*\right)$$

$$= \frac{1}{2i}\left(\langle f|g\rangle - \langle g|f\rangle\right)$$

$$\hookrightarrow \langle f|g\rangle = \langle (\hat{A} - \langle\hat{A}\rangle)\Psi \,|\, (\hat{B} - \langle\hat{B}\rangle)\Psi\rangle$$

$$= \langle \Psi | (\hat{A} - \langle\hat{A}\rangle)(\hat{B} - \langle\hat{B}\rangle)\Psi\rangle$$

$$= \langle \Psi | \left(\hat{A}\hat{B} - \langle\hat{A}\rangle\hat{B} - \hat{A}\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle\right)\Psi\rangle$$

$$= \langle\Psi|\hat{A}\hat{B}\Psi\rangle - \langle\hat{A}\rangle\langle\Psi|\hat{B}\Psi\rangle$$

$$- \langle\hat{B}\rangle\langle\Psi|\hat{A}\Psi\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle\underbrace{\langle\Psi|\Psi\rangle}_{1}$$

$$= \langle\Psi|\hat{A}\hat{B}\Psi\rangle - 2\langle\hat{A}\rangle\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle$$

$$= \langle\Psi|\hat{A}\hat{B}\Psi\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$$

$$\langle g|f\rangle = \langle\Psi|\hat{B}\hat{A}\Psi\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle$$

$$\hookrightarrow \langle f|g\rangle - \langle g|f\rangle = \langle\Psi|(\hat{A}\hat{B} - \hat{B}\hat{A})\Psi\rangle$$

$$= \langle\Psi|[\hat{A},\hat{B}]\Psi\rangle$$

$$\underline{\underline{[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}}} \quad \text{COMMUTATOR}$$

$\hookrightarrow \quad \sigma_A^2 \; \sigma_B^2 \geqslant \left[\frac{1}{2i} \left(\langle f | g \rangle - \langle g | f \rangle \right) \right]^2$

$$\boxed{\sigma_A^2 \; \sigma_B^2 \geqslant \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2}$$

UNCERTAINTY PRINCIPLE

$\hookrightarrow$ NOTE COMMUTATOR OF 2 HERMITIAN OPERATORS IS ANTI-HERMITIAN !

$$[\hat{A}, \hat{B}]^\dagger = (\hat{A}\hat{B} - \hat{B}\hat{A})^\dagger$$

$$= (\hat{B}^\dagger \hat{A}^\dagger - \hat{A}^\dagger \hat{B}^\dagger) \qquad \hat{A}^\dagger = \hat{A} \;, \; \hat{B}^\dagger = \hat{B}$$

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

$$= -[\hat{A}, \hat{B}]$$

$\leadsto$ EIGENVALUES OF ANTI-HERMITIAN OPERATOR ARE IMAGINARY

$\leadsto \quad \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle$ IS REAL NUMBER !

POSITION-MOMENTUM UNCERTAINTY : $\sigma_x \sigma_p$

$\hat{A} = \hat{x}$ POSITION OPERATOR

$\hat{B} = \hat{p}$ MOMENTUM OPERATOR

$= -i\hbar \dfrac{d}{dx}$

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

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{1}{2i} i\hbar \right)^2 = \left(\frac{\hbar}{2} \right)^2$$

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$$

EQUIVALENT NOTATION

$\Delta x \; \Delta p \geq \frac{\hbar}{2}$

ORIGINAL UNCERTAINTY PRINCIPLE OF HEISENBERG

↳ PAIR OF OBSERVABLES A, B FOR WHICH

$[\hat{A}, \hat{B}] \neq 0 \implies$ A, B ARE <u>IN</u>COMPATIBLE OBSERVABLES.

↓

THEY DO <u>NOT</u> HAVE A COMPLETE SET OF SHARED EIGENFUNCTIONS

↳ COMPATIBLE OBSERVABLES

$[\hat{A}, \hat{B}] = 0$ ↳ DO HAVE A COMPLETE SET OF SHARED EIGENFUNCTIONS

↳ (SEE PROBLEM 3.15!)

- MINIMUM UNCERTAINTY WAVE PACKET

↳ GROUND STATE OF H.O

$$\sigma_x \, \sigma_p = \frac{\hbar}{2} \quad \rightarrow \text{ HITS THE UNCERTAINTY LIMIT}$$

↳ EQUALITY MEANS

1) SCHWARTZ INEQUALITY BECOMES EQUALITY

$$\langle f | f \rangle \langle g | g \rangle = |\langle f | g \rangle|^2$$

$$\Updownarrow$$

$$g(x) = c\, f(x)$$

2) $$|z|^2 = |\langle f | g \rangle|^2 = \left(\mathrm{Im} \langle f | g \rangle \right)^2$$

$$\Updownarrow$$

$\langle f | g \rangle$ IS PURELY IMAGINARY $\Rightarrow c = ia$

$\therefore \quad g(x) = ia\, f(x) \qquad a$ IS REAL

↳ $f(x) \Rightarrow | (\hat{x} - \langle \hat{x} \rangle)\, \Psi \rangle$

$g(x) \Rightarrow | (\hat{p} - \langle \hat{p} \rangle)\, \Psi \rangle$

$g(x) = ia\, f(x)$

$$\left(-i\hbar \frac{d}{dx} - \langle p \rangle \right) \Psi = ia\, (x - \langle x \rangle)\, \Psi$$

SOLUTION

TRY: $\Psi(x) = A e^{\frac{i}{\hbar}\langle p\rangle x} \, \phi(x)$

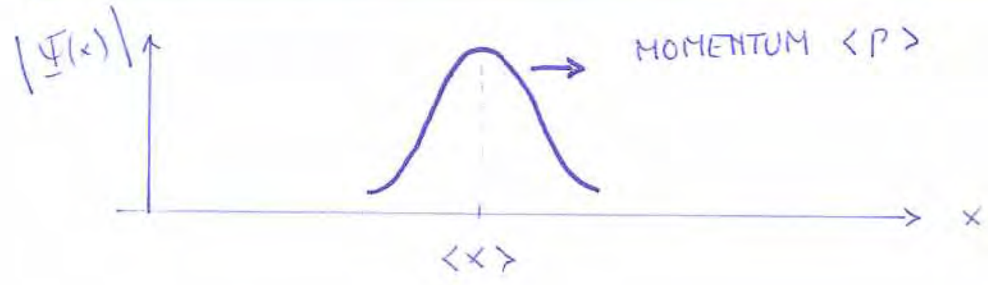
$$A e^{\frac{i}{\hbar}\langle p\rangle x}\left(-i\hbar \frac{d}{dx}\right)\phi = i a A e^{\frac{i}{\hbar}\langle p\rangle x}\left(x - \langle x\rangle\right)\phi$$

$$\downarrow$$

$$\frac{d}{dx}\phi(x) = -\frac{a}{\hbar}\left(x - \langle x\rangle\right)\phi(x)$$

SOLUTION $\quad \phi(x) = e^{-\frac{a}{2\hbar}\left(x - \langle x\rangle\right)^2}$

$$\therefore \quad \boxed{\Psi(x) = A\, e^{\frac{i}{\hbar}\langle p\rangle x} \cdot e^{-\frac{a}{2\hbar}\left(x-\langle x\rangle\right)^2}}$$



↳ CALLED: MINIMUM UNCERTAINTY GAUSSIAN WAVEPACKET

ENERGY - TIME UNCERTAINTY PRINCIPLE

$$\hookrightarrow \frac{d}{dt} \langle \hat{Q} \rangle$$

$$= \frac{d}{dt} \langle \Psi | \hat{Q} \Psi \rangle$$

$$= \langle \frac{\partial \Psi}{\partial t} | \hat{Q} \Psi \rangle + \langle \Psi | \frac{\partial \hat{Q}}{\partial t} \Psi \rangle + \langle \Psi | \hat{Q} \frac{\partial \Psi}{\partial t} \rangle$$

$$\Big\downarrow \; i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

$$= \frac{i}{\hbar} \langle \hat{H} \Psi | \hat{Q} \Psi \rangle + \langle \Psi | \frac{\partial \hat{Q}}{\partial t} \Psi \rangle - \frac{i}{\hbar} \langle \Psi | \hat{Q} \hat{H} \Psi \rangle$$

$$= \frac{i}{\hbar} \langle \Psi | \hat{H} \hat{Q} \Psi \rangle + \langle \Psi | \frac{\partial \hat{Q}}{\partial t} \Psi \rangle - \frac{i}{\hbar} \langle \Psi | \hat{Q} \hat{H} \Psi \rangle$$

$$= \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle$$

$$\boxed{\frac{d}{dt} \langle \hat{Q} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle}$$

↳ GENERALIZED UNCERTAINTY PRINCIPLE

$\hat{A} = \hat{H}$

$\hat{B} = \hat{Q}$ WHICH DOES NOT DEPEND ON TIME $\frac{\partial \hat{Q}}{\partial t} = 0$

$$\sigma_H^2 \, \sigma_Q^2 \geqslant \left(\frac{1}{2i} \langle [\hat{H}, \hat{Q}] \rangle \right)^2$$

$$= \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle Q \rangle}{dt} \right)^2$$

$$\sigma_H \, \sigma_Q \geqslant \frac{\hbar}{2} \left| \frac{d\langle Q \rangle}{dt} \right|$$

$$\sigma_H \equiv \Delta E$$

AND $\boxed{\Delta t \equiv \frac{\sigma_Q}{\left| \frac{d\langle Q \rangle}{dt} \right|}}$

$$\boxed{\Delta E \, \Delta t \geqslant \frac{\hbar}{2}}$$ ENERGY - TIME UNCERTAINTY PRINCIPLE

MEANING: $\sigma_Q = \left| \frac{d\langle Q \rangle}{dt} \right| \Delta t$

↑ RATE OF CHANGE OF $\langle Q \rangle$ PER UNIT OF TIME

Δt : TIME IT TAKES FOR EXPECTATION VALUE $\langle Q \rangle$ TO CHANGE BY ONE STANDARD DEVIATION

↳ EXAMPLE :

- FOR STATIONARY STATE :

ENERGY IS UNIQUELY DETERMINED $\Rightarrow \Delta E = 0$

$$\Downarrow$$

$$\Delta t = \infty$$

(ALL OBSERVABLES ARE CONSTANT IN TIME $\frac{d}{dt}\langle Q \rangle = 0$)

- LINEAR COMBINATION OF 2 STATIONARY STATES.

$$\Psi(x,t) = a\,\psi_1(x)\,e^{-\frac{i}{\hbar}E_1 t} + b\,\psi_2(x)\,e^{-\frac{i}{\hbar}E_2 t}$$

a, b, ψ_1, ψ_2 REAL

$$|\Psi(x,t)|^2 = a^2\psi_1^2 + b^2\psi_2^2 + 2ab\,\psi_1\psi_2\cos\left(\frac{E_2 - E_1}{\hbar}t\right)$$

PERIOD OF OSCILLATION $\tau = \dfrac{2\pi\hbar}{E_2 - E_1}$

$\Delta E = E_2 - E_1$ (ROUGHLY)

$\Delta t = \tau$ (ROUGHLY)

$$\therefore \quad \Delta E\,\Delta t \sim 2\pi\hbar = (4\pi)\frac{\hbar}{2} \geq \frac{\hbar}{2}$$

(see PROBLEM 3.18 !)

⟹ 3.6 DIRAC NOTATION

- STATE $|\Psi\rangle$

  $|x\rangle$ POSITION EIGENSTATE

  $\Psi(x,t) = \langle x|\Psi\rangle$

  ↳ W.F. IN COORDINATE SPACE

- $|p\rangle$ MOMENTUM EIGENSTATE $\qquad \hat{p}\,|p\rangle = p\,|p\rangle$

  $\Phi(p,t) = \langle p|\Psi\rangle$

  ↳ W.F. IN MOMENTUM SPACE

- $|n\rangle$ STATIONARY STATE $\qquad \hat{H}\,|n\rangle = E_n\,|n\rangle$

  $c_n(t) = \langle n|\Psi\rangle$

- OPERATORS : TRANSFORM ONE VECTOR INTO ANOTHER

  $$|\beta\rangle = \hat{Q}\,|\alpha\rangle$$

  BASIS $|e_n\rangle$

  $$|\alpha\rangle = \sum_n a_n\,|e_n\rangle$$

  $$|\beta\rangle = \sum_n b_n\,|e_n\rangle$$

  $$\boxed{Q_{nm} \equiv \langle e_n|\,\hat{Q}\,|e_m\rangle}$$

- DIRAC 's BRA & KET NOTATION

↳ $$|\alpha\rangle \Leftrightarrow \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix}$$

$\Downarrow$

'KET'

$$\langle\alpha| \Leftrightarrow \begin{pmatrix} a_1^* & \dots & a_n^* \end{pmatrix}$$

$\Downarrow$

'BRA'

$$|\alpha\rangle = \sum_n a_n |e_n\rangle$$

$$\langle\alpha| = \sum_n a_n^* \langle e_n|$$

↳ PROJECTION OPERATOR $\hat{P} \equiv |\alpha\rangle\langle\alpha|$

$$\hat{P}|\beta\rangle = \langle\alpha|\beta\rangle\, |\alpha\rangle$$

↳ IF $\{|e_n\rangle\}$ IS ORTHONORMAL BASIS (DISCRETE)

$$\boxed{\begin{aligned} \langle e_n|e_m\rangle &= \delta_{nm} \\ \sum_n |e_n\rangle\langle e_n| &= 1 \end{aligned}}$$ $\Rightarrow$ COMPLETENESS

$$\sum_n |e_n\rangle \underbrace{\langle e_n|\alpha\rangle}_{a_n}$$

$$= \sum_n a_n |e_n\rangle$$

$$= |\alpha\rangle$$

$$\therefore \quad \sum_n |e_n\rangle\langle e_n| = 1$$

↳ IF $\{|e_z\rangle\}$ IS DIRAC ORTHONORMALIZED BASIS

$$\boxed{\begin{aligned} &\langle e_z|e_{z'}\rangle = \delta(z-z') \\ &\int dz \; |e_z\rangle\langle e_z| = 1 \end{aligned}}$$

$$|\Psi\rangle = \int dz \; |e_z\rangle \underbrace{\langle e_z|\Psi\rangle}_{\Psi(z)}$$

$$\underbrace{\langle e_{z'}|\Psi\rangle}_{\Psi(z')} = \int dz \; \underbrace{\langle e_{z'}|e_z\rangle}_{\delta(z-z')} \; \Psi(z) \overset{!}{=} \Psi(z')$$

CHAPTER 4 : QUANTUM MECHANICS IN 3D

⇒ 4.1 SCHRÖDINGER EQ. IN SPHERICAL COORDINATES

- GENERALIZATION TO 3D

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

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = \frac{1}{2m}\left(\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2\right)$$

$$\hat{P}_x \rightarrow -i\hbar \frac{\partial}{\partial x}$$

$$\hat{P}_y \rightarrow -i\hbar \frac{\partial}{\partial y}$$

$$\hat{P}_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

$$\therefore \quad \hat{\bar{P}} \rightarrow -i\hbar \bar{\nabla}$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2 \Psi + V\Psi = i\hbar \frac{\partial \Psi}{\partial t}}$$

WITH $V(\bar{r}, t)$

$\bar{r}\ (x, y, z)$

↓

CARTESIAN COORDINATES

LAPLACIAN $\left\| \nabla^2 \equiv \bar{\nabla}.\bar{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right.$

↳ NORMALIZATION

$|\Psi(\bar{r},t)|^2 \, d^3\bar{r}$ PROBILITY TO FIND PARTICLE IN THE (INFINITESIMAL) VOLUME $d^3\bar{r}$ AT TIME t

$$\int d^3\bar{r} \; |\Psi(\bar{r},t)|^2 = 1$$

↳ IF $V(\bar{r},t) = V(\bar{r})$ TIME INDEPENDENT

⇓

COMPLETE SET OF STATIONARY STATES

$$\Psi_n(\bar{r},t) = \psi_n(\bar{r}) \, e^{-\frac{i}{\hbar}E_n t}$$

$\psi_n(\bar{r})$ SATISFIES TIME INDEPENDENT SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n$$

IN GENERAL

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

↓ GENERAL SOLUTION

$$\Psi(\bar{r},t) = \sum_n c_n \psi_n(\bar{r}) \, e^{-\frac{i}{\hbar}E_n t}$$

- SEPARATION OF VARIABLES

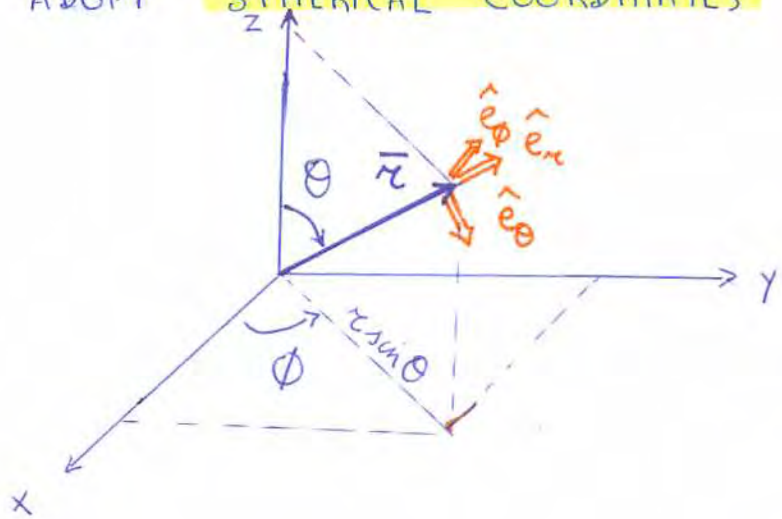
↳ FOR CENTRAL POTENTIAL $V(\bar{r}) = V(r)$

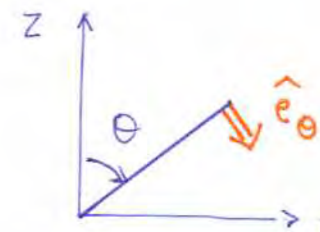
$r = |\bar{r}|$

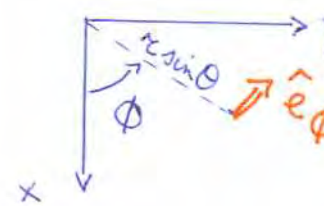
V : DEPENDS ONLY ON DISTANCE FROM ORIGIN

$\Downarrow$

ADOPT SPHERICAL COORDINATES







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

$$\hat{e}_r = \sin\theta\cos\phi\,\hat{i} + \sin\theta\sin\phi\,\hat{j} + \cos\theta\,\hat{k}$$
$$\hat{e}_\theta = \cos\theta\cos\phi\,\hat{i} + \cos\theta\sin\phi\,\hat{j} - \sin\theta\,\hat{k}$$
$$\hat{e}_\phi = -\sin\phi\,\hat{i} + \cos\phi\,\hat{j}$$

$$\bar{\nabla} f = \left(\frac{\partial f}{\partial x}\right)\hat{i} + \left(\frac{\partial f}{\partial y}\right)\hat{j} + \left(\frac{\partial f}{\partial z}\right)\hat{k}$$

$$= (\bar{\nabla}_r f)\,\hat{e}_r + (\bar{\nabla}_\theta f)\,\hat{e}_\theta + (\bar{\nabla}_\phi f)\,\hat{e}_\phi$$

$$\rightsquigarrow (\bar{\nabla}_r f) = \hat{e}_r \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right)\underbrace{\sin\theta\cos\phi}_{\frac{\partial x}{\partial r}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{\sin\theta\sin\phi}_{\frac{\partial y}{\partial r}} + \left(\frac{\partial f}{\partial z}\right)\underbrace{\cos\theta}_{\frac{\partial z}{\partial r}}$$

$$= \frac{\partial f}{\partial r}$$

$$\rightsquigarrow (\bar{\nabla}_\theta f) = \hat{e}_\theta \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right)\underbrace{\cos\theta\cos\phi}_{\frac{1}{r}\frac{\partial x}{\partial \theta}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{\cos\theta\sin\phi}_{\frac{1}{r}\frac{\partial y}{\partial \theta}} + \left(\frac{\partial f}{\partial z}\right)\underbrace{(-\sin\theta)}_{\frac{\partial z}{\partial \theta}}$$

$$= \frac{1}{r}\frac{\partial f}{\partial \theta}$$

$$\rightsquigarrow (\bar{\nabla}_\phi f) = \hat{e}_\phi \cdot \bar{\nabla} f$$

$$= \left(\frac{\partial f}{\partial x}\right)\underbrace{(-\sin\phi)}_{\frac{1}{r\sin\theta}\frac{\partial x}{\partial \phi}} + \left(\frac{\partial f}{\partial y}\right)\underbrace{(\cos\phi)}_{\frac{1}{r\sin\theta}\frac{\partial y}{\partial \phi}} \quad \frac{\partial z}{\partial \phi}$$

$$= \frac{1}{r\sin\theta}\frac{\partial f}{\partial \phi}$$

$$\boxed{\bar{\nabla} = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi}}$$

$$\bar{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

EXPRESS LAPLACIAN $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

IN POLAR COORDINATES. (HOMEWORK!)

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

TIME-INDEP
↳ SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)\right.$$

$$\left.+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi = E\psi$$

SEPARATION OF VARIABLES

$$\underline{\underline{\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)}}$$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right.$$

$$\left.+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]+V(r)\,RY = E\,RY$$

$\Downarrow$ DIVIDE BY RY

$\times\left(-\frac{2mr^2}{\hbar^2}\right)$

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

$$+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0$$

FIRST $\{\ \}$ DEPENDS ONLY ON r

SECOND $\{\ \}$ DEPENDS ONLY ON θ, ϕ

$\Downarrow$

EACH $\{\ \}$ IS CONSTANT

$\downarrow$

DENOTE BY $\ell(\ell+1)$

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

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

1° EQ: RADIAL EQ.

2° EQ: ANGULAR EQ.

• ANGULAR EQUATION

$$\boxed{\sin\theta\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-\ell(\ell+1)\sin^2\theta\, Y}$$

SOLUTION: TRY SEPARATION OF VARIABLES

$$Y(\theta,\phi)=\Theta(\theta)\,\Phi(\phi)$$

$$\underbrace{\left\{\frac{1}{\Theta}\sin\theta\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right)+\ell(\ell+1)\sin^2\theta\right\}}_{\text{DEPENDS ONLY ON }\theta}+\underbrace{\frac{1}{\Phi}\,\frac{\partial^2\Phi}{\partial\phi^2}}_{\text{DEPENDS ONLY ON }\phi}=0$$

$$\boxed{\frac{1}{\Theta}\sin\theta\,\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right)+\ell(\ell+1)\sin^2\theta=m^2}$$

$$\boxed{\frac{1}{\Phi}\,\frac{\partial^2\Phi}{\partial\phi^2}=-m^2}$$

↳ ϕ EQUATION:

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi$$

$$\boxed{\Phi(\phi) = e^{im\phi}}$$

m CAN BE BOTH POSITIVE & NEGATIVE

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

SAME PHYSICAL POINT IN SPACE

$$\Downarrow$$

$$e^{im2\pi} = 1$$

$$\Downarrow$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

INTEGER

↳ θ EQUATION

$$\boxed{\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[\ell(\ell+1)\sin^2\theta - m^2\right]\Theta = 0}$$

$$\Downarrow$$

TURN THIS INTO EQ. FOR $X = \cos\theta$

$$\frac{d}{d\theta} = \frac{dx}{d\theta} \cdot \frac{d}{dx} = -\sin\theta \frac{d}{dx}$$

ANGULAR EQ. BECOMES

$$-\sin^2\theta \frac{d}{dx}\left(-\sin^2\theta \frac{d\Theta}{dx}\right) + \left[\ell(\ell+1)\sin^2\theta - m^2\right]\Theta = 0$$

$\Downarrow \qquad \sin^2\theta = 1 - x^2$

$$(1-x^2)\frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + \left[\ell(\ell+1)(1-x^2) - m^2\right]\Theta = 0$$

$\Downarrow$

$$(1-x^2)^2 \frac{d^2\Theta}{dx^2} - 2x(1-x^2)\frac{d\Theta}{dx} + \left[\ell(\ell+1)(1-x^2) - m^2\right]\Theta = 0$$

$\Downarrow$ DIVIDE BY $(1-x^2)$

$$\boxed{(1-x^2)\frac{d^2\Theta}{dx^2} - 2x\frac{d\Theta}{dx} + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right]\Theta = 0}$$

↳ SOLUTIONS ARE ASSOCIATED LEGENDRE FUNCTIONS

$$\Theta(\theta) = A\, P_\ell^m(\cos\theta)$$

↳ ASSOCIATED LEGENDRE FUNCTIONS

$$\boxed{P_\ell^m(x) \equiv (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_\ell(x)}$$

WITH $P_\ell(x)$: LEGENDRE FUNCTIONS (POLYNOMIAL)

NOTE $P_\ell^0(x) = P_\ell(x)$

LEGENDRE POLYNOMIALS ARE DEFINED BY RODRIGUES FORMULA

$$\boxed{P_\ell(x) \equiv \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2-1)^\ell}$$

ℓ IS POSITIVE INTEGER

$\ell = 0, 1, 2, \ldots$

↳ SPECIAL CASES : P_ℓ

$$P_0(x) = 1$$

$$P_1(x) = \frac{1}{2} \frac{d}{dx} (x^2-1) = x$$

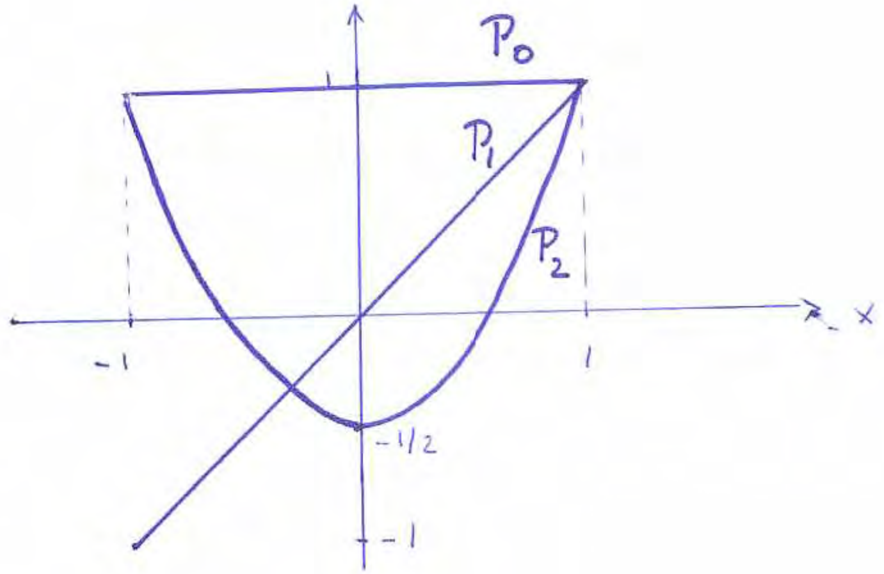
$$P_2(x) = \frac{1}{4.2} \frac{d^2}{dx^2} (x^2-1)^2 = \frac{1}{2} \frac{d}{dx} \left((x^2-1) \; x \right)$$

$$= \frac{1}{2} (3x^2-1)$$

⇝ IN GENERAL $P_\ell(x)$ IS POLYNOMIAL OF DEGREE ℓ IN x

⇝ ℓ EVEN → P_ℓ IS EVEN FUNCTION IN x

ℓ ODD → P_ℓ IS ODD FUNCTION IN x



SPECIAL CASES : P_ℓ^m

FOR ANY $\ell \Rightarrow (2\ell+1)$ POSSIBLE VALUES OF m

$$m = -\ell, -\ell+1, \dots, 0, 1, \dots \ell-1, \ell$$

- $P_0^0 = 1$
- $P_1^m = \left(\sqrt{1-x^2}\right)^m \dfrac{d^m}{dx^m} P_1(x) = \left(\sqrt{1-x^2}\right)^m \dfrac{d^m}{dx^m} x$

$$\rightsquigarrow \quad P_1^0 = x$$

$$\rightsquigarrow \quad P_1^1 = \sqrt{1-x^2}$$

- $P_2^0 = P_2 = \frac{1}{2}\left(3x^2-1\right)$

$m \neq 0 \quad P_2^m = \left(1-x^2\right)^{\frac{m}{2}} \dfrac{d^m}{dx^m} \quad \dfrac{1}{2}\left(3x^2-1\right)$

$\rightsquigarrow P_2^1(x) = \sqrt{1-x^2}\; 3x$

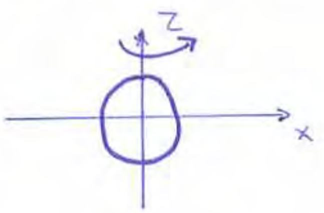
$\rightsquigarrow P_2^2(x) = 3(1-x^2)$

FOR m ODD P_ℓ^m IS POLYNOMIAL MULTIPLIED BY $\sqrt{1-x^2}$

FOR m EVEN P_ℓ^m IS POLYNOMIAL.

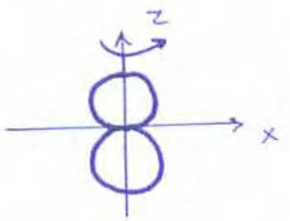
PLOT MAGNITUDE OF FUNCTION $P_\ell^m(\cos\theta)$ AT THE DIRECTION θ (ANGULAR PLOT)

$P_0^0 = 1$

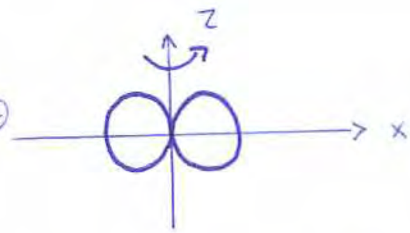


SPHERE

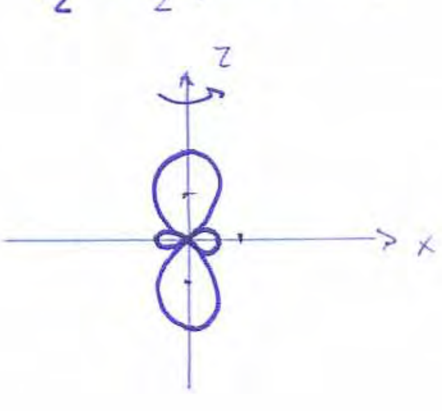
$P_1^0 = \cos\theta$



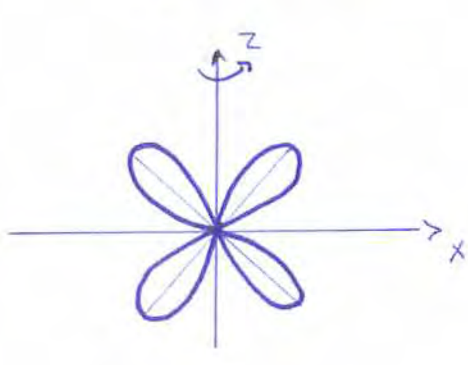
$P_1^1 = \sin\theta$



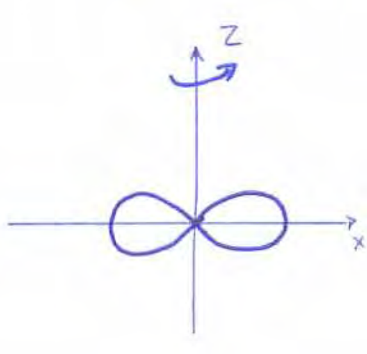
$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$



$P_2^1 = 3\sin\theta\cos\theta$



$P_2^2 = 3\sin^2\theta$



↳ NORMALIZATION

⇝ $\int d^3\bar{r}\ |\psi|^2 = 1$

⇝ $d^3\bar{r} = r^2 \sin\theta\ dr\ d\theta\ d\phi$

⇝ $\psi(\bar{r}) = R(r)\, Y(\theta,\phi)$

$$\int dr\ r^2\ |R(r)|^2 \int d\phi\ d\theta \sin\theta\ |Y(\theta,\phi)|^2 = 1$$

CONVENIENT CHOICE TO NORMALIZE R & Y SEPARATELY

$$\boxed{\begin{aligned} &\int_0^\infty dr\ r^2\ |R(r)|^2 = 1 \\ &\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\ |Y(\theta,\phi)|^2 = 1 \end{aligned}}$$

$$Y(\theta,\phi) = Y_{\ell m}(\theta,\phi) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi\ (\ell+m)!}}\ e^{im\phi}\, P_\ell^m(\cos\theta)$$

↳ $m \geq 0$

SPHERICAL HARMONICS

$$Y_{\ell\,-m}(\theta,\phi) = (-1)^m\, Y_{\ell m}^*(\theta,\phi)$$

RADIAL EQUATION

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

CHANGE OF VARIABLES

$$U(r) \equiv r R(r)$$

$$R = \frac{U}{r}$$

$$\frac{dR}{dr} = \frac{1}{r^2}\left(r \frac{dU}{dr} - U\right)$$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = \cancel{\frac{dU}{dr}} + r \frac{d^2U}{dr^2} - \cancel{\frac{dU}{dr}}$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2U}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{V_{eff}} U = E U}$$

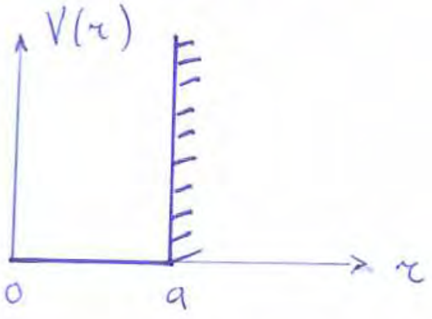
V_{eff} EFFECTIVE POT.

$\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ REPULSIVE CENTRIFUGAL POT.

GROWS FOR LARGER ℓ

NORMALIZATION : $\boxed{\int_0^\infty dr \, |U(r)|^2 = 1}$

↳ INFINITE SPHERICAL WELL



PARTICLE CONFINED IN SPHERE OF RADIUS a

∴ SOLVE SCHRÖDINGER EQ. FOR W.F. & EIGENVALUES

$r \geq a: \quad U(r) = 0$

$r < a: \quad -\frac{\hbar^2}{2m}\frac{d^2U}{dr^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}U = EU$

$$\boxed{E \equiv \frac{\hbar^2 k^2}{2m}} \qquad \boxed{\frac{d^2U}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right]U}$$

• $\ell = 0$ $\qquad \frac{d^2U}{dr^2} = -k^2 U$

$\Downarrow$

$U(r) = A\sin(kr) + B\cdot\cos(kr)$

$R = \frac{1}{r}U$!

$R(r=0)$ FINITE $\Rightarrow B = 0$

$R(r=a) = 0 \Rightarrow k = \frac{n\pi}{a}$

$$\therefore \boxed{R(r) = \frac{A}{r}\sin\left(\frac{n\pi}{a}r\right)} \qquad \boxed{E_{n0} = \frac{\hbar^2 n^2 \pi^2}{2m\,a^2}}$$

$\uparrow$ $\ell = 0$

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

NORMALIZE

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

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

$$\Downarrow$$

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

$\therefore$ ANGULAR PART $\quad \ell = 0, \quad m = 0$

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \qquad \left(\text{INDEED} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, \frac{1}{4\pi} = 1 \right)$$

$$\psi_{n\ell m} \rightarrow \boxed{\psi_{n00}(\bar{r}) = \sqrt{\frac{1}{2\pi a}} \, \frac{1}{r} \sin\left(\frac{n\pi}{a} r\right)}$$

- SOLUTION FOR ARBITRARY ℓ.

$$\rightsquigarrow \quad U(r) = A r\, j_\ell(kr) + B r\, n_\ell(kr)$$

$j_\ell(x)$: SPHERICAL BESSEL FUNCTION OF ORDER ℓ

$n_\ell(x)$: SPHERICAL NEUMANN FUNCTION OF ORDER ℓ

$$\rightsquigarrow \quad \boxed{\begin{aligned} j_\ell(x) &= (-1)^\ell x^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x} \\ n_\ell(x) &= -(-1)^\ell x^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x} \end{aligned}}$$

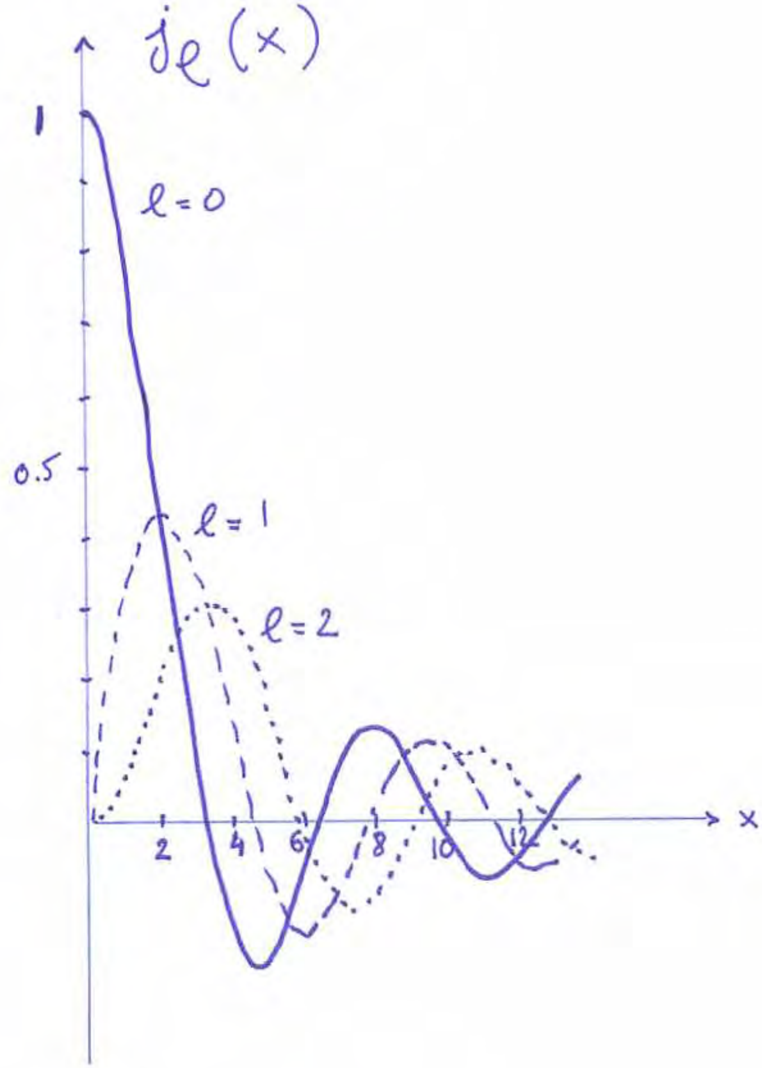
$$\rightsquigarrow \quad j_0(x) = \frac{\sin x}{x}$$

$$j_1(x) = -x\left(\frac{1}{x}\frac{d}{dx}\right)\frac{\sin x}{x}$$

$$= \frac{\sin x}{x^2} - \frac{\cos x}{x}$$

$$j_2(x) = x^2\left(\frac{1}{x}\frac{d}{dx}\right)^2 \frac{\sin x}{x}$$

$$= x^2\left(\frac{1}{x}\frac{d}{dx}\right)\left(-\frac{\sin x}{x^3} + \frac{\cos x}{x^2}\right) = \frac{3\sin x - 3x\cos x - x^2 \sin x}{x^3}$$



$$n_0(x) = -\frac{\cos x}{x}$$

$$n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

$$n_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3}{x^2}\sin x.$$

NOTE $n_\ell(x) \xrightarrow[x \to 0]{} \infty \implies B = 0$

⇝ CHOOSE k SUCH THAT

$$\underline{\underline{j_\ell(ka) = 0}}$$

⇓

ZEROES OF BESSEL FUNCTIONS.

$$\boxed{k = \frac{1}{a}\beta_{n\ell}}$$

n-th ZERO OF BESSEL FUNCTION ℓ.

$$\boxed{E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2}$$

EACH LEVEL $n\ell$
IS $(2\ell+1)$ FOLD DEGENERATE
$\forall \ell \Rightarrow m = -\ell, \dots, 0, \dots, \ell$

$$\therefore \boxed{\psi_{n\ell m}(\bar{r}) = A_{n\ell}\, j_\ell\left(\beta_{n\ell}\frac{r}{a}\right) Y_{\ell m}(\theta,\phi)}$$

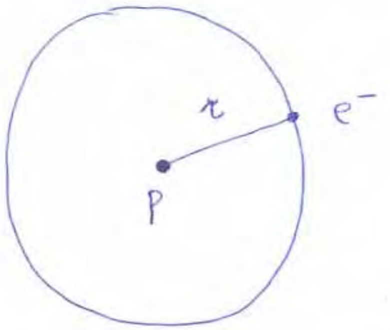
NORMALIZATION.

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

⇒ HYDROGEN ATOM

- COULOMB POTENTIAL

↳



POTENTIAL ENERGY :

$$\boxed{V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}}$$

ε_0 : PERMITTIVITY OF SPACE

$$\varepsilon_0 \simeq 8.854 \; 10^{-12} \; \frac{C^2}{J\,m}$$

↳ RADIAL EQ.

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu}$$

- **RADIAL WAVE FUNCTION** (FOR BOUND STATES)

↳ $$\boxed{K \equiv \frac{\sqrt{-2mE}}{\hbar}} \qquad E = -\frac{\hbar^2 K^2}{2m}$$

$$\frac{1}{K^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\varepsilon_0\hbar^2}\frac{1}{K^2 r} + \frac{\ell(\ell+1)}{K^2 r^2}\right]u$$

⇓ USE $\boxed{\rho \equiv Kr}$

$$\boxed{\rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2 K}}$$

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

↳ **ASYMPTOTIC BEHAVIOR** $r \to \infty$, $\rho \to \infty$

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

⇓

$$u(\rho) = Ae^{-\rho} + \cancel{Be^{\rho}}$$

BLOWS UP FOR $\rho \to \infty$

↳ BEHAVIOR FOR $r \to 0$

$\frac{1}{\rho^2}$ TERM DOMINATES

$$\frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

$$\Downarrow$$

$$u(\rho) = C \rho^{\ell+1} + \cancel{D \rho^{-\ell}}$$

BLOWS UP FOR $\rho \to 0$

$\therefore$ CONVENIENT TO TAKE OUT BEHAVIORS OF SOLUTION FOR $\rho \to \infty$ & $\rho \to 0$

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

$$\frac{du}{d\rho} = \rho^{\ell} e^{-\rho} \left[(\ell + 1 - \rho) v + \rho \frac{dv}{d\rho} \right]$$

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

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

↳ WRITE SOLUTION AS POWER SERIES IN ρ

$$\boxed{v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j}$$

⇓

DETERMINE COEFFICIENTS

$$\frac{dv}{d\rho} = \sum_{j=1}^{\infty} j\, c_j\, \rho^{j-1} = \sum_{j=0}^{\infty} (j+1)\, c_{j+1}\, \rho^j$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=\cancel{1}\,0}^{\infty} j(j+1)\, c_{j+1}\, \rho^{j-1}$$

$$\leadsto \rho \sum_{j=0}^{\infty} j(j+1)\, c_{j+1}\, \rho^{j-1}$$

$$+ \; 2(\ell+1-\rho) \sum_{j=0}^{\infty} (j+1)\, c_{j+1}\, \rho^j$$

$$+ \; \left[\rho_0 - 2(\ell+1)\right] \sum_{j=0}^{\infty} c_j\, \rho^j = 0$$

⇓

EQUATING COEFFICIENT OF POWER ρ^j

$$\boxed{\begin{gathered} j(j+1)\, c_{j+1} + 2(\ell+1)(j+1)\, c_{j+1} \\ - 2j\, c_j + [\rho_0 - 2(\ell+1)]\, c_j = 0 \end{gathered}}$$

$$\Downarrow$$

$$\boxed{c_{j+1} = \frac{[2(j+\ell+1) - \rho_0]}{(j+1)(j+2\ell+2)}\, c_j}$$

↳ SOLVE RECURSIVELY STARTING FROM c_0

↳ FOR $j \gg$ (i.e. SOLUTION FOR LARGE ρ)

$$c_{j+1} \simeq \frac{2j}{j(j+1)}\, c_j = \frac{2}{j+1}\, c_j$$

$$\downarrow$$

$$c_j = \frac{2^j}{j!}\, c_0$$

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0\, e^{2\rho}$$

$$\downarrow$$

$$u(\rho) = c_0\, \rho^{\ell+1} e^{\rho}$$

BLOWS UP !

↳ PHYSICAL SOLUTIONS ONLY CORRESPOND WITH A SERIES WHICH <u>TERMINATES</u> !

SUPPOSE MAX VALUE OF j IS j_{max}

$$c_{j_{max}+1} = 0$$

$$2(j_{max} + l + 1) - \rho_0 = 0$$

DEFINE $\boxed{n \equiv j_{max} + l + 1}$

↳ PRINCIPAL QUANTUM NUMBER (INTEGER)

$$\boxed{\rho_0 = 2n}$$

$$\Downarrow$$

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{\hbar^2}{2m} \frac{m^2 e^4}{(2\pi\varepsilon_0)^2 \hbar^4 \rho_0^2}$$

$$= -\frac{m e^4}{8\pi^2 \varepsilon_0^2 \hbar^2 4n^2}$$

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \equiv \frac{E_1}{n^2}}$$

BOHR'S FORMULA

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

$$\boxed{\begin{aligned} E_1 &= -\left[\frac{m}{2} \frac{1}{\hbar^2} \left(\frac{e^2}{4\pi \varepsilon_0} \right)^2 \right] \\ &= -13.6 \ eV \end{aligned}}$$

BINDING ENERGY OF GROUND STATE LEVEL OF HYDROGEN ATOM

$$\begin{cases} \rho_0 = \dfrac{m e^2}{2\pi \varepsilon_0 \hbar^2 K} \\ \rho_0 = 2n \end{cases}$$

$$\boxed{K = \left(\frac{m e^2}{4\pi \varepsilon_0 \hbar^2} \right) \frac{1}{n} \equiv \frac{1}{a n}}$$

$$\boxed{a \equiv \frac{4\pi \varepsilon_0 \hbar^2}{m e^2} = 0.529 \ 10^{-10} \ m}$$

BOHR RADIUS

$$\rho = K r = \frac{r}{a} \frac{1}{n}$$

$$\boxed{c_{j+1} = \frac{2(j + \ell + 1 - n)}{(j+1)(j + 2\ell + 2)} c_j}$$

GROUND STATE $n = 1$

$$n = j_{max} + \ell + 1$$

$$\Downarrow$$

$$n = 1 \iff j_{max} = 0 \;,\; \ell = 0$$

$$U_{n\ell}(r) = U_{10}(r) = c_0 \left(\frac{r}{a}\right) e^{-r/a}$$

$$R_{10}(r) = \frac{U_{10}(r)}{r} = \frac{c_0}{a} e^{-r/a}$$

$$\int_0^\infty dr\, r^2 \, |R_{10}(r)|^2 = 1 \qquad \text{NORMALIZATION}$$

$$\Downarrow$$

$$1 = \frac{|c_0|^2}{a^2} \int_0^\infty dr\, r^2 e^{-2r/a} = |c_0|^2 \frac{a}{8} \underbrace{\int_0^\infty dx\, x^2 e^{-x}}_{2}$$

$$\Downarrow$$

$$c_0 = \frac{2}{\sqrt{a}}$$

$$\therefore \boxed{\psi_{n\ell m}(\vec{r}) \Rightarrow \psi_{100}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \cdot \frac{2}{\sqrt{a}} \frac{1}{a} e^{-r/a}}$$

↳ FIRST EXCITED STATE $n = 2$

$$E_2 = -\frac{13.6\ eV}{4} = -3.4\ eV$$

$$n = j_{max} + \ell + 1$$

$$n = 2 \iff j_{max} + \ell = 1$$

2 POSSIBLE VALUES OF ℓ

$$\ell = 0 \rightarrow j_{max} = 1$$

$$\ell = 1 \rightarrow j_{max} = 0$$

- $\ell = 0$ $\quad R_{20}(r) = \frac{1}{r}\left(\frac{r}{2a}\right) \cdot e^{-r/2a} c_0 \left(1 - \frac{r}{2a}\right)$

$c_1 = -c_0$

$$\boxed{R_{20}(r) = \frac{c_0}{2a}\left(1 - \frac{r}{2a}\right) e^{-r/2a}}$$

- $\ell = 1$ $\quad R_{21}(r) = \frac{1}{r}\left(\frac{r}{2a}\right)^2 e^{-r/2a} \cdot c_0$

$$\boxed{R_{21}(r) = \frac{c_0}{4a^2}\, r\, e^{-r/2a}}$$

↳ ARBITRARY n

$$n = j_{max} + \ell + 1$$

$$\downarrow$$

$$\ell = n - 1 - j_{max}$$

POSSIBLE VALUES OF $\ell = 0, 1, \ldots, n-1$

FOR EACH ℓ : $(2\ell + 1)$ VALUES OF m

- DEGENERACY OF EACH LEVEL n

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

- POLYNOMIAL $v(\rho)$

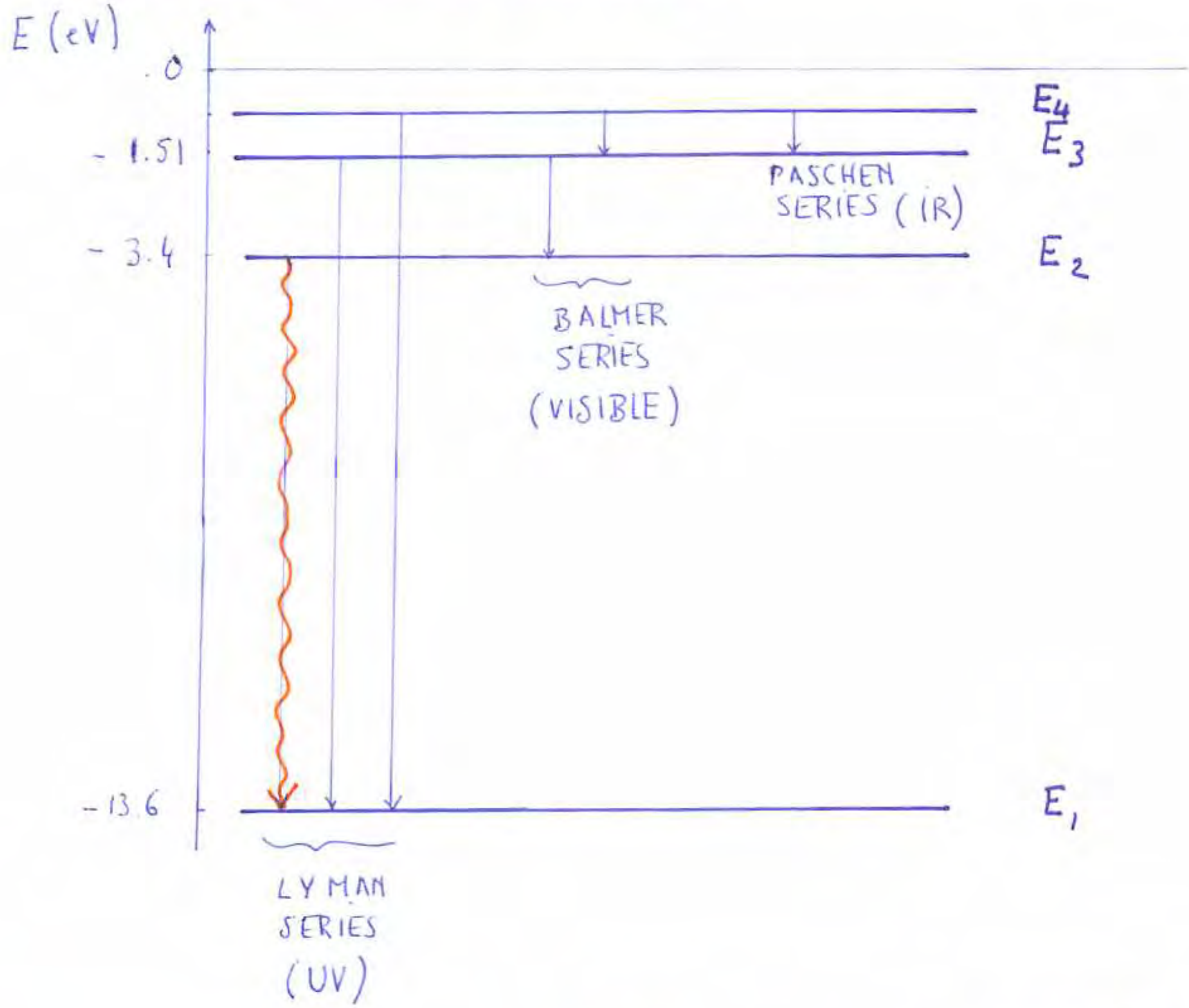
IS A SO-CALLED ASSOCIATED LAGUERRE POLYNOMIAL

$$v(\rho) \equiv L^{2\ell+1}_{n-\ell-1}(2\rho)$$

$$L^{p}_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

LAGUERRE $\longrightarrow$ $$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

SPECTRUM OF HYDROGEN



PHOTON IS EMITTED WHEN e^- FALLS INTO DEEPER BOUND STATE

PHOTON IS ABSORBED WHEN e^- IS EXCITED

↳ ENERGY IS CONSERVED

∴ PHOTON HAS TO TAKE THE DIFFERENCE IN ENERGY

TRANSITION FROM $E_i > E_f$

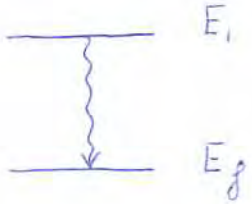
$\Downarrow$

$$E_\gamma = E_i - E_f$$

$$= (-13.6\ \text{eV}) \cdot \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

↳ PLANCK's FORMULA

$$\begin{cases} E_\gamma = h\nu \\ \dfrac{1}{\lambda} = \dfrac{\nu}{c} \end{cases} \qquad (\lambda \nu = c)$$



$$\longrightarrow \quad \frac{1}{\lambda} = \frac{1}{hc} E_\gamma$$

$$= \frac{(-E_1)}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\downarrow \qquad -E_1 = \frac{m}{2} \left(\frac{e^2}{4\pi \varepsilon_0} \right)^2 \frac{1}{\hbar^2}$$

$$\boxed{\frac{1}{\lambda} = \underbrace{\left[\frac{m}{4\pi c \hbar^3} \cdot \left(\frac{e^2}{4\pi \varepsilon_0} \right)^2 \right]}_{R\text{ : RYDBERG CONSTANT}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)}$$

$$R = 1.097\ 10^7\ m^{-1}$$

⇒ 4.3 ANGULAR MOMENTUM

- DEFINITIONS

↳ CLASSICAL

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

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

↳ QUANTUM

$$p_x \to -i\hbar \frac{\partial}{\partial x}$$

$$p_y \to -i\hbar \frac{\partial}{\partial y}$$

$$p_z \to -i\hbar \frac{\partial}{\partial z}$$

- EIGENVALUES OF ANGULAR MOMENTUM OPERATOR

↳ $[L_x, L_y] = [y p_z - z p_y, z p_x - x p_z]$

$$= [y p_z, z p_x] - [y p_z, x p_z] - [z p_y, z p_x] + [z p_y, x p_z]$$

$$= y p_x \underbrace{[p_z, z]}_{-i\hbar} - 0 - 0 + x p_y \underbrace{[z, p_z]}_{i\hbar}$$

$$= i\hbar (x p_y - y p_x) = i\hbar L_z$$

$$\therefore \quad \begin{aligned} [L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y \end{aligned}$$

$\hookrightarrow$ L_x, L_y, L_z ARE INCOMPATIBLE OBSERVABLES

GEN. UNCERTAINTY RELATION

$$\sigma_A^2 \, \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

$$\sigma_{L_x}^2 \, \sigma_{L_y}^2 \geq \frac{\hbar^2}{4} \langle L_z \rangle^2$$

NO EIGENSTATES OF BOTH L_x & L_y

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

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y \\ &\quad + L_z [L_z, L_x] + [L_z, L_x] L_z \end{aligned}$$

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

$$= 0$$

$$\therefore \quad \left\| \begin{array}{l} [L^2, L_x] = 0 \\ [L^2, L_y] = 0 \\ [L^2, L_z] = 0 \end{array} \right.$$

$\therefore$ SIMULTANEOUS EIGENSTATES OF e.g. L^2 AND L_z DO EXIST

↳ LADDER OPERATORS

$$L_\pm = L_x \pm i L_y$$

$$[L_z, L_\pm] = \underbrace{[L_z, L_x]}_{i\hbar L_y} \pm i \underbrace{[L_z, L_y]}_{(-i\hbar) L_x}$$

$$= \pm \hbar (L_x \pm i L_y)$$

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

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

$\rightsquigarrow$ IF f IS EIGENFUNCTION OF L^2, L_z

$$\Downarrow$$

$L_\pm f$ IS ALSO EIGENFUNCTION OF L^2, L_z

$$\left\| \begin{aligned} L^2 f &\equiv \lambda f \\ L_z f &\equiv \mu f \end{aligned} \right.$$

λ, μ : EIGENVALUES

$\hookrightarrow$ $L^2 (L_\pm f) = L_\pm (L^2 f) = \lambda (L_\pm f)$

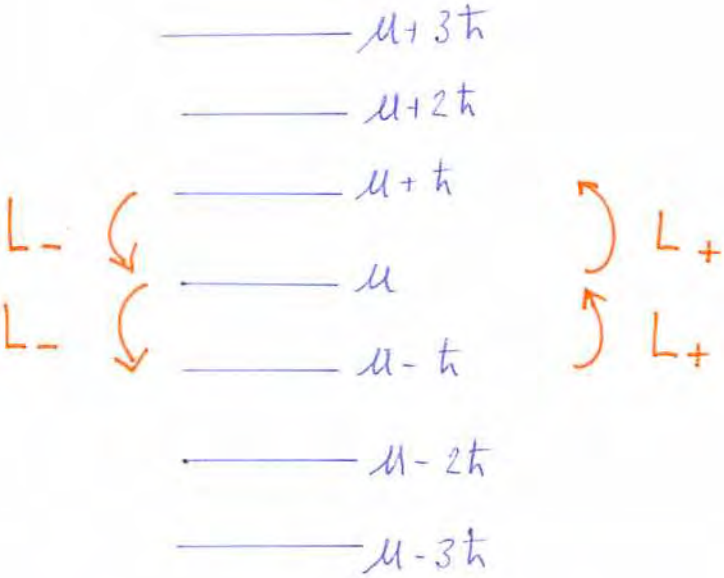
SAME EIGENVALUE

$\hookrightarrow$ $L_z (L_\pm f) = L_\pm \underbrace{L_z f}_{\mu f} \pm \hbar L_\pm f$

$$= (\mu \pm \hbar)(L_\pm f)$$

$L_\pm f$ IS EIGENFUNCTION OF L_z

WITH EIGENVALUE $\mu \pm \hbar$



MAX. VALUE OF L_z (GIVEN BY TOTAL ANG. MOMENTUM)

$$L_+ \, f_{top} = 0$$

MIN VALUE OF L_z

$$L_- \, f_{bottom} = 0$$

DEFINE $\quad L_z \, f_{top} = (\hbar \ell) \, f_{top}$

↳ EIGENVALUE OF TOP STATE

$$L_z \, f_{bottom} = (\hbar \bar{\ell}) \, f_{bottom}$$

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 + L_y^2 \mp i \underbrace{(L_x L_y - L_y L_x)}_{i\hbar L_z}$$

$$= L^2 - L_z^2 \mp i (i\hbar L_z)$$

$$\underline{\underline{L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z}}$$

$$\rightsquigarrow \quad L^2 f_{top} = \lambda f_{top}$$

$$= (L_- L_+ + L_z^2 + \hbar L_z) f_{top}$$

$$= (0 + \hbar^2 \ell^2 + \hbar^2 \ell) f_{top}$$

$$= \hbar^2 \ell(\ell + 1) f_{top}$$

$$\boxed{\lambda = \hbar^2 \ell(\ell+1)}$$

EIGENVALUE OF L^2

$$\rightsquigarrow \quad L^2 f_{bottom} = \lambda f_{bottom}$$

$$= \left(L_+ L_- + L_z^2 - \hbar L_z \right) f_{bottom}$$

$$= \hbar^2 \bar{\ell} (\bar{\ell} - 1) f_{bottom}$$

$$\lambda = \hbar^2 \bar{\ell} (\bar{\ell} - 1)$$

$$\ell (\ell + 1) = \bar{\ell} (\bar{\ell} - 1)$$

$$\Downarrow$$

$\cancel{\bar{\ell} = \ell + 1}$ NOT POSSIBLE $\bar{\ell} < \ell$

$\bar{\ell} = -\ell$ 2ℓ IS INTEGER

$\hookrightarrow \ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$

DENOTE EIGENVALUE OF L_z : $\mu = \hbar m$

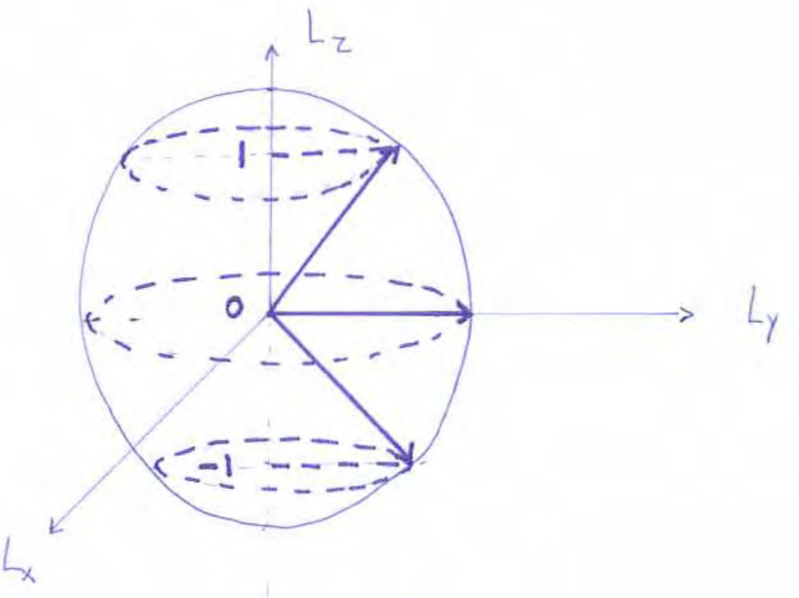
$m = -\ell, \ldots, +\ell$ (LADDER)

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

$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$; $m = -\ell, \ldots, \ell$

EXAMPLE $\ell = 1$

MAGNITUDE OF ANGULAR MOM: $\sqrt{\ell(\ell+1)} = \sqrt{2} \simeq 1.4$



- EIGENFUNCTIONS OF L^2, L_z

$$\bar{L} = -i\hbar\, \bar{r} \times \bar{\nabla}$$

$$\bar{r} = r\, \hat{e}_r$$

$$\bar{\nabla} = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

$$\hat{e}_r \times \hat{e}_\theta = \hat{e}_\phi$$

$$\hat{e}_r \times \hat{e}_\phi = -\hat{e}_\theta$$

$$\hookrightarrow \boxed{\bar{L} = -i\hbar \left(\hat{e}_\phi \frac{\partial}{\partial \theta} - \hat{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial \phi} \right)}$$

EXPRESS $\hat{e}_\phi$, $\hat{e}_\theta$ IN $\hat{\imath}, \hat{\jmath}, \hat{k}$

$\downarrow$

$\rightsquigarrow$ READ OFF L_x, L_y, L_z

$\rightsquigarrow$ CONSTRUCT L_z, $L^2 = L_x^2 + L_y^2 + L_z^2$

$\rightsquigarrow$ VERIFY

$$\left\| \begin{aligned} L_z f_\ell^m &= \hbar m f_\ell^m \\ L^2 f_\ell^m &= \hbar^2 \ell(\ell+1) f_\ell^m \end{aligned} \right.$$

$$\Downarrow$$

$$\boxed{f_\ell^m(\theta,\phi) = Y_{\ell m}(\theta,\phi)}$$

SPIN

⇒ INTRODUCTION

- ORBITAL ANGULAR MOMENTUM L

  ↳ EIGENSTATES $| \ell m \rangle$ (IN KET NOTATION)

  ↳ $L^2 |\ell m\rangle = \hbar^2 \ell(\ell+1) |\ell m\rangle$

  ↳ $L_z |\ell m\rangle = \hbar m |\ell m$

  ↳ $\ell = 0, 1, 2, \dots$ INTEGER VALUES !

  $m = -\ell, \dots, +\ell$ ($2\ell+1$ values)

  ↳ $L_\pm |\ell m\rangle = \hbar \sqrt{\ell(\ell+1) - m(m\pm 1)}\, |\ell\, m\pm 1\rangle$ (HW)

- INTRINSIC ANGULAR MOMENTUM S (SPIN)

  ↳ SATISFIES SAME ALGEBRA

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

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

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

↳ S CAN HAVE BOTH ↗ INTEGER ↘ HALF INTEGER VALUES

EIGENSTATES $|s\, s_z\rangle$

$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$

$s_z = -s, \ldots, +s$

↳ $S^2 |s\, s_z\rangle = \hbar^2 s(s+1)\, |s\, s_z\rangle$

↳ $S_z |s\, s_z\rangle = \hbar\, s_z\, |s\, s_z\rangle$

↳ SPIN IS AN <u>INTRINSIC</u> PROPERTY OF PARTICLE

VISIBLE MATTER IN UNIVERSE IS COMPOSED OF PARTICLES OF SPIN 1/2

↗ LEPTONS (ELECTRON, MUON, TAU)

↘ QUARKS (COME IN 6 'FLAVORS' UP, DOWN, STRANGE, CHARM, BOTTOM, TOP)

↓

MAKE UP PROTONS, NEUTRONS

$\Rightarrow$ SPIN 1/2

- EIGENSTATES $\quad s_z = \pm \frac{1}{2}$

$$|\tfrac{1}{2}\ +\tfrac{1}{2}\rangle \qquad (\uparrow \quad \text{SPIN UP})$$

$$|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle \qquad (\downarrow \quad \text{SPIN DOWN})$$

IN COLUMN VECTOR NOTATION

$$|\tfrac{1}{2}\ +\tfrac{1}{2}\rangle \iff \chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle \iff \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- SPIN OPERATOR IN MATRIX NOTATION

$$\leadsto \quad S^2 \chi_\uparrow = \hbar^2 \frac{3}{4} \chi_\uparrow$$

$$S^2 \chi_\downarrow = \hbar^2 \frac{3}{4} \chi_\downarrow$$

$$S^2 = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad 2 \times 2 \quad \text{MATRIX.}$$

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar^2 \frac{3}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\hookrightarrow \quad \begin{pmatrix} a \\ c \end{pmatrix} = \hbar^2 \frac{3}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar^2 \frac{3}{4} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\hookrightarrow \quad \begin{pmatrix} b \\ d \end{pmatrix} = \hbar^2 \frac{3}{4} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\therefore \quad \boxed{S^2 = \hbar^2 \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}$$

$$\leadsto \quad S_z \chi_\uparrow = \hbar \frac{1}{2} \chi_\uparrow$$

$$S_z \chi_\downarrow = - \hbar \frac{1}{2} \chi_\downarrow$$

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

$$\leadsto \quad S_\pm \, | s \, s_z \rangle = \hbar \sqrt{s(s+1) - s_z(s_z \pm 1)} \; | s \; s_z \pm 1 \rangle$$

$$S_+ \chi_\uparrow = 0$$

$$S_+ \chi_\downarrow = \hbar \sqrt{\frac{3}{4} + \frac{1}{4}} \; \chi_\uparrow = \hbar \chi_\uparrow$$

$$\Bigg\| \quad S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- \chi_\uparrow = \hbar \sqrt{\tfrac{3}{4} + \tfrac{1}{4}}\ \chi_\downarrow = \hbar\, \chi_\downarrow$$

$$S_- \chi_\downarrow = 0$$

$$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$\rightsquigarrow$ $$S_\pm = S_x \pm i S_y$$

$$S_x = \frac{1}{2}\left(S_+ + S_- \right)$$

$$S_y = -\frac{i}{2}\left(S_+ - S_- \right)$$

$$\boxed{S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}$$

$\rightsquigarrow$ NOTATION $\underline{\underline{\bar{S} = \frac{\hbar}{2}\,\bar{\sigma}}}$

$\bar{\sigma}\ (\sigma_x, \sigma_y, \sigma_z)$: PAULI SPIN MATRICES (HERMITIAN)

$$\boxed{\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

- GENERAL SPIN STATE

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix}$$

NORMALIZED $\quad |a|^2 + |b|^2 = 1 \qquad (\chi^+ \chi = 1)$

⇝ $|a|^2$: PROBABILITY TO FIND χ IN $\chi_\uparrow$ STATE

$|b|^2$: PROBABILITY TO FIND χ IN $\underbrace{\chi_\downarrow}_{\text{EIGENSTATES OF } S_z}$ STATE

⇝ WHAT ARE EIGENSTATES, EIGENVALUES OF S_x ?

$$S_x \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \lambda \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \lambda \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

EIGENVALUES $\quad \begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0$

$$\Downarrow$$

$$\lambda^2 = \left(\frac{\hbar}{2}\right)^2$$

$$\underline{\underline{\lambda = \pm \frac{\hbar}{2}}}$$

EIGENSTATES :

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\beta = \pm \alpha$$

$$S_x \chi_\uparrow^{(x)} = + \frac{\hbar}{2} \chi_\uparrow^{(x)} , \quad \chi_\uparrow^{(x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

NORMALIZED

$$S_x \chi_\downarrow^{(x)} = - \frac{\hbar}{2} \chi_\downarrow^{(x)} , \quad \chi_\downarrow^{(x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$\rightsquigarrow$ GENERAL SPINOR

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = \frac{a+b}{\sqrt{2}} \chi_\uparrow^{(x)} + \frac{a-b}{\sqrt{2}} \chi_\downarrow^{(x)}$$

$\frac{1}{2} |a+b|^2$: PROBABILITY TO FIND χ IN $\chi_\uparrow^{(x)}$ STATE

$\frac{1}{2} |a-b|^2$: PROBABILITY TO FIND χ IN $\chi_\downarrow^{(x)}$ STATE

- EXAMPLE : SPIN 1/2 PARTICLE IN SPIN STATE

$$\chi = \frac{1}{\sqrt{6}} \begin{pmatrix} 1+i \\ 2 \end{pmatrix}$$

DETERMINE PROBABILITIES OF MEASURING $+\frac{\hbar}{2}$ & $-\frac{\hbar}{2}$ FOR S_x AND S_z

↳ $\chi = \frac{1}{\sqrt{6}} (1+i)\, \chi_\uparrow + \frac{2}{\sqrt{6}} \chi_\downarrow$

$$P_\uparrow^{(z)} = \frac{1}{6} |1+i|^2 = \frac{1}{3}$$

$$P_\downarrow^{(z)} = \frac{4}{6} = \frac{2}{3}$$

↳ $\chi = \frac{1}{\sqrt{12}} (3+i)\, \chi_\uparrow^{(x)} + \frac{1}{\sqrt{12}} (-1+i)\, \chi_\downarrow^{(x)}$

$$P_\uparrow^{(x)} = \frac{1}{12} |3+i|^2 = \frac{10}{12} = \frac{5}{6}$$

$$P_\downarrow^{(x)} = \frac{1}{12} |-1+i|^2 = \frac{1}{6}$$

⇒ ELECTRON IN A MAGNETIC FIELD

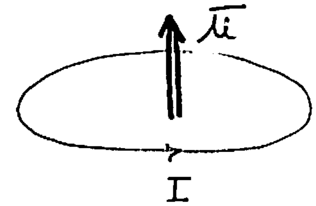
- PARTICLE WITH SPIN IS A MAGNETIC DIPOLE

↓

HAS A MAGNETIC MOMENT $\bar{\mu}$

$$\boxed{\bar{\mu} = \gamma \bar{S}}$$

cf. CURRENT LOOP



↓

PROPORTIONALITY CONSTANT :

GYROMAGNETIC RATIO.

- PLACE MAGNETIC DIPOLE IN EXTERNAL MAGNETIC FIELD $\bar{B}$

↓

INTERACTS SO AS TO ALIGN WITH $\bar{B}$

⇒ INTERACTION ENERGY (HAMILTONIAN)

$$\boxed{H = - \bar{\mu} \cdot \bar{B}}$$

IF $\bar{\mu} \parallel \bar{B}$: H IS MINIMAL $\bar{\mu} \Uparrow \uparrow \bar{B}$

$\bar{\mu}$ ANTI // $\bar{B}$: H IS MAXIMAL $\bar{\mu} \Downarrow \uparrow \bar{B}$

$$\boxed{H = - \gamma \bar{S} \cdot \bar{B}}$$

- LARMOR PRECESSION

↳ TAKE B ALONG z-AXIS . $\bar{B} = B_0\, \bar{e}_z$ ← CONSTANT

$$H = -\gamma B_0 S_z = -\gamma B_0 \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

↳ EIGENSTATES OF H ARE SAME AS S_z

$\chi_\uparrow \rightarrow$ EIGENVALUE $E_\uparrow = -\gamma B_0 \frac{\hbar}{2}$ LOWEST ENERGY

$\chi_\downarrow \rightarrow$ EIGENVALUE $E_\downarrow = +\gamma B_0 \frac{\hbar}{2}$

↳ H IS TIME-INDEPENDENT

$\therefore$ SOLUTION TO TIME DEP. SCHRÖDINGER EQ.

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

IS SUM OF STATIONARY STATES

$$\chi(t) = a\, \chi_\uparrow\, e^{-\frac{i}{\hbar} E_\uparrow t} + b\, \chi_\downarrow\, e^{-\frac{i}{\hbar} E_\downarrow t}$$

$$= \begin{pmatrix} a\, e^{\frac{i}{2}\gamma B_0 t} \\ b\, e^{-\frac{i}{2}\gamma B_0 t} \end{pmatrix}$$

$|a|^2 + |b|^2 = 1$ NORMALIZATION

a, b DETERMINED FROM INITIAL CONDITION

TAKE $a = \cos\frac{\alpha}{2}$

$b = \sin\frac{\alpha}{2}$

$$\boxed{\chi(t) = \begin{pmatrix} \cos\frac{\alpha}{2}\, e^{\frac{i}{2}\gamma B_0 t} \\ \sin\frac{\alpha}{2}\, e^{-\frac{i}{2}\gamma B_0 t} \end{pmatrix}}$$

↳ EXPECTATION VALUES OF S_x, S_y, S_z OVER TIME ?

$$\langle S_x \rangle = \frac{\hbar}{2} \chi^+(t) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \chi(t)$$

$$= \frac{\hbar}{2} \left[\cos\frac{\alpha}{2}\, e^{-\frac{i}{2}\gamma B_0 t} \quad \sin\frac{\alpha}{2}\, e^{\frac{i}{2}\gamma B_0 t} \right] \begin{bmatrix} \sin\frac{\alpha}{2}\, e^{-\frac{i}{2}\gamma B_0 t} \\ \cos\frac{\alpha}{2}\, e^{+\frac{i}{2}\gamma B_0 t} \end{bmatrix}$$

$$= \frac{\hbar}{2} \cdot \sin\frac{\alpha}{2} \cos\frac{\alpha}{2} \underbrace{\left(e^{-i\gamma B_0 t} + e^{i\gamma B_0 t} \right)}_{2\cos\gamma B_0 t}$$

$$\boxed{\langle S_x \rangle = \frac{\hbar}{2} \sin\alpha \cdot \cos(\gamma B_0 t)}$$

$$\langle S_y \rangle = \frac{\hbar}{2} \chi^{+}(t) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \chi(t)$$

$$= \frac{\hbar}{2} \sin\frac{\alpha}{2} \cos\frac{\alpha}{2} (-i) \underbrace{\left(e^{-i\gamma B_0 t} - e^{i\gamma B_0 t} \right)}_{-2i \sin \gamma B_0 t}$$

$$\boxed{\langle S_y \rangle = -\frac{\hbar}{2} \sin\alpha \, \sin(\gamma B_0 t)}$$

$$\langle S_z \rangle = \frac{\hbar}{2} \chi^{+}(t) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \chi(t)$$

$$= \frac{\hbar}{2} \left(\cos^2\frac{\alpha}{2} - \sin^2\frac{\alpha}{2} \right)$$

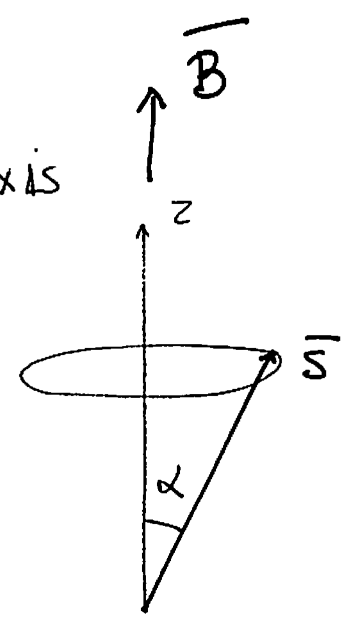
$$\boxed{\langle S_z \rangle = \frac{\hbar}{2} \cos\alpha}$$

$\langle \bar{S} \rangle$ MAKES AN ANGLE α w.r.t. z-AXIS

& PRECESSES AROUND z-AXIS

WITH ANGULAR FREQUENCY $\boxed{\omega = \gamma B_0}$

LARMOR PRECESSION



$\langle \bar{S} \rangle$ EVOLVES ACCORDING TO CLASSICAL EXPECTATIONS

• STERN - GERLACH EXPERIMENT

↳ e^- IN <u>IN</u>HOMOGENEOUS MAGN. FIELD

'POTENTIAL' $-\bar{\mu}\cdot\bar{B}$
ENERGY

GRADIENT OF POTENTIAL ENERGY

⇓

FORCE $\bar{F} = -\bar{\nabla} V$

FORCE ON MAGNETIC DIPOLE

$$\boxed{\bar{F} = \bar{\nabla}(\bar{\mu}\cdot\bar{B})}$$

$\bar{\mu}$ IS CONSTANT

(IF) $\bar{B}$ IS CONSTANT

↓

$\bar{F} = 0$

↳ $$\bar{B}(x,y,z) = -\alpha x\,\hat{e}_x + (\alpha z + B_0)\,\hat{e}_z$$

↑ UNIFORM

α SMALL

INHOMOGENEITY

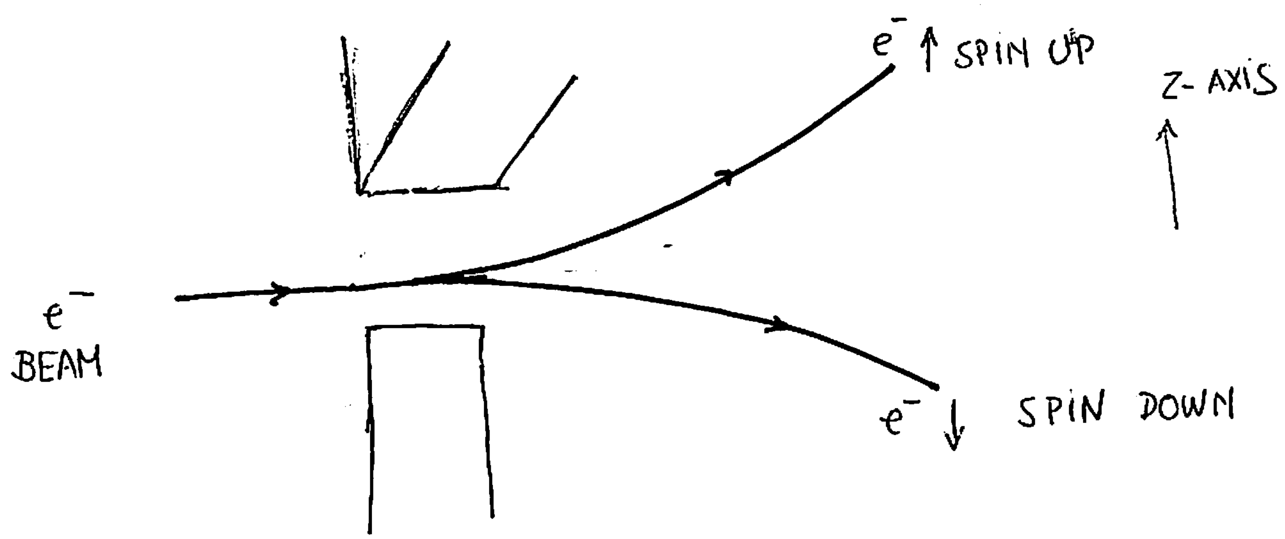
$$\bar{\mu}\cdot\bar{B} = -\alpha x\,\gamma S_x + (\alpha z + B_0)\,\gamma S_z$$

$$\boxed{\bar{F} = +\alpha\gamma\,(-S_x\,\hat{e}_x + S_z\,\hat{e}_z)}$$

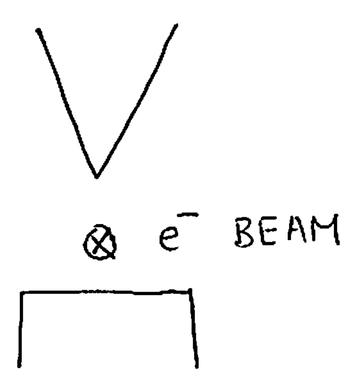
$\langle S_x \rangle$ AVERAGES TO 0 OVER TIME
DUE TO LARMOR PRECESSION
AROUND B_0

$\therefore$ NET FORCE $\underline{\underline{F_z = \alpha \gamma S_z}}$

DEPENDING OF $S_z = \pm \frac{\hbar}{2}$
THERE IS FORCE ON e^- WHICH PULLS IT IN
EITHER ONE OR THE OTHER DIRECTION



FRONT VIEW

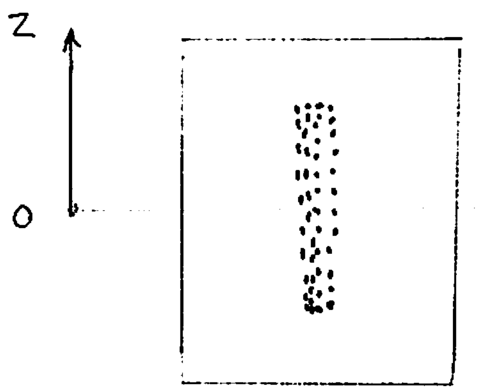


↳ EXPERIMENT DONE IN 1922 BY STERN & GERLACH (USING ATOMIC BEAMS) SILVER ATOMS

MEASURES z-COMPONENT OF SPIN !

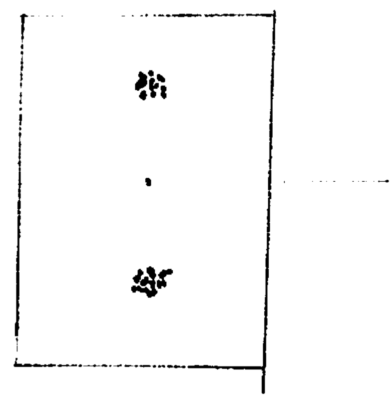
CLASSICAL MECHANICS

ALL e^- HAVE SAME $\bar{S}$ WITH RANDOM ORIENTATION



QUANTUM MECHANICS

ONLY 2 VALUES OF S_z ALLOWED



BEAM SPLITS IN 2

⇒ ADDITION OF ANGULAR MOMENTA

↳ 2 SPIN 1/2 PARTICLES

e.g. e^- SPIN 1/2
p SPIN 1/2 IN GROUND STATE ($n=1$, $\ell=0$) OF HYDROGEN ATOM
(PROTON)

4 POSSIBILITIES $\underset{e^-\ p}{\uparrow\uparrow}$, $\uparrow\downarrow$, $\downarrow\uparrow$, $\downarrow\downarrow$.

WHAT IS THE TOTAL ANGULAR MOMENTUM OF ATOM ?

$$\bar{S} = \underset{\substack{\uparrow \\ e^-\text{ SPIN}}}{\bar{S}_1} + \underset{\substack{\uparrow \\ p\text{ SPIN}}}{\bar{S}_2} \qquad \text{VECTOR ADDITION}$$

$$S_{1z}\,\chi_1 = \hbar\, s_{1z}\,\chi_1$$

$$S_{2z}\,\chi_2 = \hbar\, s_{2z}\,\chi_2$$

$$\hookrightarrow \left(S_{1z} + S_{2z}\right)\chi_1\chi_2 = \hbar\,\underbrace{\left(s_{1z} + s_{2z}\right)}_{s_z}\chi_1\chi_2$$

$\uparrow\uparrow$ $\quad s_z = +1$

$\left.\begin{matrix}\uparrow\downarrow \\ \downarrow\uparrow\end{matrix}\right\}$ $s_z = 0$ $\quad$ 2 STATES WITH 0 PROJECTION.

$\downarrow\downarrow$ $\quad s_z = -1$

TOTAL SPIN CAN BE 0 OR 1

$\underline{\underline{s = 0}}$ $\quad |s\, s_z\rangle = |0\,0\rangle$

$$= \frac{1}{\sqrt{2}} \left\{ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right\}$$

SPIN SINGLET (ANTI-SYMMETRIC)

(APPLY SPIN RAISING / LOWERING OPERATOR : HW)

$\underline{\underline{s = 1}}$ $\quad |s\, s_z\rangle \Rightarrow |1\,1\rangle = |\uparrow\uparrow\rangle$

$$|1\,0\rangle = \frac{1}{\sqrt{2}} \left\{ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right\}$$

$$|1\,-1\rangle = |\downarrow\downarrow\rangle$$

SPIN TRIPLET (SYMMETRIC).

↳ TOTAL SPIN

$$S^2 = \left(\bar{S}_1 + \bar{S}_2 \right)^2$$

$$= S_1^2 + S_2^2 + 2\, \bar{S}_1 . \bar{S}_2$$

$$\bar{S}_1 . \bar{S}_2 = \frac{1}{2} \left(S^2 - S_1^2 - S_2^2 \right)$$

$$\langle 1\, s_z | \, \bar{S}_1 . \bar{S}_2 \, | 1\, s_z \rangle = \frac{1}{2} \hbar^2 \left(2 - \frac{3}{4} - \frac{3}{4} \right) = \frac{\hbar^2}{4}$$

$$\langle 0\,0 | \, \bar{S}_1 . \bar{S}_2 \, | 0\,0 \rangle = \frac{1}{2} \hbar^2 \left(0 - \frac{3}{4} - \frac{3}{4} \right) = - \frac{3\hbar^2}{4}$$

↳ COMBINING 2 GENERAL ANGULAR MOMENTA (SPINS)

* $\frac{1}{2}\uparrow \quad \frac{1}{2}\uparrow$ ↗ $S = 0 \quad S_z = 0$
↘ $S = 1 \quad S_z = -1, 0, +1$

* j_1 COMBINE WITH j_2

WHAT IS RESULT ?

e.g. e^- IN $\ell = 1$ STATE OF HYDROGEN ATOM

& e^- HAS INTRINSIC SPIN $s = \frac{1}{2}$

WHAT IS ITS TOTAL ANGULAR MOMENTUM ? ↗ $\frac{3}{2}$ OR ↘ $\frac{1}{2}$

* GENERAL RESULT :

ALL TOTAL ANGULAR MOMENTA ARE ALLOWED

FROM $\underline{\underline{|j_1 - j_2|, \ldots, j_1 + j_2 - 1, j_1 + j_2}}$

IN STEPS OF 1

* $\bar{J}_1$ $\quad J_1^2 \, | j_1 m_1 \rangle = \hbar^2 j_1(j_1+1) \, | j_1 m_1 \rangle$

$$J_{1z} \, | j_1 m_1 \rangle = \hbar m_1 \, | j_1 m_1 \rangle$$

$\bar{J}_2$ ANALOGOUS J_2^2, J_{2z} HAVE EIGENSTATE $| j_2 m_2 \rangle$

$$\bar{J} = \bar{J}_1 + \bar{J}_2$$

$\hookrightarrow J^2, J_z$ HAS EIGENSTATE $| J M \rangle$

$$J = |j_1 - j_2|, \ \ldots, \ j_1 + j_2$$

$$M = -J, \ \ldots, \ +J$$

* $$\boxed{| JM \rangle = \sum_{m_1} \sum_{\substack{m_2 \\ m_1 + m_2 = M}} \underbrace{\langle j_1 m_1, j_2 m_2 | JM \rangle}_{} \, | j_1 m_1 \rangle | j_2 m_2 \rangle}$$

CLEBSCH - GORDON (CG)
COEFFICIENT

<u>NOTATION</u> : LESS USED NOTATION

$$C^{j_1 j_2 J}_{m_1 m_2 M} = \langle j_1 m_1, j_2 m_2 | JM \rangle$$

* <u>EXAMPLE 1</u> . $j_1 = 1$ COUPLED WITH $j_2 = \frac{1}{2}$

ORBITAL ANGULAR MOMENTUM OF e^- — SPIN OF e^-

J : $\frac{1}{2}$, $\frac{3}{2}$

e.g. $$\left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle = \sum_{\substack{m_1,\ m_2 \\ m_1 + m_2 = \frac{1}{2}}} \left\langle 1\ m_1,\ \tfrac{1}{2}\ m_2 \middle| \tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle \left|1\ m_1\right\rangle \left|\tfrac{1}{2}\ m_2\right\rangle$$

$$= \left\langle 1\ 0,\ \tfrac{1}{2}\ +\tfrac{1}{2} \middle| \tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle \left|1\ 0\right\rangle \left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle$$

$$+ \left\langle 1\ +1,\ \tfrac{1}{2}\ -\tfrac{1}{2} \middle| \tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle \left|1\ +1\right\rangle \left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle = -\sqrt{\tfrac{1}{3}}\ \left|1\ 0\right\rangle \left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle$$

$$+ \sqrt{\tfrac{2}{3}}\ \left|1\ +1\right\rangle \left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$

$\downarrow$

SUM OF SQUARES OF CG COEFF. IS 1

(BECAUSE LEFT IS NORMALIZED TO 1)

e.g. $$\left|\tfrac{3}{2}\ +\tfrac{3}{2}\right\rangle = \sum_{m_1}\sum_{m_2} \left\langle 1\, m_1, \tfrac{1}{2}\, m_2 \,\middle|\, \tfrac{3}{2}\ +\tfrac{3}{2}\right\rangle \left|1\ m_1\right\rangle \left|\tfrac{1}{2}\ m_2\right\rangle$$
$$m_1+m_2=+\tfrac{3}{2}$$

$$= \underbrace{\left\langle 1\ +1, \tfrac{1}{2}\ +\tfrac{1}{2} \,\middle|\, \tfrac{3}{2}\ +\tfrac{3}{2}\right\rangle}_{1} \left|1\ +1\right\rangle \left|\tfrac{1}{2}\ +\tfrac{1}{2}\right\rangle$$

$\left|\tfrac{3}{2}\ +\tfrac{1}{2}\right\rangle = \ldots$ (WORK IT OUT YOURSELF).

* ALSO WORKS IN REVERSE WAY

$$|j_1\, m_1\rangle\, |j_2\, m_2\rangle = \sum_{J}\sum_{M} \langle j_1\, m_1, j_2\, m_2 \,|\, J M\rangle\ |JM\rangle$$
$$J = |j_1-j_2|, \ldots j_1+j_2$$

e.g.

$$\left|\tfrac{3}{2}\ \tfrac{1}{2}\right\rangle |1\ 0\rangle = \sqrt{\tfrac{3}{5}}\ \left|\tfrac{5}{2}\ \tfrac{1}{2}\right\rangle$$
$$+ \sqrt{\tfrac{1}{15}}\ \left|\tfrac{3}{2}\ \tfrac{1}{2}\right\rangle$$
$$+ -\sqrt{\tfrac{1}{3}}\ \left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle$$

IDENTICAL PARTICLES

⇒ 2 PARTICLE SYSTEMS

• **SCHRÖDINGER EQ.**

e.g. H_2 MOLECULE

e^+e^- BOUND STATE

↳ POSITRONIUM

m_1 $\bar{r}_1$ $\quad\quad$ m_2 $\bar{r}_2$

⇝ $\Psi(\bar{r}_1, \bar{r}_2, t)$: WAVE FUNCTION

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

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\bar{r}_1, \bar{r}_2, t)$$

IF $V(\bar{r}_1, \bar{r}_2, t) = V(\bar{r}_1, \bar{r}_2)$

↳ $\Psi(\bar{r}_1, \bar{r}_2, t) = \psi(\bar{r}_1, \bar{r}_2)\, e^{-\frac{i}{\hbar}Et}$

⇝ ψ SATISFIES TIME-INDEPENDENT SCHRÖDINGER EQ.

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V(\bar{r}_1, \bar{r}_2)\psi = E\psi$$

- **SEPARATION OF CENTER OF MASS & RELATIVE MOTIONS**

IN MOST PHYSICS APPLICATIONS $V(\bar{r}_1, \bar{r}_2)$ ONLY DEPENDS ON RELATIVE COORDINATE $\bar{r} \equiv \bar{r}_1 - \bar{r}_2$

↑ DISTANCE BETWEEN PARTICLES

$$V(\bar{r}_1, \bar{r}_2) = V(\bar{r})$$

↳ THEN 2 BODY SCHRÖDINGER EQ. CAN BE SEPARATED IN 2

C.M. COORDINATE $\bar{R} \equiv \dfrac{m_1 \bar{r}_1 + m_2 \bar{r}_2}{m_1 + m_2}$

RELATIVE COORDINATE $\bar{r} = \bar{r}_1 - \bar{r}_2$

⇓

$$\bar{r}_1 = \bar{R} + \frac{m_2}{m_1 + m_2} \bar{r}$$

$$\bar{r}_2 = \bar{R} - \frac{m_1}{m_1 + m_2} \bar{r}$$

INTRODUCE REDUCED MASS $\boxed{\mu \equiv \dfrac{m_1 m_2}{m_1 + m_2}}$

$$\begin{cases} \bar{r}_1 = \bar{R} + \dfrac{\mu}{m_1}\bar{r} \\ \bar{r}_2 = \bar{R} - \dfrac{\mu}{m_2}\bar{r} \end{cases}$$

$$\bar{\nabla}_1 = \frac{\mu}{m_2}\bar{\nabla}_R + \bar{\nabla}_r$$

$$\bar{\nabla}_2 = \frac{\mu}{m_1}\bar{\nabla}_R - \bar{\nabla}_r$$

$$\hookrightarrow \quad \nabla_1^2 = \left(\frac{\mu}{m_2}\bar{\nabla}_R + \bar{\nabla}_r\right) \cdot \left(\frac{\mu}{m_2}\bar{\nabla}_R + \bar{\nabla}_r\right)$$

$$= \left(\frac{\mu}{m_2}\right)^2 \nabla_R^2 + \nabla_r^2 + \frac{2\mu}{m_2}\bar{\nabla}_R \cdot \bar{\nabla}_r$$

$$\nabla_2^2 = \left(\frac{\mu}{m_1}\right)^2 \nabla_R^2 + \nabla_r^2 - 2\frac{\mu}{m_1}\bar{\nabla}_R \cdot \bar{\nabla}_r$$

$$\hookrightarrow \quad -\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m}\nabla_2^2\psi + V(\bar{r})\psi = E\psi$$

$$-\frac{\hbar^2}{2}\left(\frac{\mu^2}{m_1 m_2^2} + \frac{\mu^2}{m_2 m_1^2}\right)\nabla_R^2\psi - \frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\nabla_r^2\psi$$

$$-\hbar^2\cancel{\left(\frac{\mu}{m_1 m_2} - \frac{\mu}{m_1 m_2}\right)}\bar{\nabla}_R \cdot \bar{\nabla}_r\psi + V(\bar{r})\psi = E\psi$$

$$\Downarrow$$

$$\frac{\mu^2}{m_1 m_2^2} + \frac{\mu^2}{m_2 m_1^2} = \frac{\mu^2}{m_1 m_2}\underbrace{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}_{\frac{1}{\mu}} = \frac{\mu}{m_1 m_2} = \frac{1}{m_1+m_2}$$

$$-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2\psi - \frac{\hbar^2}{2\mu}\nabla_r^2\psi + V(\bar{r})\psi = E\psi$$

↳ SEPARATION OF VARIABLES

$$\psi(\bar{r},\bar{R}) = \psi_R(\bar{R})\,\psi_r(\bar{r})$$

$$-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2\psi_R(\bar{R}) = E_R\,\psi_R(\bar{R})$$

$$-\frac{\hbar^2}{2\mu}\nabla_r^2\psi_r(\bar{r}) + V(\bar{r})\psi_r(\bar{r}) = E_r\,\psi_r(\bar{r})$$

$$E = E_R + E_r$$ TOTAL ENERGY

1° EQ. FREE SCHRÖDINGER EQ FOR C. M. MOTION
↓
TOTAL MASS (m_1+m_2)

2° EQ. 1 PARTICLE SCHRÖDINGER EQ.
FOR RELATIVE MOTION → REDUCED MASS μ

• BOSONS & FERMIONS

↳ 2 PARTICLE STATE : ↗ ONE PARTICLE IN STATE a : ψ_a
↘ SECOND PARTICLE IN STATE b : ψ_b

* CLASSICAL PHYSICS : PARTICLES CAN BE DISTINGUISHED

$$\psi(\bar{r}_1, \bar{r}_2) = \psi_a(\bar{r}_1)\,\psi_b(\bar{r}_2)$$

* IN QUANTUM PHYSICS PARTICLES ARE INDISTINGUISHABLE

2 WAYS TO TAKE CARE OF THIS

$$\psi(\bar{r}_1, \bar{r}_2) = A\left[\psi_a(\bar{r}_1)\,\psi_b(\bar{r}_2) \pm \psi_b(\bar{r}_1)\,\psi_a(\bar{r}_2)\right]$$

↑ NORMALIZATION

$+$: WAVE FUNCTION IS SYMMETRIC w.r.t. INTERCHANGE $1 \leftrightarrow 2$: BOSONS

$-$: WAVE FUNCTION IS ANTI-SYMMETRIC w.r.t INTERCHANGE $1 \leftrightarrow 2$: FERMIONS

↳ 'DEEP CONNECTION' (RELATIVISTIC QUANTUM FIELD THEORY) BETWEEN SYMMETRY OF WF & SPIN

$$\boxed{\begin{array}{l}\text{SPIN-STATISTICS THEOREM}\\ \text{BOSONS (SYMM. UNDER } 1 \leftrightarrow 2\text{) HAVE INTEGER SPIN}\\ \text{FERMIONS (ANTISYMM UNDER } 1 \leftrightarrow 2\text{) HAVE HALF INTEGER SPIN}\end{array}}$$

↳ PAULI EXCLUSION PRINCIPLE

2 FERMIONS CANNOT OCCUPY SAME STATE !

if $\psi_b = \psi_a$

$$\psi_-(\bar{r}_1, \bar{r}_2) = A\left[\psi_a(\bar{r}_1)\psi_a(\bar{r}_2) - \psi_a(\bar{r}_1)\psi_a(\bar{r}_2)\right]$$

$$= 0$$

↳ EXCHANGE OPERATOR P

$$P\,\psi(\bar{r}_1, \bar{r}_2) = \psi(\bar{r}_2, \bar{r}_1)$$

$$P^2 = 1$$

FOR 2 IDENTICAL PARTICLES ($m_1 = m_2$, $V(\bar{r}_1, \bar{r}_2) = V(\bar{r}_2, \bar{r}_1)$)

$$\Downarrow$$

$$[P, H] = 0$$

∴ EIGENSTATES OF H ARE EITHER SYMMETRIC OR ANTISYMM w.r.t $1 \leftrightarrow 2$

$$\boxed{\psi(\bar{r}_1, \bar{r}_2) = \pm\,\psi(\bar{r}_2; \bar{r}_1)}$$

BOSONS

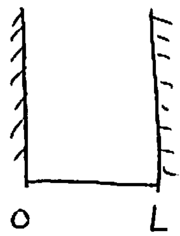
FERMIONS

• EXCHANGE FORCES

2 PARTICLES IN 1 DIM $\quad \psi_a(x)$ STATE a

$\psi_b(x)$ STATE b

e.g.



↳ DISTINGUISHABLE: $\psi(x_1, x_2) = \psi_a(x_1)\,\psi_b(x_2)$

↳ BOSONS : $\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right]$

↳ FERMIONS : $\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)\right]$

WHAT IS $\langle\ \rangle$ OF $(x_1 - x_2)^2$ DISTANCE^2 BETWEEN 1&2

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$$

↳ DISTINGUISHABLE

$$\langle x_1^2 \rangle = \int dx_1 \; x_1^2 \, |\psi_a(x_1)|^2 \underbrace{\int dx_2 \; |\psi_b(x_2)|^2}_{1}$$

$$= \langle x^2 \rangle_a$$

$$\langle x_2^2 \rangle = \langle x^2 \rangle_b$$

$$\langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b$$

↳ IDENTICAL PARTICLES

$$\langle x_1^2 \rangle = \frac{1}{2} \Big\{ \int dx_1 \; x_1^2 \; |\psi_a(x_1)|^2 \overbrace{\int dx_2 \; |\psi_b(x_2)|^2}^{1}$$

$$+ \int dx_1 \; x_1^2 \; |\psi_b(x_1)|^2 \int dx_2 \; |\psi_a(x_2)|^2$$

$$\pm \int dx_1 \; x_1^2 \; \psi_a^*(x_1)\psi_b(x_1) \int dx_2 \; \psi_b^*(x_2)\psi_a(x_2)$$

$$\pm \int dx_1 \; x_1^2 \; \psi_b^*(x_1)\psi_a(x_1) \underbrace{\int dx_2 \; \psi_a^*(x_2)\psi_b(x_2)}_{0} \Big\}$$

$$= \frac{1}{2} \left\{ \langle x^2 \rangle_a + \langle x^2 \rangle_b + 0 + 0 \right\}$$

$$\langle x_2^2 \rangle = \langle x_1^2 \rangle \qquad \text{IDENTICAL !}$$

$$\langle x_1 x_2 \rangle = \frac{1}{2} \Big\{ 2 \langle x \rangle_a \langle x \rangle_b$$

$$\pm \int dx_1 \; x_1 \; \psi_a^*(x_1)\psi_b(x_1) \int dx_2 \; x_2 \; \psi_b^*(x_2)\psi_a(x_2)$$

$$\pm \underbrace{\int dx_1 \; x_1 \; \psi_b^*(x_1)\psi_a(x_1)}_{\langle x \rangle_{ba}} \underbrace{\int dx_2 \; x_2 \; \psi_a^*(x_2)\psi_b(x_2)}_{\langle x \rangle_{ab}} \Big\}$$

$$\langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$$

$\therefore$ DISTINGUISHABLE PARTICLES

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b$$

$\therefore$ IDENTICLE PARTICLES.

$$\langle (x_1 - x_2)^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 \left| \langle x \rangle_{ab} \right|^2$$

$$\boxed{\langle (x_1 - x_2)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_d \mp 2 \left| \langle x \rangle_{ab} \right|^2}$$

INDUCES A CORRELATION BETWEEN PARTICLES. (EXCHANGE 'FORCE')

→ 'ATTRACTION' FOR BOSONS

PULLS THEM CLOSER TOGETHER

$\langle (x_1 - x_2)^2 \rangle$ DECREASES

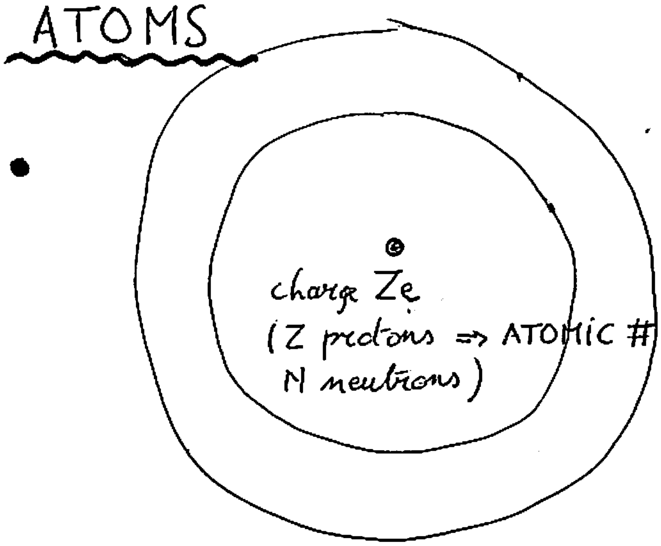
→ 'REPULSIVE' FOR FERMIONS

PUSHES THEM FURTHER APART

$\langle (x_1 - x_2)^2 \rangle$ INCREASES

TOTAL W F INCLUDES SPIN ! ↷ COVALENT BOND

⇒ ATOMS



Z ELECTRONS (MASS m)
charge $-Ze$

⇓

NEUTRAL ATOM

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_j} \right\}$$

↑ KINETIC ENERGY OF e^-

↑ POTENTIAL ENERGY OF e^- IN FIELD OF NUCLEUS OF CHARGE $+Ze$

$$+ \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)\sum_{j\neq k}^{Z} \frac{e^2}{|\bar{r}_j - \bar{r}_k|}$$

↑ POTENTIAL ENERGY DUE TO MUTUAL REPULSION OF ELECTRONS (DIFFICULT TERM!)

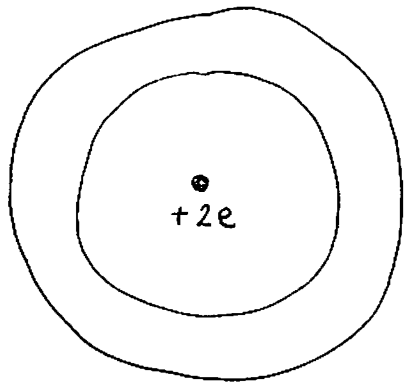
$$H\Psi = E\Psi$$

$$\Psi(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_Z)\,\chi(s_1, s_2 \ldots s_Z)$$

↑ ORBITAL W.F. ↑ SPIN W.F.

TOTAL W.F. IS ANTI-SYMM w.r.t. INTERCHANGE OF ANY 2 e^-

• **HELIUM** ($Z = 2$)



$2e^-$ ORBITING AROUND NUCLEUS OF CHARGE $+2e$

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2}$$

$$+ \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\bar{r}_1 - \bar{r}_2|}}$$

DRASTIC APPROXIMATION: DROP e^- REPULSION TERM (IGNORE)

$$H \simeq \left\{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1}\right\} + \left\{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2}\right\}$$

H OF HYDROGEN ATOM WITH NUCLEAR CHARGE $+2e$ INSTEAD OF $+e$

↳ RECALL H ATOM

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

$$E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -13.6 \text{ eV}$$

BOHR RADIUS $a \equiv \dfrac{4\pi\varepsilon_0}{e^2}\dfrac{\hbar^2}{m} \simeq 0.5\ 10^{-10}\,m$

WAVEFUNCTION $\psi_{n\ell m}(\bar{r})$

$n = 1, 2, \ldots$

$\ell = 0, 1, \ldots, n-1$

$m = -\ell, \ldots, +\ell$

GROUND STATE $\psi_{100}(\bar{r}) = \dfrac{1}{\sqrt{\pi a^3}}\, e^{-r/a}$

↳ REPLACE $e^2 \rightarrow 2e^2$

$E_1 \rightarrow 4E_1$

$a \rightarrow \dfrac{a}{2}$

He ATOM

TOTAL $E = 4\,(E_n + E_{n'})$

$$E_n = \frac{1}{n^2}(-13.6 \text{ eV})$$

↳ He GROUND STATE W.F.

$$\psi_{He,gs}(\bar{r}_1, \bar{r}_2) = \psi_{100}(\bar{r}_1)\,\psi_{100}(\bar{r}_2)$$

$$= \frac{8}{\pi a^3}\, e^{-2(r_1 + r_2)/a}$$

$$E_0 = -4 \cdot (13.6 + 13.6)\ eV$$

$$= -109\ eV$$

↳ ORBITAL W.F. IS SYMMETRIC UNDER $1 \leftrightarrow 2$

$\Downarrow$

SPIN W.F. HAS TO BE ANTI-SYMMETRIC

$$\chi = \frac{1}{\sqrt{2}} \left\{ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right\}$$ "PARAHELIUM"

↳ SPIN $S = 0$ (SINGLET)

↳ <u>EXPERIMENT</u> → G.S. IS SINGLET ☺

→ $E_0^{EXP} = -79\ eV$ ☹

<u>BUT</u> : WE IGNORED e^- REPULSION!

↳ ESTIMATE OF e^- REPULSION IN He ATOM IN ITS GROUND STATE

* TO FIRST APPROX. ASSUME e^- W.F. IS NOT AFFECTED BY e^- REPULSION

$$\psi_{He,gs}(\bar{r}_1,\bar{r}_2) = \frac{8}{\pi a^3}\, e^{-2(r_1+r_2)/a}$$

* AVERAGE VALUE OF COULOMB REPULSION BETWEEN e^-

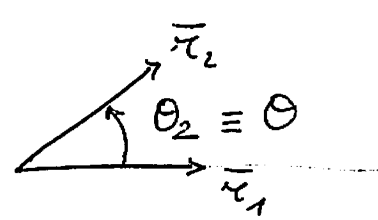
$$V_{ee} \equiv \left\langle \frac{+e^2}{4\pi\varepsilon_0}\frac{1}{|\bar{r}_1-\bar{r}_2|}\right\rangle \quad \text{IN STATE } \psi_{He,gs}$$

$$= \int d^3\bar{r}_1 \int d^3\bar{r}_2\ \psi^*_{He,gs} \cdot \frac{e^2}{4\pi\varepsilon_0\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_{12}}}\ \psi_{He,gs}$$

$$= \left(\frac{8}{\pi a^3}\right)^2 \cdot (2\pi)^2 \int dr_1\, r_1^2 \int d\cos\theta_1 \int dr_2\, r_2^2 \int d\cos\theta_2$$

$$e^{-4(r_1+r_2)/a} \cdot \frac{e^2}{4\pi\varepsilon_0\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_{12}}}$$

↓ WITHOUT LOSS OF GENERALITY



CHOOSE $\theta_1 = 0$

$\int d\cos\theta_1 \to 2$

$$V_{ee} = \left(\frac{8}{\pi a^3}\right)^2 \frac{e^2}{4\pi\varepsilon_0}(2\pi)^2 \cdot 2 \int dr_1\, r_1^2\, e^{-4r_1/a} \int dr_2\, r_2^2\, e^{-4r_2/a}$$

$$\cdot \underbrace{\int d\cos\theta \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}}$$

$$- \frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}\,\Bigg|_{-1}^{1}$$

$$\overset{\shortparallel}{\cos\theta}$$

$$= \frac{64}{a^6} \cdot \frac{8\, e^2}{4\pi\varepsilon_0} \int dr_1\, r_1\, e^{-4r_1/a} \int dr_2\, r_2\, e^{-4r_2/a}$$

$$\cdot \left\{ \sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2} \right\}$$

$$= \frac{64}{a^6} \cdot \frac{8\, e^2}{4\pi\varepsilon_0} \int dr_1\, r_1\, e^{-4r_1/a} \int dr_2\, r_2\, e^{-4r_2/a}$$

$$\cdot \underbrace{\left\{ r_1 + r_2 - |r_1 - r_2| \right\}}$$

$$= 2r_2 \qquad \text{FOR } r_1 > r_2$$

$$= 2r_1 \qquad \text{FOR } r_1 < r_2$$

$$= \frac{64}{a^6} \frac{8e^2}{4\pi\varepsilon_0} \int_0^\infty dr_1 \; r_1 \; e^{-4r_1/a}$$

$$\cdot \left\{ \int_0^{r_1} dr_2 \; r_2 \; e^{-4r_2/a} \cdot 2r_2 + \int_{r_1}^\infty dr_2 \; r_2 \; e^{-4r_2/a} \cdot 2r_1 \right\}$$

* HELP 1

$$2 \int_{r_1}^\infty dr_2 \; r_2 \; e^{-4r_2/a} = \frac{a^2}{8} \int_{4r_1/a}^\infty dx \; x \; e^{-x}$$

$$= \frac{a^2}{8} \left\{ -x e^{-x} \Big|_{\frac{4r_1}{a}}^\infty + \int_{\frac{4r_1}{a}}^\infty dx \; e^{-x} \right\}$$

$$= \frac{a^2}{8} \left\{ \frac{4r_1}{a} e^{-\frac{4r_1}{a}} + e^{-\frac{4r_1}{a}} \right\}$$

* HELP 2

$$2 \int_0^{r_1} dr_2 \; r_2^2 \; e^{-\frac{4r_2}{a}} = \frac{a^3}{32} \int_0^{\frac{4r_1}{a}} dx \; x^2 \; e^{-x}$$

$$= \frac{a^3}{32} \left\{ -x^2 e^{-x} \Big|_0^{\frac{4r_1}{a}} + 2 \int_0^{\frac{4r_1}{a}} dx \; x \; e^{-x} \right\}$$

$$= \frac{a^3}{32} \left\{ -\frac{16 r_1^2}{a^2} e^{-\frac{4r_1}{a}} - 2 x e^{-x} \Big|_0^{\frac{4r_1}{a}} + 2 \int_0^{\frac{4r_1}{a}} dx \; e^{-x} \right\}$$

$$= \frac{a^3}{32} \left\{ -\frac{16 r_1^2}{a^2} e^{-\frac{4r_1}{a}} - 2 \cdot \frac{4r_1}{a} e^{-\frac{4r_1}{a}} - 2 e^{-\frac{4r_1}{a}} + 2 \right\}$$

$$\therefore \quad V_{ee} = \frac{64}{a^6} \cdot \frac{8e^2}{4\pi\varepsilon_0} \cdot \frac{a^2}{16}$$

$$\cdot \int_0^\infty dx \; x \, e^{-x} \left\{ \frac{a^3}{32} \left[-x^2 e^{-x} - 2x e^{-x} - 2e^{-x} + 2 \right] \right.$$

$$\left. + \frac{a^2}{8} \cdot \frac{a}{4} \, x \left[x e^{-x} + e^{-x} \right] \right\}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0} \right) \cdot \frac{1}{a} \int_0^\infty dx \; x \, e^{-2x} \left\{ -\cancel{x^2} - 2x - 2 + 2e^{x} \right.$$

$$\left. + \cancel{x^2} + x \right\}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{a} \left\{ 2 \underbrace{\int_0^\infty dx \; x \, e^{-x}}_{1} - \int_0^\infty dx \; x e^{-2x} (\underset{\downarrow \, \frac{1}{4}}{x} + \underset{\downarrow \, \frac{1}{2}}{2}) \right\}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{a} \left\{ \underbrace{2 - \frac{3}{4}}_{\frac{5}{4}} \right\}$$

$$V_{ee} = \frac{5}{4a} \cdot \left(\frac{e^2}{4\pi\varepsilon_0} \right) = \frac{5}{4} \frac{m}{\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2$$

$$= \frac{5}{2} |E_1| = \frac{5}{2} \cdot (13.6 \text{ eV}) = +34 \text{ eV}$$

TOTAL ENERGY He ATOM in gs $E \simeq (-109 + 34)\,\text{eV} \simeq -75\,\text{eV}$

WITHIN 5% OF RIGHT NUMBER!

↳ EXCITED STATES

PUT ONE e^- IN H GROUND STATE

SECOND e^- IN EXCITED STATE

$$\psi_{He,\,exc.}(\bar{r}_1,\bar{r}_2) \Rightarrow \left[\psi_{100}(\bar{r}_1)\,\psi_{nlm}(\bar{r}_2) \pm \psi_{100}(\bar{r}_2)\,\psi_{nlm}(\bar{r}_1)\right]$$

2 WAYS

(+) SYMM. ORBITAL COMBINE WITH ANTI-SYMM SPIN $(S=0)$ (SINGLET) (PARAHELIUM)

(−) ANTISYMM ORBITAL COMBINE WITH SYMM SPIN $(S=1)$ (TRIPLET) (ORTHOHELIUM)

ORTHOHELIUM STATES SLIGHTLY MORE BOUND THAN PARAHELIUM STATES

SPECTROSCOPIC NOTATION $\;{}^{2S+1}L$

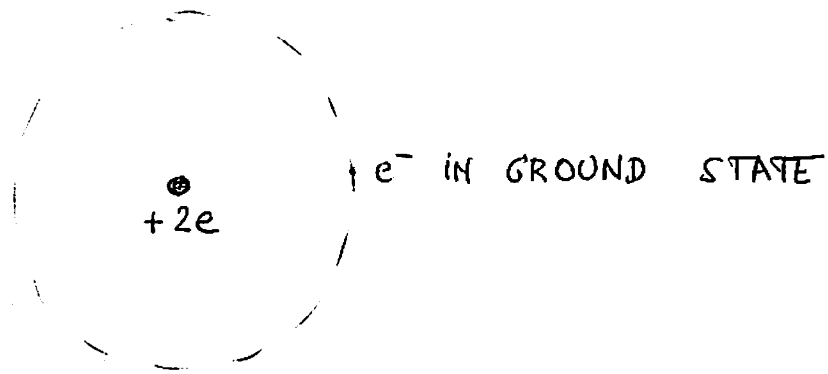
$\nearrow$ $S=0$ $\quad {}^1L \; ({}^1S, {}^1P, {}^1D, {}^1F)$

$\searrow$ $S=1$ $\quad {}^3L \; ({}^3S, {}^3P, {}^3D, {}^3F)$

$L = 0\,(S),\ 1\,(P),\ 2\,(D),\ 3\,(F)$

He EXCITED STATES ($2e^-$)

⇝ START FROM He^+ ION



ENERGY $E = -4\,(13.6\text{ eV}) = -54.4\text{ eV}$

⇝ SECOND e^- ⇒ NEUTRAL He ATOM

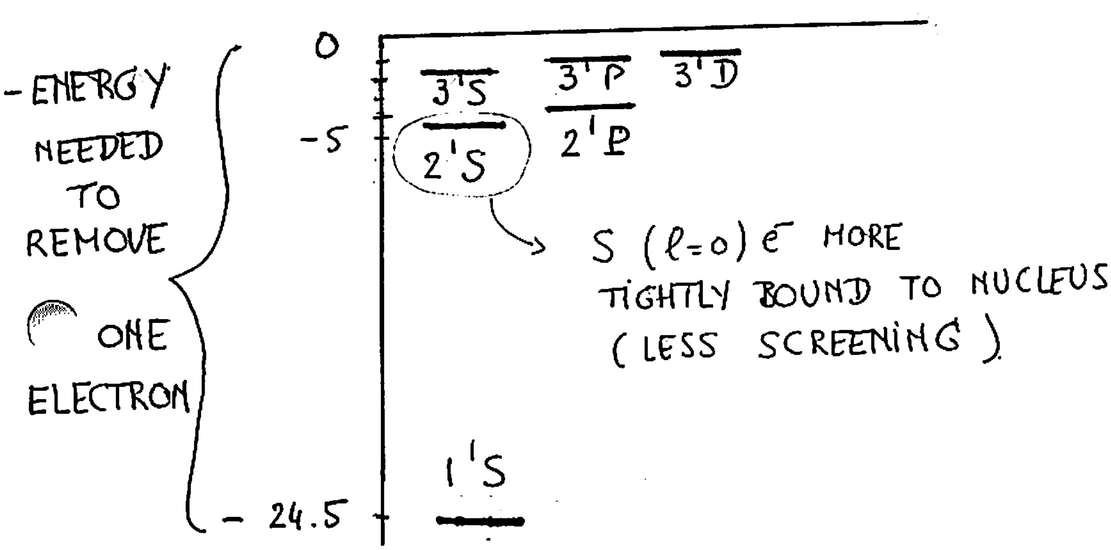
IF ONE NEGLECTS e^- REPULSION

E OF SECOND e^- WOULD ALSO BE -54.4 eV

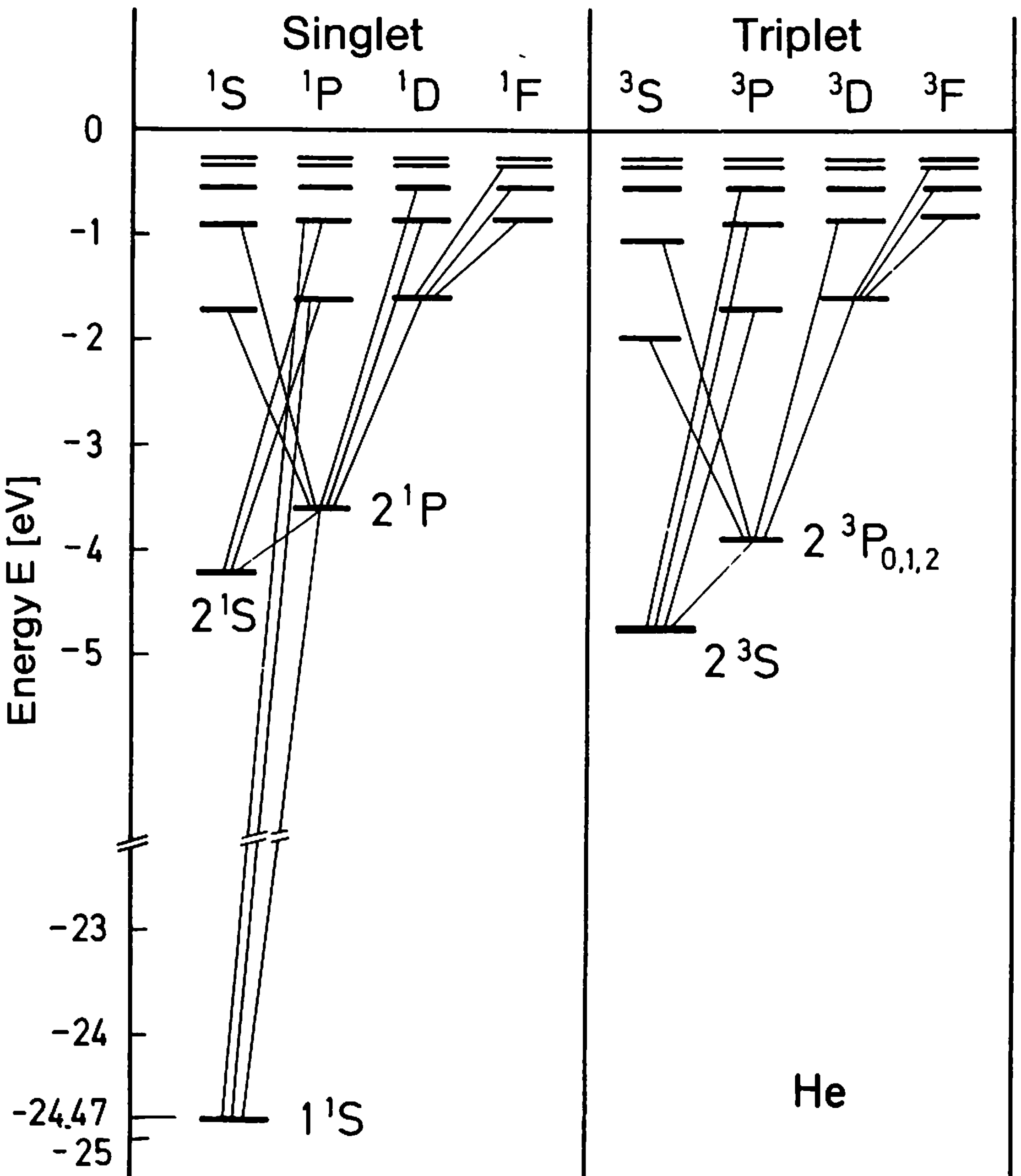
DUE TO e^- REPULSION

E OF SECOND e^- IS -24.5 eV (IF IN GROUND STATE $S=0$)

∴ TOTAL E IS $-54.4 - 24.5 \simeq -79\text{ eV}$



FOR $S=0$ (SINGLET).



(Z = 2)

Fig. 17.1. Term scheme of the He atom. Some of the allowed transitions are indicated. There are two term systems, between which radiative transitions are forbidden. These are the singlet and triplet systems. The transitions in the singlet system span an energy range of 25 eV, while those in the triplet system span only 5 eV

5.20

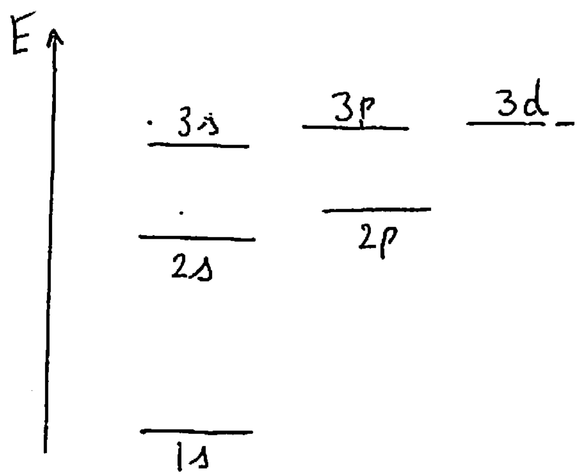
• PERIODIC TABLE

↳ TO FIRST APPROX

e^- OCCUPY ORBITALS (n, ℓ, m)

↓

ONE-PARTICLE HYDROGENIC STATES FOR NUCLEUS OF CHARGE $+Ze$



(s → $\ell = 0$ LEVELS SLIGHTLY MORE BOUND THAN $\ell \neq 0$ LEVELS)

↳ PAULI PRINCIPLE

EACH VALUE OF n (SHELL) ⇒ n^2 STATES (WITHOUT SPIN)

∴ $\underline{2n^2}$ STATES (WITH SPIN)

∴ ONLY $2\,e^-$ ↑↓ CAN OCCUPY $\underline{\underline{\text{ONE}}}$ ORBITAL n, ℓ, m

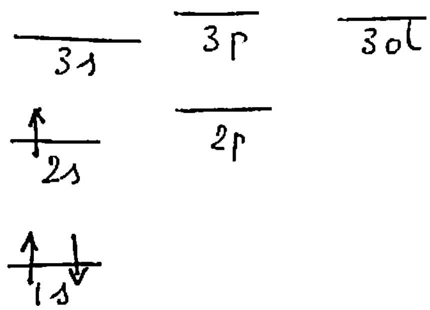
$n = 1 \Rightarrow 2e^-$

$n = 2 \Rightarrow 8e^-$

$n = 3 \Rightarrow 18e^-$

$n = 4 \Rightarrow 32\,e^-$

e.g. Li (GROUND STATE)



L : TOTAL ORBITAL ANG. MOMENTUM
S : TOTAL SPIN
J : TOTAL ANGULAR MOM.

GROUND STATE $^{2S+1}L_J$

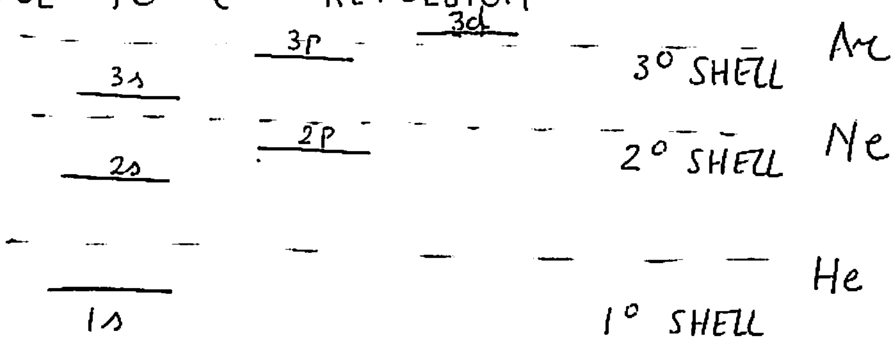
H :	$(1s)$	$^2S_{1/2}$
He :	$(1s)^2$	$^1S_0$
Li :	$(1s)^2\ (2s)$	$^2S_{1/2}$
Be :	$(1s)^2\ (2s)^2$	$^1S_0$
B :	$(1s)^2\ (2s)^2\ (2p)$	$^2P_{1/2}$
C :	$(1s)^2\ (2s)^2\ (2p)^2$	$^3P_0$

CLOSED SHELLS → NOBLE GASES : CHEMICALLY INERT

MAGIC NUMBERS : 2, 10, 18, 36, ...

DEVIATION FROM 2, 10, 28, ... $(2n^2)$

DUE TO e^- REPULSION



↳ HUND RULES

1) STATE WITH HIGHEST S HAS LOWEST ENERGY

2) STATE WITH HIGHEST L CONSISTENT WITH ANTISYMM HAS LOWEST ENERGY

3) IF SUBSHELL (n,ℓ) IS LESS THAN HALF FILLED $\Rightarrow$ $J = |L - S|$ HAS LOWEST ENERGY

↳ cf. B

IF SUBSHELL (n,ℓ) IS MORE THAN HALF FILLED $\Rightarrow$ $J = L + S$ HAS LOWEST ENERGY

5.24

Table 19.3a. Periodic Table with electron configurations, ground state terms, and ionisation energies. The filled shells and subshells are shaded

Atomic number Z	Element		Shells K $n=1$ s	L $n=2$ s	p	M $n=3$ s	p	d	N $n=4$ s	p	d	O $n=5$ s	p	LS configuration of the ground state	First ionisation potential [eV]	
1	Hydrogen	H	1											$^2S_{1/2}$	13.60	
2	Helium	He	2											$^1S_0$	24.58	
3	Lithium	Li	2	1										$^2S_{1/2}$	5.39	
4	Beryllium	Be	2	2										$^1S_0$	9.32	
5	Boron	B	2	2	1									$^2P_{1/2}$	8.30	
6	Carbon	C	2	2	2									$^3P_0$	11.26	
7	Nitrogen	N	2	2	3									$^4S_{3/2}$	14.54	
8	Oxygen	O	2	2	4									$^3P_2$	13.61	
9	Fluorine	F	2	2	5									$^2P_{3/2}$	17.42	
10	Neon	Ne	2	2	6									$^1S_0$	21.56	
11	Sodium	Na	2	2	6	1								$^2S_{1/2}$	5.14	
12	Magnesium	Mg	2	2	6	2								$^1S_0$	7.64	
13	Aluminium	Al	2	2	6	2	1							$^2P_{1/2}$	5.98	
14	Silicon	Si	2	2	6	2	2							$^3P_0$	8.15	
15	Phosphorous	P	2	2	6	2	3							$^4S_{3/2}$	10.55	
16	Sulphur	S	2	2	6	2	4							$^3P_2$	10.36	
17	Chlorine	Cl	2	2	6	2	5							$^2P_{3/2}$	13.01	
18	Argon	Ar	2	2	6	2	6							$^1S_0$	15.76	
19	Potassium	K	2	2	6	2	6		1					$^2S_{1/2}$	4.34	
20	Calcium	Ca	2	2	6	2	6		2					$^1S_0$	6.11	
21	Scandium	Sc	2	2	6	2	6	1	2					$^2D_{3/2}$	6.56	Transition elements
22	Titanium	Ti	2	2	6	2	6	2	2					$^3F_2$	6.83	
23	Vanadium	V	2	2	6	2	6	3	2					$^4F_{3/2}$	6.74	
24	Chromium	Cr	2	2	6	2	6	5	1					$^7S_3$	6.76	
25	Manganese	Mn	2	2	6	2	6	5	2					$^6S_{5/2}$	7.43	
26	Iron	Fe	2	2	6	2	6	6	2					$^5D_4$	7.90	
27	Cobalt	Co	2	2	6	2	6	7	2					$^4F_{9/2}$	7.86	
28	Nickel	Ni	2	2	6	2	6	8	2					$^3F_4$	7.63	
29	Copper	Cu	2	2	6	2	6	10	1					$^2S_{1/2}$	7.72	
30	Zinc	Zn	2	2	6	2	6	10	2					$^1S_0$	9.39	
31	Gallium	Ga	2	2	6	2	6	10	2	1				$^2P_{1/2}$	6.00	
32	Germanium	Ge	2	2	6	2	6	10	2	2				$^3P_0$	7.88	
33	Arsenic	As	2	2	6	2	6	10	2	3				$^4S_{3/2}$	9.81	
34	Selenium	Se	2	2	6	2	6	10	2	4				$^3P_2$	9.75	
35	Bromine	Br	2	2	6	2	6	10	2	5				$^2P_{3/2}$	11.84	
36	Krypton	Kr	2	2	6	2	6	10	2	6				$^1S_0$	14.00	
37	Rubidium	Rb	2	2	6	2	6	10	2	6		1		$^2S_{1/2}$	4.18	
38	Strontium	Sr	2	2	6	2	6	10	2	6		2		$^1S_0$	5.69	
39	Yttrium	Y	2	2	6	2	6	10	2	6	1	2		$^2D_{3/2}$	6.38	Transition elements
40	Zirconium	Zr	2	2	6	2	6	10	2	6	2	2		$^3F_2$	6.84	
41	Niobium	Nb	2	2	6	2	6	10	2	6	4	1		$^6D_{1/2}$	6.88	
42	Molybdenum	Mo	2	2	6	2	6	10	2	6	5	1		$^7S_3$	7.13	
43	Technetium	Tc	2	2	6	2	6	10	2	6	6	1		$^6D_{9/2}$	7.23	
44	Ruthenium	Ru	2	2	6	2	6	10	2	6	7	1		$^5F_5$	7.37	
45	Rhodium	Rh	2	2	6	2	6	10	2	6	8	1		$^4F_{9/2}$	7.46	
46	Palladium	Pd	2	2	6	2	6	10	2	6	10			$^1S_0$	8.33	
47	Silver	Ag	2	2	6	2	6	10	2	6	10	1		$^2S_{1/2}$	7.57	
48	Cadmium	Cd	2	2	6	2	6	10	2	6	10	2		$^1S_0$	8.99	
49	Indium	In	2	2	6	2	6	10	2	6	10	2	1	$^2P_{1/2}$	5.79	
50	Tin	Sn	2	2	6	2	6	10	2	6	10	2	2	$^3P_0$	7.33	
51	Antimony	Sb	2	2	6	2	6	10	2	6	10	2	3	$^4S_{3/2}$	8.64	
52	Tellurium	Te	2	2	6	2	6	10	2	6	10	2	4	$^3P_2$	9.01	
53	Iodine	J	2	2	6	2	6	10	2	6	10	2	5	$^2P_{3/2}$	10.44	
54	Xenon	Xe	2	2	6	2	6	10	2	6	10	2	6	$^1S_0$	12.13	

5.25

Table 19.3b. Periodic Table with electron configurations, ground state terms, and ionisation energies. The filled shells and subshells are shaded. (The subshells $5g$ and $6f$, $6g$, $6h$ are not shown, since there are no atoms which have electrons in these shells in their ground states)

Atomic number Z	Element		Shells N $n=4$ s	p	d	f	O $n=5$ s	p	d	f	P $n=6$ s	p	d	Q $n=7$ s	LS configuration of the ground state	First ionisation potential [eV]	
55	Cesium	Cs	2	6	10		2	6			1				$^2S_{1/2}$	3.89	
56	Barium	Ba	2	6	10		2	6			2				$^1S_0$	5.21	
57	Lanthanum	La	2	6	10		2	6	1		2				$^2D_{3/2}$	5.61	
58	Cerium	Ce	2	6	10	2	2	6			2				$^3H_4$	5.6	
59	Praseodymium	Pr	2	6	10	3	2	6			2				$^4I_{9/2}$	5.46	
60	Neodymium	Nd	2	6	10	4	2	6			2				$^5I_4$	5.51	
61	Promethium	Pm	2	6	10	5	2	6			2				$^6H_{5/2}$		
62	Samarium	Sm	2	6	10	6	2	6			2				$^7F_0$	5.6	
63	Europium	Eu	2	6	10	7	2	6			2				$^8S_{7/2}$	5.67	Rare earths
64	Gadolinium	Gd	2	6	10	7	2	6	1		2				$^9D_2$	6.16	
65	Terbium	Tb	2	6	10	9	2	6			2				—	5.98	
66	Dysprosium	Dy	2	6	10	10	2	6			2				$^5I_8$	6.8	
67	Holmium	Ho	2	6	10	11	2	6			2				$^4I_{15/2}$		
68	Erbium	Er	2	6	10	12	2	6			2				$^3H_6$	6.08	
69	Thulium	Tm	2	6	10	13	2	6			2				$^2F_{7/2}$	5.81	
70	Ytterbium	Yb	2	6	10	14	2	6			2				$^1S_0$	6.22	
71	Lutetium	Lu	2	6	10	14	2	6	1		2				$^2D_{3/2}$	6.15	
72	Hafnium	Hf	2	6	10	14	2	6	2		2				$^3F_2$	5.5	
73	Tantalum	Ta	2	6	10	14	2	6	3		2				$^4F_{3/2}$	7.7	
74	Tungsten	W	2	6	10	14	2	6	4		2				$^5D_0$	7.98	
75	Rhenium	Re	2	6	10	14	2	6	5		2				$^6S_{5/2}$	7.87	Transition elements
76	Osmium	Os	2	6	10	14	2	6	6		2				$^5D_4$	8.7	
77	Iridium	Ir	2	6	10	14	2	6	9						$^2D_{5/2}$	9.2	
78	Platinum	Pt	2	6	10	14	2	6	9		1				$^3D_3$	9.0	
79	Gold	Au	2	6	10	14	2	6	10		1				$^2S_{1/2}$	9.22	
80	Mercury	Hg	2	6	10	14	2	6	10		2				$^1S_0$	10.43	
81	Thallium	Tl	2	6	10	14	2	6	10		2	1			$^2P_{1/2}$	6.11	
82	Lead	Pb	2	6	10	14	2	6	10		2	2			$^3P_0$	7.42	
83	Bismuth	Bi	2	6	10	14	2	6	10		2	3			$^4S_{3/2}$	7.29	
84	Polonium	Po	2	6	10	14	2	6	10		2	4			$^3P_2$	8.43	
85	Astatine	At	2	6	10	14	2	6	10		2	5				9.5	
86	Radon	Rn	2	6	10	14	2	6	10		2	6			$^1S_0$	10.75	
87	Francium	Fr	2	6	10	14	2	6	10		2	6		1		4	
88	Radium	Ra	2	6	10	14	2	6	10		2	6		2		5.28	
89	Actinium	Ac	2	6	10	14	2	6	10		2	6	1	2			
90	Thorium	Th	2	6	10	14	2	6	10		2	6	2	2			
91	Protactinium	Pa	2	6	10	14	2	6	10	2	2	6	1	2			
92	Uranium	U	2	6	10	14	2	6	10	3	2	6	1	2			
93	Neptunium	Np	2	6	10	14	2	6	10	4	2	6	1	2			
94	Plutonium	Pu	2	6	10	14	2	6	10	6	2	6		2			
95	Americium	Am	2	6	10	14	2	6	10	7	2	6		2			
96	Curium	Cm	2	6	10	14	2	6	10	7	2	6	1	2			
97	Berkelium	Bk	2	6	10	14	2	6	10	8	2	6	1	2			Actinides
98	Californium	Cf	2	6	10	14	2	6	10	10	2	6		2			
99	Einsteinium	Es	2	6	10	14	2	6	10	11	2	6		2			
100	Fermium	Fm	2	6	10	14	2	6	10	12	2	6		2			
101	Mendelevium	Md	2	6	10	14	2	6	10	13	2	6		2			
102	Nobelium	No	2	6	10	14	2	6	10	14	2	6		2			
103	Lawrencium	Lw	2	6	10	14	2	6	10	14	2	6	1	2			
104	Kurchatovium		2	6	10	14	2	6	10	14	2	6	2	2			
105	Hahnium		2	6	10	14	2	6	10	14	2	6	3	2			

5.26

(Z = 3)

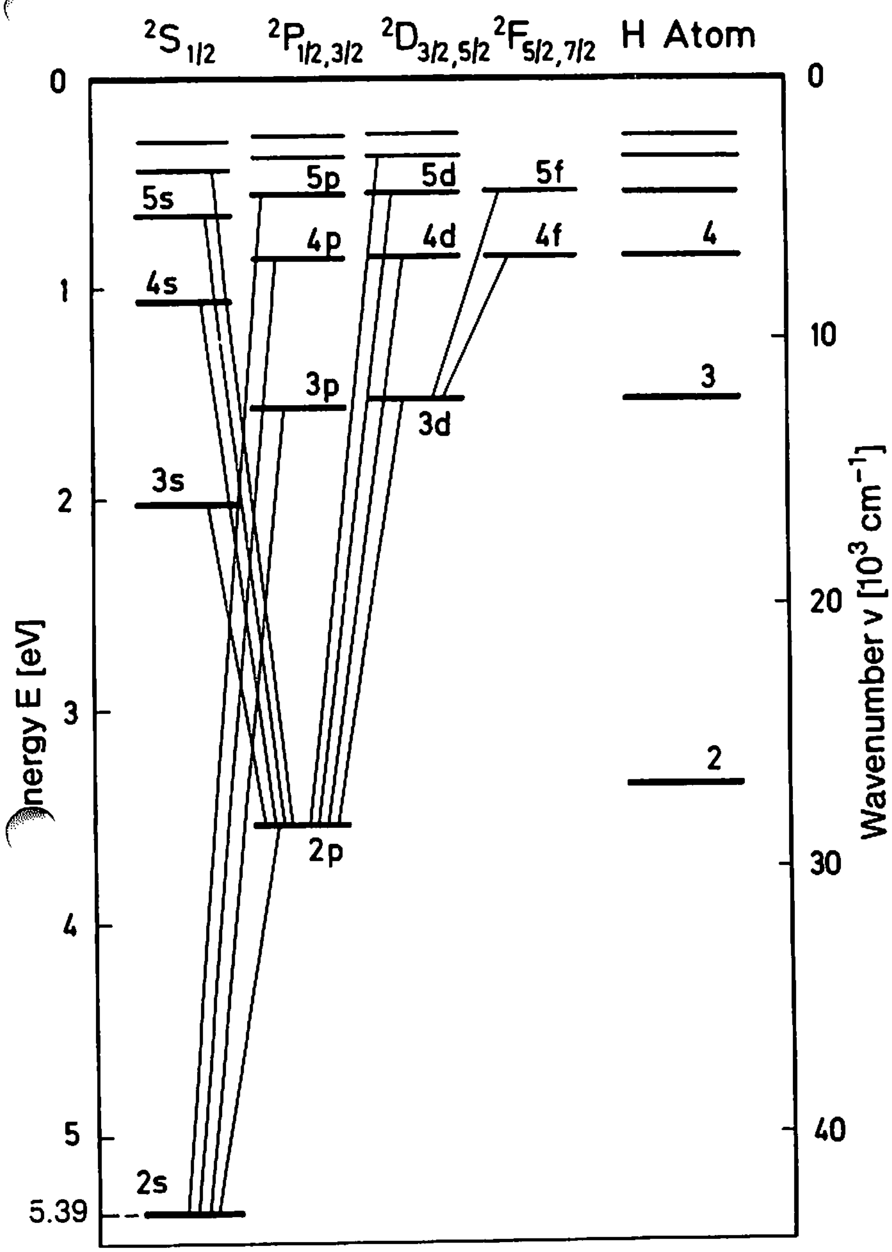
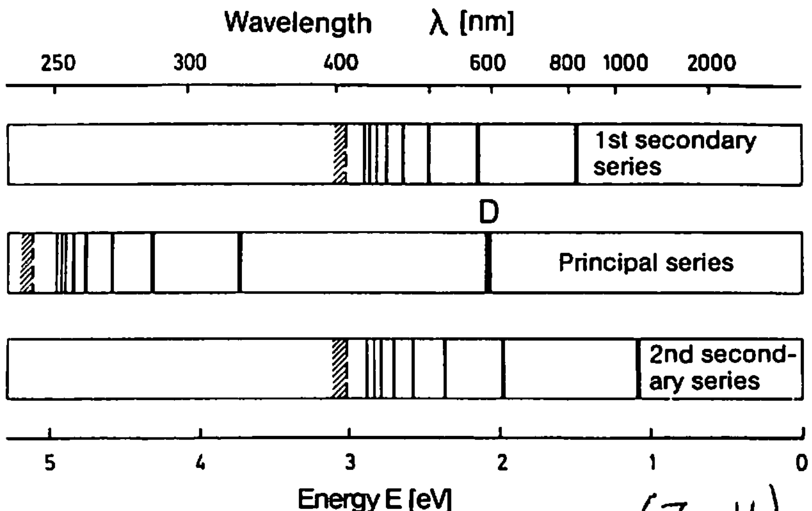


Fig. 11.5. Term diagram of the lithium atom with the most important transitions. This is called a Grotrian diagram. The term symbols given along the top of the figure are explained in Chaps. 12 and 17



(Z = 11)

Fig. 11.6. The three shortest-wave spectral series of the sodium atom. The series limits are indicated by shading. The emission spectrum is a composite of these series. In absorption spectra, normally only the principal series is observed, because in the ground state of the Na atom the highest occupied term is the $3s$ term. The yellow colour of sodium lamps is due to the longest-wave resonance line of the main series, the transition $3s \leftrightarrow 3p$. This is the sodium D line, a terminology which has been retained for historical reasons

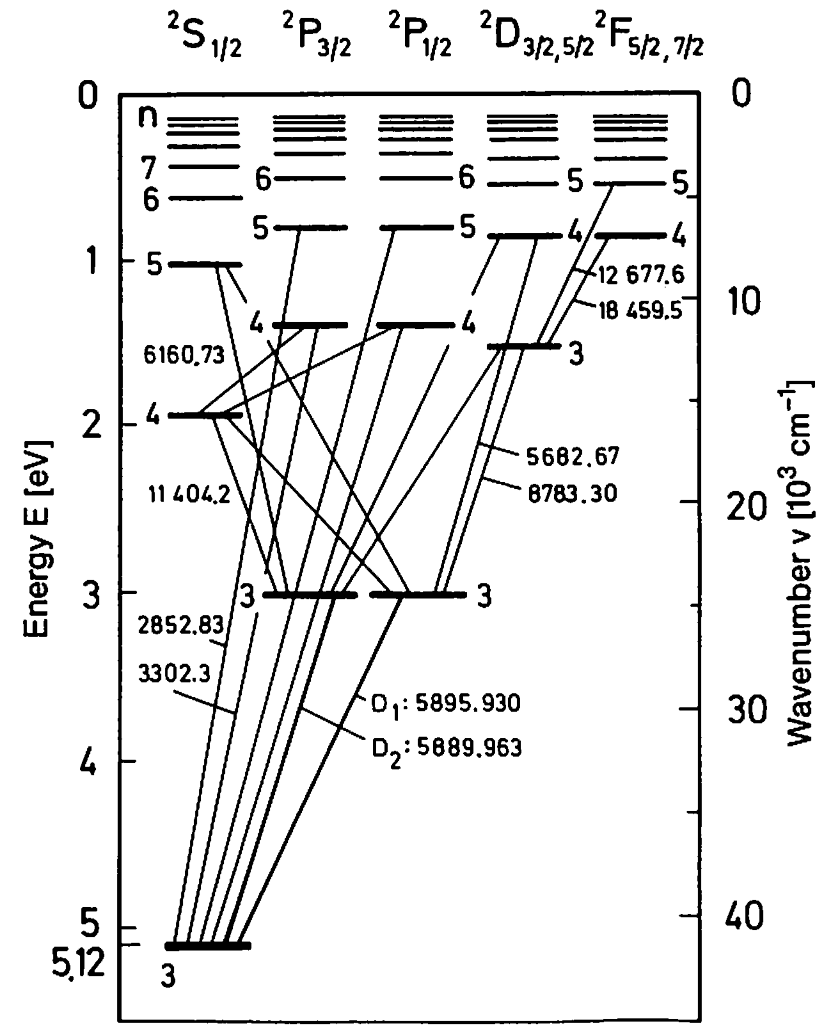


Fig. 11.7. Term scheme (Grotrian diagram) of the sodium atom. Some of the shortest-wave transitions from the principal series, the two secondary series and the Bergmann series have been included. The numbers in the diagram indicate the wavelength of the transition in Ångstrom units. The term symbols indicated on the upper edge of the figure also represent the quantum numbers for the multiplicity and the total angular momentum. These are explained in Chaps. 12 and 17

5.27

TIME - INDEPENDENT PERTURBATION THEORY

⇒ NONDEGENERATE PERTURBATION THEORY

- **INTRO**

↳ SUPPOSE WE HAVE SOLVED

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

(UNPERTURBED PROBLEM)

↳ SUPPOSE WE WANT TO SOLVE SCHRODINGER EQ. IN PRESENCE OF SMALL PERTURBATION (e.g. WEAK APPLIED MAGNETIC FIELD) H ATOM. IN

$$H = H^0 + \lambda H'$$

↑ SMALL PERTURBATION

(λ PARAMETER TO DENOTE ORDER OF PERTURBATION WILL BE TAKEN $\to 1$ IN END)

$$H \psi_n = E_n \psi_n$$

CAN WE FIND APPROXIMATE SOLUTIONS FOR ψ_n & E_n ?

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots$$

$$E_n = \underset{\substack{\Uparrow \\ \text{KNOWN}}}{E_n^0} + \lambda \underset{\substack{\Uparrow \\ \text{1-ORDER} \\ \text{CORRECTION}}}{E_n^1} + \lambda^2 \underset{\substack{\Uparrow \\ \text{2-ORDER} \\ \text{CORRECTION}}}{E_n^2} + \cdots$$

$\downarrow$ $H\psi_n = E_n \psi_n$

$$(H^0 + \lambda H^1)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$

$\downarrow$ EXPANSION IN λ

$$H^0 \psi_n^0 + \lambda (H^1 \psi_n^0 + H^0 \psi_n^1) + \lambda^2 (H^1 \psi_n^1 + H^0 \psi_n^2) + \cdots$$

$$= E_n^0 \psi_n^0 + \lambda (E_n^1 \psi_n^0 + E_n^0 \psi_n^1) + \lambda^2 (E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \cdots$$

$\downarrow$ IDENTIFY TERMS IN λ-EXPANSION

↳ TO LOWEST ORDER λ^0 :

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

ORIGINAL , UNPERTURBED PROBLEM WHICH WE HAVE SOLVED

↳ TO FIRST ORDER λ^1

$$H^1 \psi_n^0 + H^0 \psi_n^1 = E_n^1 \psi_n^0 + E_n^0 \psi_n^1$$

↳ TO SECOND ORDER λ^2 :

$$H^1 \psi_n^1 + H^0 \psi_n^2 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$$

- **FIRST - ORDER PERTURBATION THEORY**

↳ $$H^1 \psi_n^0 + H^0 \psi_n^1 = E_n^1 \psi_n^0 + E_n^0 \psi_n^1$$

$\downarrow$ TAKE INNER PRODUCT WITH $\langle \psi_n^0 |$

$$\langle \psi_n^0 | H^1 | \psi_n^0 \rangle + \langle \psi_n^0 | H^0 | \psi_n^1 \rangle$$

$$= E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle + E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$\downarrow$ $$\langle \psi_n^0 | H^0 = \langle \psi_n^0 | E_n^0$$

$$\langle \psi_n^0 | \psi_n^0 \rangle = 1$$

$$\langle \psi_n^0 | H^1 | \psi_n^0 \rangle + \cancel{E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle}$$

$$= E_n^1 + \cancel{E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle}$$

$$\Downarrow$$

$$\boxed{E_n^1 = \langle \psi_n^0 | H^1 | \psi_n^0 \rangle}$$

NOTE: WE USE THIS WHEN CALCULATING THE CORRECTION DUE TO COULOMB REPULSION BETWEEN $2e^-$ IN He ATOM:

$$H^1 = \frac{e^2}{4\pi \varepsilon_0 |\bar{r}_1 - \bar{r}_2|}$$

↳ ψ_n^1 (FIRST ORDER CORRECTION TO WAVE FUNCTION)

$$(H^0 - E_n^0)\psi_n^1 = (E_n^1 - H^1)\psi_n^0$$

ψ_m^0 FORMS COMPLETE SET

$$\boxed{\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0}$$

NOTE: TERM ψ_n^0 DOES NOT CONTRIBUTE AS $(H^0 - E_n^0)\psi_n^0 = 0$

$$\sum_{m \neq n} (H^0 - E_n^0)\, c_m^{(n)} \psi_m^0 = (E_n^1 - H^1)\, \psi_n^0$$

$\downarrow$ ψ_m^0 ARE EIGENSTATES OF H^0

$$\sum_{m \neq n} c_m^{(n)} (E_m^0 - E_n^0)\, \psi_m^0 = (E_n^1 - H^1)\, \psi_n^0$$

$\downarrow$ $\langle \psi_\ell^0 |$

$$\sum_{m \neq n} c_m^{(n)} (E_m^0 - E_n^0) \langle \psi_\ell^0 | \psi_m^0 \rangle$$

$$= E_n^1 \langle \psi_\ell^0 | \psi_n^0 \rangle - \langle \psi_\ell^0 | H^1 | \psi_n^0 \rangle$$

CASE $\ell = n$ $\quad \langle \psi_\ell^0 | \psi_m^0 \rangle = 0$

$$\rightsquigarrow \quad E_n^1 = \langle \psi_n^0 | H^1 | \psi_n^0 \rangle$$

OK! WE DERIVED THIS BEFORE

CASE $\ell \neq n$ $\quad \langle \psi_\ell^0 | \psi_m^0 \rangle = \delta_{\ell m}$

$$c_\ell^{(n)} \left(E_\ell^\circ - E_n^\circ \right) = - \langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle$$

$$c_\ell^{(n)} = \frac{\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_\ell^\circ}$$

$$\therefore \quad \boxed{ |\psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} |\psi_m^\circ\rangle }$$

ONLY APPLIES WHEN UNPERTURBED SPECTRUM is NON DEGENERATE (i.e. NO 2 ENERGIES E_n° ARE SAME)

- **SECOND ORDER PERTURBATION THEORY**

$$H' \psi_n^1 + H^\circ \psi_n^2 = E_n^\circ \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^\circ$$

$$\downarrow \quad \langle \psi_n^\circ |$$

$$\langle \psi_n^\circ | H' | \psi_n^1 \rangle + \cancel{\langle \psi_n^\circ | H^\circ | \psi_n^2 \rangle}$$

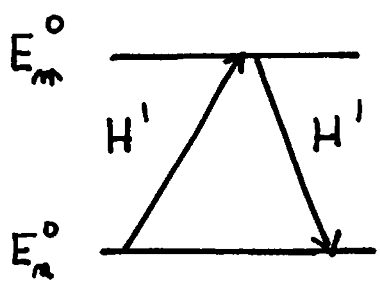
$$= E_n^\circ \cancel{\langle \psi_n^\circ | \psi_n^2 \rangle} + E_n^1 \langle \psi_n^\circ | \psi_n^1 \rangle + E_n^2$$

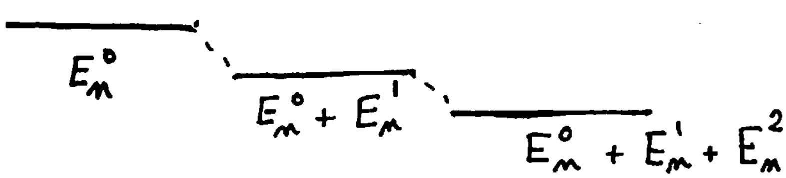
$$\downarrow \quad \langle \psi_n^\circ | H^\circ = \langle \psi_n^\circ | E_n^\circ$$

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \underbrace{\cancel{\langle \psi_n^0 | \psi_n^1 \rangle}}_{0}$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \langle \psi_n^0 | H' | \psi_m^0 \rangle$$

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$





⇒ DEGENERATE PERTURBATION THEORY

- IF IN $E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$

↓

2 ENERGIES $E_m^0 = E_n^0$ (FOR $m \neq n$)

↓

E_n^2 BLOWS UP → DERIVATION DOES NOT APPLY

- **2 - FOLD DEGENERACY**

↳ $E_a^0 = E_b^0 = E^0$

$$\left.\begin{aligned} H^0 |\psi_a^0\rangle &= E^0 |\psi_a^0\rangle \\ H^0 |\psi_b^0\rangle &= E^0 |\psi_b^0\rangle \end{aligned}\right\}$$

ANY LIN. COMB. $\alpha |\psi_a^0\rangle + \beta |\psi_b^0\rangle$ STILL SOLUTION OF H^0

$$\langle \psi_a^0 | \psi_b^0 \rangle = 0$$

↳ DUE TO PERTURBATION H'

↓

DEGENERACY BETWEEN 2 LEVELS IS LIFTED

ASSUME $|\psi\rangle$ IS SOLUTION OF $H = H^0 + \lambda H'$

($\lambda = 1$ AT END)

$$E = E^0 + \lambda E' + \lambda^2 E^2 + \cdots$$

$$|\psi\rangle = |\psi^0\rangle + \lambda |\psi'\rangle + \lambda^2 |\psi^2\rangle + \cdots$$

WITH $|\psi^0\rangle = \alpha |\psi_a^0\rangle + \beta |\psi_b^0\rangle$

$$H|\psi\rangle = E|\psi\rangle$$

$$(H^0 + \lambda H')(|\psi^0\rangle + \lambda|\psi'\rangle + \cdots)$$

$$= (E^0 + \lambda E' + \cdots)(|\psi^0\rangle + \lambda|\psi'\rangle + \cdots)$$

$$\Downarrow$$

0 - ORDER : $H^0|\psi^0\rangle = E^0|\psi^0\rangle$ ORIGINAL PROBLEM SOLVED !

1 - ORDER : $H^0|\psi'\rangle + H'|\psi^0\rangle = E^0|\psi'\rangle + E'|\psi^0\rangle$

TAKE $\langle\psi_a^0|$ & USE $|\psi^0\rangle = \alpha|\psi_a^0\rangle + \beta|\psi_b^0\rangle$

$$\langle\psi_a^0|H^0|\psi'\rangle + \langle\psi_a^0|H'|\psi^0\rangle$$

$$= E^0\langle\psi_a^0|\psi'\rangle + \alpha E'$$

$$\Downarrow \quad \langle\psi_a^0|H^0|\psi'\rangle = E^0\langle\psi_a^0|\psi'\rangle$$

$$\boxed{\alpha\langle\psi_a^0|H'|\psi_a^0\rangle + \beta\langle\psi_a^0|H'|\psi_b^0\rangle = \alpha E'}$$

NOTE : IF $\beta = 0$, $\alpha = 1$ WE FIND BACK FIRST ORDER FORMULA IN NON-DEGENERATE CASE

↳ INTRODUCE 'TRANSITION MATRIX ELEMENTS'

$$\boxed{W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle}$$

KNOWN ONCE WE SOLVED FOR $|\psi_i^0\rangle$

1- ORDER FORMULA $\quad \alpha E' = \alpha W_{aa} + \beta W_{ab} \quad (*)$

IF TAKING CONTRACTION WITH $\langle \psi_b^0 |$ INSTEAD,

WE FIND AN ANALOGOUS FORMULA $(a \leftrightarrow b)$

$$\beta E' = \beta W_{bb} + \alpha W_{ba} \quad (**)$$

$(**) \cdot W_{ab}$

$$(\beta W_{ab}) E' = (\beta W_{ab}) W_{bb} + \alpha |W_{ab}|^2$$

↓ USE $(*)$ FOR βW_{ab}

$$(\alpha E' - \alpha W_{aa})(E' - W_{bb}) = \alpha |W_{ab}|^2$$

↓ α DROPS OUT

$$E'^2 - (W_{aa} + W_{bb}) E' + W_{aa} W_{bb} - |W_{ab}|^2 = 0$$

$$\boxed{E'_\pm = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]}$$

SPECIAL CASES

$$|\psi^0\rangle = \alpha|\psi_a^0\rangle + \beta|\psi_b^0\rangle$$

$\rightsquigarrow \alpha = 1, \beta = 0 \Rightarrow W_{ba} = 0 \quad (**)$

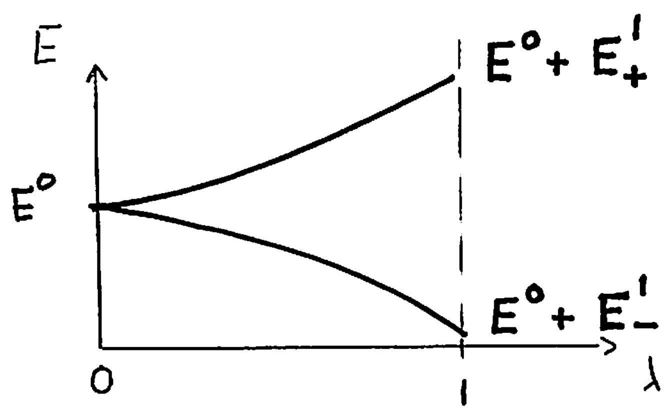
$$\underset{(*)}{E^1 =} W_{aa} \overset{!}{=} E_+^1$$

$\rightsquigarrow \alpha = 0, \beta = 1 \Rightarrow W_{ab} = 0 \quad (*)$

$$\underset{(**)}{E^1 =} W_{bb} \overset{!}{=} E_-^1$$

IN BOTH CASES WE FIND BACK RESULTS OF NON-DEGENERATE PERTURBATION THEORY

IN GENERAL



$\hookrightarrow$ DENOTES 'SWITCHING ON' THE PERTURBATION H^1 FROM 0 TO 1

↳ USEFUL THEOREM TO DETERMINE 'GOOD' LINEAR COMBINATION TO APPLY NON-DEG. P.T.

THEOREM : A HERMITIAN OPERATOR

$$[A, H^0] = [A, H'] = 0$$

IF $|\psi_a^0\rangle$ AND $|\psi_b^0\rangle$ ARE ALSO EIGENFUNCTIONS OF A :

$$A|\psi_a^0\rangle = \mu|\psi_a^0\rangle$$

$$A|\psi_b^0\rangle = \nu|\psi_b^0\rangle$$

SUCH THAT $\mu \neq \nu$

$$\Downarrow$$

$W_{ab} = 0 \Rightarrow$ WE CAN APPLY NON-DEG. PT

$$E_+^1 = W_{aa} = \langle\psi_a^0|H'|\psi_a^0\rangle$$

$$E_-^1 = W_{bb} = \langle\psi_b^0|H'|\psi_b^0\rangle$$

PROOF : $0 = \langle\psi_a^0|[A,H']|\psi_b^0\rangle$

$$= \langle\psi_a^0|AH'|\psi_b^0\rangle - \langle\psi_a^0|H'A|\psi_b^0\rangle$$

$$= (\mu-\nu)\langle\psi_a^0|H'|\psi_b^0\rangle$$

$$= (\mu-\nu)\,W_{ab} \Rightarrow \text{IF } \mu\neq\nu \Rightarrow W_{ab} = 0 \quad \blacksquare$$

• MATRIX NOTATION

2- FOLD DEGENERACY

↳ $H^0 |\psi_a^0\rangle = E^0 |\psi_a^0\rangle$

$H^0 |\psi_b^0\rangle = E^0 |\psi_b^0\rangle$

$|\psi^0\rangle = \alpha |\psi_a^0\rangle + \beta |\psi_b^0\rangle$

↳ $H = H^0 + \lambda H^1$

$E = E^0 + \lambda E^1 + \dots$

$|\psi\rangle = |\psi^0\rangle + \lambda |\psi^1\rangle + \dots$

$H|\psi\rangle = E|\psi\rangle$

TO FIRST ORDER IN PERTURBATION

2 EQS. $\begin{cases} \alpha W_{aa} + \beta W_{ab} = \alpha E^1 \\ \alpha W_{ba} + \beta W_{bb} = \beta E^1 \end{cases}$

↳ IN MATRIX NOTATION: WITH $W_{ij} \equiv \langle \psi_i^0 | H^1 | \psi_j^0 \rangle$

$$\underbrace{\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}}_{\equiv W} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

∴ E^1 : EIGENVALUES OF W MATRIX

(α, β) : GOOD LIN. COMB. OF UNPERTURBED STATES

↳ EIGENVECTORS OF W

- ## HIGHER-ORDER DEGENERACY

↳ n-FOLD DEGENERACY

$$|\psi_1^0\rangle, \; |\psi_2^0\rangle, \ldots, \; |\psi_n^0\rangle$$

ARE DEGENERATE → ENERGY E^0

↳ $n \times n$ MATRIX W

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

↳ FIRST ORDER CORRECTIONS TO ENERGY ⇒ EIGENVALUES OF W

GOOD LIN. COMB. OF UNPERTURBED STATES

$\Downarrow$

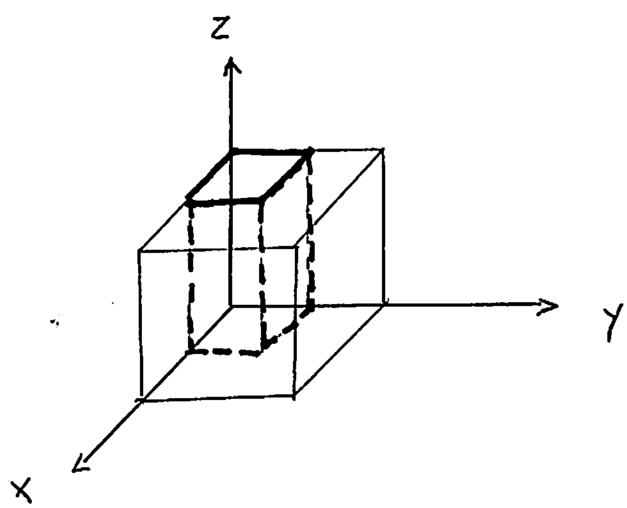
EIGENVECTORS OF W

- **EXAMPLE** : 3-DIM INFINITE CUBIC WELL WITH PERTURBATION

↳ $$H^0 = \frac{\hat{P}^2}{2m} + V(x,y,z)$$

$$V(x,y,z) = \begin{cases} 0 & , \quad 0 < x < a \\ & \quad\;\; 0 < y < a \\ & \quad\;\; 0 < z < a \\ \infty & , \quad \text{OTHERWISE} \end{cases}$$

↳ $$H' = \begin{cases} V_0 & , \quad 0 < x < a/2 \\ & \quad\;\; 0 < y < a/2 \\ 0 & , \quad \text{OTHERWISE} \end{cases}$$



PARTICLE FEELS PERTURBATION WHEN IT IS IN SMALLER BOX

↳ UNPERTURBED PROBLEM

$$\psi^{0}_{n_x n_y n_z}(x,y,z) = C \sin\left(n_x \frac{\pi}{a} x\right) \sin\left(n_y \frac{\pi}{a} y\right) \sin\left(n_z \frac{\pi}{a} z\right)$$

$$C = \left(\frac{2}{a}\right)^{3/2}$$

$$E^{0}_{n_x n_y n_z} = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \left(n_x^2 + n_y^2 + n_z^2\right)$$

⇝ GROUND STATE : $n_x = n_y = n_z = 1$

NON-DEGENERATE $E^{0}_{0} = \frac{\hbar^2}{2m} \frac{3\pi^2}{a^2}$

⇝ FIRST EXCITED STATE : $n_x = 1, \quad n_y = 1, \quad n_z = 2$

$n_x = 1, \quad n_y = 2, \quad n_z = 1$

$n_x = 2, \quad n_y = 1, \quad n_z = 1$

TRIPLY DEGENERATE

$$\psi^{0}_{a} \equiv \psi^{0}_{112}, \quad \psi^{0}_{b} \equiv \psi^{0}_{121}, \quad \psi^{0}_{c} \equiv \psi^{0}_{211}$$

ALL 3 HAVE SAME ENERGY

$$E^{0}_{1} = \frac{\hbar^2}{2m} \frac{6\pi^2}{a^2}$$

↳ PERTURBATION THEORY

$$|\psi^0\rangle \equiv \alpha\,|\psi_a^0\rangle + \beta\,|\psi_b^0\rangle + \gamma\,|\psi_c^0\rangle$$

↳ GOOD LIN. COMB OF UNPERTURBED STATES

$$W_{ij} = \langle \psi_i^0 \,|\, H' \,|\, \psi_j^0 \rangle$$

$i, j = a, b, c$

- $W_{aa} = W_{bb} = W_{cc}$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} dx \, \sin^2\left(\frac{\pi}{a}x\right) \int_0^{a/2} dy \, \sin^2\left(\frac{\pi}{a}y\right) \cdot \int_0^{a} dz \, \sin^2\left(\frac{2\pi}{a}z\right)$$

$$= \left(\frac{2}{a}\right)^3 V_0 \cdot \left(\frac{1}{2}\,\frac{a}{2}\right)\left(\frac{1}{2}\,\frac{a}{2}\right)\left(\frac{1}{2}\,a\right)$$

$$= \frac{V_0}{4}$$

- $$W_{ab} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} dx \ \sin^2\left(\frac{\pi}{a}x\right)$$

$$\cdot \int_0^{a/2} dy \ \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right)$$

$$\cdot \int_0^{a} dz \ \underbrace{\sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right)}_{\frac{1}{2}\left(\cos\frac{\pi}{a}z \ - \ \cos\frac{3\pi}{a}z\right)}$$

$$\int_0^a: \quad \cos\frac{\pi}{a}z \to 0, \quad \cos\frac{3\pi}{a}z \to 0$$

$$W_{ab} = W_{ac} = 0$$

- $$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} dx \ \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right)$$

$$\cdot \int_0^{a/2} dy \ \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right)$$

$$\cdot \int_0^{a} dz \ \sin^2\left(\frac{\pi}{a}z\right)$$

$$= \left(\frac{2}{a}\right)^3 \cdot V_0 \cdot \left(\frac{1}{2}\cdot\frac{4}{3}\frac{a}{\pi}\right)\left(\frac{1}{2}\cdot\frac{4}{3}\frac{a}{\pi}\right)\cdot\left(\frac{1}{2}a\right)$$

$$= \frac{16}{9}\frac{1}{\pi^2} V_0$$

•

$$W = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix}$$

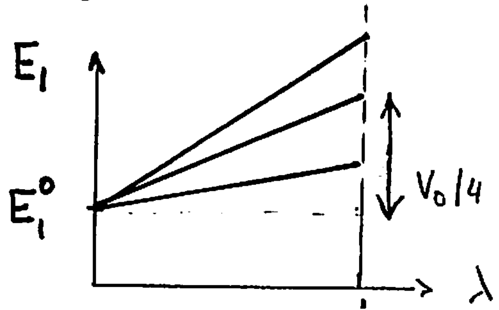
$$K \equiv \left(\frac{8}{3\pi}\right)^2$$

$$\begin{vmatrix} 1-w & 0 & 0 \\ 0 & 1-w & K \\ 0 & K & 1-w \end{vmatrix} = 0$$

$$\Updownarrow$$

$$(1-w)^3 - K^2(1-w) = 0$$

$$\begin{cases} w_1 = 1 & \Rightarrow \quad E_1^{(1)} = E_1^0 + \dfrac{V_0}{4} \\ w_2 = 1+K & \Rightarrow \quad E_1^{(2)} = E_1^0 + \dfrac{V_0}{4}(1+K) \\ w_3 = 1-K & \Rightarrow \quad E_1^{(3)} = E_1^0 + \dfrac{V_0}{4}(1-K) \end{cases}$$



↑ UNPERTURBED ENERGIES.

- GOOD UNPERTURBED STATES

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

$\rightsquigarrow \quad w = 1 \quad \Longleftrightarrow \quad \beta = \gamma = 0 \quad , \quad \alpha = 1$

$\rightsquigarrow \quad w = 1 + K \quad \Longleftrightarrow \quad \alpha = 0 \quad , \quad \beta = \gamma = \frac{1}{\sqrt{2}}$

$\rightsquigarrow \quad w = 1 - K \quad \Longleftrightarrow \quad \alpha = 0 \quad , \quad \beta = -\gamma = \frac{1}{\sqrt{2}}$

$$|\psi^0\rangle = \begin{cases} |\psi_a^0\rangle \\ \frac{1}{\sqrt{2}}\left\{|\psi_b^0\rangle + |\psi_c^0\rangle\right\} \\ \frac{1}{\sqrt{2}}\left\{|\psi_b^0\rangle - |\psi_c^0\rangle\right\} \end{cases}$$

$\downarrow$

CORRESPOND WITH 3 STATES.

• FIRST - ORDER CORRECTION TO STATES

E_m^0 ══════ } d_m FOLD DEGENERATE

E_n^0 ══════ } d_n FOLD DEGENERATE ⇒ STATES $|\psi_{n,1}^0\rangle$, $|\psi_{n,2}^0\rangle$, ... $|\psi_{n,d_n}^0\rangle$

GOOD UNPERTURBED STATES

$$\boxed{|\psi_{n_i}^0\rangle = \sum_{j=1}^{d_n} \alpha_{ij} \, |\psi_{n,j}^0\rangle}$$

↳ $i = 1 \dots d_n$

* FIRST ORDER EQ. FOR STATE n_i $(i = 1 \dots d_n)$

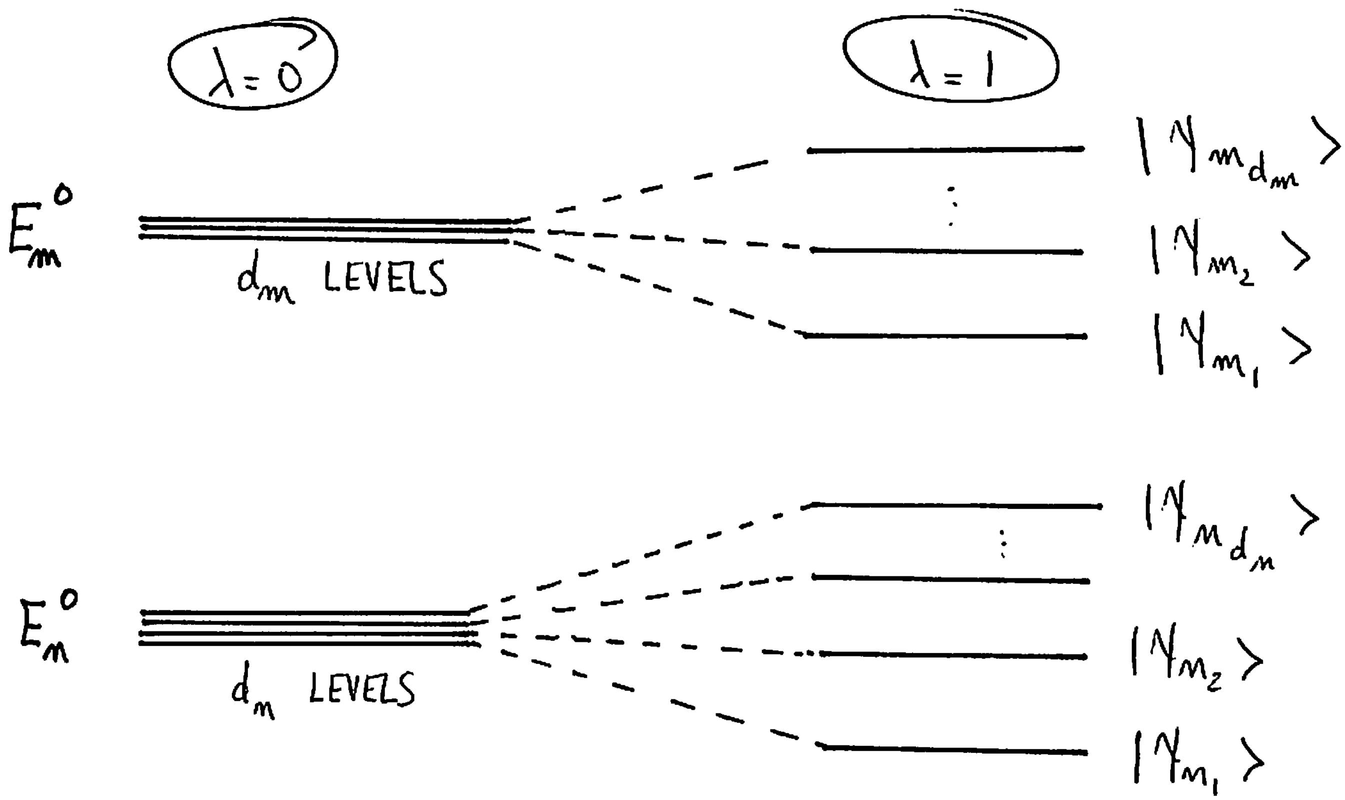
$$H^0 |\psi_{n_i}^1\rangle + H^1 |\psi_{n_i}^0\rangle = E_n^0 |\psi_{n_i}^1\rangle + E_{n_i}^1 |\psi_{n_i}^0\rangle$$

↓

$|\psi_{n_i}^1\rangle$ CAN BE EXPANDED IN COMPLETE BASIS

$$\boxed{(H^0 - E_n^0) |\psi_{n_i}^1\rangle = (E_{n_i}^1 - H^1) |\psi_{n_i}^0\rangle}$$

$$|\psi^1_{n_i}\rangle = \sum_{m \neq n} \sum_{j=1}^{d_m} c_{n_i m_j} \, |\psi^0_{m_j}\rangle$$



$$(H^0 - E^0_n) \sum_{m \neq n} \sum_{j=1}^{d_m} c_{n_i m_j} \, |\psi^0_{m_j}\rangle$$

$$= (E^1_{n_i} - H^1) \quad |\psi^0_{n_i}\rangle$$

$\Downarrow$

$$\sum_{m \neq n} \left(E_m^0 - E_n^0 \right) \sum_{j=1}^{d_m} c_{n_i m_j} \; | \psi_{m_j}^0 \rangle$$

$$= \left(E_{n_i}^1 - H^1 \right) | \psi_{n_i}^0 \rangle$$

$\Downarrow$

$$\langle \psi_{m_k}^0 | \qquad m \neq n$$

$$\left(E_m^0 - E_n^0 \right) \sum_{j=1}^{d_m} c_{n_i m_j} \; \underbrace{\langle \psi_{m_k}^0 | \psi_{m_j}^0 \rangle}_{\delta_{jk}}$$

$$= \langle \psi_{m_k}^0 | \left(\cancel{E_{n_i}^1} - H^1 \right) \qquad | \psi_{n_i}^0 \rangle$$

$$m \neq n$$

$$\left(E_m^0 - E_n^0 \right) c_{n_i m_k} = - \langle \psi_{m_k}^0 | H^1 | \psi_{n_i}^0 \rangle$$

$$\boxed{| \psi_{n_i}^1 \rangle = \sum_{m \neq n} \sum_{j=1}^{d_m} \frac{\langle \psi_{m_j}^0 | H^1 | \psi_{n_i}^0 \rangle}{E_n^0 - E_m^0} \cdot | \psi_{m_j}^0 \rangle}$$

TIME - DEPENDENT PERTURBATION THEORY

⇝ STUDY OF TIME - DEPENDENT PERTURBATIONS

⇒ TWO - LEVEL SYSTEMS

- H^0 UNPERTURBED HAMILTONIAN

↳ 2 STATES $|\psi_a\rangle \qquad H^0|\psi_a\rangle = E_a|\psi_a\rangle$

$|\psi_b\rangle \qquad H^0|\psi_b\rangle = E_b|\psi_b\rangle$

$$\langle\psi_a|\psi_b\rangle = \delta_{ab}$$

ANY STATE $|\Psi(t=0)\rangle = c_a|\psi_a\rangle + c_b|\psi_b\rangle$

$$|c_a|^2 + |c_b|^2 = 1$$

$$|\Psi(t)\rangle = c_a e^{-\frac{i}{\hbar}E_a t}|\psi_a\rangle + c_b e^{-\frac{i}{\hbar}E_b t}|\psi_b\rangle$$

c_a, c_b CONSTANTS

ALL TIME DEPENDENCE IS IN $e^{-\frac{i}{\hbar}Et}$ FOR STATIONARY STATES

• TIME-DEPENDENT PERTURBATION

↳ $H'(t)$

$\{ |\psi_a\rangle, |\psi_b\rangle \}$ FORM A COMPLETE SET

↓

WF AT TIME t CAN STILL BE EXPRESSED AS LINEAR COMBINATION OF $|\psi_a\rangle$ & $|\psi_b\rangle$

$$|\Psi(t)\rangle = c_a(t)\, e^{-\frac{i}{\hbar}E_a t}\, |\psi_a\rangle + c_b(t)\, e^{-\frac{i}{\hbar}E_b t}\, |\psi_b\rangle$$

COEFFICIENTS CAN NOW DEPEND ON TIME

$H'(t)$ CAN INDUCE TRANSITIONS BETWEEN a & b

e.g. $c_a(t=0) = 1$, $c_b(t=0) = 0$ $\overset{H'(t)}{\Longrightarrow}$ $c_a(t_1) = 0$, $c_b(t_1) = 1$ $(t_1 > 0)$

↳ $c_a(t), \; c_b(t)$?

$$H = H^0 + H'(t)$$

$$H\,|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle$$

$$\downarrow \qquad |\Psi(t)\rangle = c_a(t)\, e^{-\frac{i}{\hbar}E_a t}\, |\psi_a\rangle + c_b(t)\, e^{-\frac{i}{\hbar}E_b t}\, |\psi_b\rangle$$

$$\cancel{c_a e^{-\frac{i}{\hbar}E_a t}}\, \overset{E_a}{H^0|\psi_a\rangle} + c_b\, \cancel{e^{-\frac{i}{\hbar}E_b t} H^0}\overset{E_b}{}|\psi_b\rangle$$

$$+ c_a e^{-\frac{i}{\hbar}E_a t} H'|\psi_a\rangle + c_b e^{-\frac{i}{\hbar}E_b t} H'|\psi_b\rangle$$

$$= i\hbar \left[\dot{c}_a e^{-\frac{i}{\hbar}E_a t} |\psi_a\rangle + \dot{c}_b e^{-\frac{i}{\hbar}E_b t} |\psi_b\rangle \right]$$

$$+ c_a \cancel{E_a e^{-\frac{i}{\hbar}E_a t}} |\psi_a\rangle + c_b \cancel{E_b e^{-\frac{i}{\hbar}E_b t}} |\psi_b\rangle$$

$$\Downarrow$$

$$c_a e^{-\frac{i}{\hbar}E_a t} H'|\psi_a\rangle + c_b e^{-\frac{i}{\hbar}E_b t} H'|\psi_b\rangle$$

$$= i\hbar \left[\dot{c}_a e^{-\frac{i}{\hbar}E_a t} |\psi_a\rangle + \dot{c}_b e^{-\frac{i}{\hbar}E_b t} |\psi_b\rangle \right]$$

$$\Downarrow \qquad \langle\psi_a|$$

$$c_a e^{-\frac{i}{\hbar}E_a t} \langle\psi_a|H'|\psi_a\rangle + c_b e^{-\frac{i}{\hbar}E_b t} \langle\psi_a|H'|\psi_b\rangle$$

$$= i\hbar\, \dot{c}_a e^{-\frac{i}{\hbar}E_a t}$$

DEFINE:

$$\boxed{H'_{ab} \equiv \langle \psi_a | H' | \psi_b \rangle}$$

$$H'^{\dagger} = H' \qquad (\text{HERMITIAN})$$

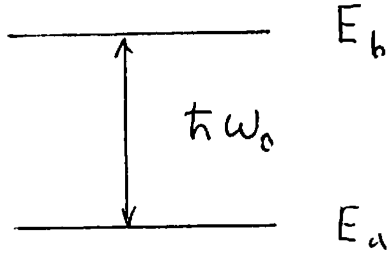
$$H'_{ba} = \left(H'_{ab} \right)^*$$

$$\boxed{\dot{c}_a = -\frac{i}{\hbar} \left[c_a H'_{aa} + c_b \, e^{-\frac{i}{\hbar}(E_b - E_a)t} H'_{ab} \right]}$$

ANALOGOUSLY

$$\boxed{\dot{c}_b = -\frac{i}{\hbar} \left[c_b H'_{bb} + c_a \, e^{-\frac{i}{\hbar}(E_a - E_b)t} H'_{ba} \right]}$$

- IMPORTANT SPECIAL CASE : $H'_{aa} = H'_{bb} = 0$



$$\hbar\omega_0 \equiv E_b - E_a$$

$$(E_b > E_a)$$

$$\boxed{\begin{aligned} \dot{c}_a &= -\frac{i}{\hbar} c_b \, e^{-i\omega_0 t} H'_{ab} \\ \dot{c}_b &= -\frac{i}{\hbar} c_a \, e^{+i\omega_0 t} H'_{ba} \end{aligned}}$$

PERTURBATION THEORY

H' SMALL

↳ SUPPOSE AT $t=0$ SYSTEM IS IN STATE a

$$c_a(t=0) = 1$$

$$c_b(t=0) = 0$$

↳ ZERO ORDER : $H' = 0$

$$c_a^{(0)}(t) = 1$$

$$c_b^{(0)}(t) = 0$$

↳ FIRST ORDER

$$\dot{c}_a^{(1)} = 0 \quad \Rightarrow \quad c_a^{(1)}(t) = 1$$

$$\dot{c}_b^{(1)} = -\frac{i}{\hbar}\, c_a^{(0)}\, e^{i\omega_0 t}\, H'_{ba}(t)$$

$$\downarrow$$

$$c_b^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, c_a^{(0)}(t')\, e^{i\omega_0 t'}\, H'_{ba}(t')$$

$$\cong -\frac{i}{\hbar}\int_0^t dt'\, e^{i\omega_0 t'}\, H'_{ba}(t')$$

↳ SECOND ORDER

$$\dot{c}_a^{(2)} = -\frac{i}{\hbar} c_b^{(1)} e^{-i\omega_0 t} H'_{ab}(t)$$

$$c_a^{(2)}(t) - \underbrace{c_a^{(2)}(0)}_{1} = -\frac{i}{\hbar} \int_0^t dt' \, c_b^{(1)}(t') e^{-i\omega_0 t'} H'_{ab}(t')$$

$$c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t dt' \, e^{-i\omega_0 t'} H'_{ab}(t') \int_0^{t'} dt'' \, e^{i\omega_0 t''} H'_{ba}(t'')$$

$$c_b^{(2)}(t) = c_b^{(1)}(t)$$

⋮

ITERATIVE PROCEDURE

↳ NORMALIZATION

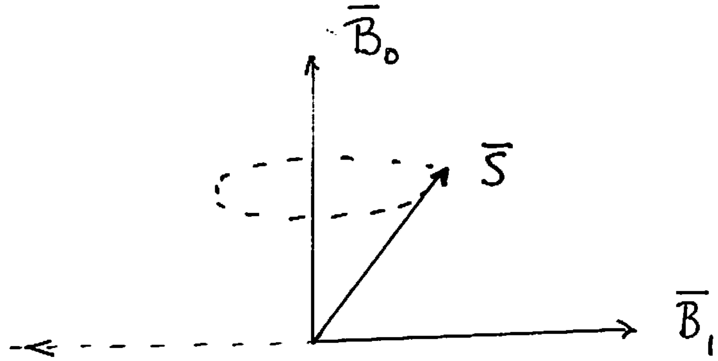
$$|c_a(t)|^2 + |c_b(t)|^2 = 1$$

↑ WILL BE APPROXIMATE TO THE GIVEN ORDER IN H'

$$\underbrace{|c_a^{(1)}(t)|^2}_{1} + \underbrace{|c_b^{(1)}(t)|^2}_{O(H'^2)} = 1 + O(H'^2)$$

• SINUSOIDAL PERTURBATION

↳

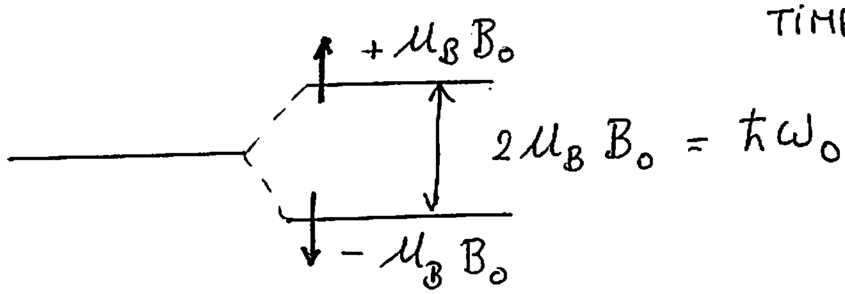


$$\bar{B} = B_0 \, \hat{e}_z + B_1 \sin\omega t \; \hat{e}_x$$

$$H^0 = + \frac{e\hbar}{2m} B_0 \, \sigma_z = \mu_B B_0 \, \sigma_z$$

$$H' = \frac{e\hbar}{2m} B_1 \sin\omega t \; \sigma_x = \underbrace{\mu_B B_1 \, \sigma_x}_{\hat{V}} \; \sin\omega t$$

⇑ TIME INDEPENDENT



↳ $H'_{ab} = \langle \psi_a | \hat{V} | \psi_b \rangle \; \sin\omega t$

FOR $\hat{V} = \mu_B B_1 \sigma_x$

$$\langle \uparrow | \hat{V} | \uparrow \rangle = 0$$

$$\langle \downarrow | \hat{V} | \downarrow \rangle = 0$$

$$V_{\uparrow\downarrow} \equiv \langle \uparrow | \hat{V} | \downarrow \rangle = \langle \downarrow | \hat{V} | \uparrow \rangle = \mu_B B_1$$

$\hookrightarrow$ 1° ORDER

$$|\psi_a\rangle = |\downarrow\rangle : c_\downarrow^{(1)}(t) = 1$$

$$|\psi_b\rangle = |\uparrow\rangle : c_\uparrow^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, e^{i\omega_0 t'}\, V_{ba}\sin\omega t'$$

$$= -\frac{i V_{ba}}{\hbar}\,\frac{1}{2i}\int_0^t dt'\left[e^{i(\omega_0+\omega)t'} - e^{i(\omega_0-\omega)t'}\right]$$

$$= -\frac{V_{ba}}{2\hbar}\left\{\frac{e^{i(\omega_0+\omega)t}-1}{i(\omega_0+\omega)} - \frac{e^{i(\omega_0-\omega)t}-1}{i(\omega_0-\omega)}\right\}$$

$\Downarrow$ FOR DRIVING FREQUENCIES

$$\omega \simeq \omega_0$$

$\uparrow$ CLOSE TO TRANSITION FREQ. ω_0

$$\omega_0 + \omega \gg |\omega_0 - \omega|$$

$$c_\uparrow^{(1)}(t) = +\frac{V_{\uparrow\downarrow}}{2i\hbar}\,\frac{e^{i(\omega_0-\omega)t}-1}{(\omega_0-\omega)}$$

$$= \frac{V_{\uparrow\downarrow}}{2i\hbar}\,\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left[e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}\right]$$

$$c_{\uparrow}^{(1)}(t) = \frac{V_{\uparrow\downarrow}}{\hbar} \frac{\sin\left[(\omega_0-\omega)t/2\right]}{(\omega_0-\omega)} e^{i(\omega_0-\omega)t/2}$$

↳ TRANSITION PROBABILITY $\downarrow \to \uparrow$ (SPIN FLIP)

$$\boxed{\begin{aligned} P_{\downarrow\to\uparrow}(t) &= \left| c_{\uparrow}^{(1)}(t) \right|^2 \\ &\simeq \frac{|V_{\uparrow\downarrow}|^2}{\hbar^2} \frac{\sin^2\left[(\omega_0-\omega)t/2\right]}{(\omega_0-\omega)^2} \end{aligned}}$$

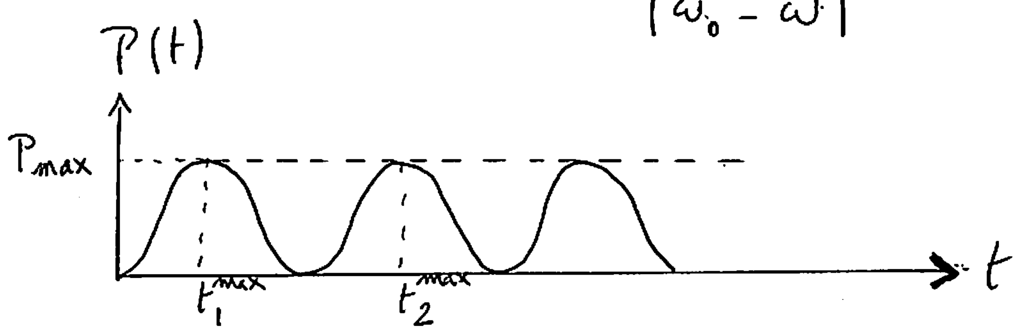
PROBABILITY OF SPIN FLIP AT TIME t

$P_{\downarrow\to\uparrow}(0) = 0$

$P_{\downarrow\to\uparrow}$ RISES TO MAX. $\dfrac{|V_{\uparrow\downarrow}|^2}{\hbar^2(\omega_0-\omega)^2} = \dfrac{(\mu_B B_1)^2}{\hbar^2(\omega_0-\omega)^2}$

$\hbar\omega_0 = 2\mu_B B_0$

AT TIMES $t_n^{max} = \dfrac{(2n+1)\pi}{|\omega_0-\omega|}$



↳ AT A TIME t

VARY ω

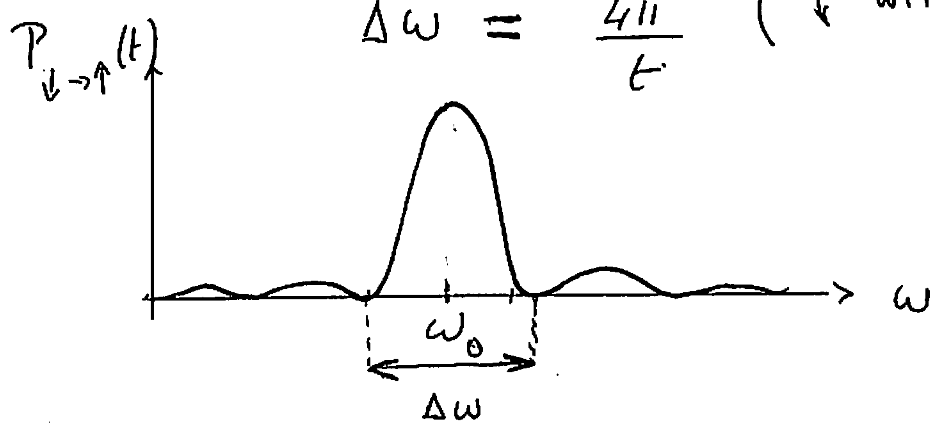
FOR $\omega \simeq \omega_0$

$$\sin^2\left[(\omega_0 - \omega)\, t/2\right] \simeq (\omega_0 - \omega)^2 \frac{t^2}{4}$$

$$P_{\downarrow\to\uparrow}(t) \simeq \left(\frac{|V_{\uparrow\downarrow}|\ t}{2\hbar}\right)^2$$ HEIGHT (↗ WITH t)

WIDTH $\quad \frac{\Delta\omega\, t}{2} = (2\pi)$

$$\Delta\omega = \frac{4\pi}{t}$$ (↓ WITH t)



RESONANCE WHEN $\omega \to \omega_0$

CAVEAT : IF $P_{\downarrow\to\uparrow}(t)$ ↗ AT SOME POINT P.T. BREAKS DOWN

↓

EXACT SOLUTION $\quad P_{\downarrow\to\uparrow}(t) \lesssim 1$ EVIDENTLY!

EXACT SOLUTION : ROTATING WAVE METHOD

↳ $H' = \hat{V} \sin\omega t$

$$= \hat{V} \frac{1}{2i} \left(e^{i\omega t} - e^{-i\omega t} \right)$$

↳ RABI'S METHOD

$$c_b(t) = -\frac{V_{ba}}{2\hbar} \left\{ \underbrace{\frac{e^{i(\omega_0+\omega)t} - 1}{i(\omega_0+\omega)}}_{\uparrow} - \underbrace{\frac{e^{i(\omega_0-\omega)t} - 1}{i(\omega_0-\omega)}}_{\uparrow} \right\}$$

FROM $e^{i\omega t}$ PART IN H' FROM $e^{-i\omega t}$ PART IN H'

FOR $\omega \simeq \omega_0$ KEEP ONLY 2° TERM

$$\boxed{H' = \hat{V} \left(\frac{i}{2} \right) e^{-i\omega t}}$$

ROTATING WAVE

↳ WITH THIS H', WE CAN SOLVE PROBLEM <u>EXACTLY</u>, <u>WITHOUT</u> USING PT

$$H'_{aa} = H'_{bb} = 0$$

$$H'_{ba} = V_{ba} \frac{i}{2} e^{-i\omega t}$$

$$H'_{ab} = H'^{*}_{ba} = V^{*}_{ab} \left(-\frac{i}{2} \right) e^{+i\omega t}$$

↳ GENERAL SOLUTION FOR $H' = \hat{V}\left(\frac{i}{2}\right) e^{-i\omega t}$

$$\begin{cases} \dot{c}_a = -\frac{i}{\hbar} c_b \, e^{-i\omega_0 t} H'_{ab} \\ \dot{c}_b = -\frac{i}{\hbar} c_a \, e^{+i\omega_0 t} H'_{ba} \end{cases}$$

$$\Downarrow$$

$$\begin{cases} \dot{c}_a = -\frac{1}{2\hbar} V^*_{ab} \, e^{i(\omega-\omega_0)t} c_b \\ \dot{c}_b = +\frac{1}{2\hbar} V_{ba} \, e^{-i(\omega-\omega_0)t} c_a \end{cases}$$

$$\ddot{c}_b = \frac{1}{2\hbar} V_{ba} \, e^{-i(\omega-\omega_0)t} \left[-i(\omega-\omega_0) c_a + \dot{c}_a \right]$$

$$= -i(\omega-\omega_0)\dot{c}_b - \frac{1}{(2\hbar)^2} |V_{ab}|^2 c_b$$

$$\boxed{\ddot{c}_b + i(\omega-\omega_0)\dot{c}_b + \frac{1}{(2\hbar)^2}|V_{ab}|^2 c_b = 0}$$

TRY $c_b \sim e^{i\lambda t}$

$$-\lambda^2 - (\omega-\omega_0)\lambda + \frac{1}{(2\hbar)^2}|V_{ab}|^2 = 0$$

$$\lambda^2 + (\omega - \omega_0)\lambda - \frac{1}{(2\hbar)^2}|V_{ab}|^2 = 0$$

$$\lambda = -\frac{(\omega - \omega_0)}{2} \pm \frac{1}{2}\sqrt{(\omega-\omega_0)^2 + \frac{|V_{ab}|^2}{\hbar^2}}$$

$$\boxed{\omega_R \equiv \frac{1}{2}\sqrt{(\omega-\omega_0)^2 + \frac{|V_{ab}|^2}{\hbar^2}}}$$

$\Uparrow$ RABI FLOPPING FREQUENCY

$$\therefore \quad c_b(t) = A\, e^{i\left[-\frac{(\omega-\omega_0)}{2} + \omega_R\right]t} + B\, e^{i\left[-\frac{(\omega-\omega_0)}{2} - \omega_R\right]t}$$

$$= e^{-i\frac{(\omega-\omega_0)}{2}t}\left[A\, e^{i\omega_R t} + B\, e^{-i\omega_R t}\right]$$

OR EQUIVALENTLY

$$c_b(t) = e^{-i\frac{(\omega-\omega_0)}{2}t}\left[C\cos\omega_R t + D\sin\omega_R t\right]$$

$$\rightsquigarrow \quad c_b(t=0) = 0 \quad \Rightarrow \quad C = 0$$

$$\| \quad c_b(t) = D\, e^{-i\frac{(\omega-\omega_0)}{2}t} \sin\omega_R t$$

$$\rightsquigarrow \quad c_a(t) = \frac{2\hbar}{V_{ba}} \dot{c}_b \, e^{+i(\omega-\omega_0)t}$$

$$= \frac{2\hbar}{V_{ba}} D \left[-\frac{i(\omega-\omega_0)}{2} \sin\omega_R t + \omega_R \cos\omega_R t \right] \cdot e^{\frac{i(\omega-\omega_0)t}{2}}$$

$$c_a(t=0) = 1 \quad \Rightarrow \quad \frac{2\hbar}{V_{ba}} D \, \omega_R = 1$$

$$D = \frac{V_{ba}}{2\hbar\omega_R}$$

$$\rightsquigarrow \quad \boxed{\begin{aligned} c_a(t) &= e^{\frac{i(\omega-\omega_0)t}{2}} \left[\cos\omega_R t - i \frac{(\omega-\omega_0)}{2\omega_R} \sin\omega_R t \right] \\ c_b(t) &= \frac{V_{ba}}{2\hbar\omega_R} e^{-\frac{i(\omega-\omega_0)t}{2}} \sin\omega_R t \end{aligned}}$$

THESE EXPRESSIONS ARE EXACT FOR $\omega \simeq \omega_0$

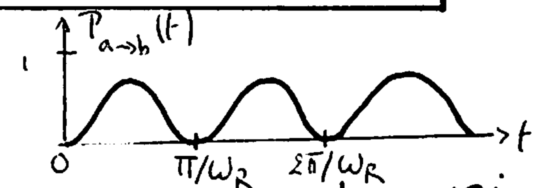
IN CONTRAST TO P.T. RESULTS

<u>CHECK</u> : $\quad |c_a(t)|^2 + |c_b(t)|^2 = 1 \qquad$ (EXACT!)

↳ PROBABILITY FOR TRANSITION $a \to b$

$$\boxed{P_{a\to b}(t) = |c_b(t)|^2 = \frac{|V_{ba}|^2}{(2\hbar\omega_R)^2} \cdot \sin^2 \omega_R t}$$

↳ EXACT RESULT $\omega \simeq \omega_0$



↳ RABI OSCILLATIONS

⇝ COMPARE WITH P.T. RESULT

$$P^{PT}_{a\to b}(t) = \frac{|V_{ba}|^2}{\left(\hbar(\omega-\omega_0)\right)^2} \cdot \sin^2\left[\frac{(\omega-\omega_0)t}{2}\right]$$

PT RESULT IS OBTAINED FOR

$$|V_{ab}| \ll \hbar(\omega-\omega_0)$$

$$\Downarrow$$

$$\omega_R = \frac{1}{2}(\omega-\omega_0)$$

⇝ PT DOES NOT HOLD VERY CLOSE TO RESONANCE ($\omega = \omega_0$)

⇝ EXACT RESULT

MAX. FOR $\omega_R t = (2n+1)\frac{\pi}{2}$

$$t = \frac{(2n+1)\pi}{2\omega_R}$$

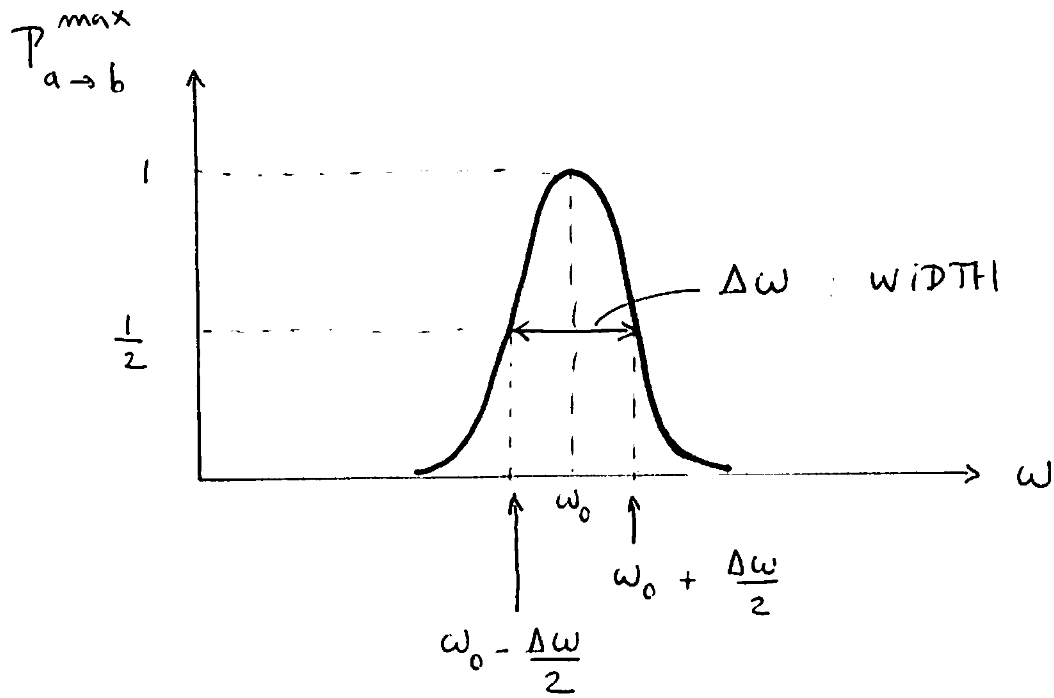
MAX PROBABILITY $P^{max}_{a\to b} = \dfrac{|V_{ba}|^2}{(2\hbar\omega_R)^2}$

WHEN $\omega = \omega_0 \Rightarrow \omega_R = \dfrac{|V_{ab}|}{2\hbar} \Rightarrow P^{max}_{a\to b} = 1$

$$P_{a \to b}^{max} = \frac{|V_{ba}|^2/\hbar^2}{(\omega - \omega_0)^2 + |V_{ba}|^2/\hbar^2}$$

$\downarrow$

RESONANCE FOR $\omega = \omega_0$

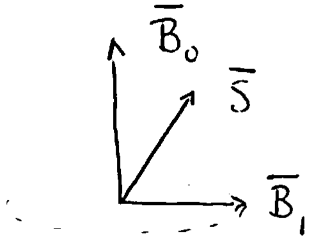


$$\frac{\Delta\omega}{2} = \frac{|V_{ba}|}{\hbar}$$

$\Delta\omega$ ALSO CALLED <u>F</u>ULL <u>W</u>IDTH AT <u>H</u>ALF <u>M</u>AXIMUM

FOR $\omega = \omega_0 \pm \frac{\Delta\omega}{2} \Rightarrow P_{a \to b}^{max} = \frac{1}{2}$

- <u>APPLICATION</u> : NUCLEAR MAGNETIC RESONANCE (NMR)



$$\omega_0 = \underset{\substack{\uparrow \\ \text{PROTON MASS}}}{\frac{e}{2M_p}} \; \underset{\substack{\parallel \\ 5.59}}{g_p} \; B_0$$

FOR $B_0 = 1\,T \Rightarrow \frac{\omega_0}{2\pi} = 4.3 \; 10^7 \, Hz$

RESONANCE FREQUENCY OBTAINED FOR RF (RADIO FREQ.) B_1 FIELD

APPENDIX : LINEAR ALGEBRA

⇒ A.1 VECTORS

- VECTOR SPACE

VECTOR SPACE CONSISTS OF VECTORS $|\alpha\rangle, |\beta\rangle, |\gamma\rangle, \ldots$

SCALARS a, b, c

WHICH IS CLOSED UNDER OPERATIONS OF VECTOR ADDITION & SCALAR MULTIPLICATION

↳ i.e. WHEN WE PERFORM THESE OPERATIONS ON ANY MEMBER OF VECTOR SPACE, WE STAY WITHIN VECTOR SPACE

① VECTOR ADDITION

↳ SUM OF 2 VECTORS IS VECTOR.

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle$$

↳ ASSOCIATIVE

$$\left(|\alpha\rangle + |\beta\rangle\right) + |\gamma\rangle = |\alpha\rangle + \left(|\beta\rangle + |\gamma\rangle\right)$$

↳ NULL VECTOR $|0\rangle$

$$|\alpha\rangle + |0\rangle = |\alpha\rangle$$

↳ $\forall\ |\alpha\rangle : \exists$ INVERSE $|-\alpha\rangle$

$$|\alpha\rangle + |-\alpha\rangle = |0\rangle$$

↳ COMMUTATIVE

$$|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle$$

(2) SCALAR MULTIPLICATION

$$a\,|\alpha\rangle = \underbrace{|\gamma\rangle}_{\text{ANOTHER VECTOR}}$$

↳ DISTRIBUTIVE w.r.t. VECTOR ADDITION

$$a\left(|\alpha\rangle + |\beta\rangle\right) = a|\alpha\rangle + a|\beta\rangle$$

↳ DISTRIBUTIVE w.r.t. SCALAR ADDITION

$$(a+b)\,|\alpha\rangle = a|\alpha\rangle + b|\alpha\rangle$$

↳ ASSOCIATIVE w.r.t. SCALAR MULTIPLICATION

$$a\left(b\,|\alpha\rangle\right) = (a.b)\,|\alpha\rangle$$

↳ $0\,|\alpha\rangle = |0\rangle$

$1\,|\alpha\rangle = |\alpha\rangle$

↳ $|-\alpha\rangle = (-1)\,|\alpha\rangle \equiv -|\alpha\rangle$

LINEAR COMBINATIONS - BASIS VECTORS

↳ LINEAR COMBINATION OF VECTORS $|\alpha\rangle, |\beta\rangle, |\gamma\rangle, \ldots$

$$a|\alpha\rangle + b|\beta\rangle + c|\gamma\rangle + \ldots$$

↳ VECTOR $|\lambda\rangle$ IS LINEARLY INDEPENDENT OF $|\alpha\rangle, |\beta\rangle, |\gamma\rangle, \ldots$

IF IT CANNOT BE WRITTEN AS LINEAR COMBINATION

↳ SET OF LINEARLY INDEPENDENT VECTORS

THAT SPANS WHOLE VECTOR SPACE IS A BASIS

(e.g. VECTORS IN 3 DIM : $\hat{i}, \hat{j}, \hat{k}$: BASIS).

EVERY OTHER VECTOR CAN BE WRITTEN AS

LINEAR COMBINATION OF BASIS VECTORS.

DIMENSION OF SPACE : # BASIS VECTORS

↳ BASIS : $|e_1\rangle, |e_2\rangle, \ldots, |e_n\rangle$

$\forall$ VECTOR : $|\alpha\rangle = a_1|e_1\rangle + a_2|e_2\rangle + \cdots + a_n|e_n\rangle$

$|\alpha\rangle \Longleftrightarrow (a_1, \ldots, a_n)$ COMPONENTS OF VECTOR

(e.g. $\bar{a} = a_x\hat{i} + a_y\hat{j} + a_z\hat{k}$)

(a_x, a_y, a_z) COMP. OF 3-DIM VECTOR

$\hookrightarrow \quad |\alpha\rangle + |\beta\rangle \Leftrightarrow (a_1 + b_1, a_2 + b_2, \dots, a_n + b_n)$

$$c|\alpha\rangle \Leftrightarrow (ca_1, ca_2, \dots, ca_n)$$

$$|0\rangle \Leftrightarrow (0, 0, \dots, 0)$$

$$|-\alpha\rangle \Leftrightarrow (-a_1, -a_2, \dots, -a_n)$$

⇒ A.2 INNER PRODUCTS

$\hookrightarrow$ IN 3-DIM : DOT PRODUCT OF 2 VECTORS

$$\bar{a}\ (a_x, a_y, a_z)$$

$$\bar{b}\ (b_x, b_y, b_z)$$

$$\bar{a}.\bar{b} = a_x b_x + a_y b_y + a_z b_z$$

$\hookrightarrow$ GENERALIZATION TO n-DIM VECTOR SPACE

INNER PRODUCT OF 2 VECTORS $|\alpha\rangle$ AND $|\beta\rangle$

$$\langle\alpha|\beta\rangle$$

$\hookrightarrow$ PROPERTIES

$$\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$$

$$\langle\alpha|\alpha\rangle \geq 0$$

$$\langle\alpha|\alpha\rangle = 0 \Leftrightarrow |\alpha\rangle = |0\rangle$$

$$\langle\alpha|\left(b|\beta\rangle + c|\gamma\rangle\right) = b\langle\alpha|\beta\rangle + c\langle\alpha|\gamma\rangle$$

↳ VECTOR SPACE + INNER PRODUCT : INNER PRODUCT SPACE

↳ NORM OF VECTOR (REAL)

$$\| \alpha \| \equiv \sqrt{\langle \alpha | \alpha \rangle} \qquad (\text{"LENGTH"})$$

(IN 3 DIM $\quad |\bar{r}| = \sqrt{\bar{r} \cdot \bar{r}}$)

UNIT VECTOR $|e_1\rangle$

$$\| e_1 \| = 1 \qquad (\text{CALLED TO BE NORMALIZED})$$

↳ 2 VECTORS ARE ORTHOGONAL

IF $\quad \langle \alpha_i | \alpha_j \rangle = 0 \qquad (i \neq j)$

↳ SET IS ORTHONORMAL

IF $\quad \langle \alpha_i | \alpha_j \rangle = \delta_{ij}$

↳ CONVENIENT TO WORK WITH ORTHONORMAL BASIS

$$|e_1\rangle, \ldots, |e_n\rangle$$

$$\langle e_i | e_j \rangle = \delta_{ij}$$

$$|\alpha\rangle = a_1 |e_1\rangle + \cdots + a_n |e_n\rangle$$

$$|\beta\rangle = b_1 |e_1\rangle + \cdots + b_n |e_n\rangle$$

$$\langle e_i | \alpha \rangle = a_i$$

$$\langle \alpha | e_i \rangle = a_i^*$$

$$\langle \alpha | \beta \rangle = \langle \alpha | \left(b_1 |e_1\rangle + \dots + b_n |e_n\rangle \right)$$

$$\boxed{\langle \alpha | \beta \rangle = a_1^* b_1 + \dots + a_n^* b_n}$$

SEE LATER:
FORMALLY INTRODUCE NOTATION (DUE TO P.A.M DIRAC)

$$\langle \alpha | = a_1^* \langle e_1 | + \dots + a_n^* \langle e_n |$$

"BRA"

$$| \beta \rangle = b_1 |e_1\rangle + \dots + b_n |e_n\rangle$$

"KET"

$$\langle \alpha | \beta \rangle = a_1^* b_1 + \dots + a_n^* b_n$$

BRACKET

↳ NORM OF VECTOR

NORM SQUARED $\langle \alpha | \alpha \rangle = |a_1|^2 + \dots + |a_n|^2$

↳ "ANGLE" OF VECTOR

- $\underline{3\text{ DIM}}$ $\cos\theta = \dfrac{\bar{a}\cdot\bar{b}}{|\bar{a}||\bar{b}|}$

- GENERALIZATION

$\langle\alpha|\beta\rangle$ COMPLEX NUMBER

$\underline{\text{BUT}}$ $$\boxed{|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle \cdot \langle\beta|\beta\rangle}$$

SCHWARTZ INEQUALITY

↳ DEFINE ANGLE: $\cos\theta \equiv \sqrt{\dfrac{\langle\alpha|\beta\rangle\langle\beta|\alpha\rangle}{\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle}}$

⇒ A.3 MATRICES

- LINEAR TRANSFORMATION $\hat{T}$

↳ $\hat{T}$ TRANSFORMS ONE VECTOR $|\alpha\rangle$ INTO ANOTHER VECTOR $|\alpha'\rangle$

$$|\alpha'\rangle = \hat{T}\,|\alpha\rangle$$

↳ OPERATION IS LINEAR

$$\hat{T}\left(a|\alpha\rangle + b\,|\beta\rangle\right) = a\left(\hat{T}|\alpha\rangle\right) + b\left(\hat{T}\,|\beta\rangle\right)$$

↳ OPERATION ON BASIS VECTORS (ORTHONORMAL)

e.g. $\hat{T}\,|e_1\rangle = T_{11}\,|e_1\rangle + T_{21}\,|e_2\rangle + \dots + T_{n1}|e_n\rangle$

$$\therefore \quad \boxed{\hat{T}\,|e_j\rangle = \sum_{i=1}^{n} T_{ij}\,|e_i\rangle} \qquad j = 1 \dots n$$

↳ $T_{ij} = \langle e_i\,|\,\hat{T}\,|\,e_j\rangle$

↳ OPERATION ON ARBITRARY VECTOR

$$|\alpha\rangle = a_1\,|e_1\rangle + \dots + a_n|e_n\rangle$$

$$= \sum_{j=1}^{n} a_j\,|e_j\rangle$$

$$\hat{T}\,|\alpha\rangle = \sum_{j=1}^{n} a_j\,\hat{T}\,|e_j\rangle$$

$$= \sum_{j=1}^{n}\sum_{i=1}^{n} a_j\,T_{ij}\,|e_i\rangle$$

$$\hat{T}\,|\alpha\rangle = |\alpha'\rangle = \sum_{i=1}^{n} a_i'\,|e_i\rangle$$

$$a_i' = \sum_{j=1}^{n} T_{ij}\, a_j$$

- MATRIX

↳ n^2 ELEMENTS $(T_{11}, T_{12}, \ldots, T_{1n}, T_{21}, T_{22}, \ldots, \ldots, T_{nn})$ UNIQUELY CHARACTERIZE A LINEAR TRANSFORMATION $\hat{T}$

$$T_{ij} = \langle e_i | \hat{T} | e_j \rangle$$

↓

FORM ELEMENTS OF A $n \times n$ MATRIX

n ROWS, n COLUMNS

$$T = \begin{pmatrix} T_{11} & T_{12} & \cdots & T_{1n} \\ T_{21} & T_{22} & \cdots & T_{2n} \\ \vdots & & & \\ T_{n1} & T_{n2} & \cdots & T_{nn} \end{pmatrix}$$

↳ SUM $\underbrace{(\hat{S} + \hat{T})}_{\hat{U}}\,|\alpha\rangle = \hat{S}\,|\alpha\rangle + \hat{T}\,|\alpha\rangle$

$\Updownarrow$

MATRICES $U = S + T$

$$U_{ij} = S_{ij} + T_{ij}$$

↳ PRODUCT OF LIN. TF.

$$|\alpha\rangle \xrightarrow{\hat{T}} |\alpha'\rangle \xrightarrow{\hat{S}} |\alpha''\rangle$$

$$|\alpha\rangle \xrightarrow{\hat{U}} |\alpha''\rangle$$

$$|\alpha'\rangle = \hat{T}\,|\alpha\rangle$$

$$|\alpha''\rangle = \hat{S}\,|\alpha'\rangle = \hat{S}\,\hat{T}\,|\alpha\rangle$$

$$|\alpha''\rangle = \hat{U}\,|\alpha\rangle$$

↳ $\hat{U} = \hat{S}\,\hat{T}$

IN COMPONENTS.

$$\begin{aligned} a''_i &= \sum_{j=1}^{n} S_{ij}\, a'_j \\ &= \sum_{j=1}^{n} S_{ij} \sum_{k=1}^{n} T_{jk}\, a_k. \\ &= \sum_{k=1}^{n} \left(\sum_{j=1}^{n} S_{ij}\, T_{jk} \right) a_k \\ &= \sum_{k=1}^{n} U_{ik}\, a_k. \end{aligned}$$

$$U_{ik} = \sum_{j=1}^{n} S_{ij}\, T_{jk}$$

$$\Updownarrow$$

$U = S\,T$ MATRIX RELATION

MATRIX MULTIPLICATION

$$U = ST$$

U_{ij} ELEMENT : ROW i OF S
MULTIPLY WITH COLUMN j OF T

$$\begin{pmatrix} U_{11} & \cdots & U_{1j} & \cdots & U_{1n} \\ \vdots & & & & \\ U_{i1} & \cdots & U_{ij} & \cdots & U_{in} \\ \vdots & & & & \\ U_{n1} & \cdots & U_{nj} & \cdots & U_{nn} \end{pmatrix} = \begin{pmatrix} S_{11} & \cdots & & S_{1n} \\ \vdots & & & \vdots \\ \boxed{S_{i1} \quad S_{i2} \quad \cdots \quad S_{in}} & & & \\ \vdots & & & \vdots \\ S_{n1} & & & S_{nn} \end{pmatrix} \begin{pmatrix} T_{11} & \cdots & T_{1j} & \cdots & T_{1n} \\ \vdots & & \vdots & & \\ T_{n1} & \cdots & T_{nj} & \cdots & T_{nn} \end{pmatrix}$$

$$U \qquad = \qquad S \qquad\qquad T$$

↳ <u>COLUMN MATRIX</u>

VECTOR $|\alpha\rangle \Leftrightarrow a = \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix}$

↳ COMPONENTS OF VECTOR.

$$|\alpha'\rangle = \hat{T}\,|\alpha\rangle$$

$$\Updownarrow$$

IN MATRIX NOTATION : $a' = Ta$

$$\begin{pmatrix} a'_1 \\ \vdots \\ a'_n \end{pmatrix} = \begin{pmatrix} T_{11} & \cdots & T_{1n} \\ \vdots & & \\ T_{n1} & \cdots & T_{nn} \end{pmatrix} \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix}$$

PROPERTIES OF MATRICES

↳ TRANSPOSE $\widetilde{T}$ OF T

$$\widetilde{T}_{ij} = T_{ji}$$ COLUMNS & ROWS INTERCHANGED

$$a = \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix} \Longrightarrow \widetilde{a} = (a_1 \dots a_n)$$

COLUMN MATRIX

ROW MATRIX.

↳ SQUARE MATRIX IS SYMMETRIC

IF $\widetilde{T} = T$

ANTI-SYMM. IF $\widetilde{T} = -T$

↳ COMPLEX CONJUGATE T^* OF MATRIX T

$$T^* = \begin{pmatrix} T^*_{11} & \dots & T^*_{1n} \\ \vdots & & \\ T^*_{n1} & \dots & T^*_{nn} \end{pmatrix}$$

$$a^* = \begin{pmatrix} a^*_1 \\ \vdots \\ a^*_n \end{pmatrix}$$

↳ REAL MATRIX , IMAGINARY MATRIX

REAL $T^* = T$

IMAG $T^* = -T$

↳ HERMITIAN CONJUGATE T^+ OF MATRIX T

(ALSO CALLED ADJOINT)

$$\boxed{T^+ \equiv \tilde{T}^*}$$

$$T^+ = \begin{pmatrix} T_{11}^* & T_{21}^* & \cdots & T_{m1}^* \\ T_{12}^* & T_{22}^* & & \\ \vdots & & & \\ T_{1m}^* & & \cdots & T_{mm}^* \end{pmatrix}$$

$$a^+ = \begin{pmatrix} a_1^* & a_2^* & \cdots & a_m^* \end{pmatrix}$$

$$= \tilde{a}^*$$

↳ HERMITIAN MATRIX

T IS HERMITIAN IF $\boxed{T^+ = T}$

↳ ANTI-HERMITIAN

T IS ANTI-HERMITIAN IF $T^+ = -T$

↳ EXAMPLES OF HERMITIAN MATRICES

2×2 $\quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

3×3 $\quad \begin{pmatrix} 2 & i & 1 \\ -i & 2 & i \\ 1 & -i & 2 \end{pmatrix}$

↳ INNER PRODUCT

$$\langle \alpha | \beta \rangle = \sum_{i=1}^{n} a_i^* b_i$$

$$\boxed{\langle \alpha | \beta \rangle = a^+ b}$$

$$= (a_1^* \dots a_n^*) \begin{pmatrix} b_1 \\ \vdots \\ b_n \end{pmatrix}$$

↳ MATRIX MULTIPLICATION IN GENERAL DOES NOT COMMUTE

i.e. $ST \neq TS$

DIFFERENCE $\Rightarrow$ COMMUTATOR $\boxed{[S,T] \equiv ST - TS}$

↳ TRANSPOSE OF PRODUCT

$$\widetilde{(ST)} = \tilde{T}\tilde{S}$$

PROOF: $(ST)_{ij} = \sum_{k=1}^{n} S_{ik} T_{kj}$

$$(\widetilde{ST})_{ij} = (ST)_{ji} = \sum_{k=1}^{n} S_{jk} T_{ki}$$

$$= \sum_{k=1}^{n} \widetilde{T}_{ik} \widetilde{S}_{kj}$$

$$= (\widetilde{T}\widetilde{S})_{ij}$$

↳ HERMITIAN CONJUGATE

$$(ST)^{+} = T^{+} S^{+}$$

↳ UNIT MATRIX $\quad I = \begin{pmatrix} 1 & & 0 \\ & \ddots & \\ 0 & & 1 \end{pmatrix}$

$$I_{ij} = \delta_{ij}$$

↳ INVERSE T^{-1} OF SQUARE MATRIX T

$$T^{-1} T = T T^{-1} = I$$

MATRIX HAS INVERSE $\Longleftrightarrow$ IT HAS A DETERMINANT $\neq 0$
$\det T \neq 0$

MATRIX WHICH HAS NO INVERSE IS SINGULAR

↳ DETERMINANT $\det T$ e.g. $\begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} \rightarrow \det T = T_{11} T_{22} - T_{12} T_{21}$

↳ INVERSE OF PRODUCT

$$(ST)^{-1} = T^{-1} S^{-1}$$

PROOF $(ST)^{-1}(ST) = I$

$$= T^{-1} \underbrace{S^{-1} S}_{I} T$$

$$= T^{-1} T \overset{!}{=} I$$

↳ UNITARY MATRIX U

$$\boxed{U^{+} = U^{-1}}$$

↳ UNITARY TRANSFORMATIONS PRESERVE INNER PRODUCTS !

MATRIX NOTATION

$$|\alpha'\rangle = \hat{U} |\alpha\rangle \iff a' = U a$$

$$|\beta'\rangle = \hat{U} |\beta\rangle \iff b' = U b$$

$$\langle \beta' | \alpha' \rangle = b'^{+} a'$$

$$= (b^{+} U^{+}) (U a)$$

$$= b^{+} \underbrace{U^{-1} U}_{I} a$$

$$= b^{+} a = \langle \beta | \alpha \rangle \quad \blacksquare \text{ QED}$$

⇒ A.4 CHANGE OF BASIS

↳ OLD BASIS $|e_i\rangle$ $i = 1 \dots n$

NEW BASIS $|f_i\rangle$ $i = 1 \dots n$

$$|e_j\rangle = \sum_{i=1}^{n} S_{ij} \, |f_i\rangle \qquad j = 1 \dots n$$

↳ $a^e = \begin{pmatrix} a_1^e \\ \vdots \\ a_n^e \end{pmatrix}$

↳ COMPONENTS OF VECTOR w.r.t. BASIS e

$a^f = \begin{pmatrix} a_1^f \\ \vdots \\ a_n^f \end{pmatrix}$

↳ COMPONENTS OF VECTOR w.r.t. BASIS f

$$a^f = S \, a^e$$

↳ MATRIX T ALSO CHANGES WHEN CHANGING BASIS

BASIS e: TRANSFORMATION $a^{e\prime} = T^e a^e$

$a^e = S^{-1} a^f$ RELATION BETWEEN ORIGINAL VECTORS IN BOTH BASES

$a^{f\prime} = S \, a^{e\prime}$ RELATION BETWEEN TRANSFORMED VECTORS IN BOTH BASES

$$a^{f'} = S . T^{e} a^{e}$$

$$= S T^{e} S^{-1} a^{f}$$

$$\equiv T^{f} a^{f} \quad \text{TRANSFORMATION IN BASIS } f$$

$$\underline{\underline{T^{f} = S T^{e} S^{-1}}}$$

T^{e}, T^{f} ARE '<u>SIMILAR</u>' MATRICES

i.e. REPRESENT SAME LINEAR TRANSFORMATION

w.r.t. DIFFERENT BASES

↳ IF BASIS e IS ORTHONORMAL

BASIS f $(a^{f} = S a^{e})$ IS ORTHONORMAL

$$\Updownarrow$$

MATRIX S IS UNITARY

<u>PROOF</u> $|\alpha\rangle = \sum_i a_i |e_i\rangle$ $\quad a^{e} = \begin{pmatrix} a_1 \\ \vdots \\ a_m \end{pmatrix}$

$|\beta\rangle = \sum_i b_i |e_i\rangle$ $\quad b^{e} = \begin{pmatrix} b_1 \\ \vdots \\ b_m \end{pmatrix}$

↳ IN ORTHONORMAL BASIS $\langle \alpha | \beta \rangle = a^{e+} b^{e}$

↳ IF $\{|f_i\rangle\}$ IS ORTHONORMAL $\langle \alpha | \beta \rangle = a^{f+} b^{f}$

$$b^{f} = S b^{e} \quad , \quad a^{f} = S a^{e} \Rightarrow a^{f+} = a^{e+} S^{+}$$

↳ DETERMINANT OF MATRIX IS LEFT UNCHANGED BY CHANGE OF BASIS

$$T^f = S T^e S^{-1}$$

$$\det T^f = \det (S T^e S^{-1})$$

$$\downarrow \qquad \det (AB) = \det A . \det B$$

$$= \det S . \det T^e . \det S^{-1}$$

$$= \underbrace{\det (\underbrace{S S^{-1}}_{I})}_{1} . \det T^e$$

$$= \det T^e$$

↳ TRACE OF MATRIX IS LEFT UNCHANGED BY CHANGE OF BASIS

$$Tr\,(T) = \sum_{i=1}^{n} T_{ii} \qquad \text{(SUM OF DIAGONAL ELEMENTS)}$$

SHOW $\quad Tr\,(T_1 T_2) = Tr\,(T_2 T_1)$ (HOMEWORK PROBLEM)

$$T^f = S T^e S^{-1}$$

$$Tr\,(T^f) = Tr\,(S T^e S^{-1})$$

$$= Tr\,(S^{-1} S T^e)$$

$$= Tr\,(T^e)$$

⇒ A.5 EIGENVECTORS & EIGENVALUES

- VECTOR $|\alpha\rangle$ WHICH TRANSFORMS INTO A SCALAR MULTIPLE OF ITSELF

$$\hat{T}\,|\alpha\rangle = \lambda\,|\alpha\rangle$$

SUCH A VECTOR $|\alpha\rangle$ IS CALLED AN EIGENVECTOR OF $\hat{T}$

λ IS CALLED ITS EIGENVALUE

- IN MATRIX NOTATION

$$T a = \lambda a \qquad (a \text{ IS NON-ZERO})$$

$$(T - \lambda I)\, a = 0$$

ZERO MATRIX

IDENTITY MATRIX.

$a \neq 0 \Rightarrow$ ONLY POSSIBLE IF $T - \lambda I$ IS SINGULAR

$$\Downarrow$$

$$\det(T - \lambda I) = 0$$

POLYNOMIAL OF DEGREE n FOR EIGENVALUES. (CHARACTERISTIC EQUATION)

HAS n COMPLEX ROOTS

(IF SOME EIGENVALUES ARE SAME ⇒ CALLED DEGENERATE

- EXAMPLE

DETERMINE EIGENVALUES & EIGENVECTORS OF

$$M = \begin{pmatrix} 2 & 0 & -2 \\ -2i & i & 2i \\ 1 & 0 & -1 \end{pmatrix}$$

↳ $\det(M - \lambda I) = 0$

$$\Updownarrow$$

$$\begin{vmatrix} 2-\lambda & 0 & -2 \\ -2i & i-\lambda & 2i \\ 1 & 0 & -1-\lambda \end{vmatrix} = 0$$

$$\Updownarrow$$

$$(2-\lambda)(i-\lambda)(-1-\lambda) + 2(i-\lambda) = 0$$

$$\Updownarrow$$

$$(i-\lambda)\lambda(\lambda-1) = 0$$

ROOTS: $\lambda_1 = 0, \ \lambda_2 = 1, \ \lambda_3 = i$ EIGENVALUES

↳ EIGENVALUE $\lambda_1 = 0$ $\Rightarrow$ EIGENVECTOR $a^{(1)}$

$$\begin{pmatrix} 2 & 0 & -2 \\ -2i & i & 2i \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = 0 \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

$$\begin{cases} 2a_1 - 2a_3 = 0 \\ -2i\,a_1 + i\,a_2 + 2i\,a_3 = 0 \\ a_1 - a_3 = 0 \end{cases}$$

$$a_1 = a_3 \quad , \quad a_2 = 0$$

WE CAN TAKE ANY VALUE OF a_1 $\sim$ MULTIPLE IS STILL EIGENVECTOR

$\downarrow$

CHOOSE $a_1 = 1$

$$\lambda_1 = 0 \quad \Longleftrightarrow \quad a^{(1)} = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$$

EIGENVALUE EIGENVECTOR

$\hookrightarrow$ EIGENVALUE $\lambda_2 = 1$ $\Rightarrow$ EIGENVECTOR $a^{(2)}$

$$\begin{pmatrix} 2 & 0 & -2 \\ -2i & i & 2i \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

$$\begin{cases} a_1 - 2a_3 = 0 \\ -2i\,a_1 + (i-1)\,a_2 + 2i\,a_3 = 0 \\ a_1 - 2a_3 = 0 \end{cases}$$

$$a_1 = 2a_3 \quad \Rightarrow \quad a_2 = \frac{2i}{i-1}\, a_3 = (1-i)\, a_3$$

CHOOSE $a_3 = 1$

$$\lambda_2 = 1 \quad \Longleftrightarrow \quad a^{(2)} = \begin{pmatrix} 2 \\ 1-i \\ 1 \end{pmatrix}$$

$\hookrightarrow$ EIGENVALUE $\underset{\sim\sim\sim}{\lambda_3 = i}$ $\Rightarrow$ EIGENVECTOR $a^{(3)}$

$$\begin{pmatrix} 2 & 0 & -2 \\ -2i & i & 2i \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = i \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

$$\begin{cases} (2-i)\,a_1 - 2a_3 = 0 \\ -2i\,a_1 + 2i\,a_3 = 0 \\ a_1 - (1+i)\,a_3 = 0 \end{cases}$$

SOLUTION $a_1 = a_3 = 0$, a_2 UNDETERMINED

CHOOSE $a_2 = 1$

$$\lambda_3 = i \quad \Longleftrightarrow \quad a^{(3)} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

- USE EIGENVECTORS AS <u>BASIS</u> (ONLY POSSIBLE IF THEY SPAN THE WHOLE VECTOR SPACE)

$$\hat{T}\,|f_1\rangle = \lambda_1\,|f_1\rangle$$

$$\hat{T}\,|f_2\rangle = \lambda_2\,|f_2\rangle$$

$$\vdots$$

$$\hat{T}\,|f_n\rangle = \lambda_n\,|f_n\rangle$$

IN THIS BASIS
$$T = \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & \ddots & \lambda_n \end{pmatrix}$$

$\downarrow$

T IS DIAGONAL

& NORMALIZED EIGENVECTORS ARE

$$f_1 = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \qquad f_2 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \qquad f_n = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}$$

↳ CHANGE BASIS TO MAKE $\hat{T}$ DIAGONAL

$\hat{T}$ IS CALLED DIAGONALIZABLE

↳ $$T^f = S\, T^e\, S^{-1}$$

T^f: IN NEW BASIS DIAGONAL; T^e: IN OLD BASIS

CHOOSE $\underline{\underline{(S^{-1})_{ij} = (a^{(j)})_i}}$

↳ COLUMNS ARE EIGENVECTORS IN OLD BASIS.

- PREVIOUS EXAMPLE

$$S^{-1} = \begin{pmatrix} 1 & 2 & 0 \\ 0 & 1-i & 1 \\ 1 & 1 & 0 \end{pmatrix} \Rightarrow S = \begin{pmatrix} -1 & 0 & 2 \\ 1 & 0 & -1 \\ i-1 & 1 & 1-i \end{pmatrix}$$

$$\begin{array}{ccc} \Uparrow & \Uparrow & \Uparrow \\ a^{(1)} & a^{(2)} & a^{(3)} \end{array}$$

$$M\,S^{-1} = \begin{pmatrix} 0 & 2 & 0 \\ 0 & 1-i & i \\ 0 & 1 & 0 \end{pmatrix}$$

$$S\,M\,S^{-1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & i \end{pmatrix}$$

- IN PRACTISE : EVERY HERMITIAN MATRIX / EVERY UNITARY MATRIX IS DIAGONALIZABLE

2 MATRICES CAN BE SIMULTANEOUSLY DIAGONALIZED BY SAME SIMILARITY MATRIX S

$\Updownarrow$

BOTH MATRICES COMMUTE

SHOW (HOMEWORK PROBLEM)

⇒ A.6 EIGENVALUES & EIGENVECTORS OF HERMITIAN MATRIX

$$\hat{T}^{+} = \hat{T}$$

- EIGENVALUES OF $\hat{T}$ ARE REAL

$$\hat{T} \mid \alpha \rangle = \lambda \mid \alpha \rangle \qquad \mid \alpha \rangle \neq \mid 0 \rangle$$

$$\langle \alpha \mid \hat{T} \mid \alpha \rangle = \lambda \langle \alpha \mid \alpha \rangle$$

NOTE: $\langle \beta \mid \hat{T} \mid \alpha \rangle = b^{+} T a$

$$\langle \alpha \mid \hat{T}^{+} \mid \beta \rangle = a^{+} T^{+} b = \left(b^{+} T a \right)^{+}$$

$$\boxed{\langle \alpha \mid \hat{T}^{+} \mid \beta \rangle = \langle \beta \mid \hat{T} \mid \alpha \rangle^{*}}$$

FOR $\mid \beta \rangle = \mid \alpha \rangle$

$\hat{T} = \hat{T}^{+}$

$$\langle \alpha \mid \hat{T} \mid \alpha \rangle = \langle \alpha \mid \hat{T} \mid \alpha \rangle^{*}$$

$$\lambda \langle \alpha \mid \alpha \rangle = \lambda^{*} \langle \alpha \mid \alpha \rangle$$

$$\lambda = \lambda^{*} \implies \lambda \text{ IS REAL} \blacksquare$$

- EIGENVECTORS OF $\hat{T}$ BELONGING TO DIFFERENT EIGENVALUES ARE ORTHOGONAL

$$\hat{T}\,|\alpha\rangle = \lambda\,|\alpha\rangle \qquad \lambda \neq \mu$$

$$\hat{T}\,|\beta\rangle = \mu\,|\beta\rangle$$

$$(1) \quad \langle\alpha|\hat{T}|\beta\rangle = \mu\,\langle\alpha|\beta\rangle$$

$$\langle\beta|\hat{T}|\alpha\rangle = \lambda\,\langle\beta|\alpha\rangle$$

$$= \langle\alpha|\hat{T}^{+}|\beta\rangle^{*} = \lambda\,\langle\beta|\alpha\rangle$$

$\Updownarrow$ TAKE $*$

$$(2) \quad \langle\alpha|\hat{T}|\beta\rangle = \lambda^{*}\,\langle\beta|\alpha\rangle^{*} = \lambda^{*}\,\langle\alpha|\beta\rangle$$

$$(1)-(2) \implies (\mu - \lambda^{*})\,\langle\alpha|\beta\rangle = 0$$

λ IS REAL $\lambda = \lambda^{*}$

AND $\lambda \neq \mu$

$\Updownarrow$

$\langle\alpha|\beta\rangle = 0$

ORTHOGONAL ■

- EIGENVECTORS OF $\hat{T}$ SPAN WHOLE VECTOR SPACE