Time-independent Schrödinger Eq.

$\boxed{\text{Stationary states}}$

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

Based on what we learned so far,

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

the Schrödinger Eq. simply implies

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = [T+V]\Psi(x,t)$$
$$= H\Psi(x,t)$$

, where $H \equiv T+V$ is called Hamiltonian.

* So far we have been only talking about $\Psi(x,0)$. Now is time to discuss how to solve the Schrödinger Eq. to find $\Psi(x,t)$ for a specified $V(x,t)$.

Most of times, the potential energy $V(x,t)$ is independent of time, that is, $V(x,t)=V(x)$.

In this case, this multivariable differential equation can be solved by "separation of variables".

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

$$\Rightarrow \frac{\partial}{\partial t}\Psi(x,t) = \psi\frac{d\varphi}{dt}$$

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{d^2\psi(x)}{dx^2}\cdot\varphi$$

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

$\Rightarrow i\hbar \frac{d\varphi}{dt}\cdot \psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\cdot\varphi + V\psi\varphi$

$\Rightarrow \quad i\hbar \frac{d\varphi}{dt}\cdot\frac{1}{\varphi} = \left(-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V\right)$

divide by $\psi\varphi$

Here left side is only a ftn of time and the right side is only a ftn of position.

In order for the equal sign to be valid for any time t and position x, both sides have to be equal to a constant, which we call "E": we will see that this constant is actually the energy of the system.

Then left side: $i\hbar\frac{d\varphi}{dt}\cdot\frac{1}{\varphi} = E$

$\Rightarrow i\hbar\frac{d\varphi(t)}{dt} = E\varphi(t)$

$\Rightarrow \boxed{\varphi(t)} = \text{const}\cdot e^{\frac{E}{i\hbar}t} = \boxed{e^{-i\frac{E}{\hbar}t}}$

, with the const $= 1$.

Right side: $-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V = E$

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

This is called "time-independent Schrödinger equation"

* So these separable solutions will look like

$\Psi(x,t) = \psi(x)\cdot e^{-i\frac{E}{\hbar}t}$, where $\psi(x)$ is a solution of the time-independent Schrödinger equation.

✱ What is special about the separable solutions?

1. They are "stationary" states, implying that expectation values of any arbitrary operators do not change over time.

<u>Proof</u>

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

$$= \int \psi^*(x)\, \cancel{e^{i\frac{E}{\hbar}t}}\, Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi(x)\, \cancel{e^{-i\frac{E}{\hbar}t}}\, dx$$

$$= \int \psi^*(x)\, Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi(x)\, dx$$

= constant of time //

for any operator $Q(x,p)$.

In particular $\langle x\rangle$ = constant. Hence

$\langle p\rangle = m\dfrac{d\langle x\rangle}{dt} = 0$; Basically nothing happens.

2. Total energy measurement always gives the fixed value of "E"

Time-independent Schrödinger eq.:

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

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

$\hat{H}$: Hamiltonian; total energy

Then the expectation value of the ~~total~~ energy

$\Rightarrow \langle H \rangle = \int \psi^* \hat{H} \psi \, dx = E \int \psi^* \psi \, dx = E$

$\langle \hat{H}^2 \rangle = \int \psi^* \hat{H} \hat{H} \psi \, dx = E^2 \int \psi^* \psi \, dx = E^2$

$\Rightarrow \sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = 0$

In other words, measurement of "H" always gives the same value of "E".

3. Any solution of the full Schrödinger Eq. (that is, $i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \Psi$), can be described by a linear combination of separable solutions. In other words,

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \varphi_n(t)$$

$$= \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}$$

$\boxed{\text{Ex.}}$ Suppose that a particle starts out in a linear combination of just two stationary states:

$$\Psi(x,0) = \frac{1}{\sqrt{5}} \psi_1(x) + \frac{2}{\sqrt{5}} \psi_2(x)$$

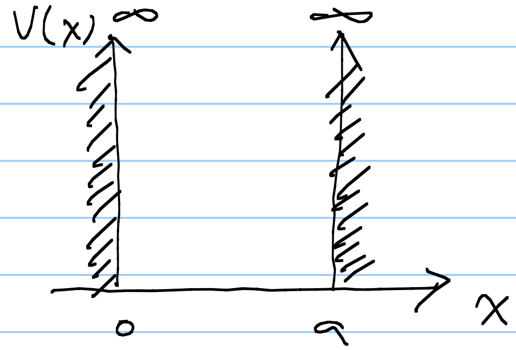
, with the corresponding energies of E_1 and E_2.

What is the wave fcn $\Psi(x,t)$ at subsequent times?

$$\Psi(x,t) = \frac{1}{\sqrt{5}} \left[\psi_1(x) e^{-iE_1 t/\hbar} + 2\psi_2(x) e^{-iE_3 t/\hbar} \right]$$

Infinite Square Well

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a \\ \infty, & \text{else} \end{cases}$$



Find the separable solutions.

$\psi_n(x)$ (called eigen functions) and

E_n (called eigen energies).

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

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

For outside wall $V(x) = \infty$, so the only solution is $\psi(x) = 0$

For $0 \le x \le a$

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

$$\Rightarrow \frac{d^2}{dx^2}\psi = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

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

This is a well-known differential equation corresponding to a classical simple harmonic oscillator equation.

Its general solution is

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

Continuity of $\psi(x)$ requires that

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

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

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

$\Rightarrow ka = n\pi \Rightarrow k_n = \frac{n\pi}{a}, \quad n = \pm 1, \pm 2, \cdots$

"−" sign gives the same solutions, so choose only "+" signs

$\Rightarrow \psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right), \quad n = 1, 2, 3, \cdots$

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

Here $\psi_n(x)$ are called eigen functions and E_n are called eigen values or eigen energies of the equation

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

Now normalize $\psi_n(x)$

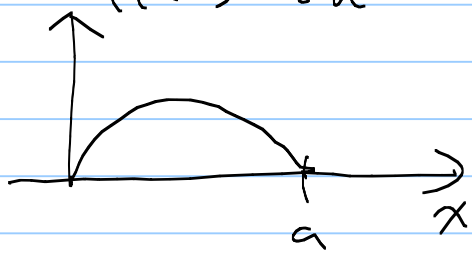
$1 = \int_0^a \psi_n^*(x)\psi_n(x)\,dx = |A|^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx$

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

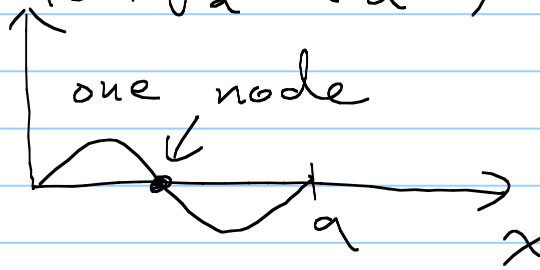
$\Rightarrow A = \sqrt{\frac{2}{a}}$

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

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



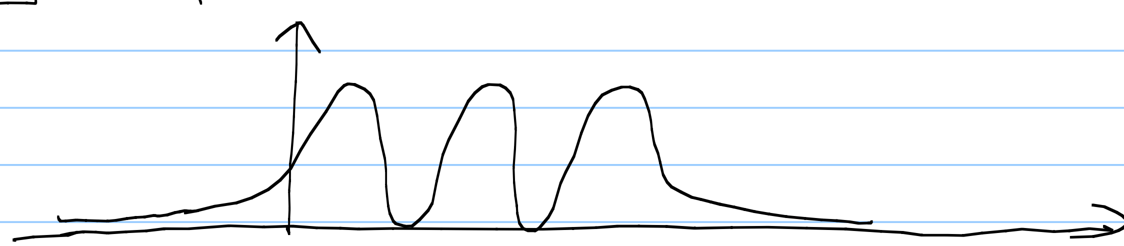
$\psi_2(x) = \sqrt{\frac{2}{a}} \sin(\frac{2\pi}{a} x)$



* Generally, ground state has "zero" number of node. Higher energy states have increasing # of nodes for any types of potential wells.

1st lowest energy state ⇒ zero node
2nd lowest energy state ⇒ one node
3rd " " ⇒ two node
⋮
n " ⇒ (n−1) node

$\boxed{\text{Ex.}}$ $|\psi_n(x)|^2$



How many eigen functions have energies lower than this eigen function?

Ans: two

* Eigen functions are orthonormal, implying

$$\int \psi_m^*(x)\,\psi_n(x) = \delta_{mn} \text{ (Kronecker-delta)}$$

check yourself that $\int_0^a \sin(\frac{m\pi}{a}) \sin(\frac{n\pi}{a})\,dx$

$$= 0 \text{ if } m \neq n$$

* Eigen functions are "complete", implying that any arbitrary function satisfying the boundary conditions enforced by the potential can be expressed by the linear combinations of these eigen functions.

In other words

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

$\uparrow$

For any arbitrary shape, we can always find appropriate "c_n" values.

* How do we find c_n values?

Use the "Fourier trick":

$$\int \psi_m^* \Psi(x,0)\, dx = \sum_{n=1}^{\infty} c_n \int \psi_m^* \psi_n(x)\, dx$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

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

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

$\uparrow$

For the infinite well

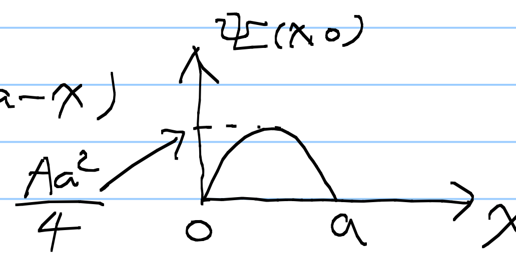
Once c_n evalued this way,

$$\Psi(x,t) = \sum c_n \psi_n(x)\, e^{-i\frac{E_n}{\hbar}t}$$

$$= \sqrt{\frac{2}{a}} \sum c_n \sin\left(\frac{n\pi}{a}x\right) e^{-i\frac{n^2\pi^2\hbar}{2ma^2}\cdot t}$$

$\boxed{\text{Ex.}}$ $\Psi(x,0) = Ax(a-x)$

for $0 \le x \le a$



Find $\Psi(x,t)$.

First, normalize it

$$1 = \int_0^a |\Psi(x,0)|^2 dx = A^2 \int_0^a x^2(a-x)^2 dx$$

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

Second, evaluate c_n.

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

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

$$= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}}\, x(a-x)\, dx$$

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

$$= \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0) - \cos(n\pi) \right]$$

$$= \begin{cases} 0, & \text{for } n \text{ even} \\ \dfrac{8\sqrt{15}}{(n\pi)^3}, & \text{for } n \text{ odd} \end{cases}$$

$$\therefore \Psi(x,t) = \sum c_n \psi_n(x)\, e^{-i\frac{E_n}{\hbar}t}$$

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

* $|c_n|^2$ is the probability of yielding E_n with the energy measurement.

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

$\Rightarrow \langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n$: constant over time

; conservation of energy

$\boxed{\text{Ex}_1}$ With $\psi_1(x)$ and $\psi_2(x)$ the eigen ftns of the infinite potential well with $E_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$ and $E_2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2$ respectively, if

$$\Psi(x,0) = \frac{1}{\sqrt{5}}\left(\psi_1(x) + 2\psi_2(x)\right)$$

(a) What is the probability of the energy measurement yielding

$$E_1,\ E_2,\ \text{and}\ \frac{E_1+E_2}{2}\ ?$$

Ans: $P(E_1) = \frac{1}{5}$, $P(E_2) = \frac{4}{5}$

$$P\left(\frac{E_1+E_2}{2}\right) = 0$$

(b) What is $\langle H \rangle$?

Ans: $\langle H \rangle = \frac{1}{5}E_1 + \frac{4}{5}E_2$

(c) If measurement of H yields E_1, what is the wave function immediately after the measurement?

Ans: $\Psi(x,0) = \psi_1(x)$

(d) A while after (c), if you measure H again, what is the probability of getting E_2 ?, Ans: zero