Classical & Quantum Waves

Solving the Schrödinger eq.

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

$\hbar$: reduced planck's constant $\frac{h}{2\pi}$

m: particle mass

$V(x,t)$: potential energy function

$\Psi(x,t)$: particle wavefunction

- Probability of finding a particle b/t $a \leq x \leq b$ is:

$$P(x,t) = \int_a^b |\Psi(x,t)|^2 dx \quad \text{where} \quad |\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t)$$

complex conjugate ($+i \rightarrow -i$)

- Common technique used to solving S.E. is separation of variables;

$$\Rightarrow \Psi(x,t) = \psi(x)\,\phi(t)$$

depends only on position — depends only on time

* only works if $V(x,t)$ is independent of time, but this is often the case

- Substitute into S.E.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[\psi(x)\,\phi(t)\right] + V(x)\psi(x)\phi(t) = i\hbar\frac{\partial}{\partial t}\left[\psi(x)\,\phi(t)\right]$$

taking derivatives ⟶

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

- Rearrange so x-terms on one side, t terms on the other

$$\underbrace{\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right]}_{\text{Does not depend on } t} = \underbrace{i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}}_{\text{Does not depend on } x}$$

$$\Rightarrow \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = K$$

space-dependent eq.

&

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = K$$

a constant (no t or x-dependence)

time-dependent eq.

$\longrightarrow$

- Let's start w/ the time-dependent eq.

$$i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = k \overset{\text{rewrite}}{\Rightarrow} \frac{d\phi(t)}{dt} = -\frac{ik}{\hbar}\phi(t)$$

$$\Downarrow$$

$$\phi(t) = e^{-ikt/\hbar}$$

- rewrite $\phi(t)$ using Euler's eq. $e^{i\theta} = \cos(\theta) + i\sin(\theta)$

$$\Rightarrow \phi(t) = \cos\left(\frac{kt}{\hbar}\right) - i\sin\left(\frac{kt}{\hbar}\right) = \cos\left(\frac{2\pi kt}{h}\right) - i\sin\left(\frac{2\pi kt}{h}\right)$$

$\hbar = h/2\pi$

~~Clearly~~, By inspection

angular frequency ω → $\frac{2\pi k}{h} \times t$ can be rewritten as ωt, w/ $\omega = \frac{2\pi k}{h}$

$$\omega = \frac{2\pi k}{h} = 2\pi f \Rightarrow$$

$$\Rightarrow k = hf$$

- What else $= hf$? $E = hf$ from Einstein-de Broglie

$$\Rightarrow k = E \ ! \Rightarrow \boxed{\phi(t) = e^{-iEt/\hbar}}$$

- So now we have $\psi(x,t) = \psi(x)\,\phi(t) = \psi(x)\,e^{-iEt/\hbar}$

- Now we need to solve the space-dependent eq. for $\psi(x)$

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x)\right] = K = E$$

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

Time-independent Schrödinger equation

where $\psi(x)$ are "Eigenfunctions" (in German)

which means "characteristic function"

// Solving/using S.E.

~~Example: The infinite square well (using S.E.)~~

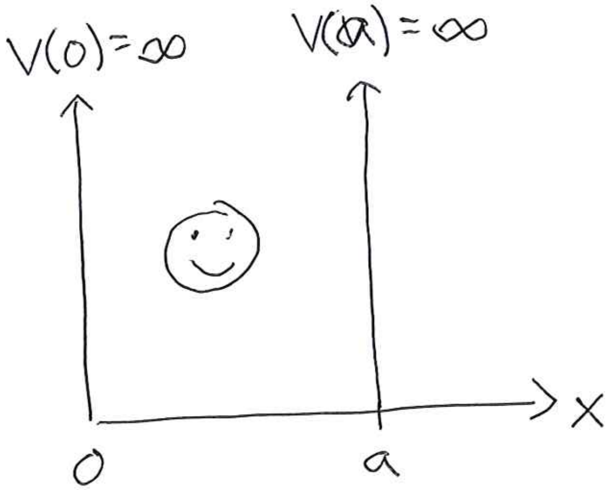
- ~~Consider a particle~~

Typical flow of a problem:

- You are given a function $V(x)$ that defines the physical situation
- Solve time-independent S.E. for $\psi(x)$
- Multiply by $\phi(t)$ to give the full $\psi(x,t) = \psi(x)\,\phi(t)$
- ~~Take~~ calculate probability $P = \int |\psi(x)|^2\,dx$ to find probability of finding the particle in a certain position

Problem: $\boxed{\text{The infinite square well}}$

- Consider a particle of mass m confined in a one-dimensional "potential well" or "box"



- Our particle can move ~~is stuck~~ inside the box but is unable to escape

$V(x)=0$ for $0 \leq x \leq a$ (inside the box)

$V(x)=\infty$ for all other x (outside the box)

- Outside the box, when $x \leq 0$ and $x \geq a$

$\psi(x)=0$

B/c probability density ~~of finding~~ $|\psi(x)|^2$ of finding particle outside the box is 0

Question: What form does $\psi(x)$ take inside the box?

· To answer this question, we need to solve the time-indep. S.E. inside the box $\boxed{20-6}$

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

w/ $V(x) = 0$ for $0 \leq x \leq a$

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

rewrite as $\dfrac{d^2\psi}{dx^2} = -k^2\psi$ w/ $k = \dfrac{\sqrt{2mE}}{\hbar}$

· Solutions: $\psi(x) = A\sin kx + B\cos kx$

· We determine constants A, B by considering the boundary conditions:

$\psi(x) = 0$ outside box

$\psi(x) \neq 0$ inside box

· Continuity of $\psi(x)$ requires that $\psi(0) = \psi(a) = 0$

$\longrightarrow$

- When $x=0$: $\psi(0) = A\sin(0) + B\cos(0) = B = 0$

$$\Rightarrow \psi(x) = A \sin kx$$

- When $x=a$: $\psi(a) = A\sin(ka) = 0$

$$\Rightarrow \sin ka = 0 \Rightarrow ka = \pm n\pi \Rightarrow k = \frac{n\pi}{a} \text{ for } n = 1, 2, \ldots$$

($A=0$ is trivial solution w/ particle not in box)

- Boundary constraints thus give $k = \frac{n\pi}{a}$

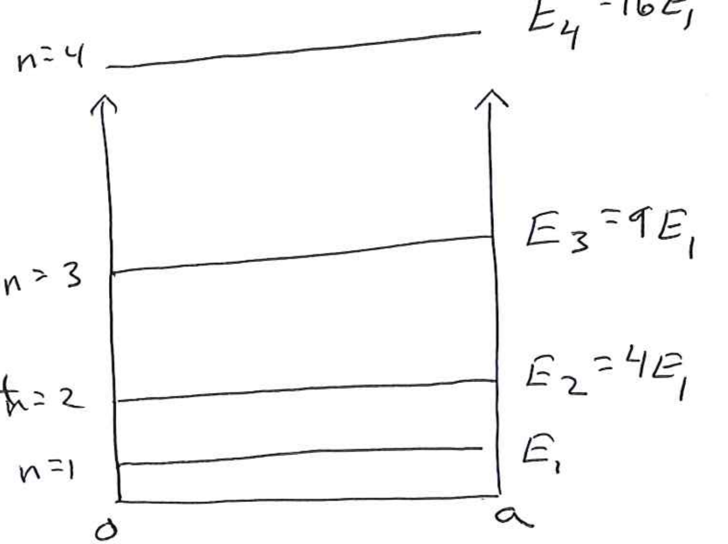
From eq: $\frac{d^2\psi}{dx^2} = -k^2\psi$ w/ $k = \frac{\sqrt{2mE}}{\hbar}$

$$\Rightarrow \frac{n\pi}{a} = \frac{\sqrt{2mE}}{\hbar}$$

$$\Rightarrow \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}} \quad n = 1, 2, 3, \ldots n$$

Energy of particle is quantized!

- Each E_n will have a different ψ_n eigenfunction



- Important! Notice that the lowest energy state is not 0, as is the case in classical physics.

- The lowest "ground state energy" or "zero point energy" is for $n=1$: $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$

- This is a general feature of quantum systems
- Can be understood in terms of Heisenberg uncertainty principle, which states that when you confine a particle in a region of space, there is an inherent uncertainty in the particles' momentum, and therefore its energy.

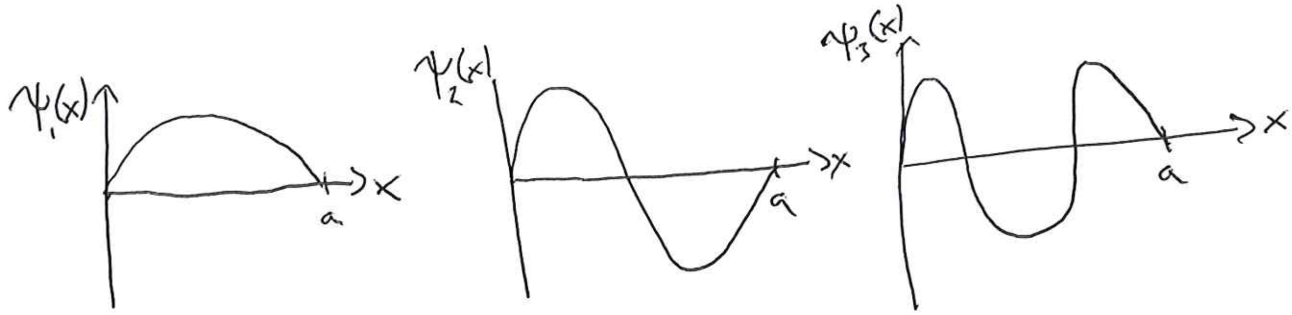
  $\rightarrow$ gives finite ground state energy

$\longrightarrow$

• Putting it all together, we derived:

$\psi(x) = A\sin(kx)$ w/ $k = \frac{n\pi}{a}$

$\rightarrow \psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right)$



$\Rightarrow$ Standing waves! Similar to waves on a string

ψ_1: "ground state", higher n-states "excited states"

• Full wavefunction: $\psi_n(x,t) = \psi_n(x)\,\phi(t) = \psi_n(x)e^{-iE_nt/\hbar}$

$$\Rightarrow \boxed{\psi_n(x,t) = A\sin\left(\frac{n\pi x}{a}\right)e^{-iE_nt/\hbar} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}}$$

• How to determine A?

$\rightarrow$ need to normalize the wavefunction using Born's probability rule

- Probability of finding particle b/t $a \le x \le b$:

$$P = \int_a^b |\Psi(x,t)|^2 dx$$

- We know that ~~the~~ probability of finding particle somewhere inside the box is 1 (ie, it is definitely in the box)

$$\Rightarrow \quad P = \int_0^a |\Psi(x,t)|^2 dx = 1$$

complex conjugate

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

$$\Psi_n(x,t) = A\sin\left(\frac{n\pi x}{a}\right)e^{-iE_n t/\hbar}$$

$$\Psi_n^*(x,t) = A\sin\left(\frac{n\pi x}{a}\right)e^{+iE_n t/\hbar}$$

$$\Rightarrow |\Psi(x,t)|^2 = A^2\sin^2\left(\frac{n\pi x}{a}\right)$$

(the exponential terms multiply to $= 1$)

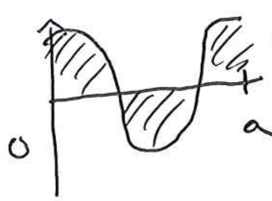
$$\Rightarrow A^2\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx = 1$$

· To evaluate, use $\sin^2(x) = [1-\cos 2x]/2$

$$\Rightarrow A^2 \underbrace{\int_0^a \frac{\left[1-\cos\left(\frac{2n\pi x}{a}\right)\right]}{2}\,dx}_{} = 1$$

$$\underbrace{\frac{1}{2}\int_0^a dx}_{\text{is } \frac{a}{2}} - \underbrace{\frac{1}{2}\int_0^a \cos\left(\frac{2n\pi x}{a}\right)dx}_{=0}$$

$= 0$ b/c integrating over one complete cycle of cosine



← shaded region sums to zero

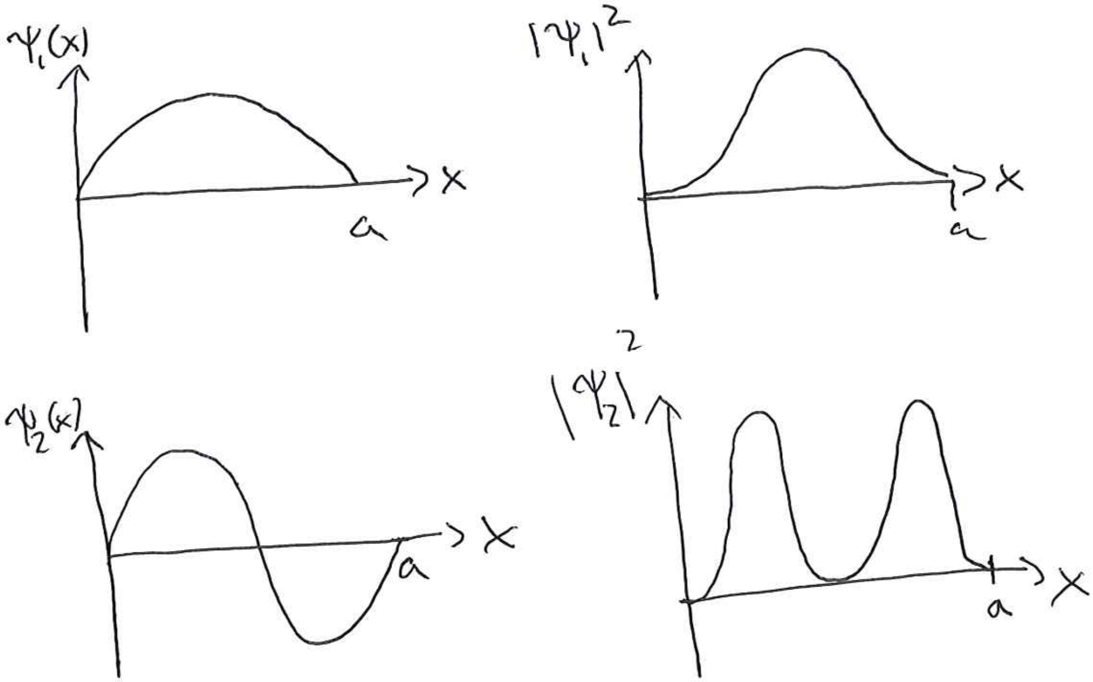
$$\Rightarrow A^2\frac{a}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

$$\Rightarrow \boxed{\psi_n(x,t) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right)e^{-iE_n t/\hbar}}$$

final answer

w/ $\boxed{E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}}$

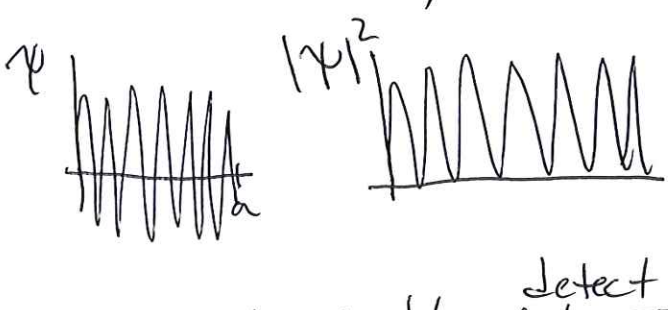
· If we now plot $|\Psi(x,t)|^2$, we can visualize where most likely to find the particle inside the box for each eigen function



ψ_1: most likely to find particle in center of box, where $|\psi_1|^2$ is maximum

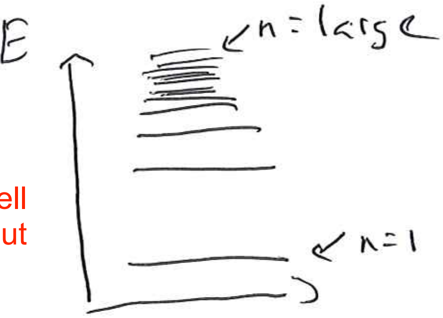
ψ_2: zero probability of finding particle in center! Most probable where $|\psi_2|^2$ maximum

· As n increases, more ψ oscillations inside box



· Eventually, for large n, oscillations so fast that no experiment could ~~determine~~ detect $|\psi|^2$ ~~separation~~ oscillations, and one measures an equal probability of finding the particle anywhere inside box

· Also, as n increases, the separation b/t quantized energy levels E_n becomes so small that one cannot detect separation, and energy possibilites appear continuous



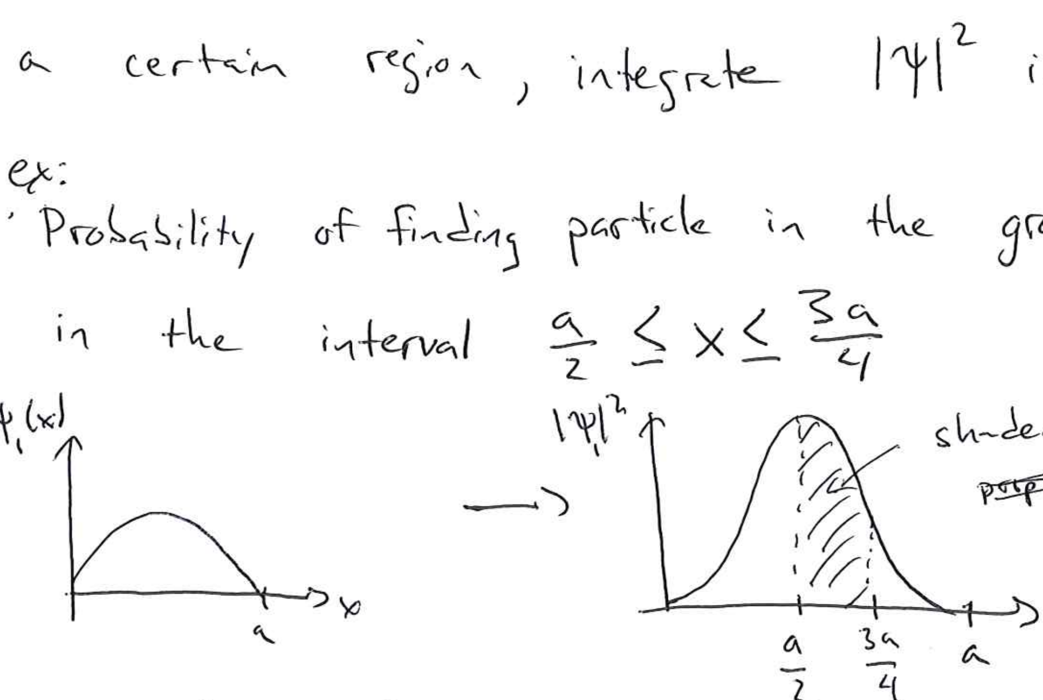
Note: This is not the case in this specific example of infinite potential well (where the opposite trend happens), but it is often the case in real systems

⇒ These two facts reproduce the "classical limit" where one would expect equal probability of finding particle anywhere in box and energy possibilities are continuous.

· To calculate probability ~~in a specific~~ of finding the particle in a certain region, integrate $|\psi|^2$ in region of interest

ex:

· Probability of finding particle in the ground state ψ_1 in the interval $\frac{a}{2} \le x \le \frac{3a}{4}$



shaded region is ~~proportional to~~ probability

$$P = \int |\Psi(x,t)|^2 \, dx$$

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

$\boxed{20-14}$

$$P = \int_{a/2}^{3a/4} |\psi_1(x,t)|^2\,dx = \int_{a/2}^{3a/4} \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right)dx \cong 0.41$$

[proof left as exercise]