G. Energy Eigenfunctions are Stationary States (as Bohr introduced)

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \quad [\text{E.g. 1D Box}]$$

Consider an energy eigenfunction (only one of them) $\psi_n(x)$

time $t=0$: $\psi_n(x)$ Prob. density $= |\psi_n(x)|^2$

time t: $\psi_n(x)e^{-iE_nt/\hbar}$ ($\because$ TDSE)

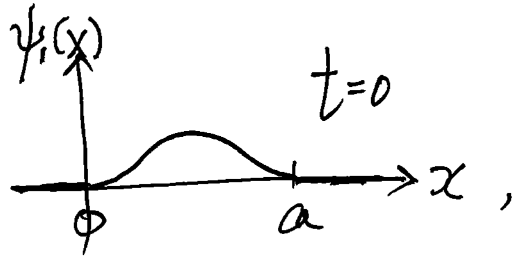
Prob. density $= \psi_n^*(x)e^{+iE_nt/\hbar}\psi_n(x)e^{-iE_nt/\hbar}$

$$= \underbrace{|\psi_n(x)|^2}_{\text{same as at } t=0} \quad \text{at time } t$$

Energy eigenfunctions are special, $|\psi_n(x)|^2$ does not change with time!

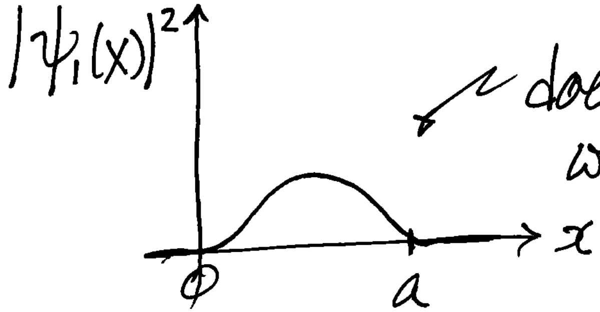
They are the "stationary states"

Question: 1D box ground state



How does it vary in time?

Probability density $|\psi_1(x)|^2$



does not vary with time!

Key Point: the property is only about <u>each individual</u> $\psi_n(x)$

e.g. $\psi_1(x)$ alone, OR $\psi_{13}(x)$ alone OR $\psi_{138}(x)$ alone

<u>Warning:</u> It is <u>not</u> about $\Phi(x) = c_1\psi_1 + c_{13}\psi_{13} + c_{138}\psi_{138}$!

Key Points:

- A single energy eigenstate : $\underbrace{\psi_n(x)}_{\text{(time 0)}} \longrightarrow \underbrace{e^{-iE_nt/\hbar}\,\psi_n(x)}_{\text{(time t)}}$

differ only by a phase factor

(but an overall phase factor doesn't matter)

Thus, "stationary".

- But $\underbrace{\Psi(0) = c_1\psi_1 + c_2\psi_2}$ $\longrightarrow$ $\underbrace{\Psi(x,t) = c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2t/\hbar}}$

NOT differ only by an overall phase factor

Thus, not stationary. Expect $|\Psi|^2$ and $\langle A \rangle$ to vary in time

H. How about general $\Phi(x,t)$ and will $\langle A \rangle$ change in time?

Think like a physicist! $\Phi(x,0) \longrightarrow \Phi(x,t)$ [initial value problem]

TDSE $\hat{H}\Phi = i\hbar\frac{\partial \Phi}{\partial t}$ governs time evolution

Key Physics Sense: $\hat{H}$ comes in whenever time evolution is considered

Time $t=0$: $\Phi(x,0) = c_1\psi_1 + c_2\psi_2 + \cdots$ $\quad (\hat{H}\psi_n = E_n\psi_n)$

"$\hat{H}$ comes in"

Time t: $\Phi(x,t) = c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2t/\hbar} + \cdots$

Will $\langle A \rangle$ change in time? Generally YES! But what's $\hat{A}$ will matter.

Special Cases (By inspection)

(i) Mean Energy $\langle E \rangle$ or $\langle H \rangle$? i.e. when $\hat{A} = \hat{H}$.

Time $t=0$, $|C_n|^2$ is probability of seeing E_n

$$\langle E \rangle(0) = \sum_{n=1}^{\infty} |C_n|^2 E_n \qquad \left(\sum_{n=1}^{\infty} |C_n|^2 = 1 \text{ from \underline{normalization}} \right)$$

Time t, $|C_n e^{-iE_nt/\hbar}|^2 = |C_n|^2$ is prob. of seeing E_n

So $$\langle E \rangle(t) = \sum_{n=0}^{\infty} |C_n|^2 E_n = \langle E \rangle(0)$$

$\therefore$ When $\underbrace{\hat{A} = \hat{H}}_{\text{Inspect this point}}$, $\langle \hat{H} \rangle \equiv \langle E \rangle$ does not change in time

(ii) How about Prob. density $|\Phi(x,t)|^2$ vs $|\Phi(x,0)|^2$?

e.g. $\left(c_1^*\psi_1^* e^{iE_1t/\hbar} + c_2^*\psi_2^* e^{iE_2t/\hbar}\right)\left(c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2t/\hbar}\right)$

$$= |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + \underbrace{c_2^* c_1 \psi_2^* \psi_1 e^{i(E_2-E_1)t/\hbar} + c_1^* c_2 \psi_1^* \psi_2 e^{-i(E_2-E_1)t/\hbar}}_{\text{have \underline{time t} in it}}$$

So, $\Phi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n e^{-iE_nt/\hbar}$ has time varying $|\Phi(x,t)|^2$

Only when $\Phi(x,t) = \psi_n e^{-iE_nt/\hbar}$, then stationary state.

General Consideration: Any $\hat{A}$, any Ψ

Will $\langle A\rangle(t) = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \hat{A}\, \Psi(x,t)\, dx$ vary with time?

Claim a result: There are $\hat{A}$ and $\hat{H}$ in the question

$$\underbrace{\frac{d\langle A\rangle}{dt}}_{\text{how } \langle A\rangle(t) \text{ varies with time}} = \frac{1}{i\hbar} \underbrace{\left\langle [\hat{A},\hat{H}] \right\rangle}_{\text{expectation value of commutator } [\hat{A},\hat{H}]} = \frac{1}{i\hbar}\int_{-\infty}^{\infty} \Psi^*(x,t)\,[\hat{A},\hat{H}]\,\Psi(x,t)\,dx$$

(assumed $\hat{A}$ has no dependence on time)

$\therefore$ If $\hat{A}$ is a quantity for which $[\hat{A},\hat{H}] = 0$ ($\hat{A}$ commutes with $\hat{H}$),
then $\frac{d\langle A\rangle}{dt} = 0$ ($\therefore$ $\langle A\rangle$ does not change in time)

Examples

(i) $\hat{A} = 1$, $\langle A \rangle = \int \Phi^*(x,t)\,\Phi(x,t)\,dx$

$$\frac{d\langle A\rangle}{dt} = \langle \underbrace{[1, \hat{H}]}_{\substack{\shortparallel \\ 0}} \rangle = \langle 0 \rangle = 0$$ $\Rightarrow$ If Φ is normalized at some time 0, it remains normalized at other times

(ii) $\hat{A} = \hat{H}$ (Energy) , $[\hat{H}, \hat{H}] = 0$

$\therefore \frac{d\langle E\rangle}{dt} = 0 \Rightarrow \langle E \rangle$ (mean energy) does not change in time

Generally, $\underbrace{[\hat{A}, \hat{H}] \neq 0}_{\langle [\hat{A}, \hat{H}] \rangle \neq 0 \text{ also}}$ and thus $\langle A\rangle(t)$ varies in time.

(iii) $\hat{A} = \hat{p}$ (momentum operator $\frac{\hbar}{i}\frac{d}{dx}$)

$$[\hat{p}, \hat{H}] = [\hat{p}, \frac{\hat{p}^2}{2m} + U(\hat{x})] = [\hat{p}, U(\hat{x})] = \frac{\hbar}{i}\frac{dU(x)}{dx}$$

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

$$= \underbrace{\frac{\hbar}{i}\left(\frac{dU}{dx}\right)}_{\text{commutator}} f(x) \quad \text{for all functions } f(x)$$

$$\therefore \frac{d\langle p\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{p}, \hat{H}]\rangle = \frac{1}{i\hbar}\left\langle \frac{\hbar}{i}\frac{dU(x)}{dx}\right\rangle = \left\langle -\frac{dU}{dx}\right\rangle$$

Classical Mechanics

$\hookrightarrow$ $\frac{dp}{dt} = -\frac{dU}{dx} = \text{Force}$

Quantum Mechanics

$\hookrightarrow$ $\frac{d\langle p\rangle}{dt} = \left\langle -\frac{dU}{dx}\right\rangle$

- about expectation values
- Ehrenfest Theorem

Key Point

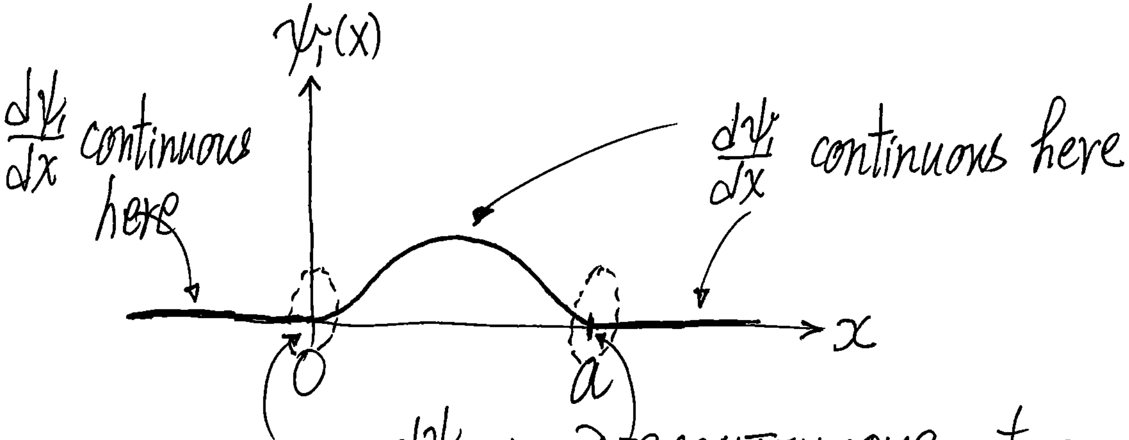
- $\dfrac{d\langle A\rangle}{dt} = \dfrac{1}{i\hbar}\left\langle [\hat{A}, \hat{H}] \right\rangle$ for general $\hat{A}$ (no time dependence) and general Φ for taking $\langle \cdots \rangle$ (the expectation value)

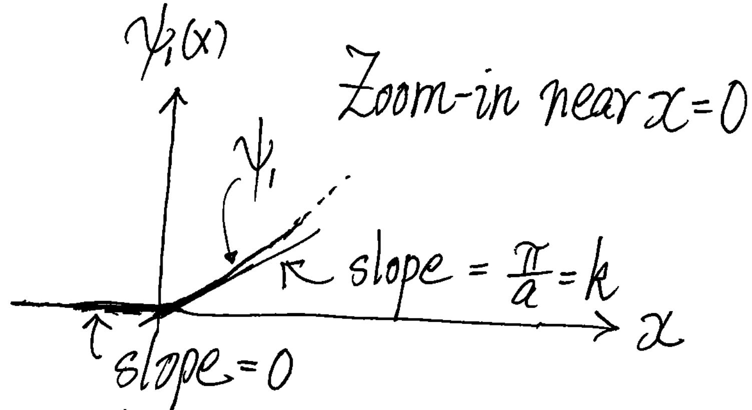
$\hat{H}$ enters because $\hat{H}$ governs the time evolution of Φ through TDSE $\quad i\hbar \dfrac{\partial \Phi}{\partial t} = \hat{H}\Phi$

I. Requirement (Boundary Condition) on Slope $\frac{d\psi}{dx}$ of wavefunctions

- Well-behaved wavefns: Continuous, single-valued
- How about $\frac{d\psi}{dx}$?
- Inspect 1D Box energy eigenfunctions $\psi_n(x)$

$$\psi_1(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a} & , \; 0 < x < a \\ 0 & , \; x \leq 0 \;\&\; x \geq a \end{cases}$$





$\frac{d\psi_1}{dx}$ is DISCONTINUOUS at $x=0$ and $x=a$

- There is a jump in slope (discontinuous) at $x=0$ and $x=a$
- Eslewhere, slope is continuous
- Recall: At $x=0$ & $x=a$, $U(x)$ has a jump of infinity
- What is the general rule on $\frac{d\psi}{dx}$?

Take-home message

- $\frac{d\psi}{dx}$ is continuous in most cases, but it is not at the locations where $U(x)$ has a jump to infinity

Let's see why TISE $\dfrac{d^2\psi(x)}{dx^2} + \dfrac{2m}{\hbar^2}[E - U(x)]\psi(x) = 0$

General Concept: Boundary Conditions (B.C.) come from integrating TISE

- Integrate over a tiny interval of x: from $x_0-\varepsilon$ to $x_0+\varepsilon$ around x_0

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon}\left(\frac{d^2\psi}{dx}\right)dx = \frac{2m}{\hbar^2}\int_{x_0-\varepsilon}^{x_0+\varepsilon}[U(x)-E]\,\psi(x)\,dx$$

$$\Rightarrow \left.\frac{d\psi}{dx}\right|_{x=x_0+\varepsilon} - \left.\frac{d\psi}{dx}\right|_{x=x_0-\varepsilon} = \frac{2m}{\hbar^2}\int_{x_0-\varepsilon}^{x_0+\varepsilon}[U(x)-E]\,\psi(x)\,dx \qquad (*)$$

General Result up to here

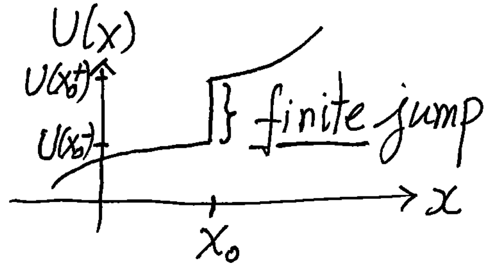
- Case (i): $U(x)$ is continuous at $x = x_0$

Take $\varepsilon \to 0$ in (*). $\text{RHS} = \dfrac{2m}{\hbar^2}\left[U(x_0) - E\right]\psi(x_0)\cdot 2\varepsilon$

$\longrightarrow 0$ as $\varepsilon \to 0$

$\therefore \left(\dfrac{d\psi}{dx}\right)$ is continuous at x_0

- Case (ii): $U(x)$ has a <u>finite discontinuity</u>



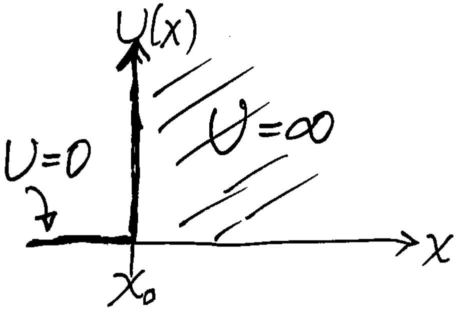
$$\text{RHS} = \frac{2m}{\hbar^2}\left[\int_{x_0-\varepsilon}^{x_0}[U(x)-E]\psi(x)dx + \int_{x_0}^{x_0+\varepsilon}[U(x)-E]\psi(x)dx\right]$$

$$= \frac{2m}{\hbar^2}\left[(U(x_0^-)-E)\psi(x_0)\varepsilon + (U(x_0^+)-E)\psi(x_0)\varepsilon\right]$$

$$= \frac{2m}{\hbar^2}\Big[\underbrace{U(x_0^-)+U(x_0^+)}_{\text{finite}} - 2E\Big]\psi(x_0)\cdot\underbrace{\varepsilon}_{\to 0} \longrightarrow 0 \quad (\text{as } \varepsilon \to 0)$$

$\therefore \left(\dfrac{d\psi}{dx}\right)$ is continuous at x_0

- Case (iii): $U(x)$ has an infinite discontinuity



$$RHS = \frac{2m}{\hbar^2}\left[U(x_0^-) + U(x_0^+) - 2E\right]\psi(x_0)\cdot\varepsilon \qquad (\varepsilon \to 0)$$

$$= \frac{2m}{\hbar^2}\Big[\underbrace{U(x_0^-) + U(x_0^+)}_{\to\infty}\Big]\psi(x_0)\cdot\underbrace{\varepsilon}_{\to 0}$$

$$= \text{finite}$$

$\therefore$ $\dfrac{d\psi}{dx}$ is discontinuous at x_0 where $U(x_0)$ has an infinite discontinuity

Summary: "$\dfrac{d\psi}{dx}$ is continuous until you hit a $\underbrace{\text{hard wall}}_{U\to\infty}$"

J. Summary

- 1D Box as 1st example : $\psi_n(x) \leftrightarrow E_n$
- Quantum confinement
- Orthonormality
- Expanding any $\Psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$ or $\Psi(x) = \sum_{n=1}^{\infty} \tilde{c}_n \phi_n(x)$ $[\hat{A}\phi_n = a_n \phi_n]$
- $|\tilde{c}_n|^2$ = Prob. of getting a_n in measurement of A on $\Psi(x)$
- Expectation value and Uncertainty [conceptual + operational]
- Energy eigenstates (one alone) are stationary states
- $\langle A \rangle(t)$ varies with time generally for general $\hat{A}$ and general Ψ
- $\frac{d\psi}{dx}$ is continuous until hitting a hard wall