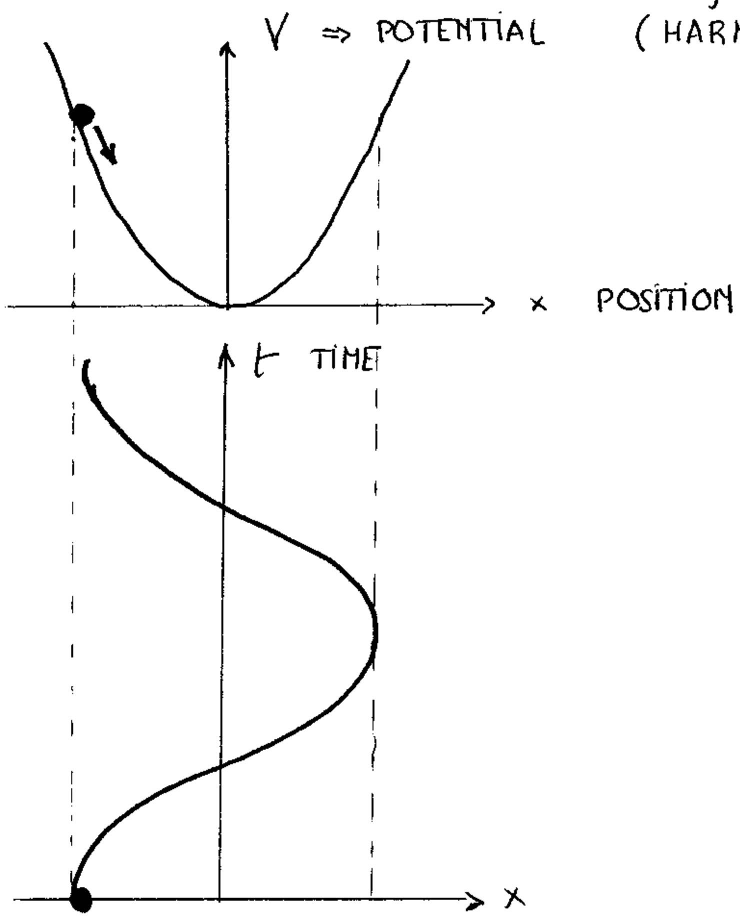
CHAPTER 1 : WAVE FUNCTION

1.1 SCHRÖDINGER EQUATION

- CLASSICAL MECHANICS



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

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

POTENTIAL

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

$\Downarrow$

POSITION $x(t)$

$\Downarrow$

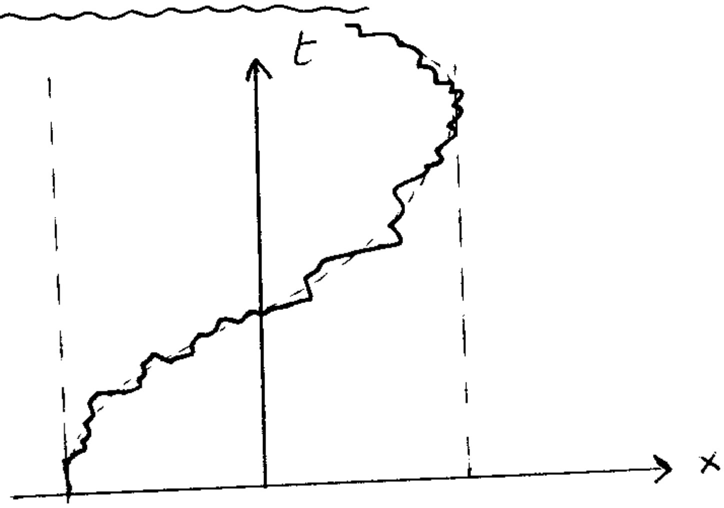
VELOCITY $v(t) = \dfrac{dx}{dt}$

$\Downarrow$

MOMENTUM $p = m v$

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

- QUANTUM MECHANICS



→ POSITION CAN NOT BE DETERMINED TO ARBITRARY ACCURACY

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

→ WE CAN ONLY SPEAK OF PROBABILITY

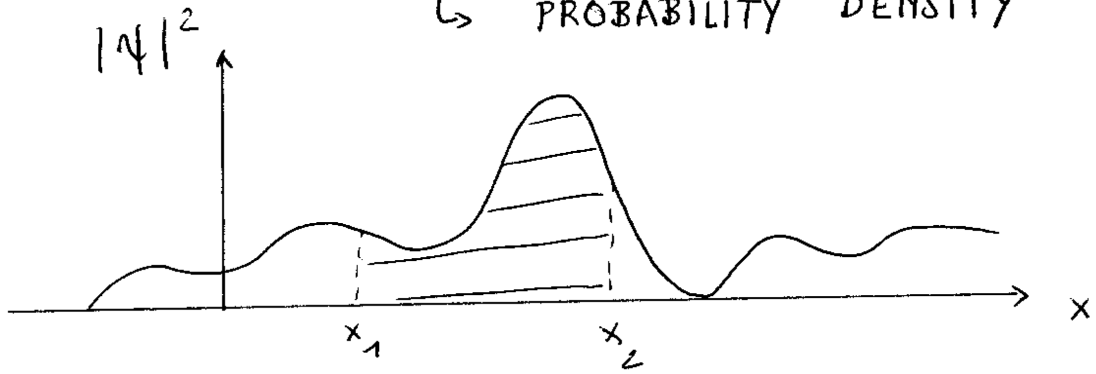
TO FIND {PARTICLE / OBJECT} AT A GIVEN TIME t

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

PARTICLE / OBJECT AT TIME t

BETWEEN x_1 AND x_2.

→ WAVE FUNCTION SATISFIES <u>SCHRÖDINGER EQ.</u>

$$\boxed{-\underbrace{\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}}_{\text{KINETIC ENERGY}} + \underbrace{V\psi}_{\text{POTENTIAL ENERGY}} = \underbrace{i\hbar\frac{\partial\psi}{\partial t}}_{\text{TOTAL ENERGY}}}$$

SOLUTION [+ { BOUNDARY / INITIAL } CONDITIONS $\psi(x,0)$]

↳ $\psi(x,t)$

$$\hbar = \frac{h}{2\pi} = 1.054\,572 \; 10^{-34} \; J.s$$

h : PLANCK's CONSTANT { RECALL : LIGHT OF FREQUENCY ν ↓ ENERGY PACKETS $E = h\nu$ (PHOTON)

→ SMALLNESS OF h : FOR MACROSCOPIC OBJECTS

FLUCTUATIONS AROUND CLASSICAL TRAJECTORY

VERY TINY ⇒ TO GOOD APPROXIMATION :

WE CAN APPLY NEWTON's EQ.

1.2 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

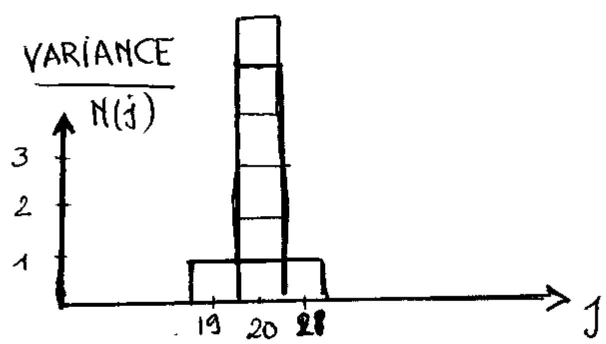
→ PROBABILITY TO FIND PERSON WITH AGE j

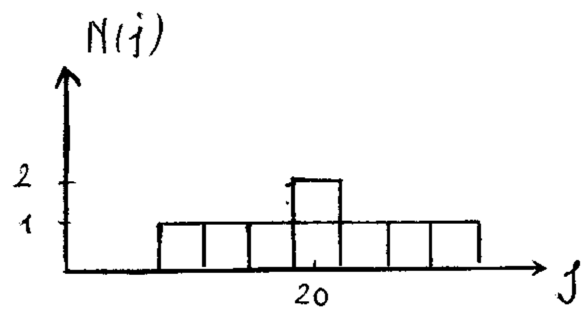
$$P(j) = \frac{N(j)}{N}$$

→ 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

$\Downarrow$

MEASURE OF SPREAD : VARIANCE σ^2

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

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

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

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

→ <u>STANDARD DEVIATION</u>

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

- CONTINUOUS VARIABLES

e.g. HEIGHT OF PERSON x

→ PROBABILITY DENSITY $\rho(x)$

* INFINITESIMAL INTERVAL

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

↳ $\rho(x)\, dx$

* FINITE INTERVAL

PROBABILITY TO FIND SOMEONE WITH HEIGHT BETWEEN a AND b

↳ $P_{ab} = \int_a^b dx\ \rho(x)$

* 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

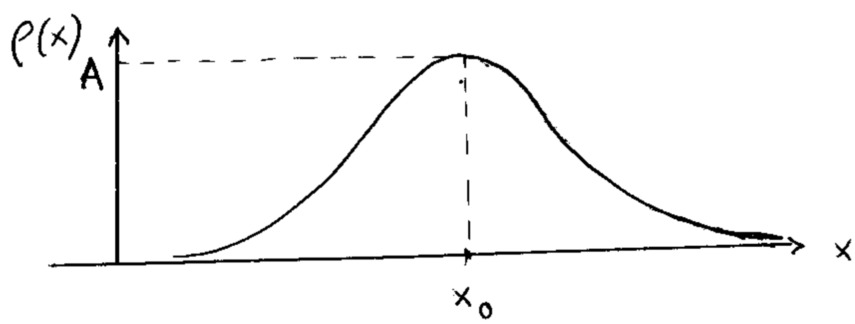
$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$$

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

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

→ EXAMPLE : GAUSSIAN DISTRIBUTION.

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



* NORMALIZATION

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

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

$x' = x - x_0$

$dx' = dx$

GAUSSIAN INTEGRAL

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

$$\Downarrow$$

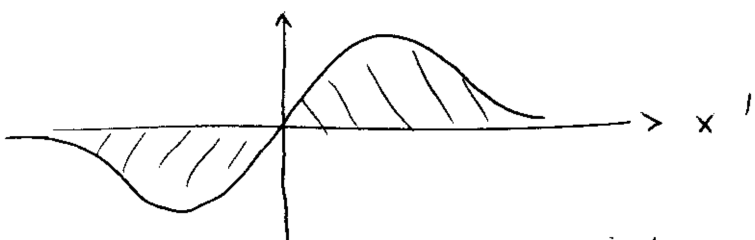
$$\underline{\underline{A = \sqrt{\frac{\lambda}{\pi}}}}$$

* 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

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

$$\underline{\underline{\langle x \rangle = x_0}}$$

* VARIANCE

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

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

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

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

$x' = x - x_0$

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

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

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

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

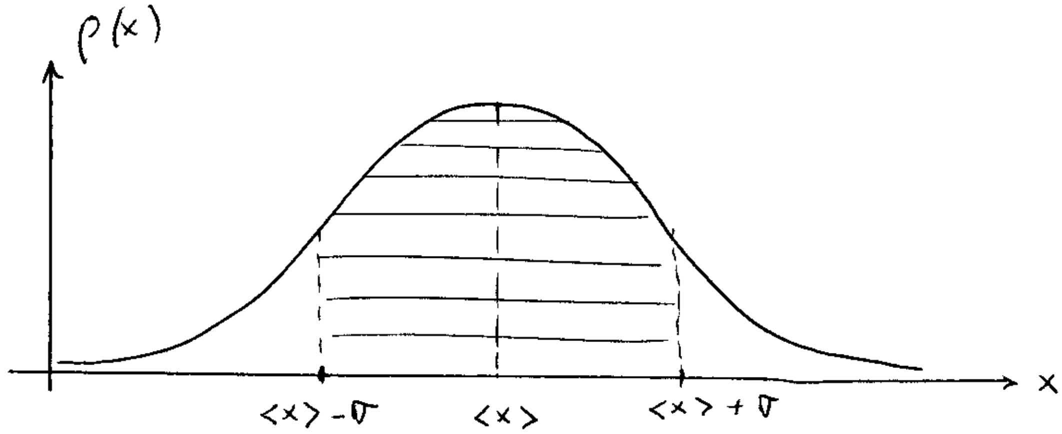
MATH HELP:

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

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

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

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



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

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

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

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

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

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

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

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

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

1.3 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

ϕ : 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 <u>NOT</u> 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

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

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

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

↳ POTENTIAL V IS REAL

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

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

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

+

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

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

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

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

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

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

$\downarrow$ 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.

1.4 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

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

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'

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

↑ POSITION 'OPERATOR'

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

↑ MOMENTUM 'OPERATOR'

$\langle T \rangle$ KINETIC ENERGY

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

$$\langle T \rangle = \int dx \, \Psi^* \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi$$

↑ KINETIC ENERGY 'OPERATOR'

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

↳ 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 $\langle p\rangle$

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

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

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

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

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

$\downarrow$ 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

$\hookrightarrow$ EXPECTATION VALUES OBEY CLASSICAL LAWS (e.g. NEWTON's LAWS)

1.5 UNCERTAINTY PRINCIPLE

→ WAVE FUNCTION Ψ

WAVELENGTH λ

$\updownarrow$

PARTICLE MOMENTUM p

PARTICLE - WAVE DUALITY IN Q.M.

DE BROGLIE FORMULA :

$$\boxed{p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}}$$

$$\hbar = \frac{h}{2\pi}$$

→ HEISENBERG'S UNCERTAINTY PRINCIPLE

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

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

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

$\sigma_p = \Delta p$

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$