Quantum mechanics. Introduction.

What is quantum mechanics?

Quantum mechanics (aka wave mechanics) is the study of ***matter*** and ***radiation*** at an atomic level.

Why was quantum mechanics developed?

In the early 20-th century some experiments produced results which could not be explained by classical physics. For instance, it was well known that electrons orbited the nucleus of an atom. However, if they did so in a manner which resembled the planets orbiting the sun, classical physics predicted that the electrons would spiral in and crash into the nucleus within a fraction of a second. Obviously that doesn't happen, or life as we know it would not exist. That incorrect prediction, along with some other experiments that classical physics could not explain, showed scientists that *something new was needed* to explain science at the atomic level.

Quantum mechanics. Introduction.

If classical physics is wrong, why do we still use it?

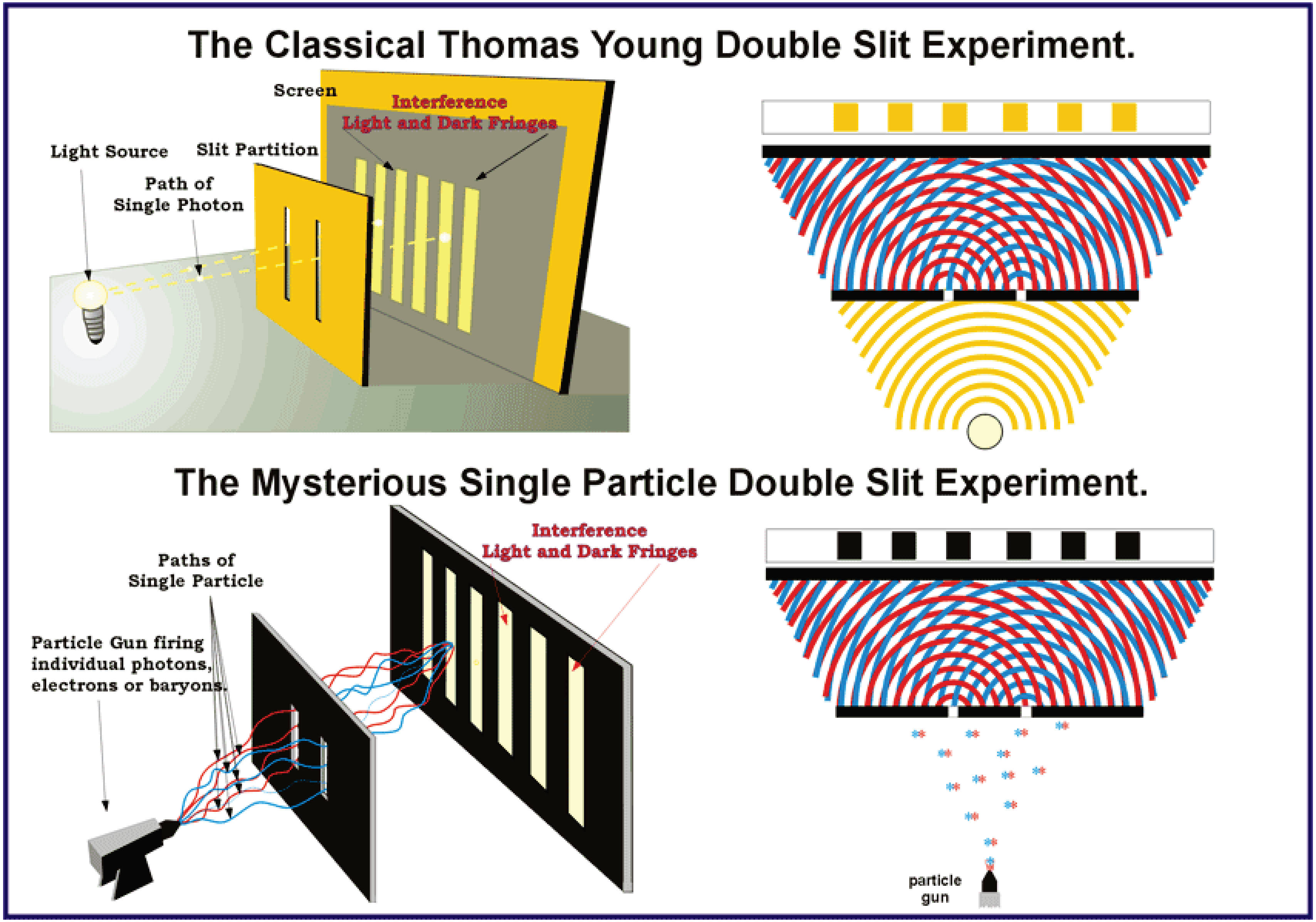
For everyday things, which are much larger than atoms and much slower than the speed of light, classical physics does an excellent job. Plus, it is much easier to use than either quantum mechanics or relativity (each of which require an extensive amount of math).

What is the importance of quantum mechanics?

The following are among the most important things which quantum mechanics can describe while classical physics cannot:

- Discreteness of energy
- The wave-particle duality of light and matter
- Quantum tunneling
- The Heisenberg uncertainty principle
- Spin of a particle

Wave-Particle Duality



Electrons exhibit weave-like behavior

Louis De Broglie

Every particle has a wavelength (de Broglie) given by $\boxed{\lambda = \frac{h}{p}}$

Question: Why don't we see particle waves (i.e., diffraction and interference) in day-to-day life?

Answer: Macroscopic objects have ***wavelengths too small*** to interact with slits, but atomic-sized objects do appear to behave like waves!

Example: ***Macroscopic Object*** – ping pong ball

$$\lambda(\text{ping pong ball}) = \frac{h}{mv} = \frac{6.63\times10^{-34}\ \text{J}\cdot\text{s}}{\left(2\times10^{-3}\ \text{kg}\right)\left(5\ \text{m/s}\right)} = \boxed{6.6\times10^{-32}\ \text{m}}$$

Immeasurably small!

Example: ***Microscopic Object*** – "slow electron" (1% speed of light)

$$\lambda(\text{electron}) = \frac{6.63\times10^{-34}\ \text{J}\cdot\text{s}}{\left(9.1\times10^{-31}\ \text{kg}\right)\left(10^{6}\ \text{m/s}\right)} = \boxed{7.3\times10^{-10}\ \text{m}}$$

Atomic Dimensions

2.4. Quantum mechanics

Probability and the Uncertainty Principle

It is impossible to describe with absolute precision events involving individual particles on the atomic scale.

Instead, we must speak of the ***average values*** (expectation values) of position, momentum, and energy of a particle such as an electron.

The theory describes the ***probabilistic nature*** of events involving small particles (atoms, electrons, elementary particles). The fact is that such quantities as the position and momentum of an electron do not exist apart from a particular uncertainty.

Heisenberg uncertainty principle

Werner Heisenberg

The magnitude of uncertainty to determine physical quantities (position, momentum, energy) is described by the ***Heisenberg uncertainty principle*** (also known as the principle of indeterminacy)

In any measurement of the position and momentum of a particle, the uncertainties in the two measured quantities will be related by

$$(\Delta x)\cdot(\Delta p_x) \geq \hbar$$

Heisenberg uncertainty principle – 2

Similarly,

The uncertainties in an energy measurement will be related to the uncertainty in the time at which the measurement was made by:

$$(\Delta E)\cdot(\Delta t) \geq \hbar$$

Heisenberg uncertainty principle – 3

Example:

What is the ***uncertainty*** in velocity for an electron in a 1 Å radius orbital in which the positional uncertainty is 1% of the radius?

$$\Delta x = 1\times 10^{-10}(\mathrm{m})\times 0.01 = 1\times 10^{-12}\ (\mathrm{m})$$

$$\Delta p = \frac{h}{2\pi\Delta x} = \frac{6.626\times 10^{-34}(\mathrm{J\cdot s})}{2\pi\times 1\times 10^{-12}(\mathrm{m})} = 1.05\times 10^{-22}\ (\mathrm{kg\cdot m/s})$$

$$\Delta v = \frac{\Delta p}{m} = \frac{1.05\times 10^{-22}(\mathrm{kg\cdot m/s})}{9.11\times 10^{-31}(\mathrm{kg})} = 1.2\times 10^{8}\ (\mathrm{m/s})$$

Huge!

Heisenberg uncertainty principle – 4

Example:

What is the ***uncertainty*** in position for a 80 kg student walking across campus at 1.3 m/s with an uncertainty in velocity of 1%.

$$\Delta p = m \times \Delta v = 80(\mathrm{kg}) \times 0.013(\mathrm{m/s}) = 1.04\ (\mathrm{kg} \cdot \mathrm{m/s})$$

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}(\mathrm{J} \cdot \mathrm{s})}{4\pi \times 1.04(\mathrm{kg} \cdot \mathrm{m/s})} = 5.07 \times 10^{-35}\ (\mathrm{m})$$

Uncertainty in position of a student is very small – **we know where you are!**

Probability – 1

The uncertainty principle brings us to an idea that we cannot properly speak of the position of an electron, but must look for the ***probability*** of finding an electron at a certain position.

Thus one of the important results of quantum mechanics is that a ***probability density function*** can be obtained for a particle in a certain environment, and this function can be used to find the expectation value of important quantities such as position, momentum, and energy.

For this purpose, it is common to define:

A ***probability density function*** $\boldsymbol{P(x)}$ describes the ***probability of finding a particle within a certain volume***.

Probability – 2

The ***probability*** of finding the particle in a range from ***x*** to **(*x* + *dx*)** is ***P*(*x*)*dx***.

Since the particle will be somewhere, the ***probability to find it*** in some point within region (-∞,∞) must be 1:

$$\boxed{\int_{-\infty}^{\infty} P(x)dx = 1}$$

if the function ***P*(*x*)** is properly chosen – normalized.

To find the ***average value*** of a function of x (***f*(*x*)**), we need only multiply the value of that function in each increment dx by the probability ($P(x)$) of finding the particle in that dx and sum over all range of x:

Average value of f(x):

$$\boxed{\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)P(x)d}$$

where $P(x)$ is ***normalized***.

The Schrödinger wave equation - 1

Erwin Schrödinger

Basic postulates:

Postulate 1.

Each particle in a physical system is described by a wave function **$\Psi(\mathbf{r},t)=\Psi(x,y,z,t)$.**

This function and its partial space derivative ($\partial\psi/\partial x + \partial\psi/\partial y + \partial\psi/\partial z$) are continuous, finite, and single valued.

Wave function can be interpreted as probability amplitude

The Schrödinger wave equation - 2

Postulate 2.

In dealing with classical quantities such as energy E and momentum p, we must relate these quantities with abstract ***quantum mechanical operators*** defined in the following way (one-dimensional case).

Classical variable	***Quantum operator***
x	x
$f(x)$	$f(x)$
$p(x)$	$\frac{\hbar}{j}\frac{\partial}{\partial x}$
E	$-\frac{\hbar}{j}\frac{\partial}{\partial t}$

The Schrödinger wave equation - 3

Postulate 3.

The ***probability*** of finding a particle with wave function Ψ in the volume ($dx \times dy \times dz$) is ($\Psi^*\Psi$) $dx \times dy \times dz$.

(Ψ^* is the complex conjugate of Ψ , obtained by reversing the sign of each j. Thus, $(e^{jx})^* = e^{-jx}$).

The product $\Psi^*\Psi$ is ***normalize***d so that $\int_{-\infty}^{\infty} \Psi^*\Psi dxdydz = 1$

and the ***average value*** $\langle Q \rangle$ of any variable Q is calculated from the wave function by using the ***quantum operator*** Q_{op} defined in postulate 2:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* Q_{op} \Psi dxdydz = 1$$

The Schrödinger wave equation - 4

The classical equation for the energy of a particle: $E_{kin} + E_{pot} = E_{tot}$

Kinetic energy E_{kin}: $E_{kin} = \frac{mV^2}{2} = \frac{p^2}{2m}$

Potential energy E_{pot}: $E_{pot} = U(\vec{r})$ (U – potential energy)

$$\frac{p^2}{2m} + U = E_{tot}$$

The Schrödinger wave equation - 5

$$\frac{p^2}{2m} + U = E_{tot}$$

In quantum mechanics we have to use the operator form for variables momentum p and energy E (postulate 2); the operators are allowed to operate on the wave function Ψ.

Classical variable	***Quantum operator***
x	x
$f(x)$	$f(x)$
$p(x)$	$\frac{\hbar}{j}\frac{\partial}{\partial x}$
E	$-\frac{\hbar}{j}\frac{\partial}{\partial t}$

$$\frac{p^2}{2m} + U = E_{tot} \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(\vec{r},t)}{\partial \vec{r}^{\,2}} + U(\vec{r})\Psi(\vec{r},t) = -\frac{\hbar}{j}\frac{\partial \Psi(\vec{r},t)}{\partial t}$$

The Schrödinger wave equation - 6

We can rewrite the equation using conventional notation:

$$\nabla^2\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(\vec{r},t)}{\partial \vec{r}^2} + U(\vec{r})\Psi(\vec{r},t) = -\frac{\hbar}{j}\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

$$\Downarrow$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t}}$$

– the Schrödinger wave equation.

Note: the wave function **Ψ** in the Schrödinger wave equation includes both *space* and *time* dependencies.

The Schrödinger wave equation - 7

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t}$$

where **Ψ**(**r**,*t*)=**Ψ**(*x*,*y*,*z*,*t*) is a function of ***space*** coordinates and ***time*** (!);

U(**r**) – potential energy (field). (It may have very complex form)

Wave functions are ***solutions to the Schrodinger wave equation***. The wave function, **Ψ**(*x*, *t*) describes physical state of the particle, such as its momentum, energy etc. and also where the particle is (in terms of probability).

This is quite complex differential equation – typically it is very difficult to solve it and find **Ψ**(**r**,*t*).

In many cases, it is possible to solve the wave equation by breaking it into two equations by the technique of separation of ***space*** coordinates and ***time*** variables.

Let **Ψ**(*x*,*t*) be represented by the product $\psi(x)\times\phi(t)$

The Schrödinger wave equation - 8

Let $\Psi(x,t)$ be represented by the product $\psi(x)\times\phi(t)$:

$$\Psi(x,t)=\psi(x)\times\phi(t)$$

Substituting this product in ***the Schrödinger wave equation***

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

we have:

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

Now the variables can be ***separated***!

The Schrödinger wave equation - 9

Separation of variables allows us to derive two independent equations:

(1) ***the time-dependent Schrödinger equation*** in one dimension:

$$\boxed{\frac{\partial \phi(t)}{\partial t} + \frac{jE}{\hbar}\phi(t) = 0}$$

[We are not going to discuss the time-dependent Schrödinger wave equation in this course]

(2) ***the time-independent Schrödinger equation.***

To derive time-independent Schrödinger equation, we have to recall quantum operator to determine energy:

$$-\frac{\hbar}{j}\frac{\partial}{\partial t}$$

The Schrödinger wave equation - 10

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

Using quantum energy operator: $-\frac{\hbar}{j}\frac{\partial}{\partial t}$

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

Thus, eliminating time dependent function $\phi(t)$ we have:

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

or

$$\boxed{\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2m}{\hbar^2}\left[E-U(x)\right]\psi(x)=0}$$

The Schrödinger wave equation - 11

The time-independent (stationary) Schrödinger equation:

$$\boxed{\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2m}{\hbar^2}[E-U(x)]\psi(x)=0}$$

Solution of this equation, wave function $\psi(x)$, describes a particle in stationary state.

Constant E corresponds to the energy of the particle when particular solutions are obtained, such that a wave function ψ_n corresponds to a particle energy E_n.

This equation is the basis of wave mechanics. From it we can determine ***the wave functions*** for particles in various simple systems.

For calculations involving electrons, the potential term $U(x)$ usually represents electrostatic or magnetic field.

Particle in potential well – 1

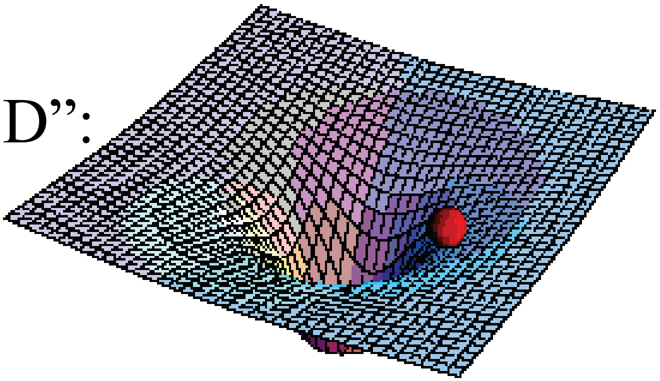
(“particle in a box”)

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\left[E - U(x)\right]\psi(x) = 0$$

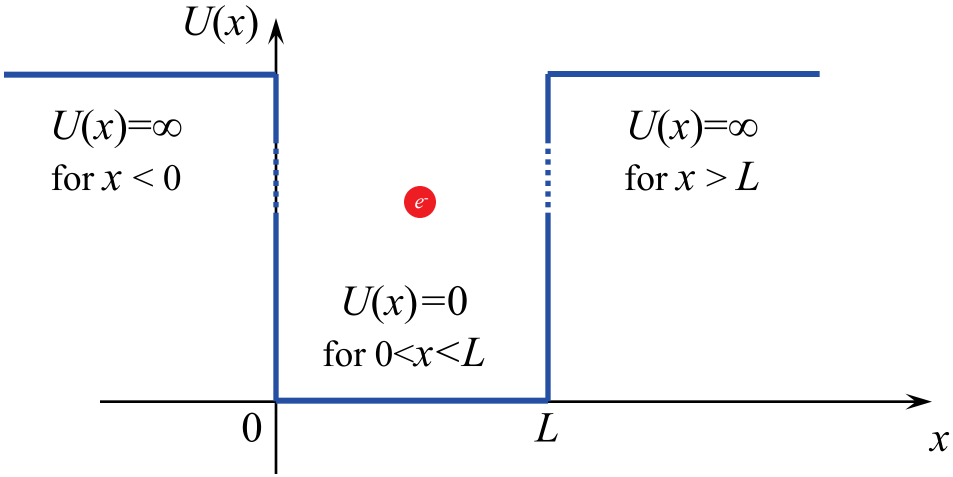
It is quite difficult to find solutions to the Schrödinger wave equation for most realistic potential fields *U*(*x*).

“1-D”: $U(x) = -\frac{q^2}{x}$

“2-D”:

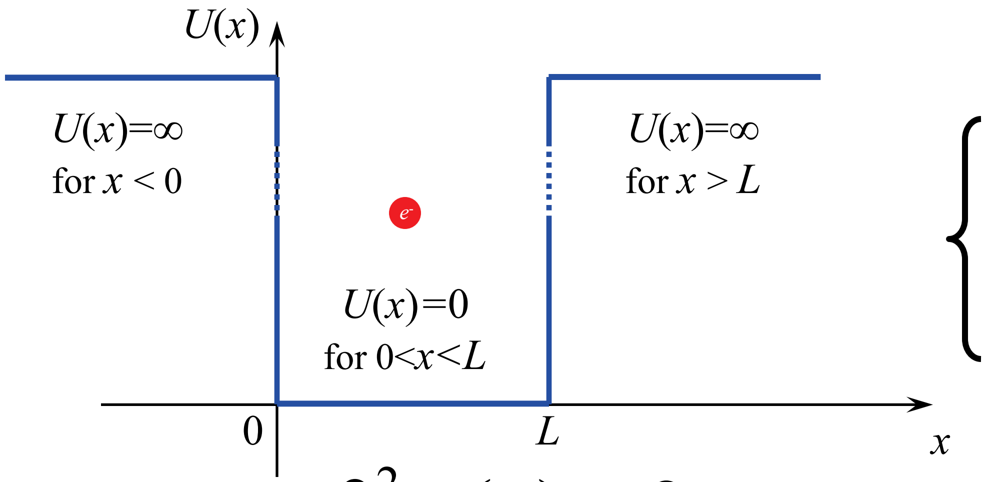


The simplest problem is the potential energy well with infinite boundaries - “***particle in a box***”



“1-D”

Particle in potential well – 2



$$\begin{cases} U(x) = 0 \text{ for } 0 < x < L \\ U(x) = \infty \text{ for } x < 0 \text{ and } x > L \end{cases}$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\left[E - U(x)\right]\psi(x) = 0$$

For free particle (electron) of mass m inside one-dimensional potential well ($U(x) = 0$) Schrödinger time-independent (stationary) equation:

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \qquad \text{for } 0 < x < L$$

Particle in potential well – 3

This Schrödinger equation for free particle (electron) of mass *m* inside one-dimensional well ($U(x) = 0$)

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \qquad \text{for } 0 < x < L$$

has general solution: $\psi(x) = Ae^{jkx} + Be^{-jkx}$

Shape of the potential well dictates the ***boundary conditions***: the solution ($\psi(x)$) must have ***zero*** values at the walls of the well ($x = 0$ and $x = L$). This is due to the fact that probability to find particle outside the well must be zero: $|\psi(x)|^2=0$ for any $x < 0$ and $x > L$.

Thus, the ***boundary conditions***: $\boxed{\psi(0) = 0\ ; \quad \psi(L) = 0}$

Particle in potential well – 4

General solution of the equation $\psi(x) = ae^{jkx} + be^{-jkx}$

can be given in more simple form: $\left(e^{\pm j\theta} = \cos\theta \pm j\sin\theta\right)$

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

We must examine boundary conditions to choose a solution:

Solution should satisfy boundary condition: $\psi(x=0) = 0$
At $x = 0$ we have: (1) $A\sin(k0) = 0$; (2) $B\cos(k0) \neq 0$

$$\Downarrow$$

$\psi(x) = A\sin(kx)$ satisfies boundary condition $\psi(0) = 0$
and $\psi(x) = B\cos(kx)$ – does not.

The solution of the equation is $\psi(x) = A\sin(kx)$

Particle in potential well – 5

Thus, the solution of the Schrödinger equation for free particle inside one-dimensional potential well is $\psi(x) = A\sin(kx)$

Parameter k can be found by substituting solution $\psi(x) = A\sin(kx)$ into equation

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}E\psi(x) = 0 \qquad \text{for } 0 < x < L$$

$$\frac{\partial^2 A\sin(kx)}{\partial x^2} + \frac{2m}{\hbar^2}EA\sin(kx) = 0$$

$$\frac{d\sin(x)}{dx} = \cos(x)$$

$$\frac{d\cos(x)}{dx} = -\sin(x)$$

$$-Ak^2\sin(kx) + \frac{2m}{\hbar^2}EA\sin(kx) = 0$$

$$-k^2 + \frac{2mE}{\hbar^2} = 0 \qquad \Rightarrow \qquad \boxed{k = \sqrt{\frac{2mE}{\hbar^2}}}$$

Particle in potential well – 6

On the other hand, according to the boundary conditions $\psi(x)$ has to be zero at $x = 0$ and $x = L$.

k ***must*** then be some ***integer multiple*** of π/L:

$$k = \frac{n\pi}{L} \quad \text{where n = 1, 2, 3, …}$$

$$\boxed{k = \sqrt{\frac{2mE}{\hbar^2}}} \quad \text{and} \quad \boxed{k = \frac{n\pi}{L}} \quad \Rightarrow \quad \sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L} \quad \Rightarrow \quad \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

This formula shows what values of energy the particle in the potential well may have.

The energy is <u>quantized</u> **!!!**

The integer ***n*** is called a ***quantum number.***

Particle in potential well – 7

In order to find amplitude *A* of the wave function $\psi(x) = A\sin(kx)$, – the solution of the Schrödinger equation, – we have to use Postulate 3 stating that probability to find particle anywhere from -∞ to ∞ is 1. Actually, the probability to find particle in the region from 0 to *L* is 1:

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = \int_{0}^{L} \psi^*(x)\psi(x)dx = 1$$

[Using formula from table of integrals: $\int(\sin x)^2\,dx = \frac{1}{2}x - \frac{1}{4}\sin 2x + C$]

$$\int_{-\infty}^{\infty} \psi^*\psi dx = \int_{0}^{L} A^2\left[\sin\left(\frac{n\pi}{L}x\right)\right]^2 dx = A^2\,\frac{L}{n\pi}\int_{0}^{L}\left[\sin\left(\frac{n\pi}{L}x\right)\right]^2 d\left(\frac{n\pi}{L}x\right) =$$

$$= \frac{A^2L}{n\pi}\left[\frac{1}{2}\left(\frac{n\pi}{L}x\right) - \frac{1}{4}\sin\left(2\frac{n\pi}{L}x\right)\right]_0^L = \frac{A^2L}{n\pi}\left[\frac{1}{2}\left(\frac{n\pi}{L}L\right)\right] = \frac{A^2L}{2}$$

Particle in potential well – 8

Based on Postulate 3: $\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1$

$$\frac{A^2L}{2} = 1 \quad \Rightarrow \quad \boxed{A = \sqrt{\frac{2}{L}}}$$

Conclusion:

Free particle of mass ***m*** in one-dimensional potential well ($U(x) = 0$) is described by Schrödinger time-independent (stationary) equation:

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}E\psi(x) = 0 \qquad \text{with solution} \qquad \psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$

Particle in potential well – 9
Summary

Free particle of mass m in one-dimensional potential well ($U(x) = 0$) is described by wave functions

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

For each allowable value of $\boldsymbol{n}$ the particle may have only certain value of energy given by

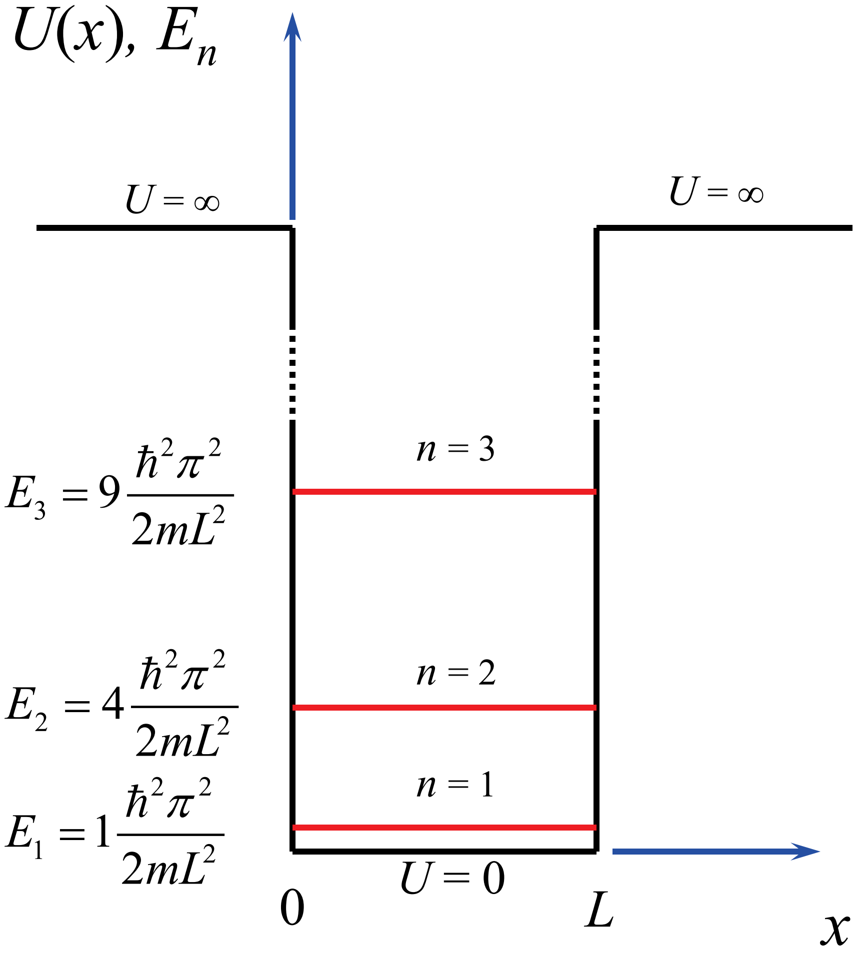
$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

This formula describes energy spectrum of the particle in the potential well.

- The energy of a particle in potential well is ***quantized***.
- The integer $\boldsymbol{n}$ is called a ***quantum number***.
- The particular wave function $\psi_n(x)$ and corresponding to it energy E_n describe the ***quantum state*** of the particle.

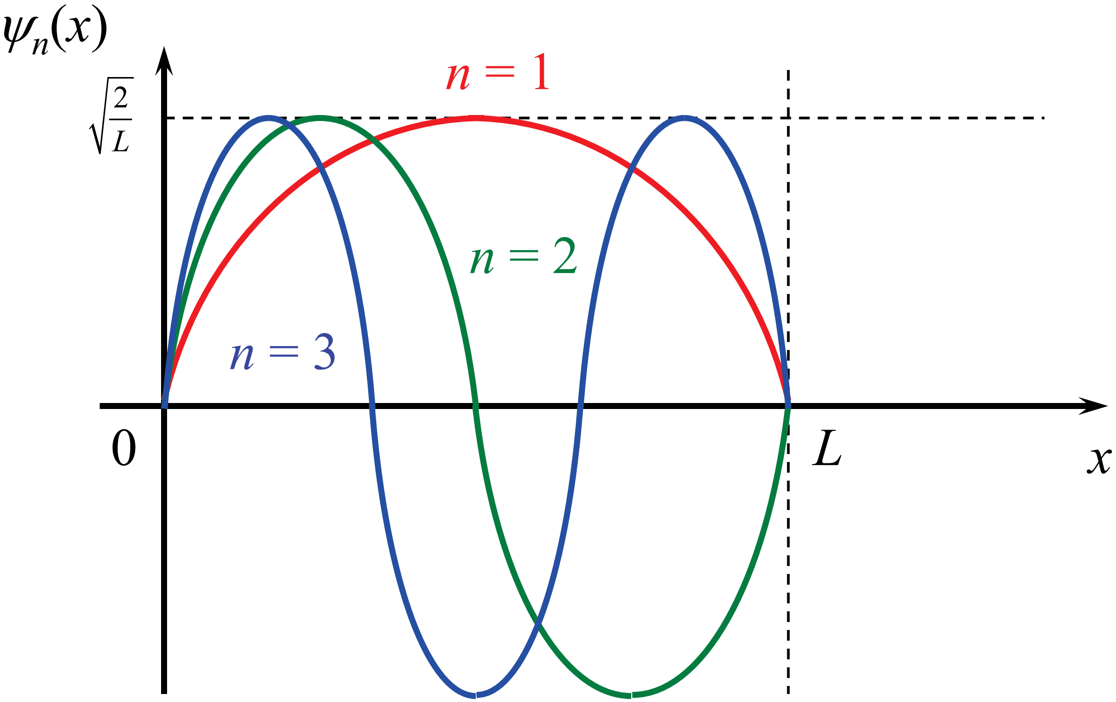
Particle in potential well – 10

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

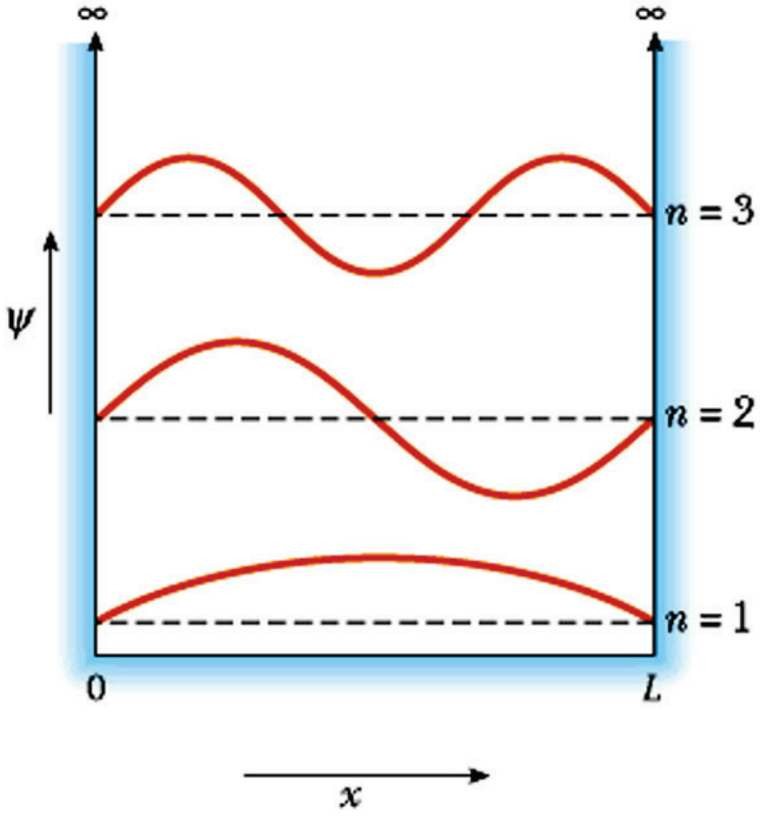


Particle in potential well – 11

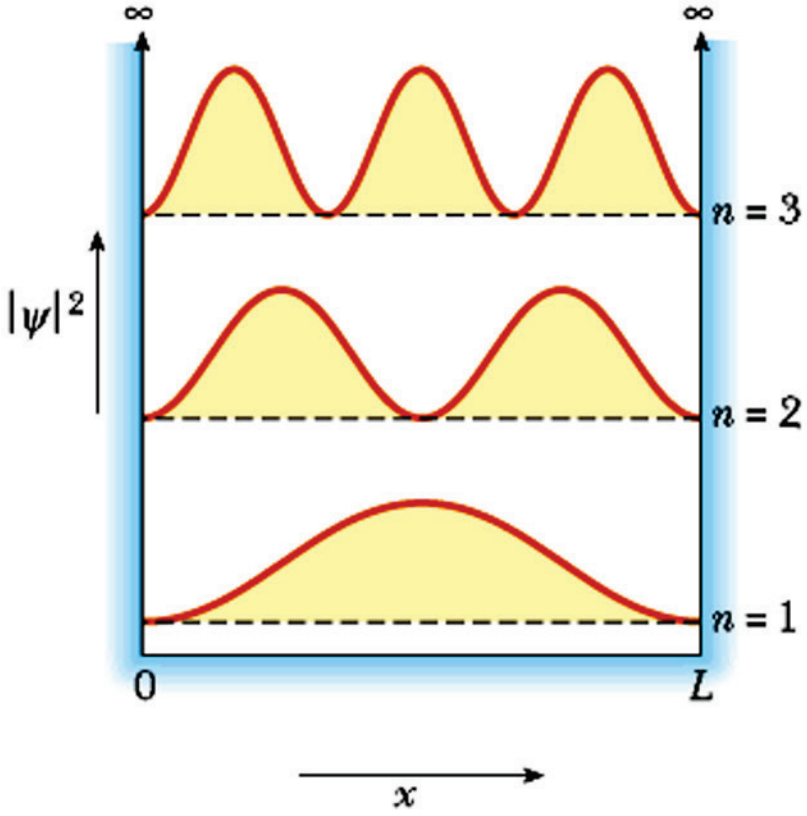
$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x}$$



Particle in potential well – 12

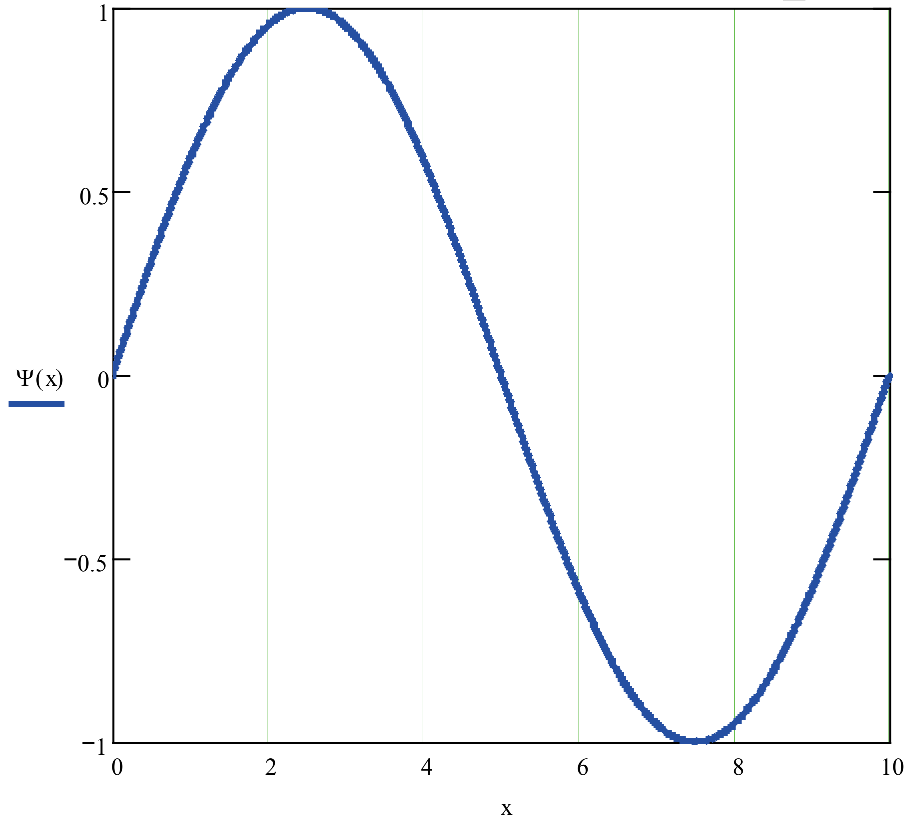


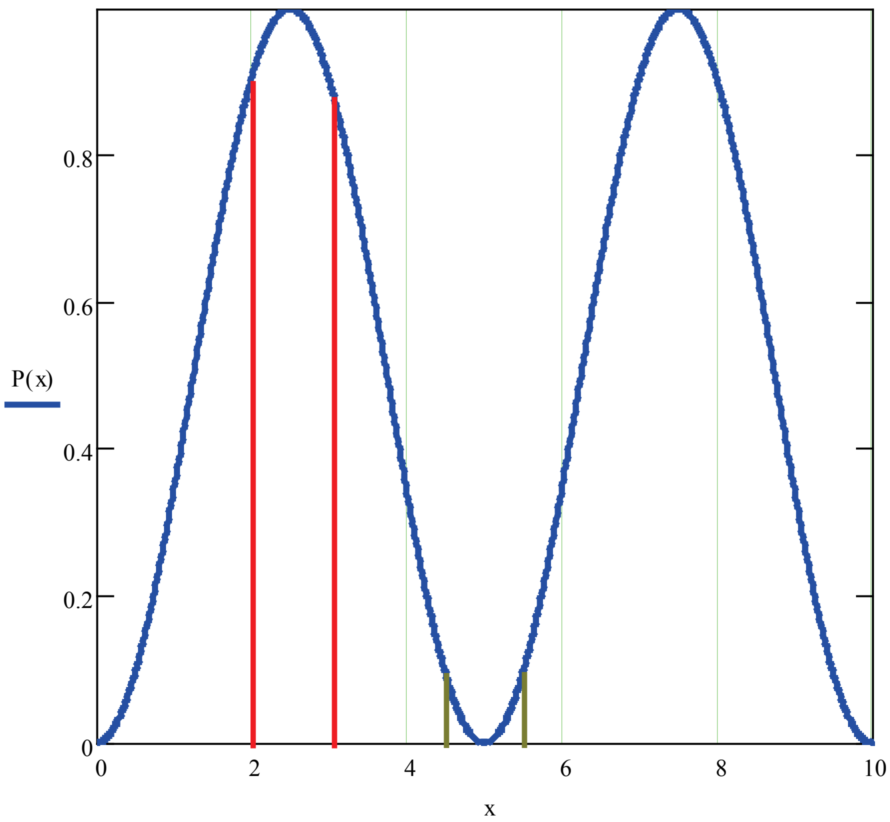
Wave function $\psi_n(x)$.



Probability of finding a particle at a position x inside the well is proportional to $|\psi_n(x)|^2$

Particle in potential well – 13





Probability to find electron in the interval from $x = 2$ to $x = 3$ is

$$\frac{\int_{2}^{3} \left|\Psi_{2}(x)\right|^{2} dx}{\int_{0}^{10} \left|\Psi_{2}(x)\right|^{2} dx} = 0.194 \approx 20\%$$

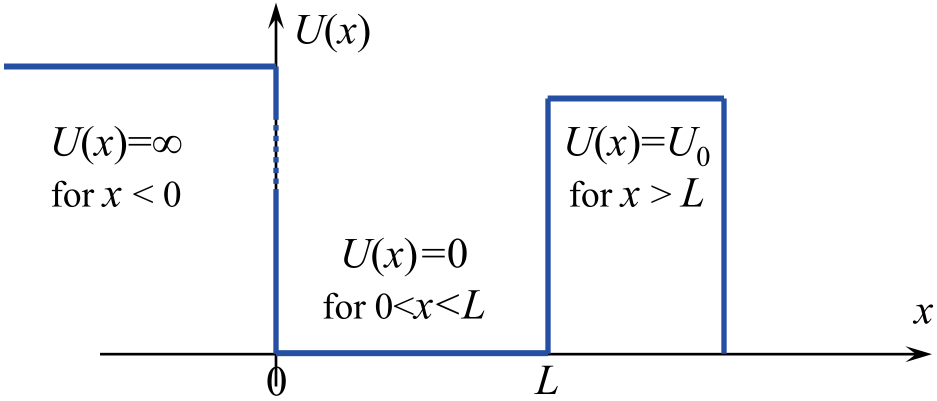
Probability to find electron in the interval from $x = 4.5$ to $x = 5.5$ is

$$\frac{\int_{4.5}^{5.5} \left|\Psi_{2}(x)\right|^{2} dx}{\int_{0}^{10} \left|\Psi_{2}(x)\right|^{2} dx} = 0.0000065 \approx 0.00065\%$$

Tunneling – 1

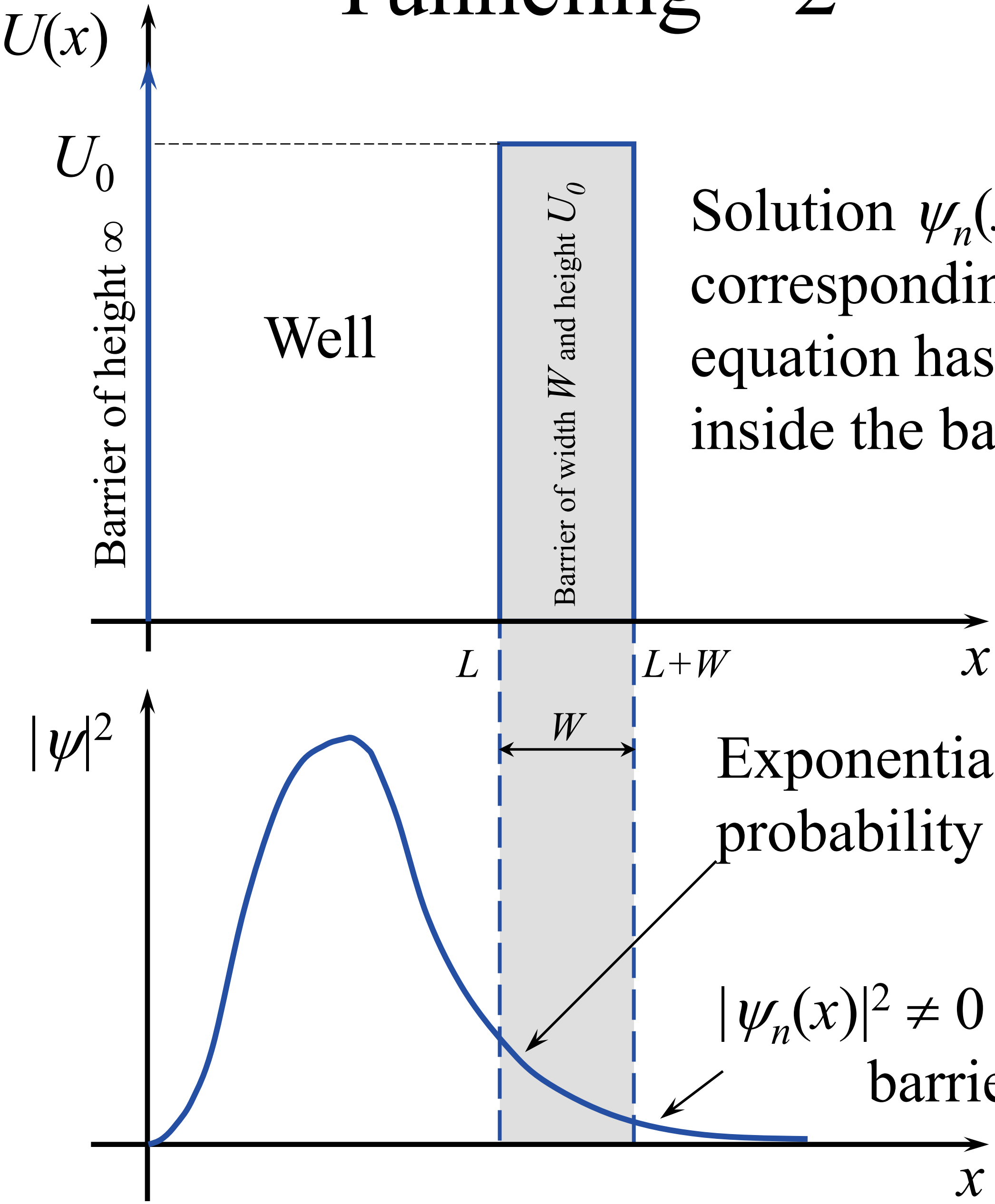
The wave functions are relatively easy to obtain for the potential well with infinite walls, since the boundary conditions force wave function ψ_n to be zero at the walls.
Such shape of potential well models quite unrealistic situation.

A ***finite potential well*** is more appropriate model of cases existing in real world.



In this case, process of quantum mechanical ***tunneling*** of an electron through a barrier of finite height and thickness may take place.

Tunneling – 2

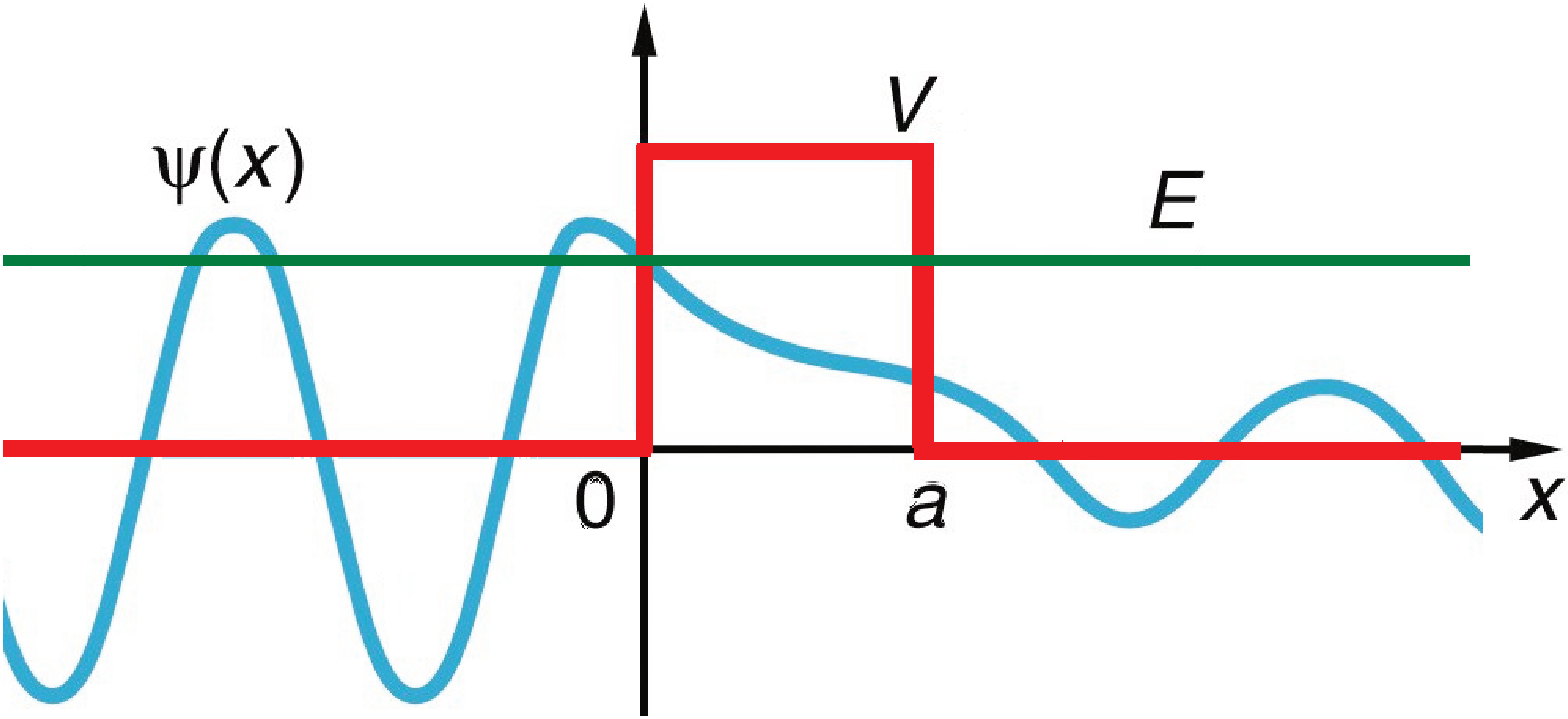


Solution $\psi_n(x)$ of corresponding Schrödinger equation has nonzero value inside the barrier and beyond it.

Exponential decrease of probability inside barrier

$|\psi_n(x)|^2 \neq 0$ beyond barrier

Tunneling – 3



Tunneling – 4

When the barrier width and height is not infinite, the boundary conditions do not force ψ to zero at the barrier. Instead, we must use the condition that ψ and its slope $d\psi/dx$ are continuous at each boundary of the barrier (postulate 1).

Thus ψ must have a ***nonzero*** value within the barrier and also on the other side.

Since ψ has a value to the right of the barrier, $\psi^*\psi$ exists there also, implying that there is ***some none-zero probability*** of finding the particle beyond the barrier.

The particle does not go ***over*** the barrier! – particle's total energy is less than the barrier height U_0.

The mechanism by which the particle "penetrates" the barrier is called ***tunneling***.

It is ***impossible*** to explain effect of tunneling using classical concept. Quantum mechanical tunneling is bound to the ***uncertainty principle***.

Tunneling is important only over very small dimensions, but it can be of great importance in the conduction of electrons in solid-state devices: p-n junctions, field-effect transistors.