Schrödinger's Wave Equation and its Applications to One Dimensional Problems

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Schrödinger's Wave Equation (Derivation)

Erwin Schrödinger
1887-1961

- **Considering a complex plane wave:** $\Psi(x,t) = Ae^{i(kx-\omega t)}.$
- Now the Hamiltonian of a system is : $H = T + V$
- **Here 'V' is the potential energy and 'T' is the kinetic energy.**
- **We already know that 'H' is the total energy i.e.**

$$E = \frac{p^2}{2m} + V(x).$$

- **So,**

$$\frac{\partial \Psi}{\partial t} = -i\omega Ae^{i(kx-\omega t)} = -i\omega\Psi(x,t)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 Ae^{i(kx-\omega t)} = -k^2\Psi(x,t)$$

$p = \frac{2\pi\hbar}{\lambda}$ and $k = \frac{2\pi}{\lambda}$

$$k = \frac{p}{\hbar}.$$

- Here 'λ' is the wavelength and 'k' is the wave-number.

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi(x,t).$$

- Now multiplying Ψ (x, t) to the Hamiltonian we get,

$$E\Psi(x,t) = \frac{-\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi(x,t).$$

$$E = \hbar\omega,$$

$$E\Psi(x,t) = \frac{\hbar\omega}{-i\omega}\Psi(x,t).$$

- **This is known as time independent Schrödinger's Wave Equation.**
- Now combining the right parts, we can get the Schrodinger Wave Equation as

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

- This equation is known as the ***Time Dependent Schrödinger Equation*.**
- **This equation tells us how the initial information about the system changes with time according to a particular physical circumstance that a system finds itself in.**

Application of Schrödinger's equation to One Dimensional Problem

- The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape.
- The solutions to the problem give possible values of E and ψ that the particle can possess.
- E represents allowed energy values and ψ(x) is a wave-function, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.
- To solve the problem for a particle in a 1-dimensional box, we must follow the *recipe for Quantum Mechanics*:
  - ❖ One dimensional Schrödinger Equation
  - ❖ Define the Potential Energy, V
  - ❖ Solve the Schrödinger Equation
  - ❖ Define the wave-functions
  - ❖ Solve for the allowed energies

One-Dimensional Quantum Mechanics

The Schrödinger Equation

Consider an atomic particle with mass m and mechanical energy E in an environment characterized by a potential energy function $U(x)$.

The Schrödinger equation for the particle's wave function is

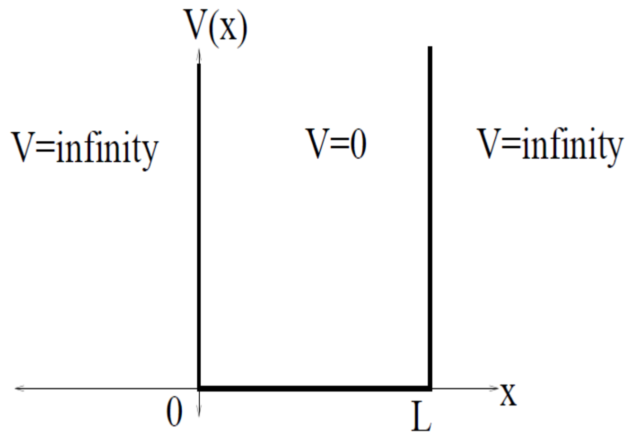
$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}[E - U(x)]\psi(x) \qquad \text{(the Schrödinger equation)}$$

Conditions the wave function must obey are

1. $\psi(x)$ and $\psi'(x)$ are continuous functions.
2. $\psi(x) = 0$ if x is in a region where it is physically impossible for the particle to be.
3. $\psi(x) \rightarrow 0$ as $x \rightarrow +\infty$ and $x \rightarrow -\infty$.
4. $\psi(x)$ is a normalized function.

Define the Potential Energy V

- **We confine the particle to a region between x = 0 and x = L Let us write the potential (the potential of infinite depth) as**



$$
\begin{aligned}
V(x) &= 0 \quad \text{for } 0 \le x \le L \\
&= \infty \quad \text{otherwise}
\end{aligned}
$$

- **The potential energy is plotted as a function of a single variable. as shown in Fig.**
- **The potential energy is *0 inside the box (V=0 for 0<x<L) and goes to infinity at the walls of the box (V=∞ for x<0 or x>L).***
- ***We* assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box.**
- **This is necessary to apply the proper boundary conditions while solving the Time Independent Schrödinger Equation (TISE) for infinitely deep square well.**

How to solve Schrödinger Equation?

•The Time-independent Schrödinger equation (TISE) for a particle of mass m moving in one direction with energy E is $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$ or $\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}(E-V)\psi=0$

- This equation can be modified for a particle of mass m free to move parallel to the x-axis with zero potential energy (V = 0 everywhere).
- Out side the box the solution is trivial.
- It is ZERO i.e. $\psi=0$
- Inside the box the TISE reduces to
- This equation has well known solution as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}E\psi=0$$

$$\Leftrightarrow \frac{\partial^2\psi}{\partial x^2}+k^2\psi=0 \ (\because k^2=\frac{2m}{\hbar^2}E)$$

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

- *$\psi(x)$ determines the stationary states (V=0) inside the box .*
- *Boundary* conditions, the probability of finding the particle at x=0 or x=L is zero

•implies (*$\psi(x)=0$*) .

- When x=0 , then sin (0)=0 and cos (0)=1 ; therefore

$$\psi(0)=A\sin(0)+B\cos(0)=0 \Rightarrow B=0$$

- Then for x=L, the following is true

$$\psi(L)=A\sin(kL)=0 \Rightarrow kL=0,\pi,2\pi,3\pi,.....n\pi$$

$$\therefore kL=n\pi\,(\forall n=1,2,3,...)$$

How to find out the Wave function?

Yes, you are right! – n cannot be zero, because for $n=0$ we would have $\Psi=0$ for all values of x, which would mean: "There is no particle in the box". So, the "physically acceptable" solutions for k are:

$$k_n = \frac{n\pi}{L}, \quad \text{where} \quad n = 1,2,3,\dots \quad (\text{a natural integer}).$$

Accordingly, for the possible quantum states of the particle in the box are the wave function can take the forms:

For $0 \le x \le L$:

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right), \quad \text{where} \quad n = 1,2,3,\dots , \text{ and}$$

$$\psi_n(x) = 0 \quad \text{for all} \quad x < 0 \text{ and } x > L.$$

But there is still an arbitrary constant A in this solution! This function fulfills the Schroedinger Equation for <u>any</u> value of A! Is this an acceptable situation? And if not, how can we find the "good" value?

Yes, you are right! The A constant has to take a concrete value. But how to find this value? There is still one "resource" we have Not used – namely, any wave function in QM MUST BE …

YES! – MUST BE NORMALIZED!

In other words, it must satisfy:

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

For our well, the normalization condition takes a simpler form:

$$\int_{0}^{L} |\psi_n(x)|^2 dx = 1$$

Particle in the Infinite Potential Well

Let's carry out the calculations:

$$\int_0^L |\psi_n(x)|^2 dx = \int_0^L A^2 \sin^2\left(\frac{n\pi}{L}x\right)dx$$

Let's use a "dummy variable" $y \equiv \frac{n\pi}{L}x$

then $x = \frac{L}{n\pi}y$ and $dx = \frac{L}{n\pi}dy$

The lower limit is still 0, but the upper limit has to be changed to:

$$y_{\text{upper\_limit}} = \frac{n\pi}{L}x_{\text{upper\_limit}} = \frac{n\pi}{L}L = n\pi$$

$$= A^2 \frac{L}{n\pi}\int_0^{n\pi} \sin^2(y)dy$$

Particle in the Infinite Potential Well

$$\boxed{\int_0^{n\pi} \sin^2(y)\,dy = \frac{n\pi}{2}}$$

So, we can continue from the preceding slide:

$$= A^2 \frac{L}{n\pi} \times \frac{n\pi}{2} = \frac{A^2 L}{2} = 1$$

From which we obtain immediately:

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

and the complete solution for $\psi(x)$:

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

Energy Eigen values

One more very important thing – we also want to know the energies corresponding to all these possible quantum states of the particle in the well.

Good news! It is really straightforward to obtain the energies from the results we already have. Look:

The wavenumber k is related to the energy as:

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \text{so} \quad E = \frac{\hbar^2 k^2}{2m}$$

But, as we have found, the allowed values of k are: $k_n = \dfrac{n\pi}{L}$

Combining the two, we get:

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \qquad (n = 1,2,3\ldots).$$

Allowed energy Eigen values

- The normalized wave-functions for a particle in a 1-dimensional box:

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

- **The allowed energies for a particle in a box:**

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

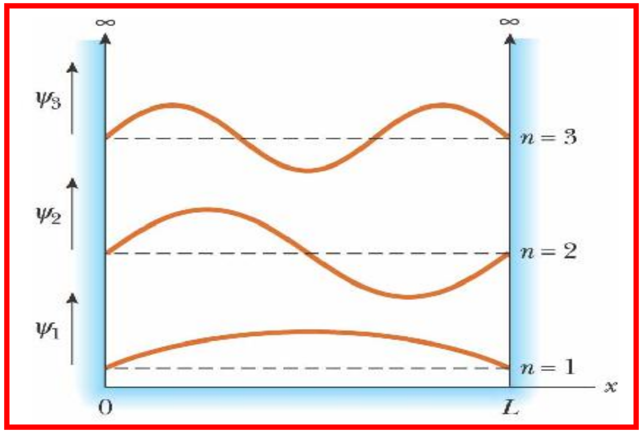
- **interpretation:** 1. The energy of a particle is quantized.

2. The lowest possible energy of a particle is **NOT zero.**

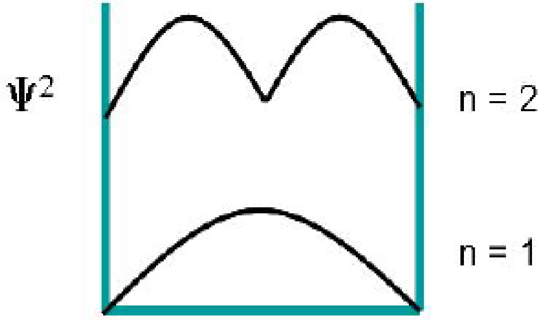
$$E_0 = \frac{\hbar^2 \pi^2}{2mL^2} = \frac{h^2}{8mL^2} \,(\, for \;\; n = 1)$$

- **This is called the zero-point energy (ground state energy) and means the particle can** never be at rest because it always has some kinetic energy.

- **This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.**
- **The wave-functions for a particle in a box at the n=1, n=2 and n=3 energy levels look like as figure.**



- **The probability of finding a particle a certain spot in the box is determined by Squaring ψ .**
- **The probability distribution for a particle in a box at the n=1 and n=2 energy levels looks like as given in figure.**



Average Momentum of Particle in a Box (Infinite Potential Well)

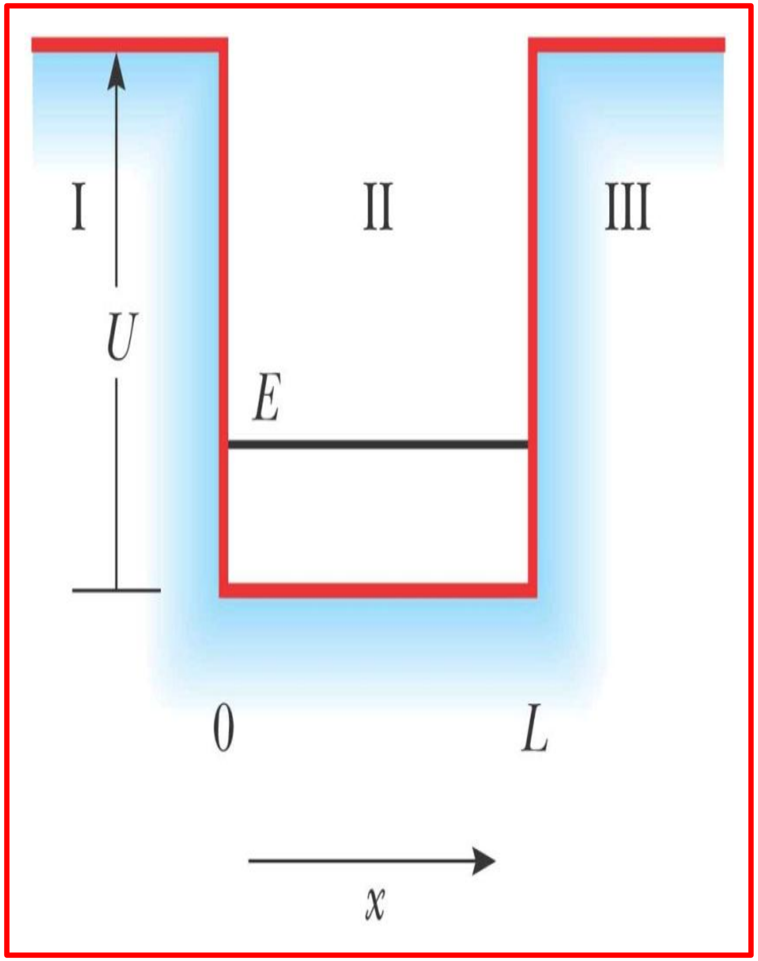
$$< p >= \int_0^L \Psi^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi^*(x)dx = \int_0^L [\sqrt{\frac{2}{L}}\sin kx]\frac{\hbar}{i}\frac{\partial\sqrt{\frac{2}{L}}\sin kx}{\partial x}dx$$

$$= \frac{2}{L}\frac{\hbar}{i}k\int_0^L \sin(kx)\cos(kx)dx = 0$$

- **Can evaluate the integral and show it is zero**
- **Can note that the right hand side is either 0 or imaginary, but momentum cannot be imaginary so it must be zero**

Finite Potential Well

- **The potential energy is zero ($U(x) = 0$) when the particle is $0 < x < L$ (Region II)**
- **The energy has a finite value ($U(x) = U$) outside this region, i.e. for $x < 0$ and $x > L$ (Regions I and III)**
- **We also assume that energy of the particle, E, is less than the "height" of the barrier, i.e. $E < U$**



Finite Potential Well

Schrödinger Equation

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

I. $x < 0;\ U(x) = U$

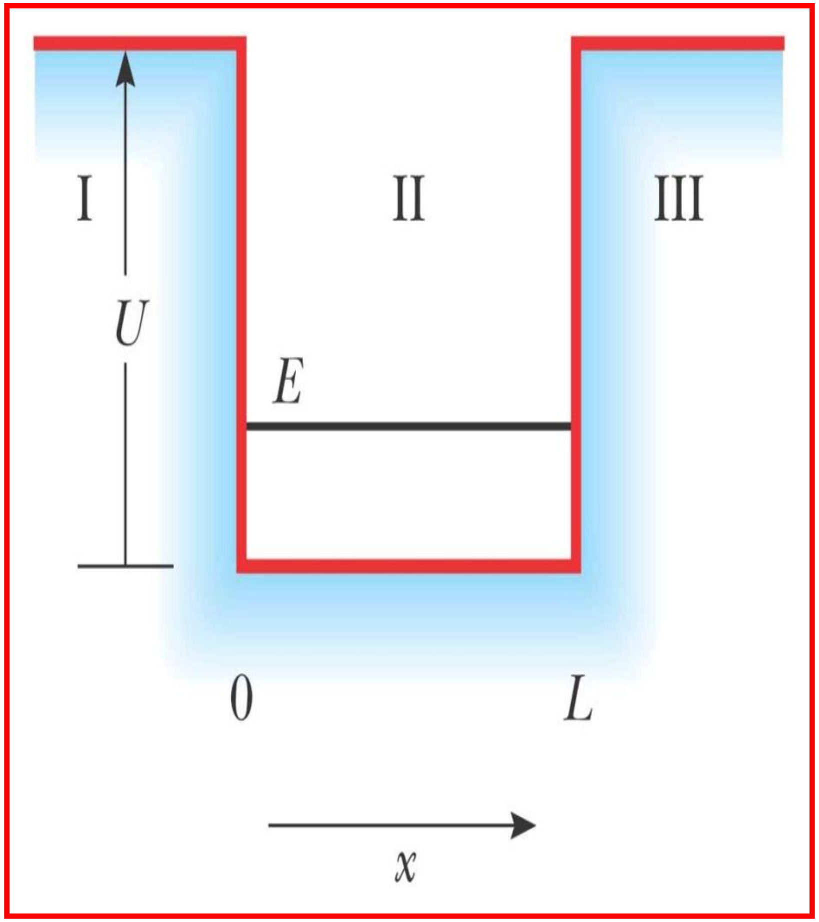
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_I}{dx^2}+U\psi_I=E\psi_I$$

II. $0 < x < L;\ U(x) = 0$

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

III. $x > L;\ U(x) = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{III}}{dx^2}+U\psi_{III}=E\psi_{III}$$

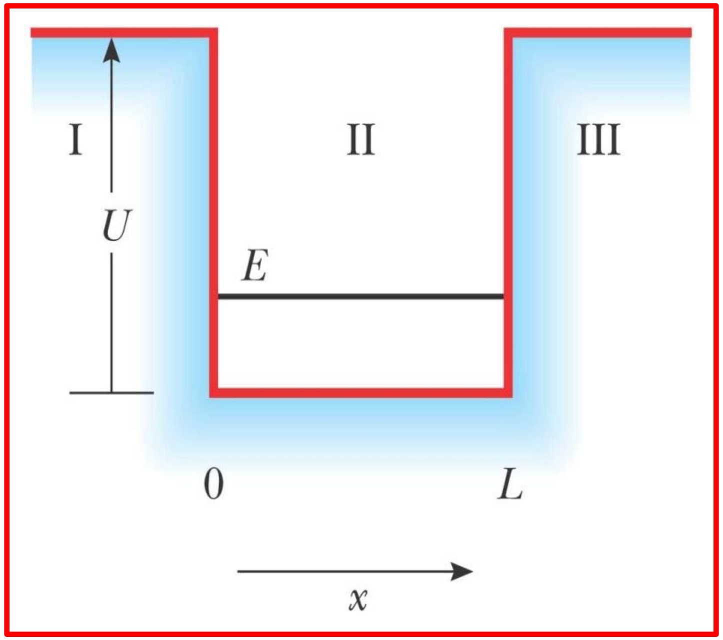


Finite Potential Well: Region II

- $U(x) = 0$ because V=0
  - This is the same situation as previously for infinite potential well
  - The allowed wave functions are sinusoidal
- The general solution of the Schrödinger equation is

$$\psi_{II}(x) = F \sin kx + G \cos kx$$

  - where F and G are constants



- The boundary conditions , however, no longer require that $\psi(x)$ be zero at the sides of the well

Finite Potential Well: Regions I and III

- The Schrödinger equation for these regions is

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

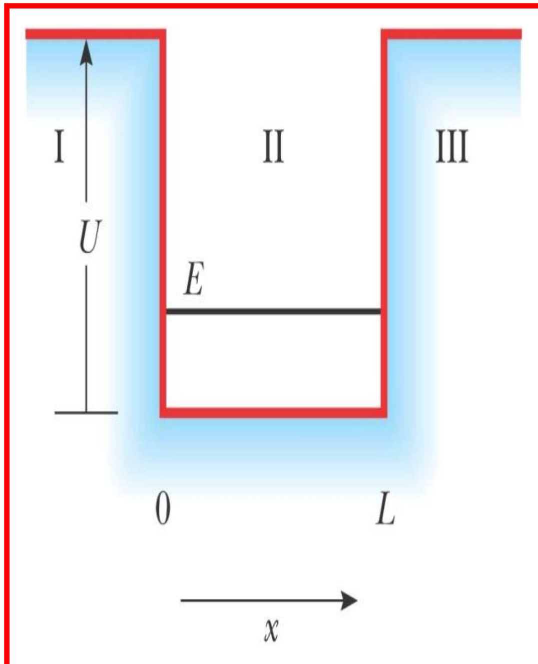
- It can be re-written as

$$\boxed{\frac{d^2\psi}{dx^2} = \frac{2m(U-E)}{\hbar^2}\psi = C^2\psi, \text{ where } C^2 \equiv \frac{2m(U-E)}{\hbar^2}}$$

- The general solution of this equation is

$$\psi(x) = Ae^{Cx} + Be^{-Cx}$$

  - *A* and *B* are constants
  - Note (*E*-*U*) is the negative of kinetic energy, -E_k
  - In region II, *C* is imaginary and so have sinusoidal solutions we found
  - In both regions I and III, $C = \frac{\sqrt{2mU}}{\hbar}$ and $\psi(x)$ is exponential

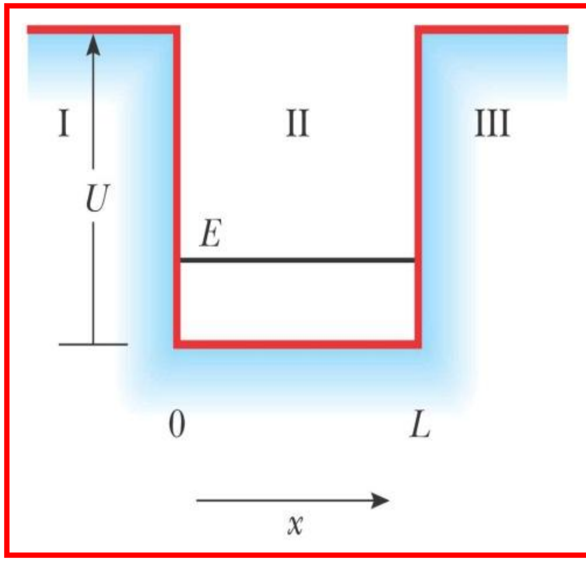


Finite Potential Well – Regions I and III

- Requires that wave-function, $\psi(x) = Ae^{Cx} + Be^{-Cx}$ not diverge as $x \rightarrow \mp\infty$
- So in region I, $B = 0$, and $\psi_I(x) = Ae^{Cx}$
  - to avoid an infinite value for $\psi(x)$ for large negative values of x
- In region III, $A = 0$, and

  $$\psi_{III}(x) = Be^{-Cx}$$

  - to avoid an infinite value for $\psi(x)$ for large positive values of x



Finite Potential Well

- **The wave-function and its derivative must be *single-valued* for all x**
  - **There are two points at which wave -function is given by two different functions: $x = 0$ and $x = L$**
- **Thus, we equate the two expressions for the wave-function and its derivative at $x = 0, L$.**
  - **This, together with the normalization condition, determines the amplitudes of the wave-function and the constants in the exponential term.**
  - **This determines the allowed energies of the particle**

$$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$$

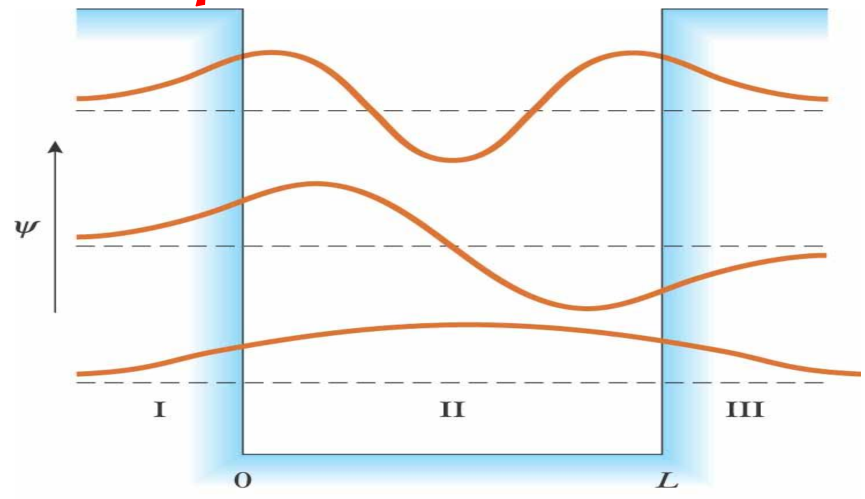
$$\frac{d\psi_{\mathrm{I}}}{dx}(0) = \frac{d\psi_{\mathrm{II}}}{dx}(0)$$

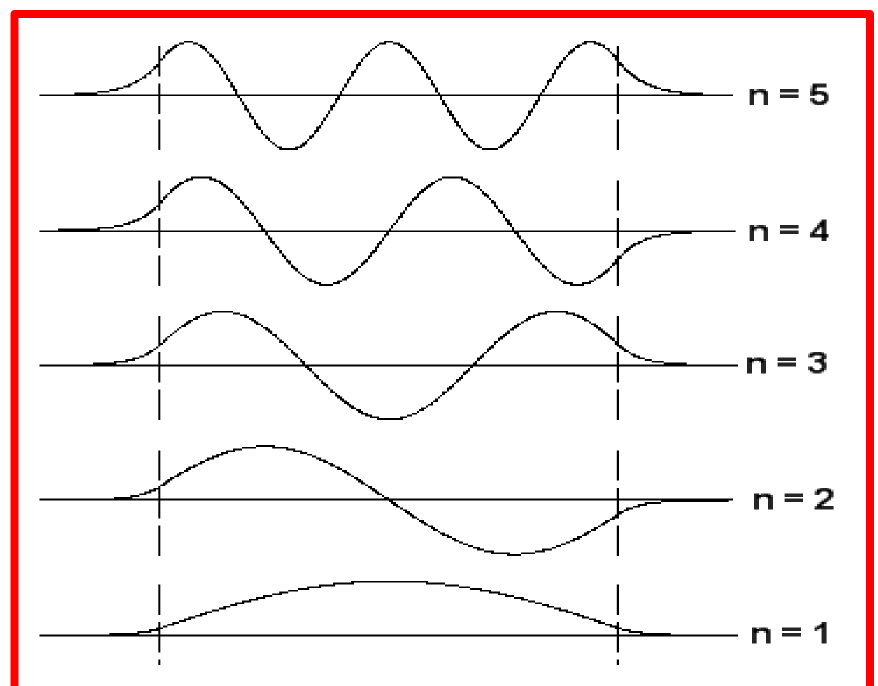
$$\psi_{\mathrm{II}}(L) = \psi_{\mathrm{III}}(L)$$

$$\frac{d\psi_{\mathrm{II}}}{dx}(L) = \frac{d\psi_{\mathrm{III}}}{dx}(L)$$

Finite Potential Well
Graphical Results for $\psi(x)$

- Outside the potential well, classical physics forbids the presence of the particle
- Quantum mechanics shows the wave function decays exponentially to zero

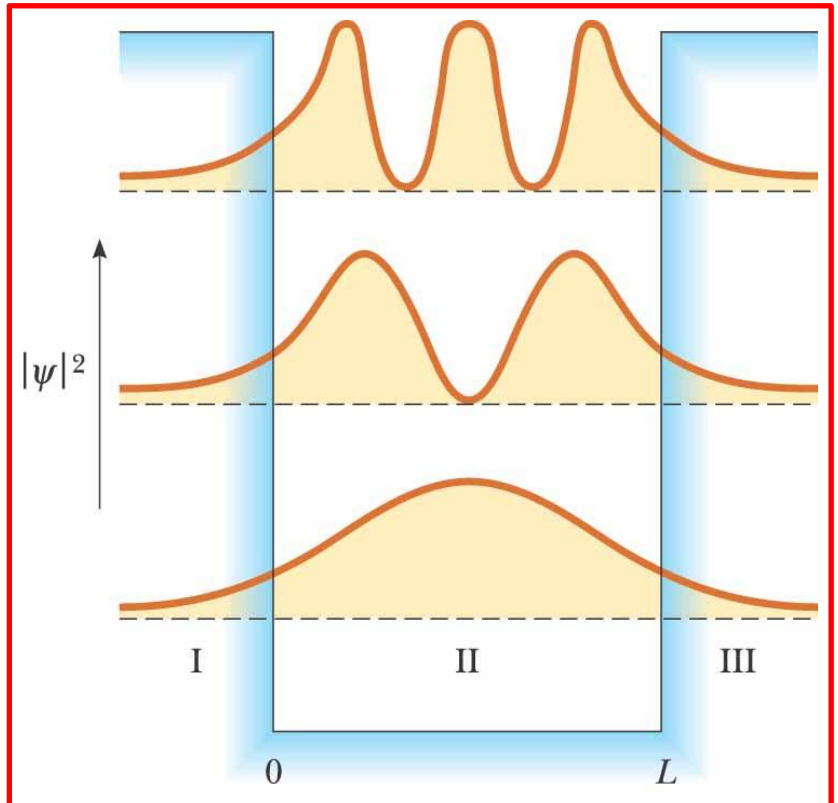




Finite Potential Well

Graphical Results for Probability Density, $|\ \psi(x)\ |^2$

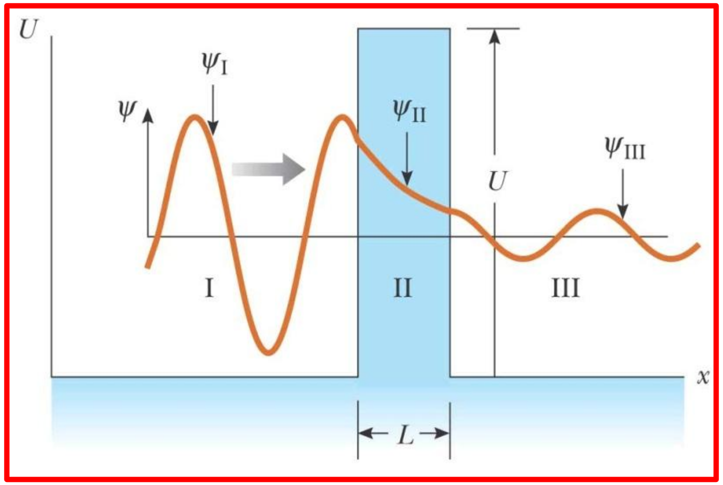
- The probability densities for the lowest three states are shown
- The functions are smooth at the boundaries
- Outside the box, the probability of finding the particle decreases exponentially, **but it is not zero!**



http://phys.educ.ksu.edu/vqm/html/probillustrator.html

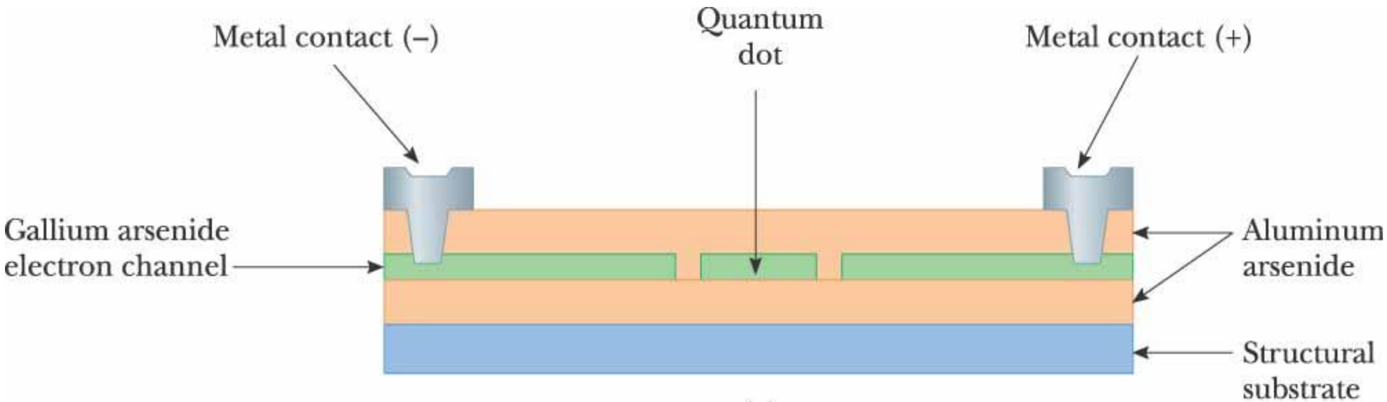
Tunneling

- The potential energy has a constant value *U* in the region of width *L* and zero in all other regions
- This a called a barrier
- *U* is the called the barrier height. Classically, the particle is reflected by the barrier
  - Regions II and III would be *forbidden*



- According to quantum mechanics, all regions are accessible to the particle
  - The probability of the particle being in a classically forbidden region is low, but not zero
  - Amplitude of the wave is reduced in the barrier
  - A fraction of the beam penetrates the barrier
  - http://phys.educ.ksu.edu/vqm/html/qtunneling.html
  - http://phet.colorado.edu/web-pages/simulations-base.html

More Applications of Tunneling
Resonant Tunneling Device



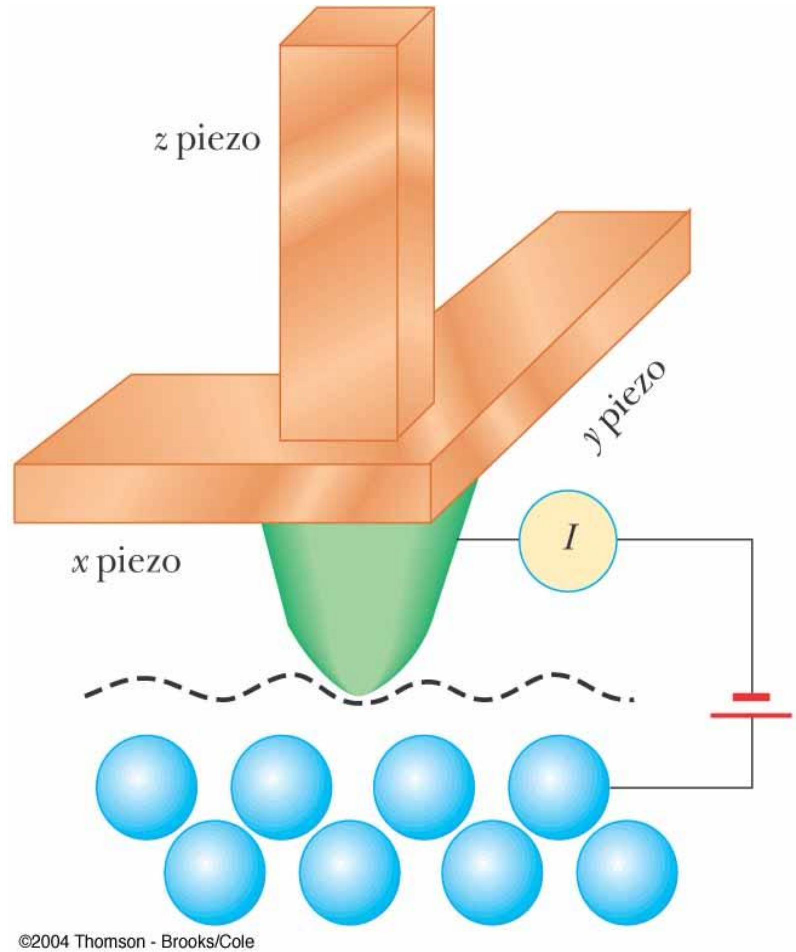
(a)

- Electrons travel in the gallium arsenide
- They strike the barrier of the quantum dot from the left
- The electrons can tunnel through the barrier and produce a current in the device

More Applications of Tunneling

Scanning Tunneling Microscope

- An electrically conducting probe with a very sharp edge is brought near the surface to be studied
- The empty space between the tip and the surface represents the "barrier"
- The tip and the surface are two walls of the "potential well"



Simple Harmonic Oscillator

- **To explain blackbody radiation Planck postulated that the energy of a simple harmonic oscillator is quantized**
  - **In his model vibrating charges act as simple harmonic oscillators and emit EM radiation**
- **The quantization of energy of harmonic oscillators is predicted by QM.**
- *Let's write down the Schrödinger Equation for SHO*
- *For SHO the potential energy is*

$$\boxed{U(x) = \frac{kx^2}{2} = \frac{m\omega^2 x^2}{2} \qquad \omega = \sqrt{\frac{k}{m}}}$$

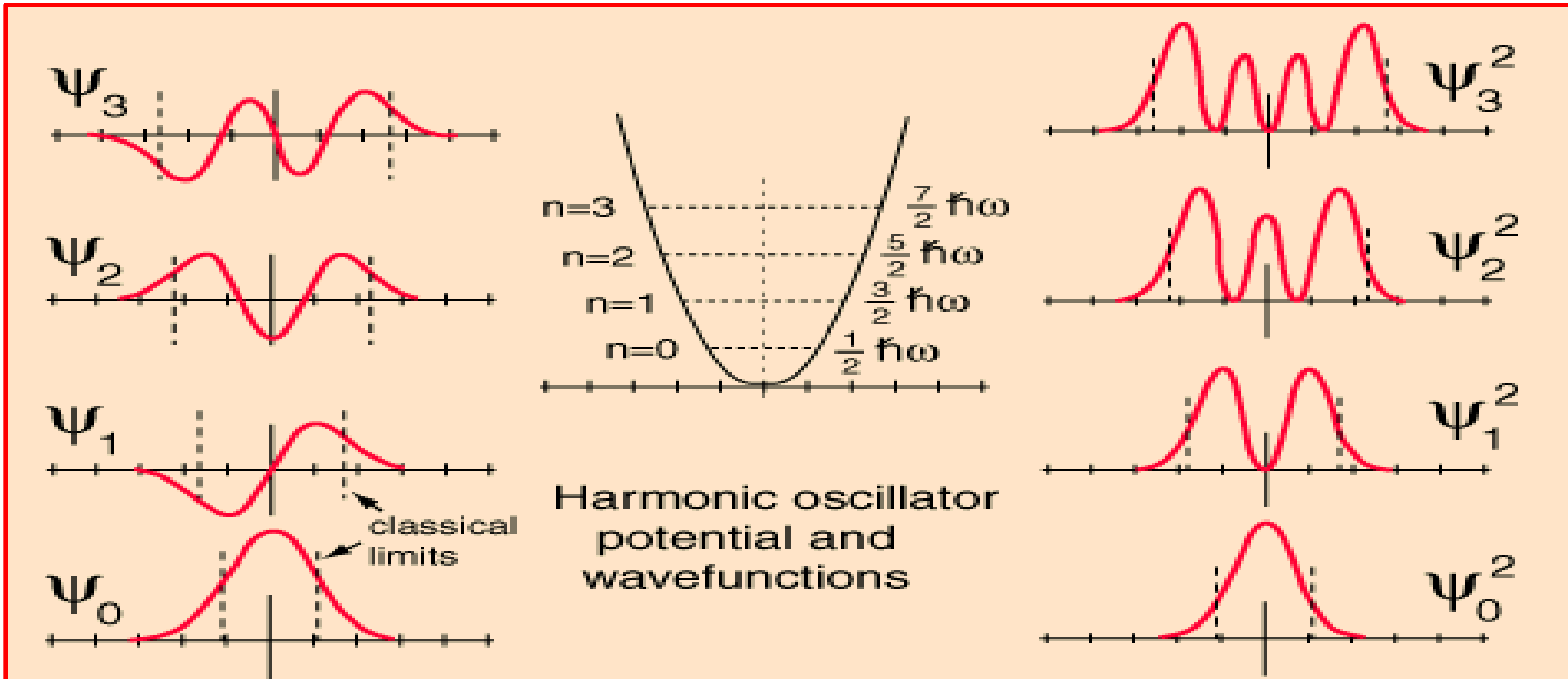
- *Time independent Schrödinger Equation for SHO in one -Dimension*

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial^2 x} + \frac{m\omega^2 x^2}{2}\psi(x) = E\psi(x)}$$

Simple Harmonic Oscillator

- **Solutions of time-independent Schrödinger equation for 1D harmonic oscillator**

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+\frac{m\omega^2x^2}{2}\psi(x)=E\psi(x)}$$



Simple Harmonic Oscillator

- **Planck's expression for energy of SHO**

$$\boxed{E = nh\nu}$$

- **Energy of SHO obtained from the solution of the Schrödinger equation**
  - *Thus, the Planck formula arises from the Schrödinger equation naturally*
  - *$n = 0$ is the ground state with energy ½hν*

$$E = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)h\nu$$

$$n = 0,1,2,3,\ldots$$

$$\hbar = \frac{h}{2\pi}; \quad \omega = 2\pi\nu$$

Term ½ *hν* tells us *that quantum SHO always* oscillates. *These are called zero point vibrations*

Simple Harmonic Oscillator

- *Energy of SHO from the Schrödinger equation*

$$\boxed{E = nh\nu + \frac{1}{2}h\nu}$$

- *The zero point energy ½hν is required by the Heisenberg uncertainty relationship*
- *The term of ½hν is important for understanding of some physical phenomena*
- *For example, this qualitative explains why helium does not become solid under normal conditions*
  - **the "zero point vibration" energy is higher than the "melting energy" of helium**
- *Force between two metal plates*

Good Luck