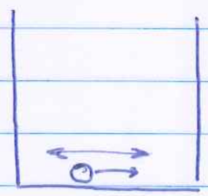
Quantum infinite well (rigid box)

Let's for a moment construct the probability density for a classical particle, bouncing b/w the walls.



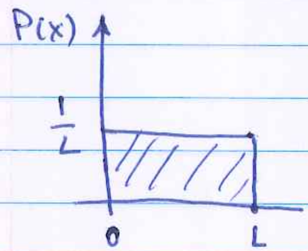
If the collisions with the wall are pectectly elastic (and we will always assume they are), then the energy of the particle is constant E

The particle moves with the constant speed $v = \sqrt{2E/m}$ (since $E = mv^2/2$) from one wall to another. Then what is the probability to catch the particle b/w x_0 and $x_0 + \Delta x$?
It takes the particle time L/v to cross the box, and the time it spends b/w x_0 and $x_0 + \Delta x$ is $\Delta x / v$. Thus, the probability to catch the particle there is ~~Δx~~ ~~time~~

$$P_{x,x+\Delta x} = \frac{\text{time b/w } x \text{ and } x+\Delta x}{\text{time to cross the box}} = \frac{\Delta x}{L}$$

probability density $P(x) = P(\Delta x)/\Delta x = 1/L$ constant

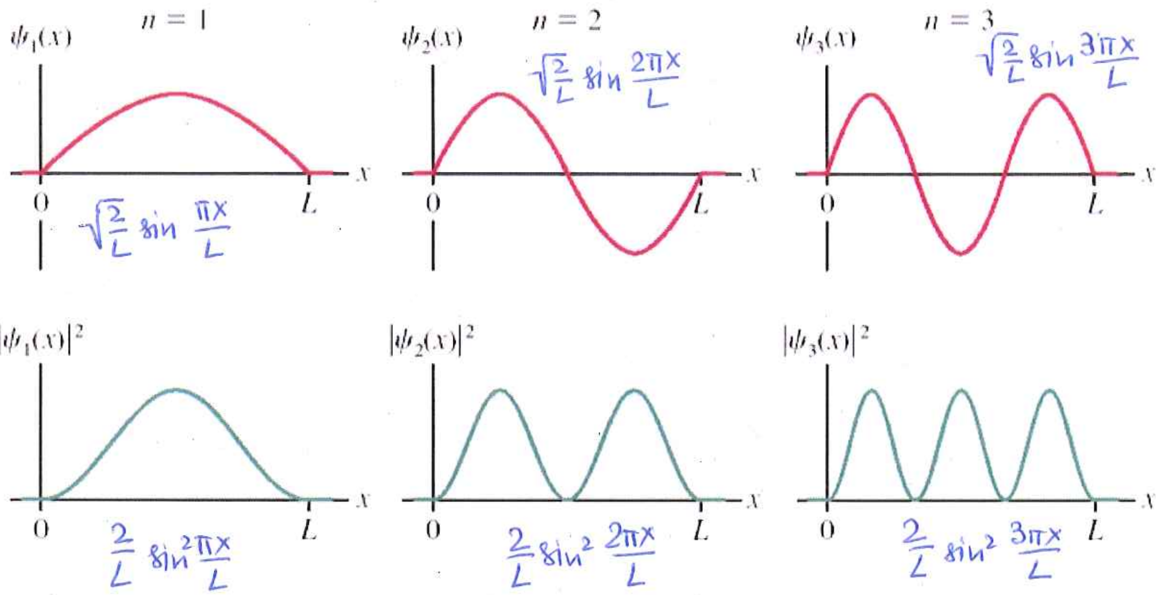
For a classical particle in a rigid box

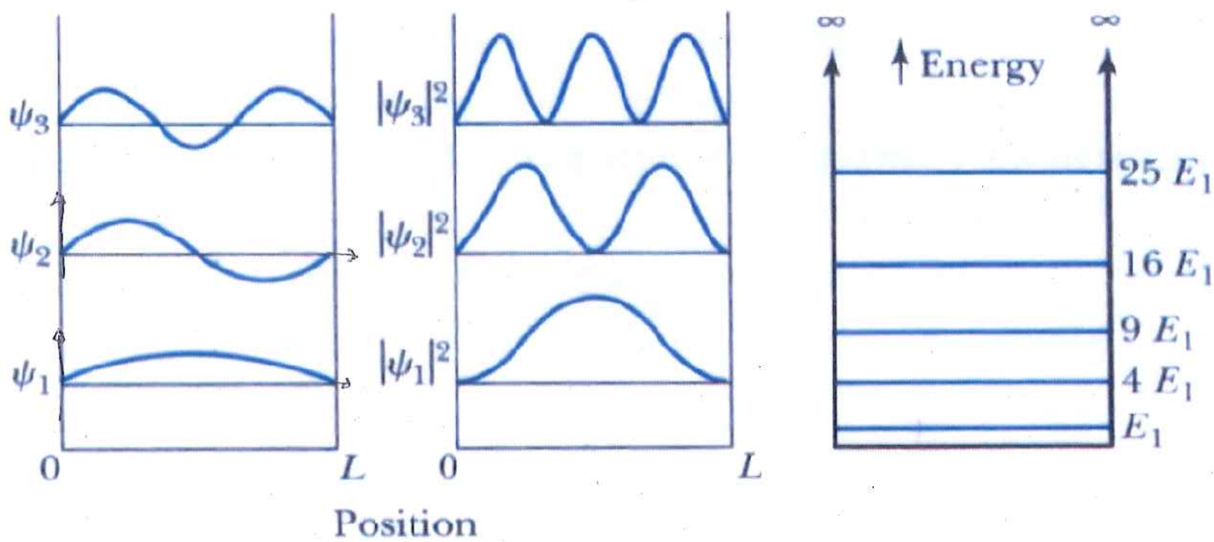


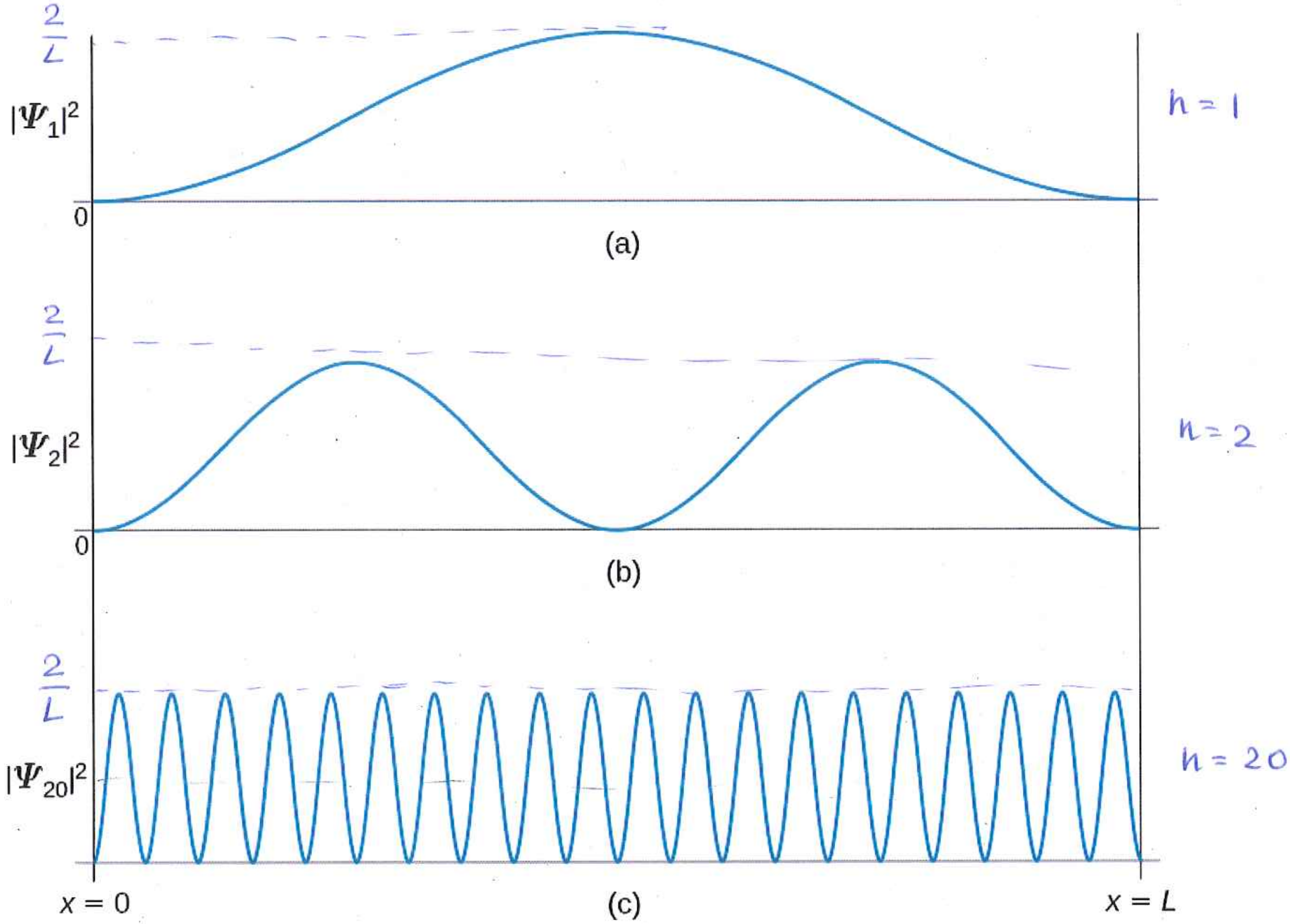
Cohrespondence principle: behavior of systems described by quantum mechanics must reproduce classical physics in the limit of large quantum numbers.

$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2}$ eigenstate $\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L}$

FIGURE 41.7 Wave functions and probability densities for a particle in a rigid box of length L.




ψ_3
ψ_2
ψ_1
0
L
$|\psi_3|^2$
$|\psi_2|^2$
$|\psi_1|^2$
0
L
Position
∞
Energy
∞
$25\ E_1$
$16\ E_1$
$9\ E_1$
$4\ E_1$
E_1



(a)

(b)

(c)

for very large n $P_n(x) \approx \frac{1}{L}$ (since the average of $\sin^2 x = \frac{1}{2}$)

What we established in QM so far

At the moment we consider <u>bound</u> <u>states</u>: the case in which a classical particle is localized in a region of space. Such region is called "classically - allowed" region.

~~Bound states are descr~~

If a quantum particle is localized, its energy spectrum consists of descreet states, typically numbered $n = 1$ (or 0) to $n = \infty$, each state is characterized by a specific value of energy E_n and a specific wave function $\psi_n(x)$, such that

Schrodinger equation: $$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + U(x)\psi_n(x) = E_n \cdot \psi_n(x)$$

Full wave function includes a time-dependent phase factor

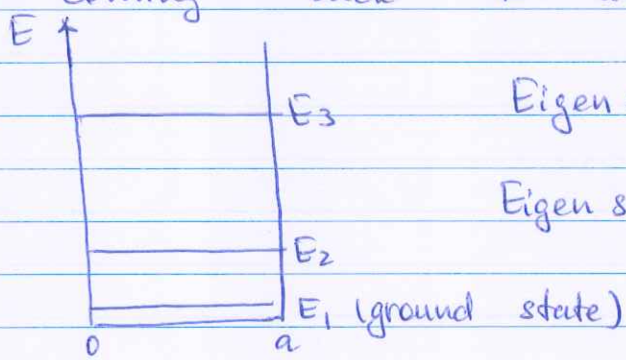
$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_nt/\hbar}$$

Note: for now, we are going to work in coordinate representation for all wave - functions. That means we are going to assume that we can ~~measure~~ determine position x precisely, and we can write a wave function as a function of x $\Rightarrow \psi_n(x)$

In principle, it is possible to use a different representation, for example momentum (p) representation in which the values of p are defined, and x becomes an operator. If the calculations are carried out properly, both approaches will give same spectrum of energies E_n, even though the functional dependence of the corresponding state wavefunction would be different $\psi_n(x)$ or $\psi_n(p)$

Often, the ~~sto~~ values of energy for stationary states E_n are called eigenenergies, and the states n — eigen states.
Often the notation $|n\rangle$ is used to denote the quantum state without specifying its representation. So $|n\rangle$ ~~is~~ (called "ket") is more general way to write $\psi_n(x)$.
In the same notation bra → $\langle n|$ — corresponds to $\psi^*_n(x)$

Coming back to an infinite well



Eigen energies $E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$

Eigen states: $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a}$

If a particle has energy E_n, it is in a stationary state $\psi_n(x)$, and it is going to stay there forever (stationary state!)
No matter how many time you measure particle's energy it stays the same (that is why it is an energy eigenstate)

Does this mean that a particle inside such box will only exist in states with energies E_n and wavefunction $\psi_n(x)$?

No!

But its state won't be stationary it will undergo time evolution — measurable time dependence.

Reminder: quantum superposition
a particle can be simultaneously in more than one state.
However, its wave function is still a solution of the Schrodinger equation

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

Since we already found a ~~set~~ set of solutions of this equation
$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_nt/\hbar}$, we are going to write ~~any~~ the wavefunction of any particle in such potential $U(x)$ as a combination of the wavefunctions $\psi_n(x,t)$

$$\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar} + \ldots + c_n\psi_n(x)e^{-iE_nt/\hbar} + \ldots$$

where $c_1, c_2 \ldots c_n$ - complex numbers
(it is like writing a vertor in the basis of 3 unit vectors)
If we put this expression in the Schrodinger eqn

$$c_1E_1\psi_1e^{-iE_1t/\hbar} + c_2E_2\psi_2e^{-iE_2t/\hbar} + \ldots + c_nE_n\psi_ne^{-iE_nt/\hbar} = c_1\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + U(x)\psi_1\right]}_{E_1\psi_1}e^{\frac{-iE_1t}{\hbar}}$$

+ .. same for every term

We guarantee that our wavefunction is a solution

Average energy $\langle E\rangle = |c_1|^2E_1 + |c_2|^2E_2 + \ldots + |c_n|^2E_n + \ldots$

Probability to find a particle in a state E_n is $p_n = |c_n|^2$

How to calculate $\{c_n\}$ - ?

Important mathematical note

One can check that

$$\int_0^a \sin\frac{\pi n x}{a}\sin\frac{\pi m x}{a}\,dx = 0 \quad \text{if} \quad n \neq m$$

Eigen states are <u>orthogonal</u>

It is a general ~~express~~ rule that in any potential

$$\int_{-\infty}^{+\infty} \psi_n(x)\,\psi_m^*(x)\,dx = \delta_{nm} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

That can help us to find c_n, if we know the wavefunction $\psi(x)$ at $t=0$

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x) + \ldots \quad c_n\psi_n(x) \qquad \times\ \psi_m^*(x)$$

and integrate

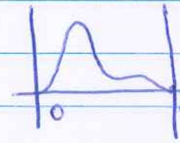
$$\int_{-\infty}^{+\infty}\psi(x)\psi_m^*(x)\,dx = c_1\int_{-\infty}^{+\infty}\psi_1(x)\psi_m^*(x)\,dx + \ldots + \underbrace{c_m\underbrace{\int_{-\infty}^{+\infty}\psi_m(x)\psi_m^*(x)\,dx}_{=1}}_{\text{only non-zero term!}} + \ldots$$

$$c_m = \int_{-\infty}^{+\infty}\psi(x)\psi_m^*(x)\,dx$$

Let's assume that at $t=0$

$$\psi(x) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x)$$

$$P(x) = \frac{1}{2}\left(\sin\frac{\pi x}{a} + \sin\frac{2\pi x}{a}\right)^2$$



$P(x, t=0)$
particle is mostly at the left half of the box

$$\psi(x,t) = \frac{1}{\sqrt{2}}\psi_1(x)\, e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}}\psi_2(x)\, e^{-iE_2 t/\hbar} =$$

$$= \frac{1}{\sqrt{2}}\sin\frac{\pi x}{a}\, e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}}\sin\frac{2\pi x}{a}\, e^{-4iE_1 t/\hbar} \qquad \left(E_2 = 4E_1 = \frac{4\pi^2\hbar^2}{2ma^2}\right)$$

$$P(x,t) = \psi(x,t)\cdot\psi^*(x,t) = |\psi(x,t)|^2 = \frac{1}{2}\left(\sin\frac{\pi x}{a}e^{-iE_1 t/\hbar} + \sin\frac{2\pi x}{a}e^{-i4E_1 t/\hbar}\right) \times \left(\sin\frac{\pi x}{a}e^{iE_1 t/\hbar} + \sin\frac{2\pi x}{a}e^{i4E_1 t/\hbar}\right)$$

$$P(x,t) = \frac{1}{2}\sin^2\frac{\pi x}{a} + \frac{1}{2}\sin^2\frac{2\pi x}{a} + \frac{1}{2}\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}\left(e^{i3E_1 t/\hbar} + e^{-i3E_1 t/\hbar}\right) =$$

$$= \frac{1}{2}\sin^2\frac{\pi x}{a} + \frac{1}{2}\sin^2\frac{2\pi x}{a} + \sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}\underbrace{\cos\left(\frac{3E_1 t}{\hbar}\right)}_{\text{time dependence}}$$