Particle in a Box

$$H = T + V \Rightarrow \frac{\underset{\sim}{p}^2}{2m} + V(\underset{\sim}{x})$$

The equation for eigenkets of $\underset{\sim}{H}$ and energy eigenvalue, E:

$$\underset{\sim}{H}|E\rangle = \left(\frac{\underset{\sim}{p}^2}{2m} + V(\underset{\sim}{x})\right)|E\rangle = E|E\rangle$$

Project on to eigenkets of $\underset{\sim}{x}$

$$\int \langle x|\left(\frac{\underset{\sim}{p}^2}{2m} + V(\underset{\sim}{x})\right)|x'\rangle dx' \langle x'|E\rangle = E\underbrace{\langle x|E\rangle}_{\psi(x)}$$

$$\int \langle x|\frac{\underset{\sim}{p}^2}{2m}|x'\rangle\langle x'|E\rangle dx' = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

$$\int \langle x|V(\underset{\sim}{x})|x'\rangle\langle x'|E\rangle dx' = \int V(x)\,\delta(x-x')\langle x'|E\rangle dx'$$
$$= V(x)\,\psi(x)$$

So, the eigenequation for $\underset{\sim}{H}$ becomes the differential equation:

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

$V(x) \rightarrow$ sometimes not continuous, so

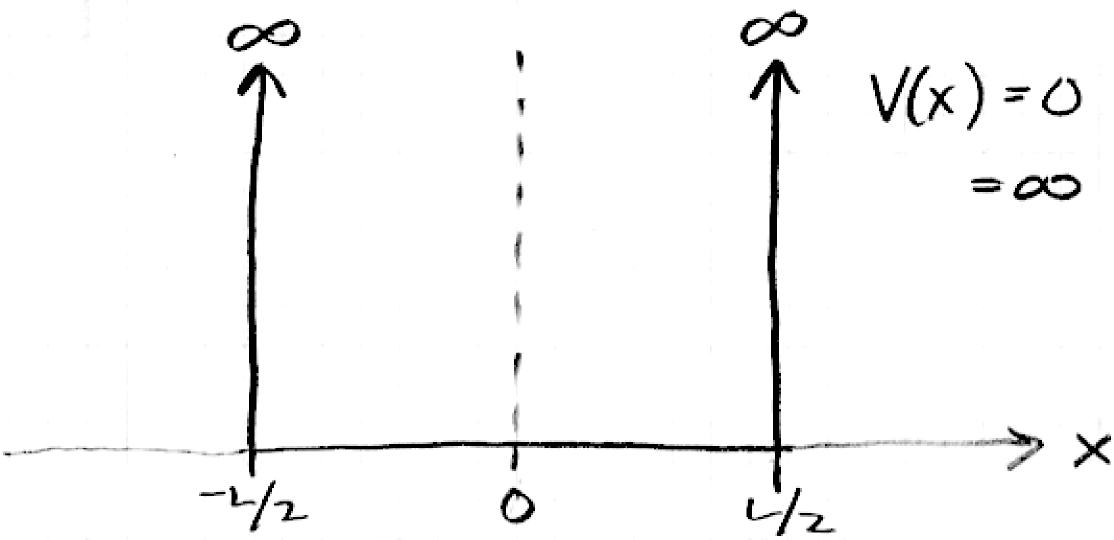
$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left(\underline{V(x)} - E\right)\psi$$

not continuous

not continuous, however: $\int \frac{d^2\psi}{dx^2} \propto \frac{d\psi}{dx}$ will be continuous and so will $\psi \propto \int \frac{d\psi}{dx}$

The most peculiar (but common) situation arises when $V(x)$ has a jump of infinite height; this occurs for the "particle in a box." In that case, $\frac{d\psi}{dx}$ has a discontinuity, but $\psi(x)$ does not.

Particle in a Box



$V(x) = 0 \quad |x| < \frac{L}{2}$
$\quad\;\; = \infty \quad |x| \geq \frac{L}{2}$

region I: $\quad x \leq -L/2 \quad (V(x) = \infty)$

II: $\quad |x| < L/2 \quad (V(x) = 0)$

III: $\quad x \geq L/2 \quad (V(x) = \infty)$

argue: $\psi_{I}(x) = \psi_{III}(x) = 0$

- physically: particle cannot penetrate where it would need an infinite amount of energy

- Mathematically, could imagine solving

$$V(x) = \begin{cases} V_0 & x \leq -L/2 \quad \text{Region I} \\ 0 & |x| < L/2 \quad \text{II} \\ V_0 & x \geq L/2 \quad \text{III} \end{cases}$$

if you do, you find that as $V_0 \to \infty$,
$\psi_I(x) = \psi_{III}(x) = 0$

<u>$\psi(x)$ still continuous</u>

so $\psi_{II}(-L/2) = \psi_{II}(L/2) = 0$

In region II, $V(x) = 0$, so for eigenfunctions of energy,

$$\frac{d^2\psi_{II}}{dx^2} = -\frac{2mE}{\hbar^2}\psi_{II}$$

or $\quad \psi_{II} \propto e^{\pm ikx} \quad \left(\frac{d^2\psi_{II}}{dx^2} = (\pm ik)^2\psi_{II}\right)$

$$\frac{d^2\psi_{II}}{dx^2} = -k^2\psi_{II}$$

OK if $\quad k^2 = \frac{2mE}{\hbar^2}$

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

then $\boxed{\psi_{II}(x) = Ae^{ikx} + Be^{-ikx}}$

to make $\psi_{II}(-L/2) = \psi_{II}(L/2) = 0$

need: $A e^{-ikL/2} + B e^{ikL/2} = 0$

$A e^{ikL/2} + B e^{-ikL/2} = 0$

or $$\underbrace{\begin{bmatrix} e^{-ikL/2} & e^{ikL/2} \\ e^{ikL/2} & e^{-ikL/2} \end{bmatrix}} \begin{bmatrix} A \\ B \end{bmatrix} = 0$$

for non trivial A & B (that is, $A \neq 0, B \neq 0$) the matrix must be singular, and have determinant 0

$$\begin{vmatrix} e^{-ikL/2} & e^{ikL/2} \\ e^{ikL/2} & e^{-ikL/2} \end{vmatrix} = e^{-ikL} - e^{ikL} = 0$$

$$= -2i \sin(kL) = 0$$

$$kL = 0, \pm\pi, \pm 2\pi, \ldots$$

or $k = \frac{n\pi}{L}$ $\quad n = 0, \pm 1, \pm 2, \ldots$

now plug back in to solve for A & B

$$\begin{pmatrix} e^{-in\pi/2} & e^{in\pi/2} \\ e^{in\pi/2} & e^{-in\pi/2} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0$$

both yield the same equation:

$$e^{-in\pi/2} A + e^{in\pi/2} B = 0$$

$$B = -e^{-in\pi} A$$

$n = \text{even}(0, \pm 2, \pm 4, \ldots)$ $B = -A$ $\quad n = \text{odd}(\pm 1, \pm 3, \ldots)$ $B = A$

<u>$n=0$</u>: yields $\psi(x)=0$, which is trivial

<u>$n=\pm 1, \pm 3, \ldots$</u> $B=A$ so

$$\psi_{II}(x)=\psi_n(x)=A\left(e^{\frac{in\pi}{L}x}+e^{\frac{-in\pi}{L}x}\right)$$
$$=2A\cos\left(\frac{n\pi}{L}x\right)$$

normalization:

$$1=\int_{-L/2}^{L/2}dx\,|\psi_n(x)|^2=4|A|^2\int_{-L/2}^{L/2}\cos^2\left(\frac{n\pi}{L}x\right)dx \qquad z=\frac{n\pi}{L}x$$

$$=4|A|^2\left(\frac{L}{n\pi}\right)\left[\int_{-n\pi/2}^{n\pi/2}\underbrace{\cos^2 z}_{\cos^2 z=\frac{1}{2}(1+\cos 2z)}dz=\frac{1}{2}\int_{-n\pi/2}^{n\pi/2}(1+\cos 2z)dz=\underbrace{\frac{1}{2}\left(z+\frac{1}{2}\sin 2z\right)\Big|_{-n\pi/2}^{n\pi/2}}_{\frac{1}{2}n\pi}\right]$$

$$1=4|A|^2\cdot\left(\frac{L}{n\pi}\right)\frac{1}{2}n\pi=2|A|^2L$$

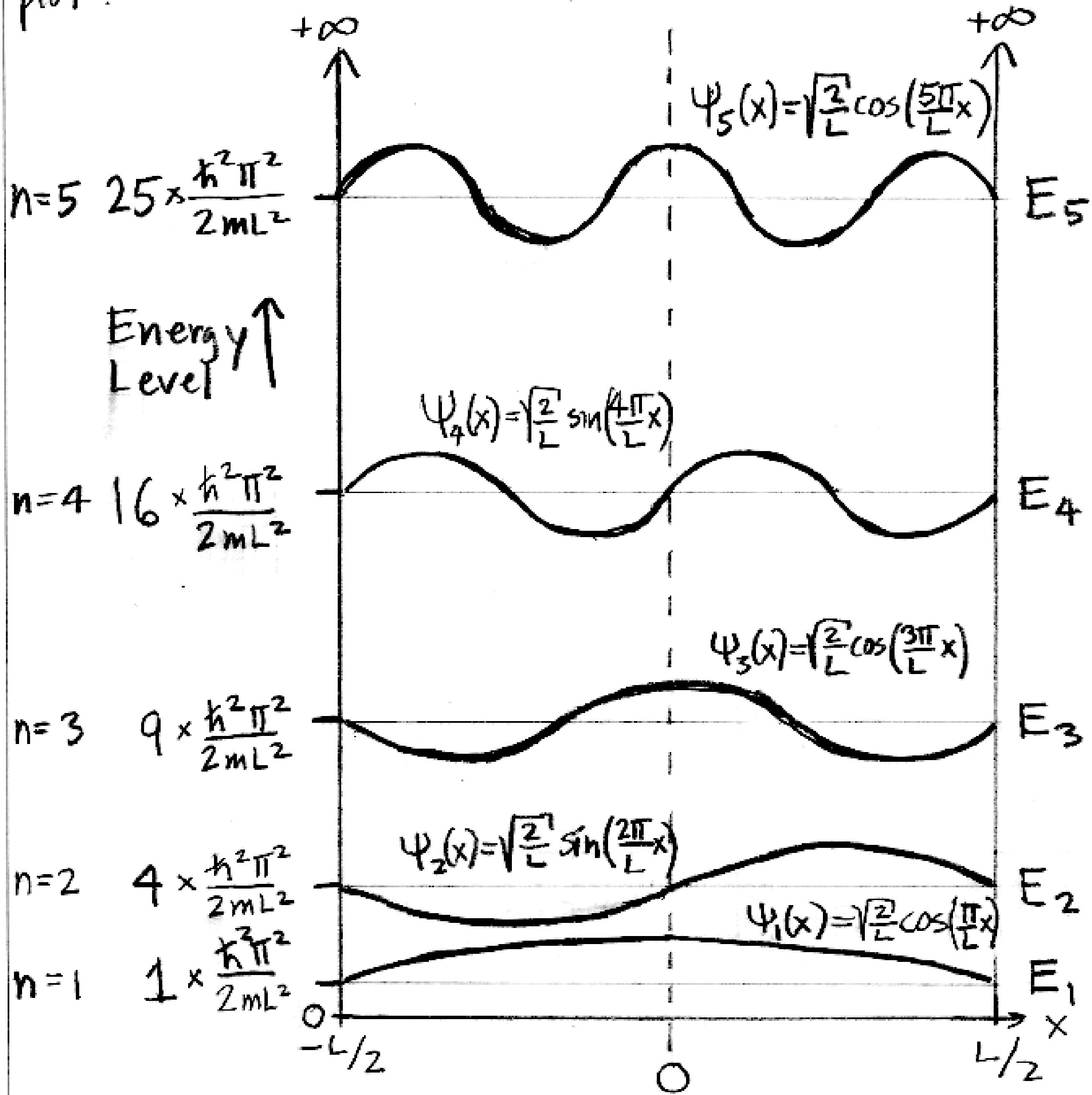
$$|A|=\frac{1}{\sqrt{2L}} \Rightarrow \boxed{\psi_n(x)=\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi}{L}x\right) \quad n=1,3,5,\ldots \text{ (– ones are no different)} \quad E_n=\frac{\hbar^2k^2}{2m}=\frac{\hbar^2\pi^2n^2}{2mL^2}}$$

Similarly, for the <u>even</u> values of n:

$n=\pm 2, \pm 4, \ldots$

$$\boxed{\psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \quad n=2,4,6,\ldots \text{ (– ones just change sign)} \quad E_n=\frac{\hbar^2k^2}{2m}=\frac{\hbar^2\pi^2n^2}{2mL^2}}$$

Sometimes these wavefunctions are simultaneously displayed with the energy eigenvalues in the following plot:



note: odd n have <u>even</u> wavefunctions

even n have <u>odd</u> wavefunctions

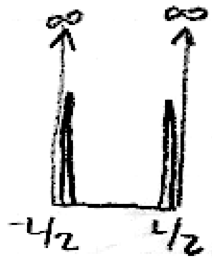
<u>Note</u>: the ground state does <u>not</u> have $E = 0$! A bit of a surprise, but this can be viewed as a result of the uncertainty principle.

Uncertainty Principle:

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

but $\frac{L}{2} \geq \Delta x$ ⇐ why? maximum dispersion when particle spends its time at walls of box.

(particle in box)



$$|\psi(x)|^2 = \tfrac{1}{2}\delta(x+\tfrac{L}{2}) + \tfrac{1}{2}\delta(x-\tfrac{L}{2})$$

$$\langle x \rangle = \int dx \, x |\psi(x)|^2 = \tfrac{1}{2}(-\tfrac{L}{2}) + \tfrac{1}{2}(\tfrac{L}{2}) = 0$$

$$\Delta x^2 = \int dx (x-0)^2 |\psi(x)|^2 = \tfrac{1}{2}\tfrac{L^2}{4} + \tfrac{1}{2}\tfrac{L^2}{4}$$

$$\Delta x = L/2 \quad)$$

so

$$\frac{L}{2}\Delta p \geq \frac{\hbar}{2}$$

$$\Delta p \geq \hbar / L$$

0, state at rest

Then $E = \langle \underset{\sim}{H} \rangle = \dfrac{\langle p^2 \rangle}{2m} = \dfrac{\cancel{\langle p \rangle^2} + (\Delta p)^2}{2m} = \dfrac{(\Delta p)^2}{2m}$

$$E \geq \frac{1}{2m}\left(\frac{\hbar}{L}\right)^2 = \frac{\hbar^2}{2mL^2}$$

for the $n=1$ state,

$$E_1 = \pi^2 \cdot \frac{\hbar^2}{2mL^2} > \frac{\hbar^2}{2mL^2} \qquad \left(\begin{matrix}\text{since} \\ \pi^2 \sim 9 > 1\end{matrix}\right)$$

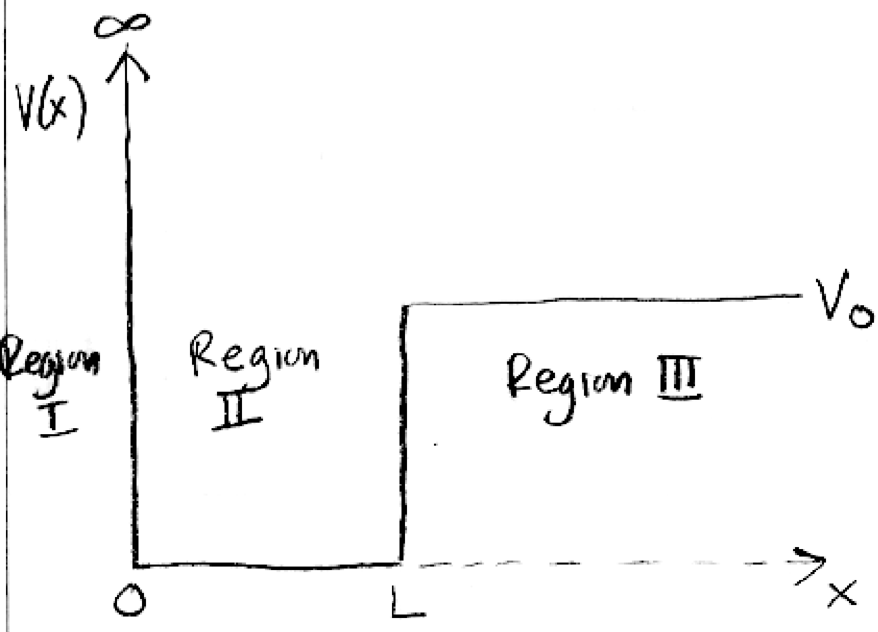
But the lower bound on E qualitatively describes why the ground state is not at 0 energies.

Quantization

$\underset{\sim}{x}$ and $\underset{\sim}{p}$ had continous eigenvalues

The Particle in a Box has discrete energy and momentum eigenvalues. Sometimes this is called "quantization," and quantization arises because bound states are localized. The connection is: states with energies not equal to the quantized values have the vast majority of their probability density away from the potential, and so they are not localized.

To discuss this, it is useful to consider the potential below:



Still: Region I, $\psi(x) = 0$ (infinite energy to get in)

Region II: $\psi_{II}(x) = \underline{A\sin(kx)}$ $E = \frac{\hbar^2 k^2}{2m}$

free, but must $\psi_{II}(0) = 0$.

Region III: function depends on whether $E < V_0$ or $E > V_0$.

Case A

$E \leq V_0$: $\dfrac{d^2\psi_{III}}{dx^2} = \dfrac{2m}{\hbar^2}\underbrace{(V_0 - E)}_{\geq 0 \text{ since } V_0 \geq E}\psi_{III}$

set $K \equiv \left[\dfrac{2m}{\hbar^2}(V_0 - E)\right]^{1/2}$ (real number) $V_0 \geq E$

then $\psi_{III}(x) = Be^{-Kx} + Ce^{Kx}$

Case B

$E > V_0$: $\dfrac{d^2\psi_{III}}{dx^2} = \dfrac{2m}{\hbar^2}\underbrace{(V_0 - E)}_{< 0 \text{ since } V_0 < E}\psi_{III} = \dfrac{-2m}{\hbar^2}|V_0 - E|\psi_{III}$

with $k \equiv \left[\dfrac{2m}{\hbar^2}|V_0 - E|\right]^{1/2}$

$\psi_{III} = Be^{-ikx} + Ce^{ikx}$ ← The i provides the − sign

Only Case A results in quantization however. How? Two points:

#1 must match $\psi(x)$ and $\psi'(x)$ at the interface between region II and region III

$\psi(x)$: $A \sin kL = Be^{-KL} + Ce^{KL}$

$\psi'(x)$: $Ak \cos kL = -KBe^{-KL} + KCe^{KL}$