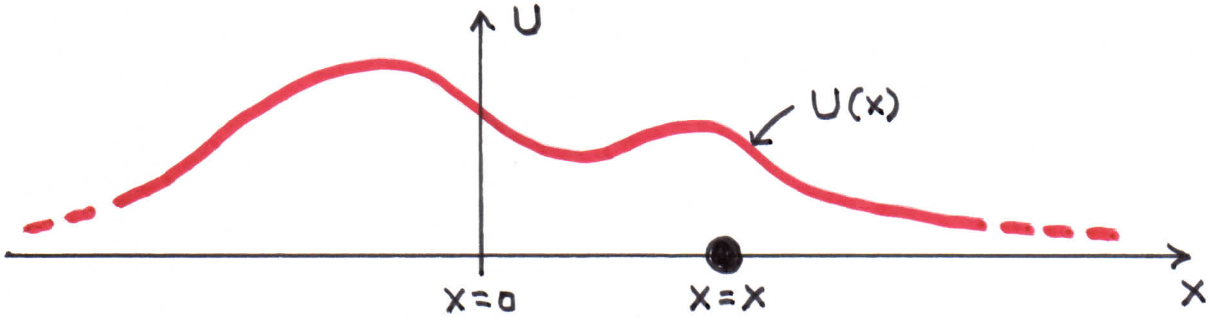
Preliminary



Consider an isolated system with a single (point mass) particle in a potential energy field U(x) [for simplicity the system will be 1-D with the particle constrained to move along the x-axis. In classical mechanics we may be interested in the following quantities:

(1) particle position vs. time: $x(t)$

(2) particle velocity vs. time: $v(t)$

(3) kinetic energy vs. time: $K(t)$

(4) potential energy vs. time: $U(x[t])$

(5) particle momentum vs. time: $p(t)$

(6) limits of motion: X_{max}, X_{min} (if any)

⋮

Analysis of a Mechanical System (1-D Classical)

Method: Integration of Energy Equation

system isolated (single mass)

$$\frac{1}{2}mv^2 + U(x) = E = \underline{\text{constant}}$$

$$\frac{1}{2}m\dot{x}^2 + U(x) = E$$

we assume here that E is known

$$\dot{x}^2 = \frac{2(E - U(x))}{m}$$

$$\frac{dx}{dt} = \sqrt{\frac{2}{m}}\sqrt{E - U(x)}$$

$$\frac{dx}{\sqrt{E-U(x)}} = \sqrt{\frac{2}{m}}\,dt$$

$$\int_{x_0}^{x} \frac{dx}{\sqrt{E-U(x)}} = \sqrt{\frac{2}{m}}\int_0^t dt$$

get $t = \sqrt{\frac{m}{2}}\int_{x_0}^{x}\frac{dx}{\sqrt{E-U(x)}}$

Invert this and get $\underline{x = f(t)}$

Then $v(t) = \dot{f}(t)$

$K(t) = \frac{1}{2}m\left[\dot{f}(t)\right]^2$

$E = K(t) + U(x[t])$

Alternate method: Solving Differential Equation of N2

$$F = ma \qquad \text{note: } F(x) = -\frac{dU(x)}{dx}$$

$$F(x) = m\ddot{x}$$

$$\ddot{x} - \frac{1}{m}F(x) = 0$$

Solve 2nd order O.D.E and get functional solution which includes 2 undetermined constants (call c_1 and c_2) $x = f(c_1, c_2, t)$

Find c_1 and c_2 by setting

$x(t=0) = x_0$ and

$\dot{x}(t=0) = v_0$

$E = K(t) + U(x[t])$

Operators

quantity	classical physics	quantum mechanics
position	x	$\hat{x} = x$
momentum	$p = mv$	$\hat{p} = -i\hbar \, d/dx$
K.E.	$K = \frac{1}{2}mv^2$	$\hat{K} = \frac{-\hbar^2}{2m} d^2/dx^2$
P.E.	$U(x)$	$\hat{U} = U(x)$
total E	$E = K + U$	$\hat{E} = \hat{K} + \hat{U}$

If a particle has a well-defined quantity (momentum, total energy, etc.), it will have a wave function for which

$\widehat{\text{operator}}\,\Psi(x) =$ specific value of quantity $\Psi(x)$

$\Psi(x)$ is an eigenfunction of $\hat{p}$

eg $\hat{p}\,\Psi(x) = p\,\Psi(x)$

p is an eigen-value of $\hat{p}$

Examples of Operators

eg Consider the differential operator $\hat{a} = 5\frac{d}{dx}$

$$\hat{a}(10e^{6x}) = 5\frac{d}{dx}(10e^{6x}) = 300e^{6x}$$

$$\hat{a}(10e^{6x}) = 30(10e^{6x})$$

this is an eigenfunction of $\hat{a}$

this is an eigenvalue of the operator $\hat{a}$ associated with the eigenfunction $10e^{6x}$

eg Consider the same operator as above $\hat{a} = 5\frac{d}{dx}$

$$\hat{a}(x^2-3x) = 5\frac{d}{dx}(x^2-3x) = 10x-15$$

$$\hat{a}(x^2-3x) \neq \text{constant}(x^2-3x)$$

this is not an eigenfunction of operator $\hat{a}$

Schrödinger Equation

classical mechanics

$$\left.\begin{aligned} &\tfrac{1}{2}mv^2 + U(x) = E \\ \text{or}\quad &\frac{p^2}{2m} + U(x) = E \end{aligned}\right\} \text{total energy equation}$$

quantum mechanics

$$\hat{K}\,\psi(x) + \hat{U}(x)\,\psi(x) = E\,\psi(x)$$

or

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

this is a second order ordinary D.E.

The 3-D version of the Schrödinger Equation:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + U(x,y,z)\,\psi = E\,\psi$$

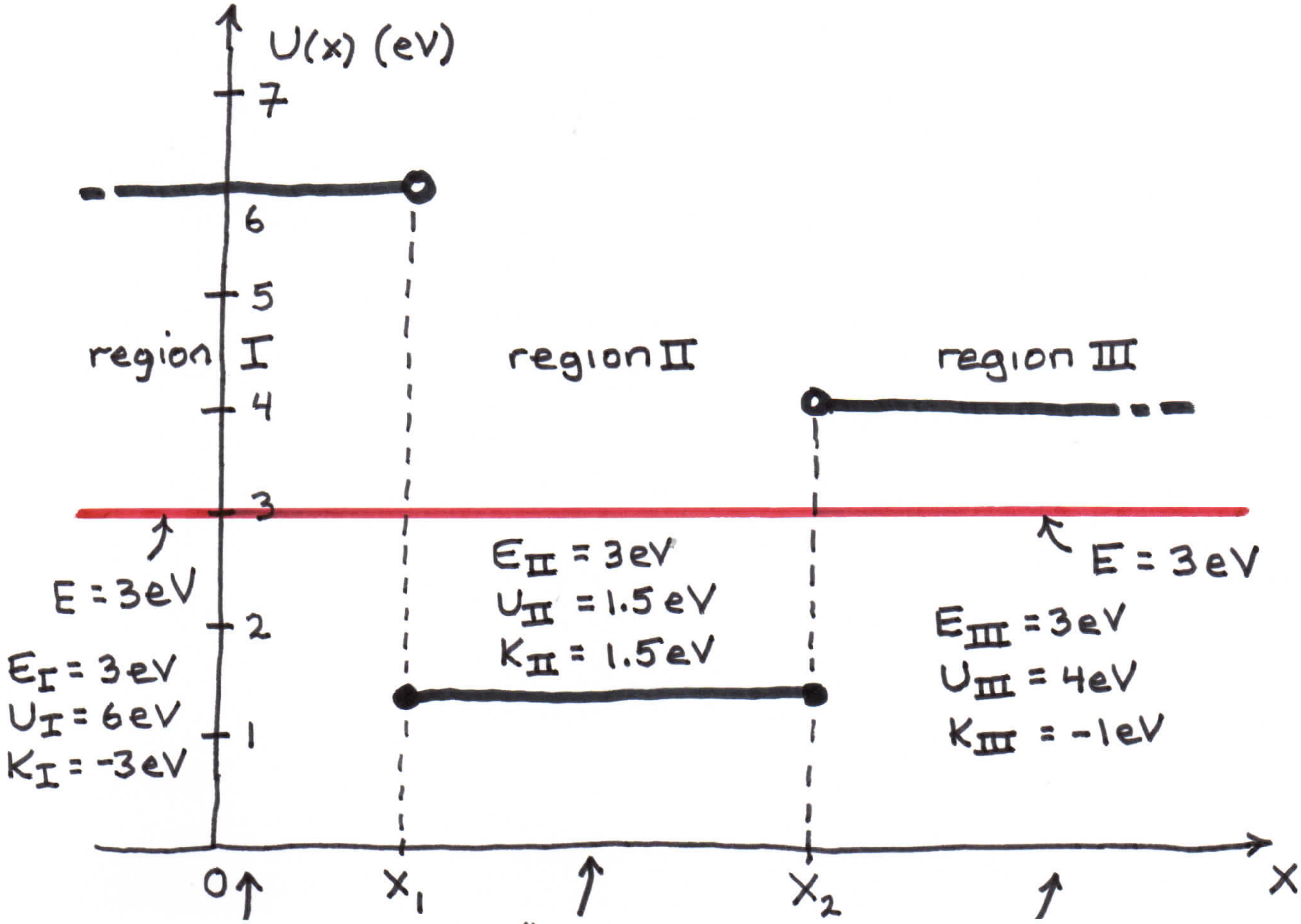
where $\psi = \psi(x,y,z)$

Erwin Schrödinger

* Austrian Physicist
* 1926 - paper on wave mechanics, formalizing the Schrödinger Equation and using it to yield correct values for the energy eigenvalues for the hydrogen atom
* 1926 - paper solving the quantum harmonic oscillator, rigid rotor, diatomic molecule

Nobe Prize in physics 1933

Step Function Potential Energy



$$-\frac{\hbar^2}{2m}\psi_I'' + (6-3)\psi_I = 0 \qquad -\frac{\hbar^2}{2m}\psi_{II}'' + (1.5-3)\psi_{II} = 0 \qquad -\frac{\hbar^2}{2m}\psi_{III}'' + (4-3)\psi_{III} = 0$$

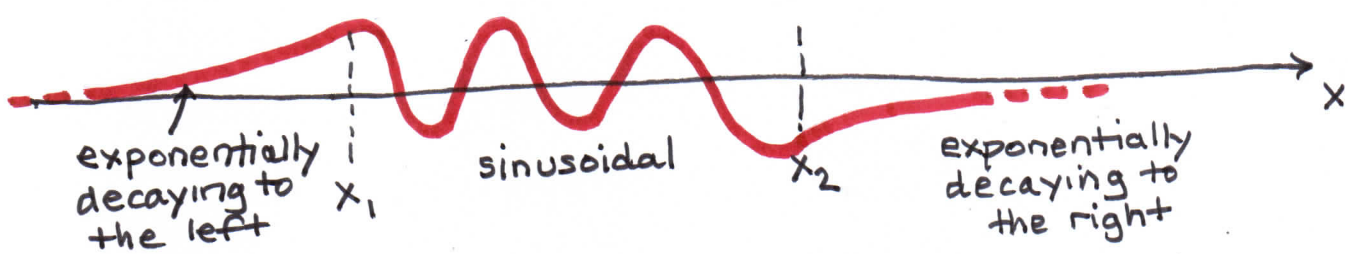
$$\psi_I = c_1 \exp\left\{-\sqrt{\frac{2m(6-3)}{\hbar^2}}\,x\right\} + c_2 \exp\left\{+\sqrt{\frac{2m(6-3)}{\hbar^2}}\,x\right\}$$

$$\psi_{II} = c_3 \sin\sqrt{\frac{2m(3-1.5)}{\hbar^2}}\,x + c_4 \cos\sqrt{\frac{2m(3-1.5)}{\hbar^2}}\,x$$

$$\psi_{III} = c_5 \exp\left\{-\sqrt{\frac{2m(4-3)}{\hbar^2}}\,x\right\} + c_6 \exp\left\{+\sqrt{\frac{2m(4-3)}{\hbar^2}}\,x\right\}$$

$$\psi_I(x_1) = \psi_{II}(x_1) \qquad \psi_{II}(x_2) = \psi_{III}(x_2)$$

$$\psi_I'(x_1) = \psi_{II}'(x_1) \qquad \psi_{II}''(x_2) = \psi_{III}''(x_2)$$



Card Game

Use a full deck of cards (52 cards, 4 suits, 3 face cards [J, Q, K] in each suit,). You agree to playing gambling game with the "dealer". He shuffles the cards, and then lets you cut them. You turn over the card where you've cut the deck and reveal it. Here are the rules:

1. If the card is a red ace, the dealer pays you $10.00.
2. If the card is a black face card, the dealer pays you $3.00.
3. If the card is a numbered spade, the dealer pays you $2.00.
4. If the card is not one of the above, you pay the dealer $2.00.

Expected Gain per Play

outcome	gain g_i	P_i	$P_i g_i$
red ace	+\$10	$\frac{2}{52}$	$+\frac{20}{52}$
black face	+\$3	$\frac{6}{52}$	$+\frac{18}{52}$
numbered spade	+\$2	$\frac{9}{52}$	$+\frac{18}{52}$
other	−\$2	$\frac{35}{52}$	$-\frac{70}{52}$

$$-\frac{14}{52} = -\$0.27$$

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Expectation Values

The expectation value of a physical quantity q of a quantum mechanical system whose wave function is $\Psi(x)$:

$$\langle q \rangle \equiv \int_{-\infty}^{\infty} \Psi(x)^* \hat{q}\, \Psi(x)\, dx$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi(x)^* x\, \Psi(x)\, dx$$

expectation value of the x-position of the particle

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi(x)^* \left[-i\hbar \frac{d}{dx}\right] \Psi(x)\, dx$$

expectation value of the momentum of the particle

$$\langle K \rangle = \int_{-\infty}^{\infty} \Psi(x)^* \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right] \Psi(x)\, dx$$

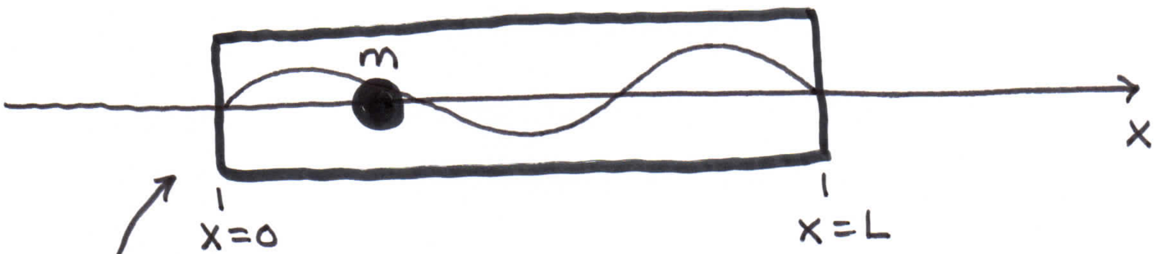
expectation value of the kinetic energy of the particle

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi(x)^* \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right] \Psi(x)\, dx$$

expectation value of the total energy of the system

Expectation Value Example

1-D Particle in a Box:



$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi 3 x}{L}\right)$$

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi_3(x)^* \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x) \right] \psi_3(x)\, dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi 3 x}{L}\right) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 0 \right] \sqrt{\frac{2}{L}} \sin\left(\frac{\pi 3 x}{L}\right) dx$$

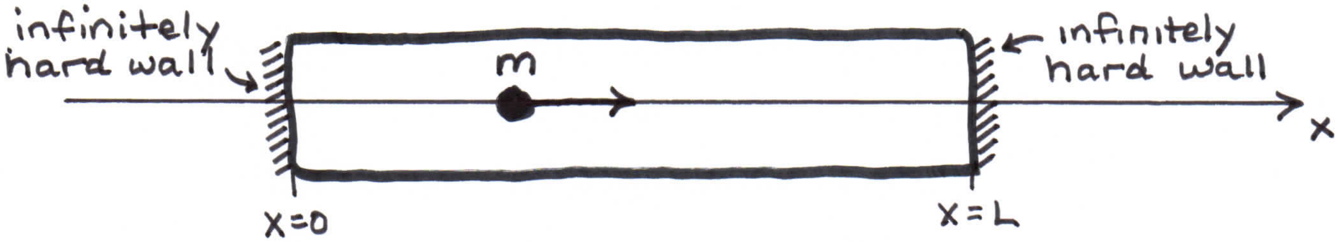
$$= \frac{2}{L} \int_0^L -\frac{\hbar^2}{2m} \left(\frac{\pi 3}{L}\right)^2 (-1) \sin^2\left(\frac{\pi 3 x}{L}\right) dx$$

$$= \frac{18 \hbar^2 \pi^2}{2 m L^3} \int_0^L \sin^2\left(\frac{\pi 3 x}{L}\right) dx = \frac{18 \hbar^2 \pi^2}{2 m L^3} \left(\frac{1}{2} L\right)$$

$$= \frac{18 \; \pi^2}{4 m L^2} \left(\frac{h}{2\pi}\right)^2 = \boxed{\frac{3^2 h^2}{8 m L^2}}$$

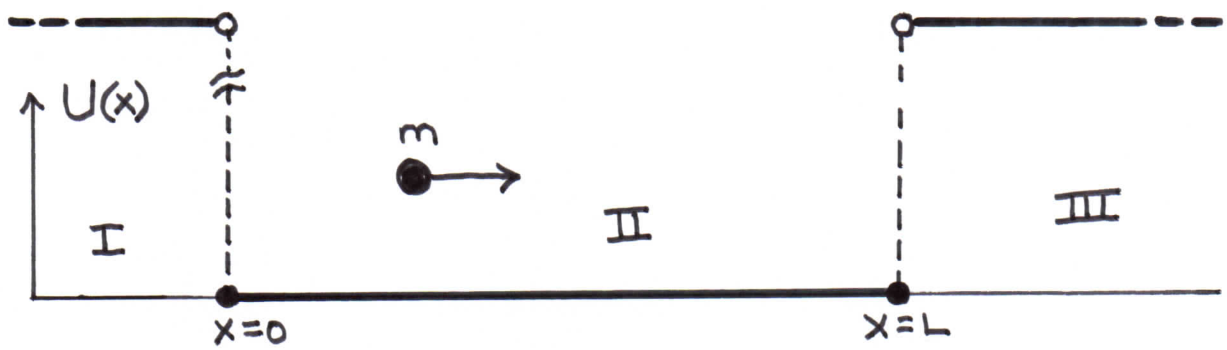
$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_3(x)^* x \, \psi_3(x)\, dx \dashrightarrow \text{can show} = \boxed{\tfrac{1}{2} L}$$

Particle in a 1-D Box



* **Wave mechanical approach:** Find all allowed energies and their associated wave functions.

* **Display potential energy function**



region I: $x < 0$ $\quad U_I(x) = \text{infinite}$

region II: $0 \le x \le L$ $\quad U_{II}(x) = 0$

region III: $x > L$ $\quad U_{III}(x) = \text{infinite}$

* **Write Schrödinger Equation for each region**

region I: $-\frac{\hbar^2}{2m}\psi_I'' + \text{inf.}\,\psi_I = E\psi_I$

region II: $-\frac{\hbar^2}{2m}\psi_{II}'' + 0\,\psi_{II} = E\psi_{II}$

region III: $-\frac{\hbar^2}{2m}\psi_{III}'' + \text{inf.}\,\psi_{III} = E\psi_{III}$

$\psi_I(x)$ must be 0 and $\psi_{III}(x)$ must be 0

*** Solve** $-\frac{\hbar^2}{2m}\psi_{II}'' = E\psi_{II}$ undetermined (as of yet) constant

$$-\frac{\hbar^2}{2m}\psi_{II}'' - E\psi_{II} = 0$$

$$\psi_{II}'' + \frac{2mE}{\hbar^2}\psi_{II} = 0$$

General solution to the above is:

$$\psi_{II}(x) = c_1 \sin\sqrt{\frac{2mE}{\hbar^2}}\,x + c_2 \cos\sqrt{\frac{2mE}{\hbar^2}}\,x$$

Apply the boundary condition $\psi_I(0) = 0 = \psi_{II}(0)$

$$0 = c_1 \sin\sqrt{\frac{2mE}{\hbar^2}}(0) + c_2 \cos\sqrt{\frac{2mE}{\hbar^2}}(0)$$

$$\boxed{0 = c_2}$$

So $\psi_{II}(x) = c_1 \sin\sqrt{\frac{2mE}{\hbar^2}}\,x$

Apply the boundary condition $\psi_{II}(L) = \psi_{III}(L) = 0$

$$0 = c_1 \sin\sqrt{\frac{2mE}{\hbar^2}}\,L$$

← c_1 cannot be 0 or you would have no wave function at all

this will be 0

if $\sqrt{\frac{2mE}{\hbar^2}}\,L = n\pi$ any integer 1, 2, 3, 4, ...

$$\sqrt{\frac{2mE}{\hbar^2}}\,L = n\pi \rightarrow E = \frac{n^2\pi^2\hbar^2}{2mL^2} \text{ or } \boxed{\frac{n^2h^2}{8mL^2} = E_n}$$

These are the allowed energies →

So $\psi_{II}(x) = c_1 \sin\sqrt{\frac{2mE}{\hbar^2}}\,x$ ← synthesize with $E = \frac{n^2h^2}{8mL^2}$

$$\psi_{n\,II}(x) = c_1 \sin\left(\frac{n\pi x}{L}\right)$$

This must be normalized and so demand

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

$$\int_{-\infty}^{0} \overbrace{|\psi_{I}(x)|^2}^{0} dx + \int_{0}^{L} c_1^2 \sin^2\left(\frac{n\pi x}{L}\right) dx + \int_{L}^{\infty} \overbrace{|\psi_{III}(x)|^2}^{0} dx = 1$$

$$c_1^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$c_1 = \sqrt{\frac{2}{L}}$$

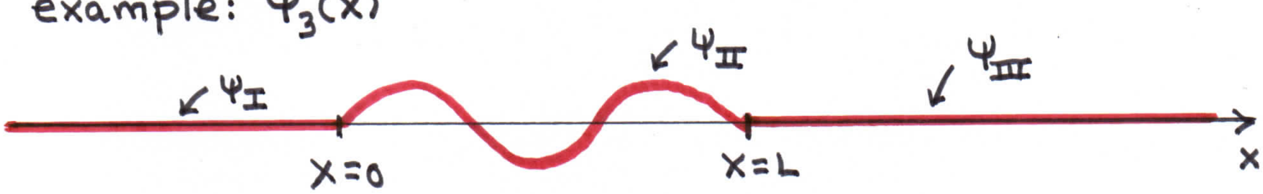
So $\psi_{II}(x) \rightarrow \boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)}$

allowed wave functions of the particle in a 1-D box

$$\boxed{E_n = \frac{n^2h^2}{8mL^2}}$$

allowed energies associated with those quantum status

example: $\psi_3(x)$



$$\hat{E} = \hat{K} + \hat{U} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + 0$$

inside box

total energy operator

kinetic energy operator

potential energy operator

$$\hat{E}\Psi = E\Psi$$ ← solve

results for particle in a 1-D box

$$\Psi_1 = \sqrt{2/L}\,\sin\left(\frac{\pi}{L}x\right) \longleftrightarrow E_1 = \frac{h^2}{8mL^2}$$

$$\Psi_2 = \sqrt{2/L}\,\sin\left(\frac{2\pi}{L}x\right) \longleftrightarrow E_2 = \frac{2^2h^2}{8mL^2}$$

$$\Psi_3 = \sqrt{2/L}\,\sin\left(\frac{3\pi}{L}x\right) \longleftrightarrow E_3 = \frac{3^2h^2}{8mL^2}$$

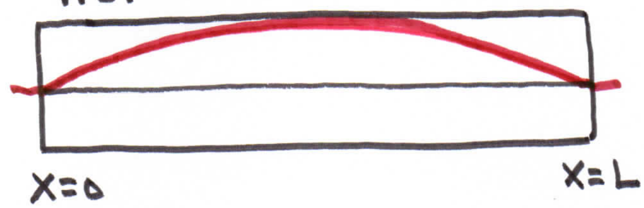
$\vdots$ $\qquad\qquad\qquad\qquad$ $\vdots$

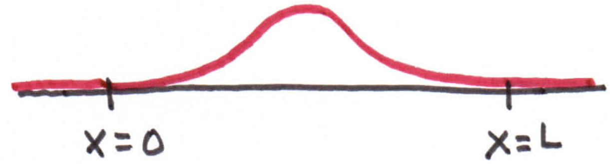
these are eigenfunctions of the total energy operator $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

these are the eigenvalues of the total energy operator $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ associated w/ the eigenfunctions Ψ_n

Particle in a 1-D Box

n=1

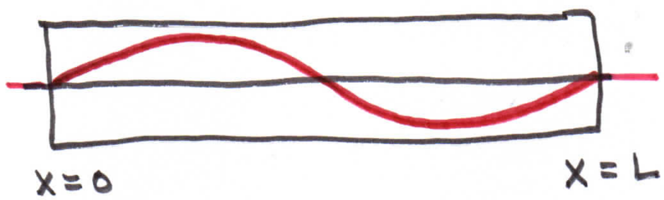


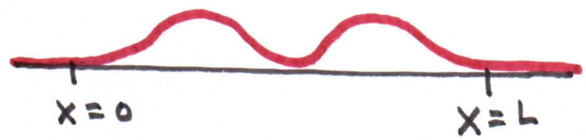


$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$

$|\psi_1(x)| = \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right)$

n=2

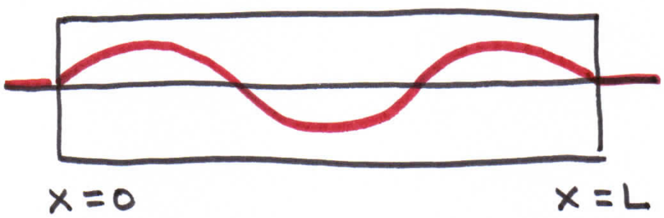


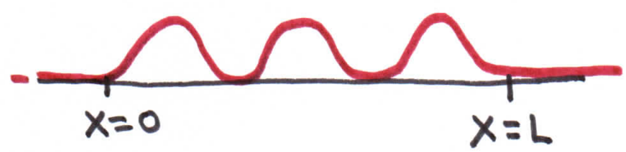


$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$

$|\psi_2(x)|^2 = \frac{2}{L} \sin^2\left(\frac{2\pi x}{L}\right)$

n=3

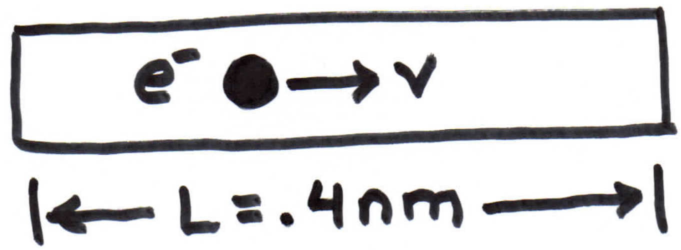




$\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right)$

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

Particle in a 1-D Box



$$E_n = \frac{n^2 h^2}{8 m_e L^2} \qquad n = 1, 2, 3, \ldots$$

Use $E_n = \dfrac{n^2 (hc)^2}{8 m_e c^2 L^2}$

$$E_1 = \frac{1^2 (1240)^2}{8(511{,}000)(.4)^2} = 2.35\,\text{eV}$$

$$E_2 = \frac{2^2 (1240)^2}{8(511{,}000)(.4)^2} = 9.40\,\text{eV}$$

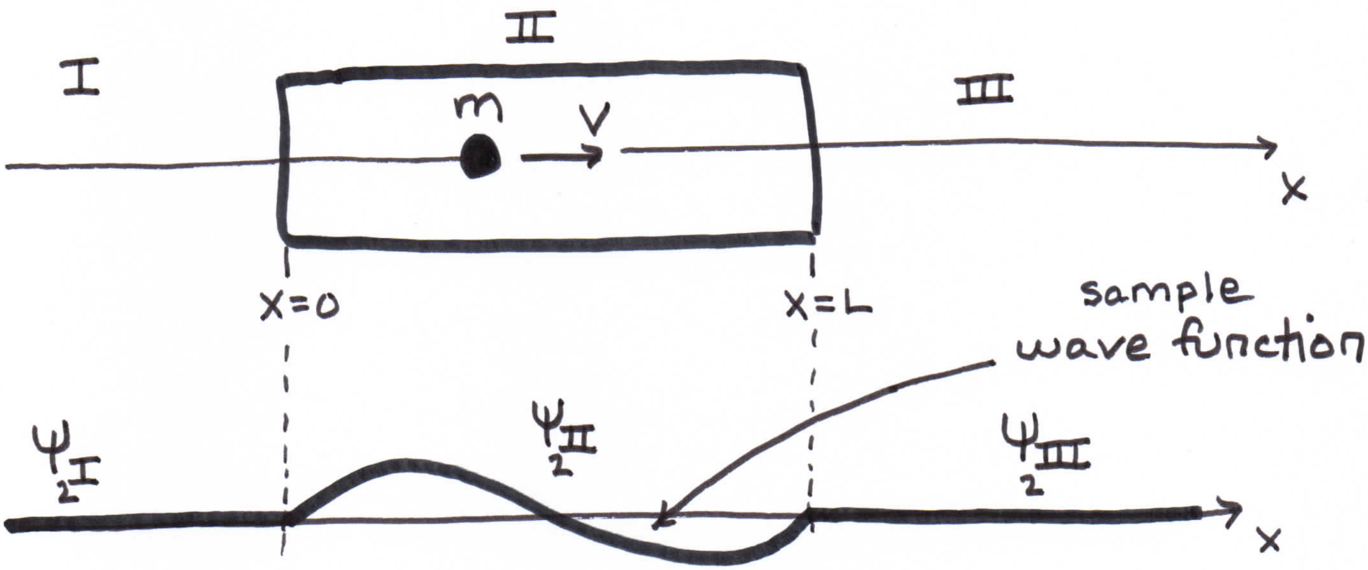
$$E_3 = 21.16\,\text{eV}$$

$$E_4 = 37.61\,\text{eV}$$

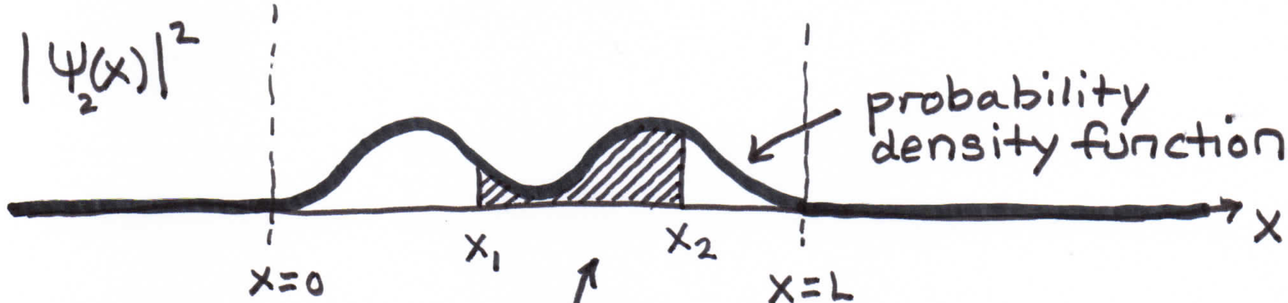
$\vdots$

energy spectrum

Probability Density



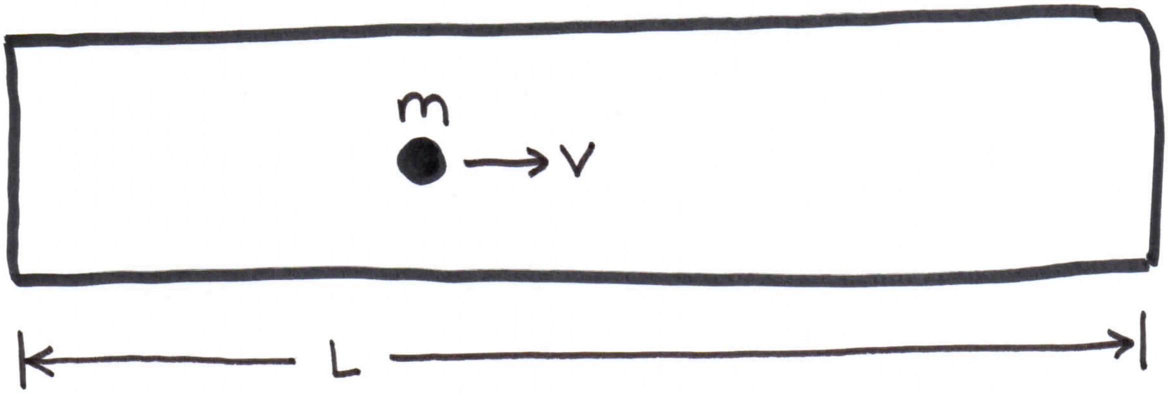
$$\psi_2(x) = \begin{cases} 0 \text{ for } x \leq 0 \\ \sqrt{2/L}\,\sin\left(\frac{\pi 2}{L}x\right) \text{ for } 0 \leq x \leq L \\ 0 \text{ for } x \geq L \end{cases}$$



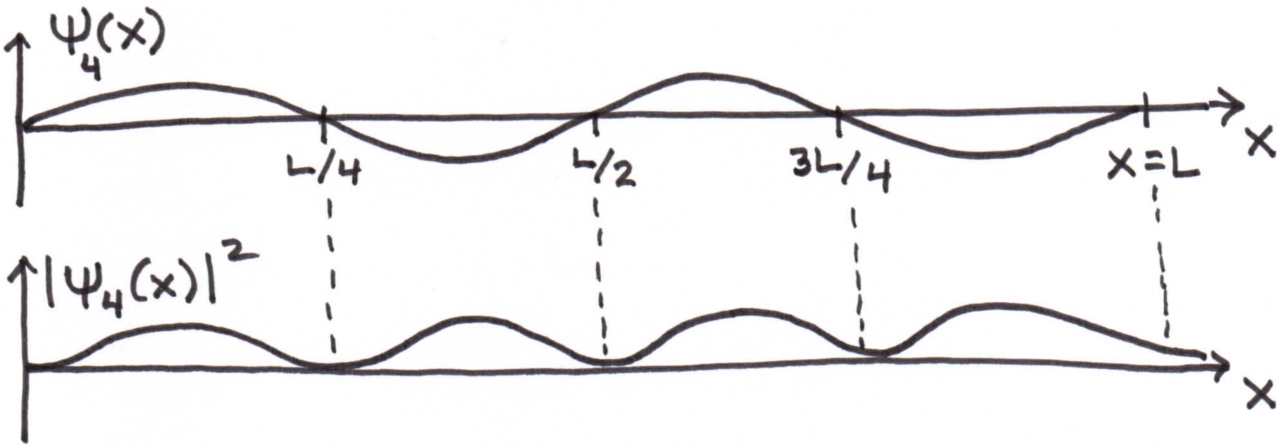
Probability of detecting the particle (with the above wave function) between $x = x_1$ and $x = x_2$ is

$$P(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} |\psi_2(x)|^2 dx$$

1-D Box Example



$n = 4$ (3rd excited state)



What is probability that particle would be found between $x = \frac{L}{4}$ and $\frac{L}{2}$

$$\psi_4(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{4\pi x}{L}\right)$$

$$P\left(\frac{L}{4} < x < \frac{L}{2}\right) = \int_{L/4}^{L/2} \left(\frac{2}{L}\right) \sin^2\left(\frac{4\pi x}{L}\right) dx$$

$$= \boxed{.25 \text{ or } 25\%}$$