

Chapter 2

Now the real work starts: **how do we solve the Sch. Eq.?**

In general, the Sch. Eq. has a **time-dependent** potential:

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

where $V=V(x,t)$. For example, the $V(x,t)$ of an electric field $\mathbf{E}(x,t)$.

Start with something *simpler*: a **time independent** potential $V=V(x)$. Then use "**separation of variables**".

Assume:

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

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\varphi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \varphi$$

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

Divide by $\psi\varphi$ to get:

$$\underbrace{i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt}}_{\text{Function of } t \text{ only}} = \underbrace{-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V(x)}_{\text{Function of } x \text{ only}} = E$$

(constant with important physical meaning)

Time dependence is easy here!

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = E \quad \Rightarrow \quad \frac{d\varphi}{dt} = -\frac{iE}{\hbar} \varphi$$

$$\varphi(t) = e^{-iEt/\hbar}$$

Coordinate dependence is not easy! ☹️

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

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

Constant to be found

The solutions of this time-indep. Sch. Eq. are important for 3 reasons [(1,2) given here, (3) later]:

(1) They are stationary states: $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$

$$|\Psi(x, t)|^2 = \Psi^* \Psi = \psi^* e^{+iEt/\hbar} \psi e^{-iEt/\hbar} = |\psi(x)|^2$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx.$$

Constant
in time

All expectation values of operators $O(x,p)$ are constant in time.

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = 0$$

(2) They have "sharp" energies.

$$\underbrace{H(x, p) = \frac{p^2}{2m} + V(x)}_{\text{Classical "Hamiltonian"}} \xrightarrow[\text{rules}]{\text{QM}} \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

$p \rightarrow (\hbar/i)(\partial/\partial x)$

Now the time-indep. Sch. Eq. looks "simple":

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

Then, the constant E is the energy !

$$\langle H \rangle = \int \psi^* \underbrace{\hat{H}\psi}_{E\psi} dx = E \int |\psi|^2 dx = E \underbrace{\int |\Psi|^2 dx}_{=1} = E$$

Why E is "sharp"?

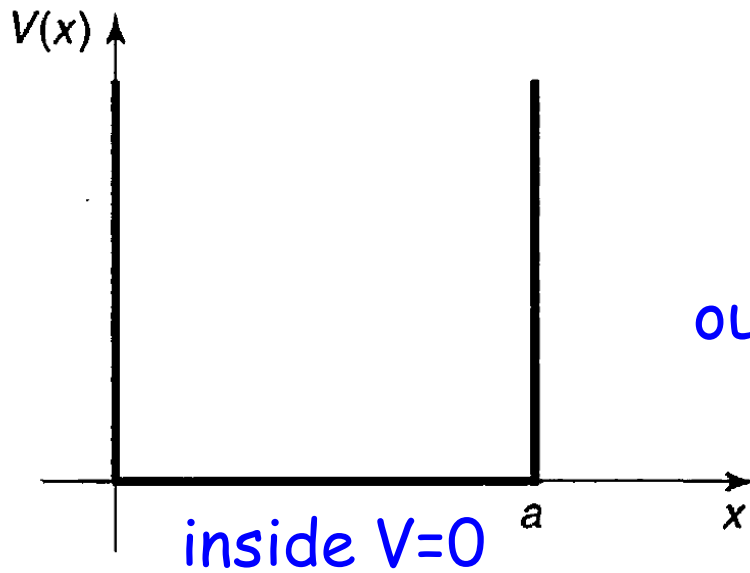
$$\hat{H}^2\psi = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2\psi$$

$$\langle H^2 \rangle = \int \psi^* \hat{H}^2\psi dx = E^2 \underbrace{\int |\psi|^2 dx}_{=1} = E^2$$

$$\text{Thus: } \sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0$$

sharp!

The infinite square well



$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a. \\ \infty, & \text{otherwise} \end{cases}$$

outside



$$\psi(x) = 0$$

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



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

$$k \equiv \frac{\sqrt{2mE}}{\hbar}$$

**E is to be determined.
"Inside" the potential
E will be discrete.**

The diff. eq. $\frac{d^2\psi}{dx^2} = -k^2\psi$ has as a solution:

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

A and B are constants fixed by boundary conditions.

In this case, the only bound. cond. we know is

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

The first one is easy:

$$\psi(0) = A \underbrace{\sin 0}_{=0} + B \underbrace{\cos 0}_{=1} = B = 0$$

The second one becomes:

$$\psi(a) = A \sin ka \quad \text{or} \quad \sin ka = 0$$

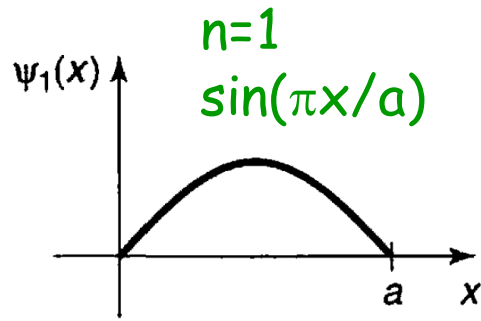
$$ka = \cancel{0}, \pm\pi, \pm 2\pi, \pm 3\pi, \dots$$

A=0 or k=0 leads to zero wave function, not normalizable.
The "-" solutions are redundant because $\sin(x)$ is odd.

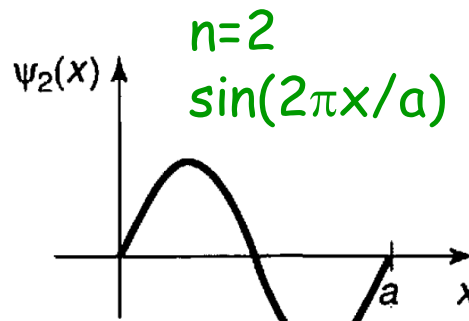
Only
solutions
are then:

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1, 2, 3, \dots$$

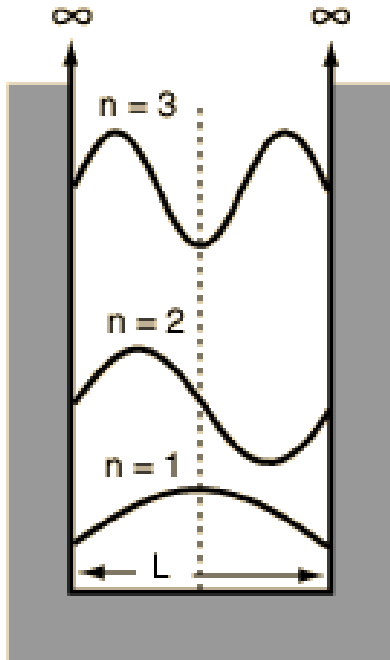
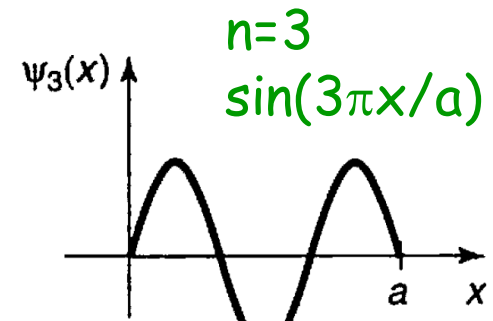
Note that this is a **discrete** set of solutions, thus energies will be discrete.



ground state

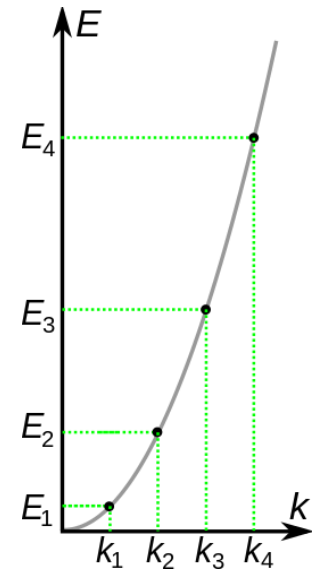


excited states



$x = 0$ at left wall of box.

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$



Energies are **quantized** in QM, while in classical mechanics inside the well you can have any energy.