## 3-1. The time-independent SE

$$i\hbar \frac{\partial \Psi}{\partial t} = \underset{\text{Hamiltonian }\underline{\underline{\text{operator}}}}{\underline{\underline{\overset{\curvearrowright}{H}}}}\,\Psi(x,t) \longleftarrow \text{acts to the } \underline{\underline{\text{right}}} \text{ on the wave function}$$

Underline **Operator** : operates (changes) the wave function. The simplest change one can anticipate is multiplication by a constant

$$\underset{\text{eigenfunction}}{H\Psi} = \underset{\text{eigenvalue}}{a}\,\Psi$$

|| This simplest scenario is called the eigenvalue problem

Time-independent Hamiltonian:

$$H = \frac{p^2}{2m} + \underset{\text{does } \underline{\underline{\text{not}}} \text{ explicitly depend on } t}{\underline{\underline{V(x)}}}$$

The wave function can be factored into <u>space-dependent</u> and <u>time-dependent</u> parts:

$$\Psi(x,t) = T(t)\,u(x)$$

$$i\hbar\, u(x) \frac{dT(t)}{dt} = \left[-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)\,u(x)\right] T(t)$$

$$i\hbar \frac{1}{T}\frac{dT}{dt} = \frac{1}{u(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)\,u(x)\right] = \overset{\boxed{\text{constant}}}{\overset{\downarrow}{\textcircled{E}}}$$

Time-dependent part: $T(t) = c\, e^{-iEt/\hbar}$

Space-dependent part:

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

Constant shift of the potential does not change the solution, but shifts the energy by that constant. This is analogous to classical mechanics where $-\frac{dV}{dx} = F$ (force) determines the equations of motion.

## 3-2 Eigenvalue equations

$$\underline{\hat{O}\,f(x) = g(x)}$$

operator $\hat{O}$ acting on $f(x)$ and producing $g(x)$

Linear operators: $\hat{L}\,[f_1 + f_2] = \hat{L}f_1 + \hat{L}f_2$

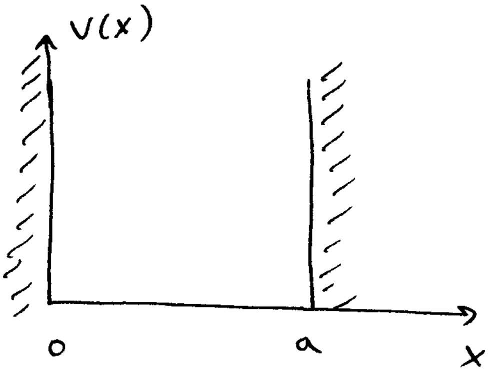
$$\hat{L}(cf) = c\,\hat{L}f$$

SE is a linear equation, i.e. the sum of solutions is a solution. The general form of the wave function is ($V(x)$ does not depend on t)

$$\psi(x,t) = \underbrace{\sum c_n u_n(x)\, e^{-iE_nt/\hbar}}_{\text{discrete spectrum}} + \underbrace{\int dE\, \underbrace{C(E)}_{\text{density of states}}\, u_E(x)\, e^{-iEt/\hbar}}_{\text{continuous spectrum}}$$

# 3-3. Particle in a box

$$V(x) = \begin{cases} \infty, & x < 0 \\ 0, & 0 < x < a \\ \infty, & x > a \end{cases}$$



In order to avoid infinite term $V(x)\,u(x)$ in the SE at $x<0$, $x>a$, $u(x) \equiv 0$ in those regions.

at $0 \le x \le a$ : $$\frac{d^2u}{dx^2} + \underbrace{\frac{2mE}{\hbar^2}}_{k^2,\ \underline{\underline{E>0}}\ !} u(x) = 0$$

Solution :

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

$$u(0) = 0 \quad \rightarrow \quad B = 0$$

$$u(a) = 0 \quad \rightarrow \quad k_n a = \pi n$$

Energy levels : $$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 a^2 \hbar^2}{2ma^2}}$$

Wave function : $$\boxed{u_n = \underline{\underline{\sqrt{\frac{2}{a}}}} \sin\left(\frac{\pi n x}{a}\right)}$$

normalization constant

$$\int_0^a dx\, u_n^*(x)\, u_m(x) = \delta_{nm}$$

orthonormality conditions : <u>same</u> functions are <u>normalized</u> + <u>different</u> functions are <u>orthogonal</u>

## Physical results :

1. Nonzero minimum energy:

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

$n=0$ would correspond to $u_0 \equiv 0$, no state at all. $p=0$ would mean $\Delta p = 0$ and that violates the uncertainty principle

$\Delta x \approx a$, $\Delta p = \frac{\hbar}{a}$, $E \approx \frac{\hbar^2}{2ma^2}$, in qualitative agreement with the exact result

2. $\langle p \rangle = 0$ ← true for any real wave function

$$\langle p \rangle = \int_0^a dx\, u_n(x) \overbrace{\Big(-i\hbar \underset{\substack{\uparrow \\ \text{changes sign under } x \to -x}}{\frac{\partial}{\partial x}}\Big)\, u_n(x)}^{\text{invariant under } x \to -x \ ((-1)\times(-1))}$$

$$\langle p^2 \rangle = 2m E_n > 0$$

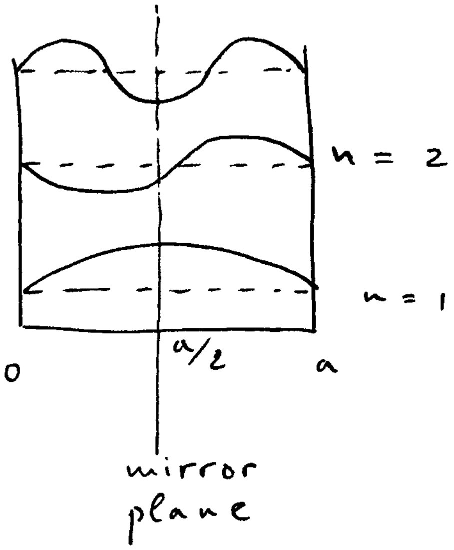
$$\Delta p = \sqrt{\langle p^2 \rangle} = \pi\hbar/a$$

3. $\langle K \rangle$ grows with the number of nodes
($\psi_n(x) = 0$ makes a node)

$$\langle K \rangle = \frac{\hbar^2}{2m} \cdot \int_0^a dx \left| \frac{du_n(x)}{dx} \right|^2 \longleftarrow \langle K \rangle \text{ is larger when } u_n(x) \text{ oscillat} \text{ a lot}$$

! number of nodes $= n - 1$

4.



$\underline{\underline{n \text{ odd}}} \rightarrow u_n(x)$ is invariant to reflection in the mirror plane

$\underline{\underline{n \text{ even}}} \rightarrow u_n(x) \rightarrow -u_n(x)$ under reflection

Shift of the variable $x \rightarrow x - \frac{a}{2}$ to place the mirror plane at the origin

$$\sin\left(\frac{n\pi x}{a}\right) \rightarrow \sin\left(\frac{n\pi x}{a} - \frac{n\pi}{2}\right) =$$

$$= \sin\frac{n\pi x}{a}\cos\frac{n\pi}{2} - \cos\frac{n\pi x}{a}\sin\frac{n\pi}{2}$$

$n = 1, 3, 5, \ldots (2m+1)$, $\quad u_n \propto \underline{\underline{\cos\frac{n\pi x}{a}}}$

even function in respect to $x \rightarrow -x$

$n = 2, 4, 6, \ldots 2m$, $\quad u_n \propto \underline{\underline{\sin\frac{n\pi x}{a}}}$

odd function in respect to $x \rightarrow -x$

## Particle in a box density of states:

$$E \propto n^2, \qquad \frac{dE}{E} = 2\,\frac{dn}{n}$$

$$\frac{dn}{dE} = \frac{n}{2E} = \frac{2ma^2}{\hbar^2\pi^2}\,\frac{1}{n}$$

number of available states decays as $1/n$

## 3-4. The expansion postulate

**Expansion postulate of QM:**

Arbitary "well-behaved" wave function can be expanded in eigenfunctions of a Hermitian operator corresponding to a physical observable

**Reminder:** Hermitian operator has real expectation values

**Particle in the box:**

$$\hat{H} u_n = E_n u_n, \qquad u_n = \sqrt{\frac{2}{a}}\,\sin\frac{\pi n x}{a}$$

↗ Hermitian operator

↑ physical observable, energy

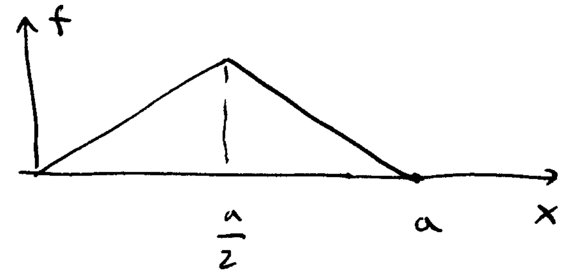
The above statement seems to suggest that any function in $x \in [0, a]$ can be expanded in $u_n(x)$:

$$f(x) = \sum a_n u_n(x) = \sqrt{\tfrac{2}{a}} \sum a_n \sin\left(\frac{\pi n x}{a}\right)$$

$\underline{f(0) = f(a) = 0}$ — f(x) must satisfy the same boundary conditions as $u_n(x)$. That what means "well-behaved"

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

Example :



$$f(x) = \begin{cases} x, & 0 \le x \le \frac{a}{2} \\ a-x, & \frac{a}{2} \le x < a \end{cases}$$

$$a_n = \frac{(2a)^{3/2}}{\pi^2 n^2} \sin \frac{n\pi}{2}$$

$$a_{2m} = 0$$

If an arbitrary function satisfying the same boundary condition con be expanded in $u_n(x)$, $u_n(x)$ forms a complete set

Therefore, if $u_n(x)$ are all eigenfunctions of a Hermition operator, they form a complete set.

In application to the particle in a box, any physical property one measures for that particle (e.g., momentum) will form a complete set of states (functions).

For a time-dependent wave function:

$$\Psi(x,t) = \sum A_n u_n(x) e^{-iE_nt/\hbar}$$

## Physical interpretation of the expansion coefficients

$H u_n(x) = E_n u_n(x)$ ← Hamiltonian eigenvalue problem (measuring energy!)

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

$$= \int_0^{\infty} \Psi^*(x) u_n(x) \sum_n A_n E_n = \sum \underline{\underline{|A_n|^2}} E_n$$

weight of eigenstate n in the observed average energy

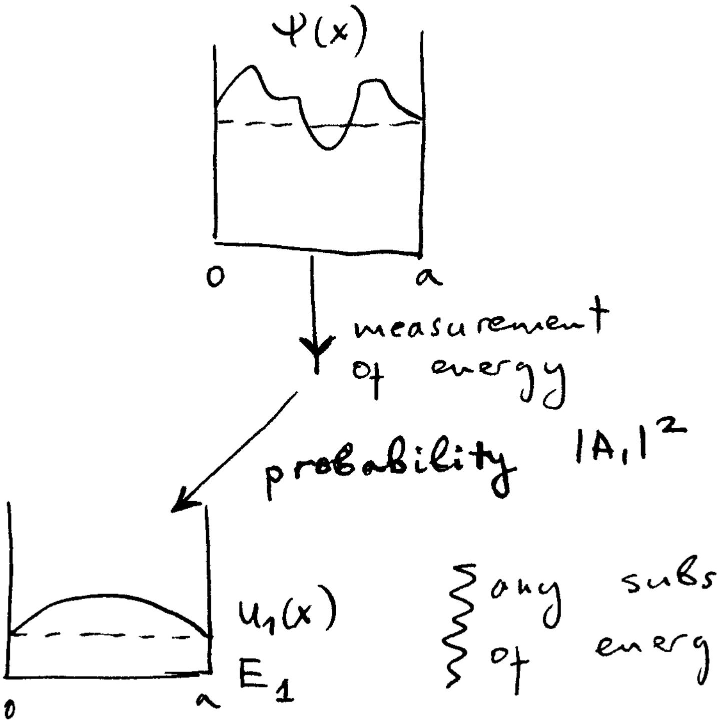
$$E_{av} = \langle H \rangle = \sum E_n \underline{\underline{P_n}}$$

probability to find a given energy level $E_n$

**Postulate:** measurement of the energy gives rise to one of the eigenvalues of the energy operator (Hamiltonian)

$|A_n|^2 = P_n$ ← $A_n$ is the probability amplitude for finding the particle in state $E_n$

Any measurement projects a state which is a mixture of eigenstates into an eigenstate of the observable



any subsequent measurement of energy will give $E_1$. !

**Example**

$$\psi(x) = \begin{cases} A\,\frac{x}{a}\,, & 0 < x < \frac{a}{2} \\ A\left(1-\frac{x}{a}\right), & \frac{a}{2} < x < a \end{cases} \quad \text{at } t=0$$

Probability of getting $E_n$ in the energy measurement ( $A=\sqrt{12/a}$ )

$$A_n = \sqrt{\frac{2}{a}} \int_0^a dx\, \psi(x) \sin\frac{n\pi x}{a} = \sqrt{\frac{24}{a}}\left[ \int_0^{a/2} \frac{x}{a} \sin\frac{n\pi x}{a}\, dx + \right.$$

$$\left. + \int_{a/2}^{a} \left(1-\frac{x}{a}\right) \sin\frac{n\pi x}{a}\, dx \right]$$

$$|A_n|^2 = \frac{96}{\pi^4 n^4} \qquad n \text{ odd}$$

$$= 0 \qquad n \text{ even}$$

## 3-5. Free particle

If one wants to measure the momentum, one has to solve the eigenvalue problem for the momentum operator

$$\hat{p}\, u_p(x) = p\, u_p(x)$$

$$\frac{\hbar}{i}\frac{\partial u_p(x)}{\partial x} = p\, u_p(x) \longrightarrow u_p(x) = c\, e^{\frac{ipx}{\hbar}}$$

Normalization

$$\int_{-\infty}^{\infty} dx\, u_p^*(x)\, u_{p'}(x) = |c|^2 \int_{-\infty}^{\infty} e^{\frac{ix}{\hbar}(p-p')}\, dx = 2\pi\hbar |c|^2 \delta(p-p'$$

$$c = \frac{1}{\sqrt{2\pi\hbar}} \qquad \boxed{u_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipx/\hbar}}$$

$$\boxed{\int_{-\infty}^{\infty} u_p^*(x)\, u_{p'}(x)\, dx = \delta(p-p')}$$

Normalization for continuous indices is performed on the Dirac delta function instead of the Kronecker symbol in the case of discrete variables

The physical significance of Fourier transform is that it provides the expansion of a wave function in eigenstates of the momentum operator (Hermitian operator corresponding to a physical observable).

<u>Degeneracy</u> : there may be more than one independent eigenfunction that corresponds to the same eigenvalue

$e^{ikx}$ and $e^{-ikx}$ are <u>two independent</u> solutions of the SE for a free particle

Degeneracy is commonly linked to the energy operator :

$$\underbrace{\psi_1 = e^{ikx}, \quad \psi_2 = e^{-ikx}}$$

$$H\psi_1 = H\psi_2 = \frac{\hbar^2 k^2}{2m}\psi_1 = \frac{\hbar^2 k^2}{2m}\psi_2$$

Two states with degenerate energies may produce different eigenvalues for another operator :

$$\hat{p}\, e^{ikx} = \hbar k\, e^{ikx} , \qquad \hat{p}\, e^{-ikx} = \ominus \hbar k\, e^{-ikx}$$

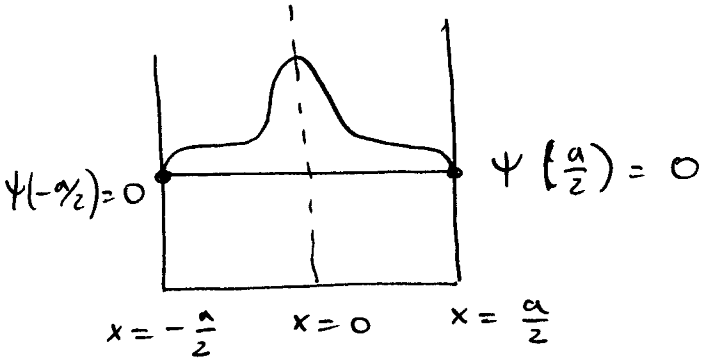
One can use a linear combination of the two solutions

$$\cos kx = \frac{1}{2}\left(e^{ikx} + e^{-ikx}\right),$$

$$\sin kx = \frac{1}{2i}\left(e^{ikx} - e^{-ikx}\right)$$

these two now behave differently under the <u>parity operation $x \to -x$</u>

## 3-6. Parity



$$\boxed{\psi(x,t)=\sum_m A_m\sqrt{\frac{2}{a}}\cos\frac{\pi x(2m+1)}{a}\times e^{-iE_{2m+1}t/\hbar}}$$

$$\psi\left(\frac{a}{2},t\right)=\sum A_m\sqrt{\frac{2}{a}}\cos\frac{\pi(2m+1)}{2}\ldots$$

$$=0$$

$$\psi\left(-\frac{a}{2},t\right)=0$$

Even function:

$$\psi(-x,t)=\psi(x,t)$$

The even/odd property is time independent. Evenness and oddness are constants of the motion.

Parity operator: $\boxed{P\psi(x)=\psi(-x)}$

Eigenvalues:

$$\left.\begin{aligned}P^2\psi(x)&=\psi(x)\\P\psi(x)&=\lambda\psi(x)\\P^2\psi(x)&=\lambda^2\psi(x)\end{aligned}\right\}\quad \begin{aligned}&\lambda^2=1\\&\boxed{\lambda=\pm 1}\end{aligned}$$

eigenvalues of the parity operator

Any wave function $\psi(x)$ can be expanded in eigenfunctions of the parity operator

$$\psi(x) = \psi^{(+)}(x) + \psi^{(-)}(x)$$

$$\psi^{(+)}(x) = \frac{1}{2}[\psi(x) + \psi(-x)], \quad \psi^{(-)}(x) = \frac{1}{2}[\psi(x) - \psi(-x)]$$

$$P\psi^{(+)}(x) = (+1)\psi^{(+)}(x), \quad P\psi^{(-)}(x) = (-1)\psi^{(-)}(x)$$

When an even function stays even?

$$\psi(x,0) = \psi(-x,0) \equiv \psi^{(+)}(x)$$

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi(x,t) \rightarrow i\hbar\frac{\partial P\psi}{\partial t} = PH\psi(x,t)$$

if $PH = HP$,

$$i\hbar\frac{\partial P\psi}{\partial t} = H(P\psi)$$

Therefore $P\psi$ is a solution of the same linear differential equation with the boundary condition $\psi(x,0)$. It implies that

$$P\psi(x,T) = \psi(x,t) \quad \text{and} \quad \psi(x,t) \text{ stays even}$$

Therefore $\boxed{[\hat{P}, \hat{H}] = 0}$ is the condition for $\psi^{(+)}(x,t)$ and $\psi^{(-)}(x,t)$ not to mix with time → evenness/oddness is a constant of motion

<u>Generally</u>: any operator that does not have an explicit time dependence and commutes with the Hamiltonian is a constant of motion

One can also show that $[\hat{P}, \hat{H}] = 0$ ensures that one can define a common basis set for $\hat{P}$ and $\hat{H}$, that is solutions $u_n(x)$ of the SE can be split into even and odd components: $u_n^{(+)}$ and $u_n^{(-)}$.

<u>Example</u>: $\hat{H}(t) = \frac{\hat{p}^2}{2m} + V(x,t)$

$$[\hat{H}(t), \hat{H}(t)] = 0$$

however, $\hat{H}(t)$ does not form a constant of motion $(E = E(t))$ because it involves an explicit dependence on $t$.