Lecture Notes: January 8, Tue, Class 1

Schrodinger equations for bound and unbound states

Objectives:

- Describe various properties of a wave and their relationships
- Using the separation of variables method, drive two part equations from the time-dependent Schrodinger Equation assuming Energy is constant.
- Differentiate potentials between bound and unbound states
- Formulate Schrodinger Equations for unbound states such as free, step, and barrier potentials and recognize what wave functions to use for a given potential and energy.
- Recognize the shape and the nature of wave functions associated with particles in unbound states associated with free, step, and barrier potentials.

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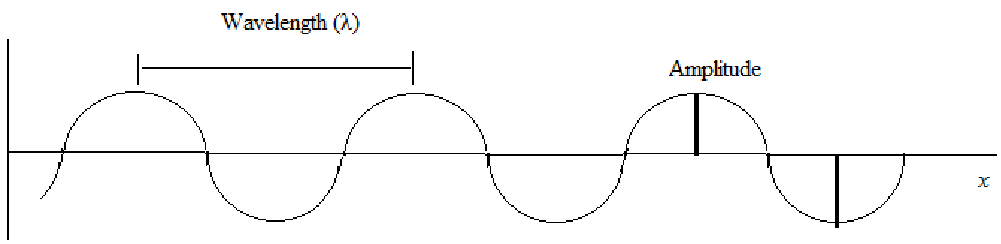
Defining Wave

When t = 0



- Amplitude: Distance from the middle to crest (or trough)
- Wavelength (λ) = distance from crest to crest OR distance from trough to trough

When x = fixed (i.e. at a given location), the propagating wave can be observed in terms of

- Period (T) = Time between passage of two successive crests.
- Frequency (ν) = Number of crest passages per unit time = $\frac{1}{T}$

Based on these properties, we can define

- Angular frequency (**ω**) $= 2\pi\nu = \frac{2\pi}{T}$
- Angular wave number (k) = $\frac{2\pi}{\lambda}$

Some quantum mechanical concepts such as p and E can be defined using wave concepts:

- Momentum (p) = $\hbar k$ = $\hbar$ $(\frac{2\pi}{\lambda})$ = $\frac{h}{\lambda}$ (de Broglie relation)
- Energy quanta (E) = $\hbar\omega$ (ω is continuous for unbound states vs. discrete for bound states)

Momentum and Energy (therefore, k and ω), are related differently from situation to situation. For example,

- Photon in free space: $\omega = ck$
- Electron in free space: E = $\frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$ or $\omega = \frac{\hbar k^2}{2m}$

Contrasting Quantum and Newtonian Mechanics
In Newtonian mechanics, we can describe the motion of a particle under a certain force in terms of the particle's mass, position, velocity and acceleration, using Newton's 2nd law. In quantum mechanics, we can describe the probability of finding the particle at a certain time and at a certain position using the Schrodinger equation. The Schrodinger equation can help us calculate expected values of variables such as position and momentum across given time and space. Newtonian mechanics is an approximation of quantum mechanics when the particle in question becomes sufficiently large.

Schrodinger Equation
The time-dependent Schrodinger Equation can be drawn from the Hamiltonian operator that corresponds to the total energy of a system:

Hamiltonian Operator (H) $H\Psi(x,t) = E\Psi(x,t)$ (e1)

Since H = Total Energy = Kinetic energy (T) + Potential energy (U)

(e1) becomes $(T+U)\Psi(x,t) = E\Psi(x,t)$ (e2)

Since $T(p) = \frac{p^2}{2m}$ $and\ U(x)$

(e2) becomes $\left(\frac{p^2}{2m} + U\right)\Psi(x,t) = E\Psi(x,t)$ (e3)

Using operator notations for $p = \frac{\hbar}{i}\frac{\partial}{\partial x}$ and $\mathrm{E} = i\hbar\,\frac{\partial}{\partial t}$

(e3) becomes the **Time-Dependent Schrodinger Equation**

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

Where

- $U(x)$ = Potential energy (position dependent)
- $\Psi(x,t)$ = Wave function of a particle
- $\Psi(x,t)$ involves real and imaginary parts (Re $\Psi(x,t)$ + i Im $\Psi(x,t)$) where $i^2 = -1$.
- $\int_a^b \Psi^*(x,t)\Psi\,(x,t)dx = \int_a^b |\Psi\,(x,t)|^2\,dx$ = P (Probability of finding the particle between a and b at time t).
- $\Psi^*(x,t)\Psi\,(x,t) = |\Psi\,(x,t)|^2$ represents probability *density*.
- $\int_{-\infty}^{\infty} |\Psi\,(x,t)|^2\,dx = 1$ (normalization)
- $\Psi(x,t)$ should be normalized for $|\Psi\,(x,t)|^2$ to represent probability density.
- $\Psi(x,t)$ and its partial derivative (= $\frac{\partial\Psi(x,t)}{\partial x}$) should be continuous everywhere.

Solving the temporal part of the Schrodinger equation.
Use a separation of variables method by defining:

$$\Psi(x,t) = \psi(x)\,\phi(t) \qquad \text{(e4)}$$

Substitute $\Psi(x,t)$ the Schrodinger equation (e3) with $\psi(x)\,\phi(t)$:

$$\frac{-\hbar}{2m}\frac{\partial^2\psi(x)\,\phi(t)}{\partial x^2} + U(x)\psi(x)\,\phi(t) = i\hbar\,\frac{\partial\,\psi(x)\,\phi(t)}{\partial t} \qquad \text{(e5)}$$

Move the part of the wave function that is constant under derivatives

$$\frac{-\hbar^2\,\phi(t)}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\psi(x)\,\phi(t) = \psi(x)i\hbar\,\frac{\partial\;\phi(t)}{\partial t} \qquad \text{(e6)}$$

Divide (e6) by $\psi(x)\,\phi(t)$, we get

$$\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = i\hbar\,\frac{1}{\phi(t)}\frac{\partial\,\phi(t)}{\partial t} \qquad \text{(e7)}$$

Since *U(x)* is time-independent (we assumed so), one way to get both sides equal regardless of space and time would be to assign a constant, *C*. If *U* (potential energy) depends on x and t, i.e. *U* (*x*, *t*), then a C cannot be assigned.

Now, from the (e7), we have two equations:

Spatial part of $\Psi(x,t)$: $$\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = \mathrm{C} \qquad \text{(e8)}$$

Temporal part of $\Psi(x,t)$: $$i\hbar\,\frac{1}{\phi(t)}\frac{\partial\,\phi(t)}{\partial t} = \mathrm{C} \qquad \text{(e9)}$$

To solve the Temporal part of $\Psi(x,t)$ (e9), rearrange it as a first order linear differential equation by multiplying $\frac{\phi(t)}{i\hbar}$ on both sides

$$\frac{\partial\,\phi(t)}{\partial t} = \frac{\mathrm{C}}{i\hbar}\,\phi(t) \qquad \text{(e10)}$$

Since a known solution for the first order linear differential equation

$$\frac{d\,f(x)}{d\,x} = \mathrm{b}\,\mathrm{f(x)} \quad \rightarrow \quad \mathrm{f(x)} = \mathrm{A}e^{bx}$$

We have a solution for (e10) as

$$\phi(t) = Ae^{(C/i\hbar)t} = Ae^{-i(C/\hbar)t} \qquad \text{(e11)}$$

Now put the temporal part of solution (e11) to the original wave function (e4) to get

$$\Psi(x,t) = \psi(x)\,\phi(t) = \psi(x)\,e^{-i(C/\hbar)t} \qquad \text{(e12)}$$

In this particular case of $\Psi(x,t)$, the following can be said:

The probability density does not depend upon time because

$$\Psi^*(x,t)\Psi\,(x,t) = \psi(x)^*\,e^{+i(C/\hbar)t}\,\psi(x)\,e^{-i(C/\hbar)t} = \psi(x)^*\,\psi(x) \qquad \text{(e13)}$$

> So, this case represents stationary states where the total Energy is constant (not depend upon time or space).

For this reason, we now substitute C with E (total energy constant) in (e8)

$$\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = \mathrm{C} = \mathrm{E}$$

We have the **time-independent Schrodinger Equation**:

$$\boldsymbol{\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\,\psi(x) = \mathrm{E}\,\psi(x)} \qquad \text{(e14)}$$

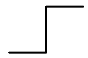
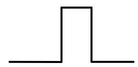
(e15) can be simply written as

$$\mathrm{H}\,\psi(x) = \mathrm{E}\,\psi(x)$$

$$\text{where H (Hamiltonian Operator)} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$$

Note that the Schrodinger time-independent equations can be solved only for certain E values as we will see quantized energy values associated with wave functions in examples.

Unbound States where where the total energy E is (1) constant and (2) greater than 0 such as

- No Potential $U(x)$= 0
- Potential Steps $U(x)$= 
- Potential Barrier $U(x)$ = 

Since the total energy is constant, the time independent Schrodinger Equation is used to describe the wave function of a particle that is unbound according to $U(x)$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\,\psi(x) = \text{E}\,\psi(x) \qquad \text{(e14)}$$

1. No Potential, $U(x)$= 0, Basically Free Particle

Since there is no potential, (e1.12) becomes:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = \text{E}\,\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\psi(x) = -\,k^2\,\psi(x) \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

Solutions:

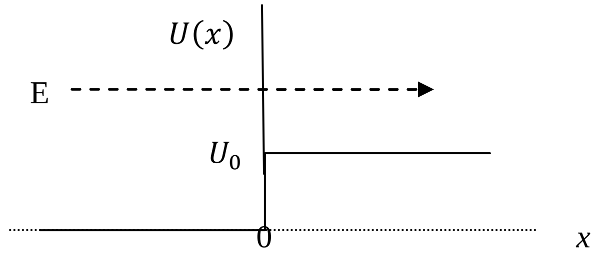
e^{+ikx} = *coskx* + *i sinkx for a particle* moving in the positive direction (→) on the *x* axis.

e^{-ikx} = *coskx* - *i sinkx for a particle* moving in the opposite direction (←) on the *x* axis.

Go to phet.colorado.edu/en/simulations/category/physics/quantum-phenomena
Select the **Quantum tunneling and wave packets** application to learn about the nature of wave functions associated with the Schrodinger equations for unbound particles.
Download the application. You need JAVA to view the application.

2. Potential Step

$$U(x) = \begin{cases} 0 & x < 0 \\ U_0 & x \geq 0 \end{cases}$$



IF E > U_0

Where $x < 0$,

- Schrodinger Equation: $\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\,\psi(x) = -\,k^2\,\psi(x)$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$
- Solution represents wave functions that move in two opposite directions
  - e^{+ikx} represents the initial wave function of *the particle* moving in the positive direction (→) on the *x* axis.
  - e^{-ikx} represents the reflected wave function of the same particle moving in the opposite direction (←) on the *x* axis.
  - $\psi_{x<0}$ = Incoming wave function + Reflected wave function
    = A e^{+ikx} + B e^{-ikx}
- Since the incoming particle is unbound, the particle can have any E value (not quantized) and thus any *k* value.

Where $x \geq 0$

- Schrodinger Equation: $\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{-2m(E-U_0)}{\hbar^2}\,\psi(x) = -\,k'^2\,\psi(x)$ where $k' = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}$
- Solution involves only the transmitted wave function, $\psi_{x\geq 0} = Ce^{ik'x}$

Wave functions in both regions should satisfy the following conditions at the boundary *x* = 0

- $\psi_{x<0}(x=0) = \psi_{x\geq 0}\,(x = 0)$ → A + B = C
- $\frac{d\psi_{x<0}}{dx}\,|_{\,x=0}$ $\frac{d\psi_{x\geq 0}}{dx}\,|_{\,x=0}$ → *k*(A – B) = *k'*C

Note: **Flux of X** = Number of X that pass the unit area and per unit time (X = particle, charge, mass, etc.) = The flow of X per unit area and per unit time.

Flux = density × velocity

Why? Velocity = distance per unit time. And, density × distance = number of X per unit area.
Thus, density × velocity = number of Xs that pass the unit area per unit time.

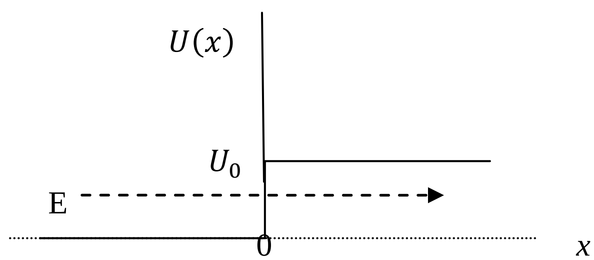
Now consider a real experiment where an instrument shoots off N particles, all of which are prepared in the same wave function ψ. The particle density? It is $N \times |\psi|^2$. What is the *particle flux*? It is $N|\psi|^2 \times v = N|\psi|^2 v = N|\psi|^2 \frac{\hbar k}{m}$. What is important is that

$$\text{Particle flux} = N|\psi|^2 \frac{\hbar k}{m} \propto |\psi|^2 k$$

Particle flux ∝ (probability density) (wave number)

- Transmission probability = $\frac{\text{transmitted particle flux}}{\text{incoming particle flux}} = \frac{|\psi_{trans}|^2 k'}{|\psi_{incoming}|^2 \; k} = \frac{C^*C\,k'}{A^*A\,k}$
  $= \frac{4kk'}{(k+k')^2} = \frac{4\sqrt{E(E-U_0)}}{(\sqrt{E}+\sqrt{E-U_0})^2}$
- Reflection probability = $\frac{\text{reflected particle flux}}{\text{incoming particle flux}} = \frac{|\psi_{reflected}|^2 k}{|\psi_{incoming}|^2 \; k} = \frac{B^*B}{A^*A}$
  $= \frac{(k-k')^2}{(k+k')^2} = \frac{(\sqrt{E}-\sqrt{E-U_0})^2}{(\sqrt{E}+\sqrt{E-U_0})^2}$

$$U(x) = \begin{cases} 0 & x < 0 \\ U_0 & x \geq 0 \end{cases}$$



IF E < U_0 → The kinetic energy of the particle < 0 where x ≥ 0

Where $x < 0$,

- Schrodinger Equation: $\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\psi(x) = -\,k^2\,\psi(x)$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$
- Solution represents wave functions that move in two opposite directions (same as E > U_0)
  - $\psi_{x<0}$ = Incoming wave function + Reflected wave function
    = A e^{+ikx} + B e^{-ikx}

Where $x \geq 0$

- Schrodinger Equation: $\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m(E-U_0)}{\hbar^2}\psi(x) = \alpha^2\psi(x)$ where $\alpha = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$
- Solution involves the wave function that would decay, $\psi_{x\geq 0}$ = C$e^{-\alpha x}$
- Note that another solution of the differential equation, $e^{\alpha x}$ does not apply a physical sense (divergent as x → ∞).
- The wave function decays exponentially after x = 0.

Wave functions in both regions should satisfy the following conditions at the boundary x = 0

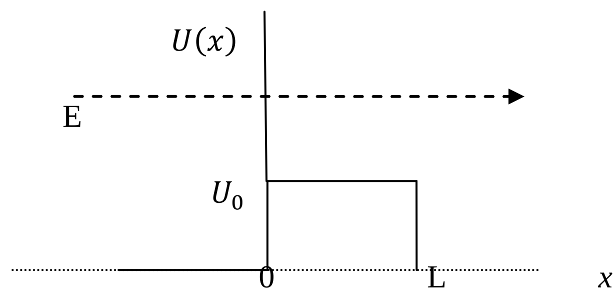
- $\psi_{x<0}(x=0) = \psi_{x\geq 0}\,(x=0)$ → A + B = C
- $\frac{d\psi_{x<0}}{dx}\Big|_{\,x=0}\ \frac{d\psi_{x\geq 0}}{dx}\Big|_{\,x=0}$ → k(A – B) = -α C

Wave number density ∝ (probability density) (wave number)

- Transmission probability = 0
- Reflection probability = $\frac{\text{reflected particle flux}}{\text{incoming particle flux}} = \frac{|\psi_{reflected}|^2\ k}{|\psi_{incoming}|^2\ \ k} = \frac{B^*B}{A^*A} = 1$

3. Potential Barrier

$$U(x) = \begin{cases} 0 & x < 0 \\ U_0 & 0 \leq\ x\ \leq L \\ 0 & x > L \end{cases}$$



IF E > U_0

Using the results from the step potential example, the following wave functions can be considered as solutions to the Schrodinger Equation under the potential barrier:

- $\psi_{x<0}$ = Incoming wave function + Reflected wave function

  = A e^{+ikx} + B e^{-ikx} where $k = \sqrt{\frac{2mE}{\hbar^2}}$

- $\psi_{0\leq\,x\,\leq\,L}$ = Incoming wave function + Reflected wave function

  = C $e^{+ik'x}$ + D $e^{-ik'x}$ where $k' = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}$

- $\psi_{x>L}$ = Transmitted wave function = Fe^{ikx} where $k = \sqrt{\frac{2mE}{\hbar^2}}$

Wave functions at the boundary should satisfy the following conditions

- $\psi_{x<0}(x=0) = \psi_{0\leq\,x\,\leq\,L}\,(x=0)$ → A + B = C + D
- $\frac{d\psi_{x<0}}{dx}\Big|_{\,x=0} = \frac{d\psi_{0\leq\,x\,\leq\,L}}{dx}\Big|_{\,x=0}$ → k (A – B) = k’(C – D)
- $\psi_{\psi_{0\leq\,x\,\leq\,L}}(x=L) = \psi_{0x>L}\,(x = \text{L})$ → C$e^{+ik'L}$ + D$e^{-ik'L}$ = Fe^{+ikL}
- $\frac{d\psi_{0\leq\,x\,\leq\,L}}{dx}\Big|_{\,x=\text{L}} = \frac{d\psi_{x>L}}{dx}\Big|_{\,x=\text{L}}$ → ik’ (C$e^{+ik'L}$ – D$e^{-ik'L}$ = ik Fe^{+ikL}

Therefore,

- Transmission probability = $\frac{\text{transmitted particle flux}}{\text{incoming particle flux}} = \frac{|\psi_{trans}|^2\ k}{|\psi_{incoming}|^2\ \ k} = \frac{F*F}{A^*A}$

$$= \frac{\frac{4\,k'^2 k^2}{(k^2 - k'^2)^2}}{sin^2(k'L) + \frac{4\,k'^2 k^2}{(k^2 - k'^2)^2}}$$

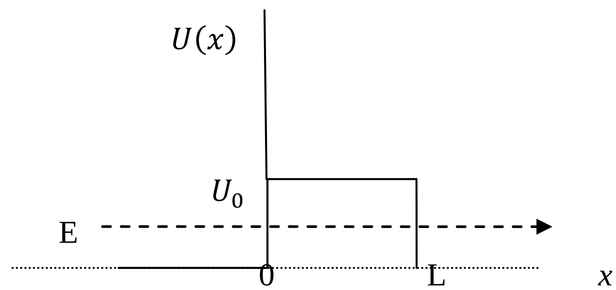
- Reflection probability $= \frac{\text{reflected particle flux}}{\text{incoming particle flux}} = \frac{|\psi_{reflected}|^2\ k}{|\psi_{incoming}|^2\ k} = \frac{B^*B}{A^*A}$

$$= \frac{sin^2(k'L)}{sin^2(k'L) + \frac{4\,k'^2 k^2}{(k^2 - k'^2)^2}}$$

(Note. Sine dependence → Resonnant Transmission $k'L = \sqrt{\frac{2m(E-U_0)}{\hbar^2}} = n\,\pi$)

Potential Barrier

$$U(x) = \begin{cases} 0 & x < 0 \\ U_0 & 0 \le x \le L \\ 0 & x > L \end{cases}$$



IF E < U_0

Using the results from the step potential example, the following wave functions can be considered as solutions to the Schrodinger Equation under the potential barrier:

- $\psi_{x<0}$ = Incoming wave function + Reflected wave function

  $=$ A e^{+ikx} + B e^{-ikx} where $k = \sqrt{\frac{2mE}{\hbar^2}}$

- $\psi_{0\le x \le L}$ = Incoming wave function + Reflected wave function

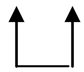
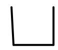
  $=$ C $e^{+\alpha x}$ + D $e^{-\alpha x}$ where $\alpha = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$

- $\psi_{x>L}$ = Transmitted wave function = Fe^{ikx} where $k = \sqrt{\frac{2mE}{\hbar^2}}$

Even though the particle does not have enough energy to overcome the potential barrier U_0, the particle can be still found on the other side of the barrier.

Bound States

Bound States represent cases when a particle's wave function is limited to a finite region of space by the potential energy, $U(x)$. We will consider wave functions and energies three such cases:

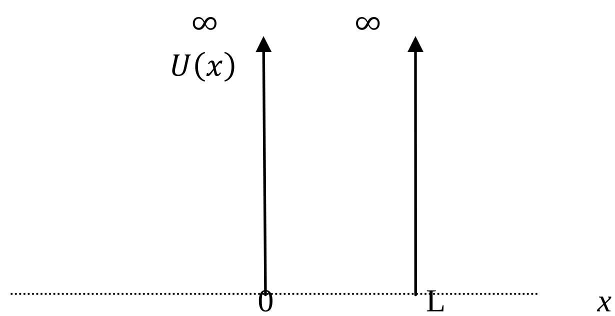
- Infinite Well $where\ U(x)$ = 
- Finite Well $where\ U(x)$ = 

We have the time-independent Schrodinger Equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\,\psi(x) = \mathrm{E}\,\psi(x) \qquad \text{(e14)}$$

Infinite Well

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



Where $x \leq 0$, wave functions CANNOT exist since the potential is infinity. → $\psi_{x\leq 0}(x) = 0$
Where $x \geq L$, wave functions CANNOT exist since the potential is infinity → $\psi_{x\geq L}(x) = 0$
Where $0 < x < L$, put $U(x) = 0$ into the time-independent Schrodinger Equation (e14),

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = \mathrm{E}\,\psi(x) \qquad \text{(e15)}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\psi(x) = -\,k^2\,\psi(x) \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

Since the wave function has to be confined inside the infinite well, we can consider $\sin(kx)$ or $\cos(kx)$ that satisfy (e15) as $\psi_{0<x<L}(x)$.

BUT, since $\psi(x)$ needs to be continuous which means

- $\psi_{x\leq 0}(x = 0) = 0$ → We take only $\sin(kx)$ for $\psi_{0<x<L}(x)$ (drop $\cos(kx)$)
- $\psi_{x\geq L}(x = 0) = 0$ → $\psi_{0<x<L}(x = L) = \sin(kL) = 0$ gives energy quantization rules

$$kL = \sqrt{\frac{2mE}{\hbar^2}}L = n\pi \qquad \text{where n =1, 2, 3, etc.}$$

$$E = \frac{n^2\,\pi^2\,\hbar^2}{2mL^2} \qquad \text{Energy quantization}$$

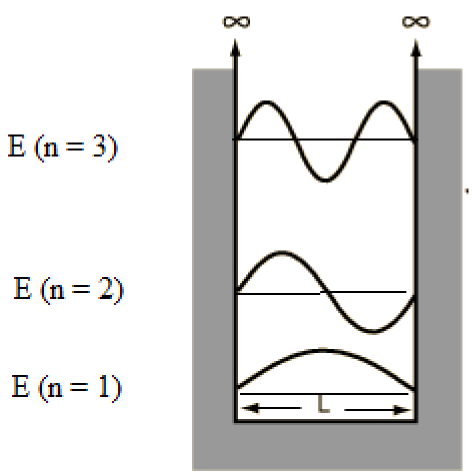
- Normalization

$$\psi_{0<x<L}(x) = A\sin(kx) = \mathrm{A}\sin(\frac{n\pi x}{L})$$

$$\int_0^L |\psi_{0<x<L}(x)|^2 = 1 = \mathrm{A}^2 \int_0^L \sin\left(\frac{n\pi x}{L}\right)^2 dx = \mathrm{A}^2\,\frac{\mathrm{L}}{2} \rightarrow \mathrm{A} = \sqrt{\frac{2}{L}}$$

THEREFORE,

- Wave function: $\psi_{0<x<L}(x) = \sqrt{\frac{2}{L}}\,\sin(\frac{n\pi x}{L})$
- Energy $E = \frac{n^2\,\pi^2\,\hbar^2}{2mL^2}$



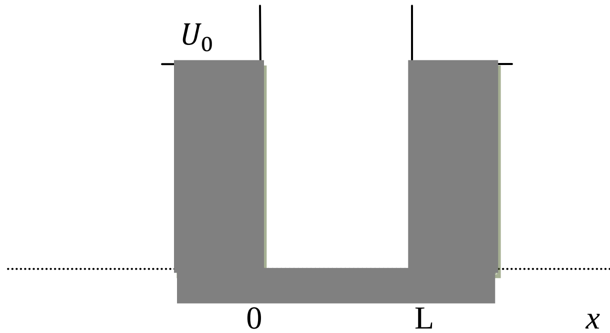
$$E\ (n=3) = 9\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

$$E\ (n=2) = 4\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

$$E\ (n=1) = 1\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

Finite Well

$$U(x) = \begin{cases} U_0 & x \le 0 \\ 0 & 0 < x < L \\ U_0 & x \ge L \end{cases}$$



where $0 < x < L$, $\psi_{0<x<L} = Ae^{ikx} + Be^{-ikx}$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$

where $x \le 0$, $\psi_{x<0}$ should decay exponentially as *x moves below zero* = $Ce^{\alpha x}$

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

where $x \ge 0$, $\psi_{x \ge 0}$ should decay exponentially as *x moves above L* = $De^{-\alpha x}$

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

Since $\psi(x)$ should be continuous everywhere, the following conditions should be met:

- $\psi_{x\le0}(x = 0) = \psi_{0<x<L}(x = 0)$
- $\frac{d\psi_{x\le0}}{dx}\Big|_{x=0} = \frac{d\psi_{0<x<L}}{dx}\Big|_{x=0}$
- $\psi_{0<x<L}(x = L) = \psi_{x\ge L}(x = L)$
- $\frac{d\psi_{0<x<L}}{dx}\Big|_{x=L} = \frac{d\psi_{x\ge L}}{dx}\Big|_{x=L}$
- $\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx$ = (normalization condition)

This means, there are five equations to be solved for A, B, C, and D. An additional parameter has to obey these relationships. That additional parameter is *k* (therefore E). Not all energy values will meet all five equations.