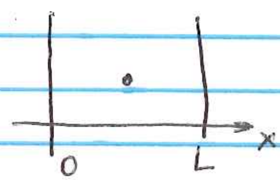
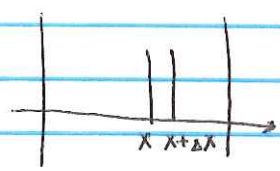
Schrodinger equation

The Schrodinger equation allows to calculate the wavefunction of an object (non-relativistic) that moves in the known potential energy $U(x)$

Wave function $\psi(x,t)$ [1D case]
Here we assume that an object can be found in a range of coordinates x



Previous exampe — a quantum particle bouncing b/w two walls $x=0$, $x=L$
Since the particle can only be $0<x<L$, the probability to find it for any $x<0$ or $x>L$ is zero, thus $\psi(x)=0$ in these regions.
To describe the probability of finding the particle in the ~~vicin~~ small vicinity of some x and time t, we need to calculate the probability density $|\psi(x,t)|^2$



Probability of finding the particle b/w x and $x+\Delta x$ (Δx is small)

$$P(x, x+\Delta x) = |\psi(x,t)|^2 \cdot \Delta x$$

Probability to fing a particle b/w $a<x<b$

$$P_{ab}(t) = \int_a^b |\psi(x,t)|^2 dx$$

If a particle can only be found b/w $x=a$ and $x=b$, $P_{ab}=1$ (we know for sure it is $a<x<b$)
so

$$\int_a^b |\psi(x,t)|^2 dx = 1 \qquad \text{Normalization}$$

For a free particle with known energy E and known momentum p the wave-function

$$\psi_{pE}(x,t) = \frac{1}{\sqrt{2\pi}}\, e^{ipx/\hbar - iEt/\hbar} = \frac{1}{\sqrt{2\pi}}\, e^{ipx/\hbar}\, e^{-iEt/\hbar}$$

This is the case of a steady-state (stationary) wave-particle, where the complex exponents $e^{ipx/\hbar}$ and $e^{iEt/\hbar}$ ~~descri~~ characterize the particle property: momentum (spatial part) and energy (temporal part)

Statement: if we let the particle move in some non-zero potential energy $U(x)$, the spatial part of ~~a~~ the stationary states will change, but the temporal dependence $e^{-iEt/\hbar}$ will not. Basically, any wave function, corresponding to a stationary (time-independent) state will oscillate in time at the frequency $E/\hbar$, corresponding to the constant total energy of this state: $\psi(x,t) = \psi(x)\, e^{-iEt/\hbar}$

Note, that a physically measurable parameter – probability distribution $|\psi(x,t)|^2$ – will not have this dependence

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

$$= \psi^*(x)\psi(x) = |\psi(x)|^2$$ (time dependence disappears)

General (time-dependent) Shrodinger eqn

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

This equation will describe <u>any</u> wave function for a given potential $U(x)$.
We are looking for specific states — time independent and hence having constant energy. For such states

$$\psi(x,t) = \psi_E(x)\, e^{-iEt/\hbar}$$

$$\frac{\partial \psi(x,t)}{\partial t} = \psi_E(x)\left(-\frac{iE}{\hbar}\right) e^{-iEt/\hbar}$$

Substituting this into the Shrodinger eqn

$$i\hbar\frac{\partial \psi(x,t)}{\partial t} = i\hbar\psi_E(x)\left(-\frac{iE}{\hbar}\right)\cancel{e^{-iEt/\hbar}} = -\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2}\cancel{e^{-iEt/\hbar}} + U(x)\,\psi_E(x)\,\cancel{e^{-iEt/\hbar}}$$

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

Time-independent Shrodinger equation
Solutions of this equation will describe a wave function of a system with total energy E. (i.e. if we measure the total energy of the particle in this state $\psi_E(x)$, ~~we will always~~ ~~meas~~ the outcome of such measurement will always be E, and the state of the system will not change)

Finding the form of the solution for a given $U(x)$ → mathematical problem

Simplest case: $U(x) = 0$

Shrodinger equation: $-\frac{\hbar^2}{2m}\frac{d^2\psi_E}{dx^2} = E\psi_E(x)$

$$\frac{d^2\psi_E}{dx^2} + \frac{2mE}{\hbar^2}\psi_E = 0$$

Solutions: oscillations $e^{\pm ikx}$ or $\sin kx, \cos kx$

For example $\psi_E(x) = A\sin kx$

$$\frac{d\psi_E}{dx} = Ak\cos kx$$

$$\frac{d^2\psi_E}{dx^2} = -Ak^2\sin kx = -k^2\psi_E(x)$$

$$-\frac{\hbar^2}{2m}\left(-k^2\psi_E(x)\right) = E\psi_E(x) \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

(analogous for $\cos kx$, $e^{\pm ikx}$)

Slightly more interesting example: constant non-zero potential

$U(x) = U_0 \quad 0 < x < L$, inpenetrable walls at $x = 0, L$

Shrodinger equation $E\psi_E(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2} + U_0\psi_E(x)$

$$(E - U_0)\psi_E(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U_0) = 0$$

a) Possible solutions: $e^{\pm ik_1 x}$, $\sin k_1 x, \cos k_1 x$

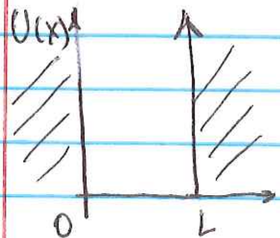
where $k_1 = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}$ if $E > U_0$

b) Possible solutions: $e^{\pm \alpha x}$

where $\alpha = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$ if $E < U_0$

(classically impossible situation)

But how do we know which functions to use?



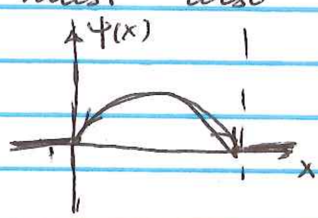
$$U(x) = \begin{cases} 0 & 0<x<L \\ \infty & x<0 \quad x>L \end{cases}$$

As we discuss, outside the probability to find the particle is zero $\Rightarrow$
$\psi(x<0) = \psi(x>L) = 0$

Insinde — we know now the solutions $\sin kx$, $\cos kx$ or $e^{\pm ikx}$. Any combination of them will work. Which one to pick?

<u>Boundary conditions</u> what separate this particle from any othe particle in this experiment.

First rule for wave functions!
$\psi(x)$ is always continuous. So if $\psi(x)=0$ for $x<0$ and $x>L$, the asymptotic for the ~~solution~~ ~~the~~ solution <u>inside</u> the walls must also approach zero.

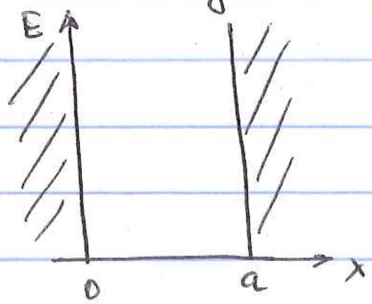


$$\lim_{x\to 0}\psi(x) = 0$$

$$\lim_{x\to L}\psi(x) = 0$$

no discontinuities
(jumps)

Returning to a rigid box



$\psi(x) = 0$ for $x < 0$ & $x > a$

Thus $\psi(x) = 0$ for $x = 0$ and $x = a$

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

$x = 0$ $\quad \psi(0) = A = 0 \quad \psi(x) = B\sin kx$

$x = a$ $\quad \psi(a) = B\sin ka = 0 \quad \Rightarrow \sin ka = 0 \quad ka = \pi \cdot n$

$k_n = \frac{\pi}{a} \cdot n$ quantization of momentum

$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$ energy levels

$\psi_n(x) = B_n \sin \frac{\pi n x}{a}$

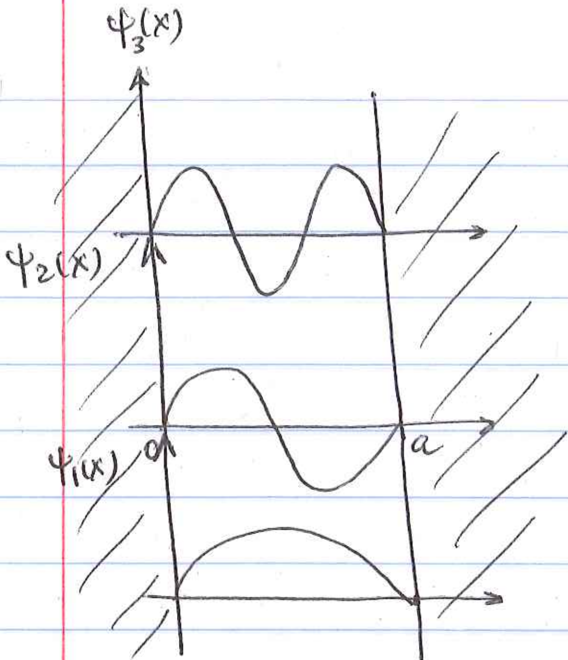
Amplitude is found from the normalization conditions: the probability to find the particle inside the well is 100%

$$\int_0^a |\psi(x)|^2 dx = |B_n|^2 \int_0^a \sin^2 \frac{\pi n x}{a} dx = \frac{a}{2} |B_n|^2 = 1$$

$|B_n| = \sqrt{\frac{2}{a}}$ notice that B_n is defined up to a phase factor

Wave function of a particle inside the rigid box

$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a}$ standing waves (as expected)

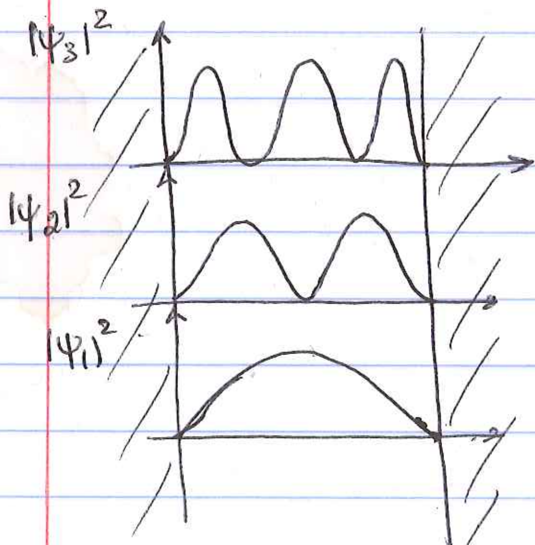


$$E_3 = \frac{9\pi^2\hbar^2}{2ma^2} = 9E_1 \qquad \psi_3 = \sqrt{\frac{2}{a}}\sin\frac{3\pi x}{a}$$

$$E_2 = \frac{4\pi^2\hbar^2}{2ma^2} = 4E_1 \qquad \psi_2(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} \qquad \psi_1(x) = \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}$$

Probability density



$$|\psi_3(x)|^2 = \frac{2}{a}\sin^2\frac{3\pi x}{a}$$

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

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

For any $n > 1$, there are points when $|\psi_n(x)|^2 = 0$ => the probability to detect the particle at these points is zero! So a quantum particle can bounce back and forth without actually passing through this point