Particle in a box

How boundary conditions and normalization determine the wave function?

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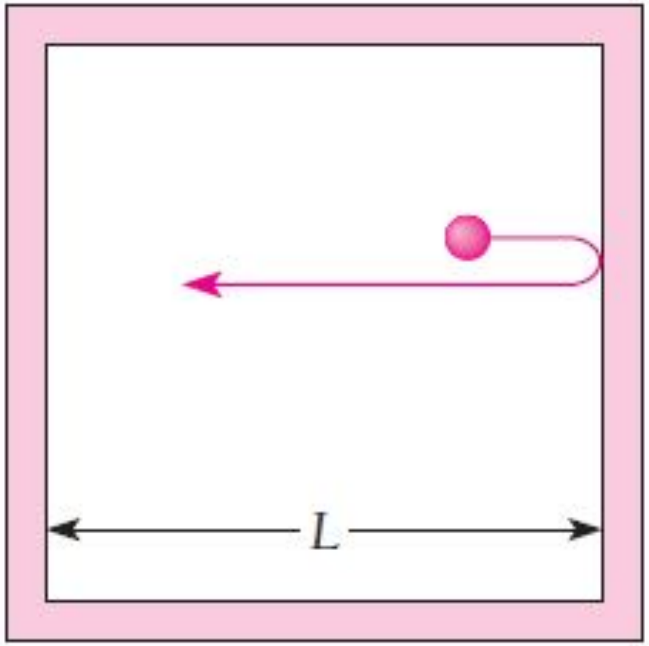
- The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely.

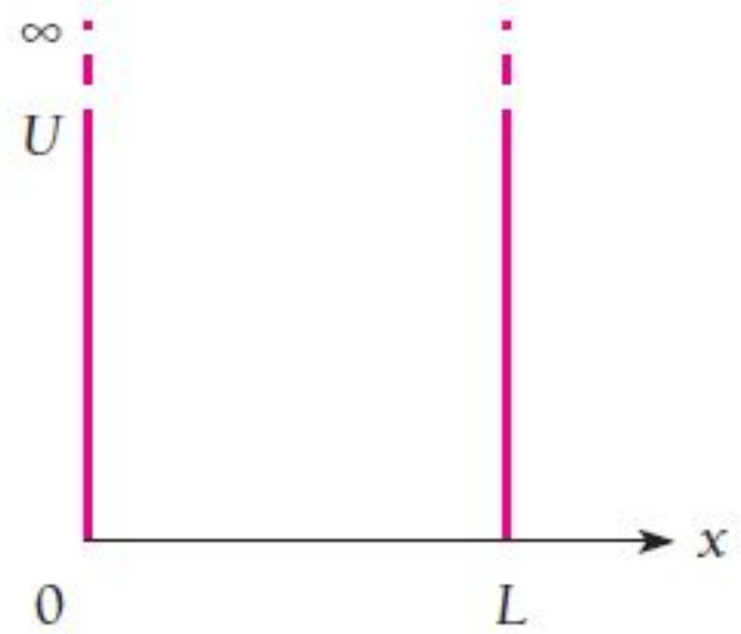
- The simplest case is that of a particle that bounces back and forth along a straight line between the walls of the box of width L.

- We shall assume that the walls of the box are infinitely hard, so the particle does not lose energy each time it strikes a wall, and that its velocity is sufficiently small so that we can ignore relativistic considerations.ok



Particle in a box with infinitely hard walls

- It is simplest quantum-mechanical problem.
- A particle of mass m is restricted to move along the x-direction between x=0 and x=L in a one-dim rigid box.



- The collision of particle with the walls is perfectly elastic. i.e. A particle does not loose energy when it collides to walls, so that its total energy stays constant.

- The potential energy U of the particle is infinite on both sides of the box, while U is a constant—say 0, inside the box.

$$U(x) = 0 \quad 0 < x < L$$

$$U(x) = \infty \quad x \leq 0$$
$$x \geq L$$

Boundary conditions

- Because the particle can not have a infinity amount of energy, it can not exist outside the box,

$$\psi(x) = 0 \;\; for \;\; x \leq 0, \\ x \geq L$$

What is ψ is within the box (0<x<L)?

Within the box, the Schrödinger Equation becomes:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \text{.....................}1$$

U=0 within the box

and its solution is:

$$\psi = A\sin\frac{\sqrt{2mE}}{\hbar}x + \mathrm{B}\cos\frac{\sqrt{2mE}}{\hbar}x \text{..............}2$$

which we can verify by substitution back into Eq.1.
A and B are constants, to be evaluated.

This solution is subject to the **boundary conditions** that, $\psi(x) = 0$ for x=0 and for x=L

At $x = 0$ $\psi(x) = 0$

$$A \sin \frac{\sqrt{2mE}}{\hbar} x + \mathrm{B} \cos \frac{\sqrt{2mE}}{\hbar} x = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

- Since $\cos 0^0 = 1$, the second term can not describe the particle because it does not vanish at x=0. Hence, we can conclude that, B=0
- Since $\sin 0^0 = 0$, the sine term always gives $\psi = 0$ at x=0, as required.

<u>At x=L</u>, $\psi(x) = 0$ only when:

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi \text{......................4} \qquad n=1,2,3\ldots$$

This result comes about because the sines of the angles π, 2π, 3π,…. are all 0

- It is clear that the energy of the particle can have only certain values, which are eigen values.

- These eigen values, constitutes the energy levels of the system, are found by solving Eq. 4) for E_n, which gives

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}} \quad \text{......................5} \qquad n=1,2,3\ldots$$

Each permitted energy is called an **energy level,** and the integer *n* that specifies an energy level E_n is called its **quantum number.**

The general conclusions of Equation 5:

1. A trapped particle cannot have an arbitrary energy, as a free particle can. Its confinement leads to restrictions on its wave function that allow the particle to have only certain specific energies which depends on the mass of the particle and on the details of how it is trapped.

2. A trapped particle cannot have zero energy. Since the de Broglie wavelength of the particle is $\lambda = h/mv$, a speed of $v = 0$ means an infinite wavelength. But there is no way to reconcile an infinite wavelength with a trapped particle, so such a particle must have at least some kinetic energy.

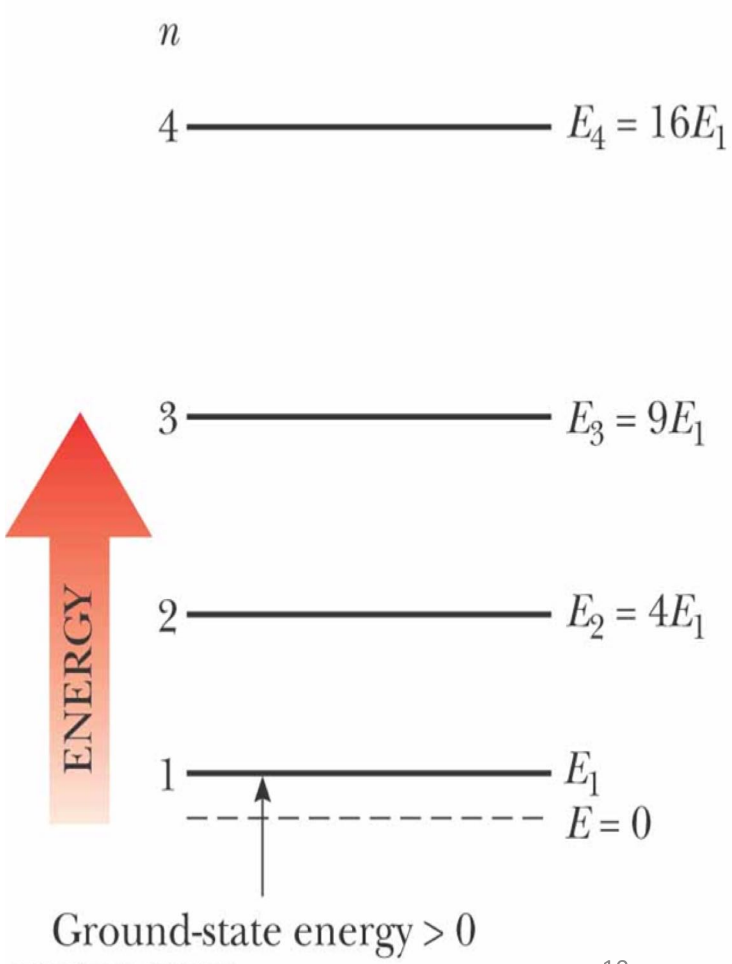
3. Because Planck's constant is so small—only 6.63x10^{-34} J.s—quantization of energy is noticeable only when *m* and *L* are also small.

Energy Level Diagram – Particle in a Box

The permitted energies for the particle in a box

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

- The lowest allowed energy, E_1 corresponds to the **ground state.**
- $E_n = n^2 E_1$ are called **excited states**
- $E = 0$ is not an allowed state as the particle can never be at rest.



Problem: An electron is in a box 0.10 nm across, which is the order of magnitude of atomic dimensions. Find its permitted energies.

Solution:

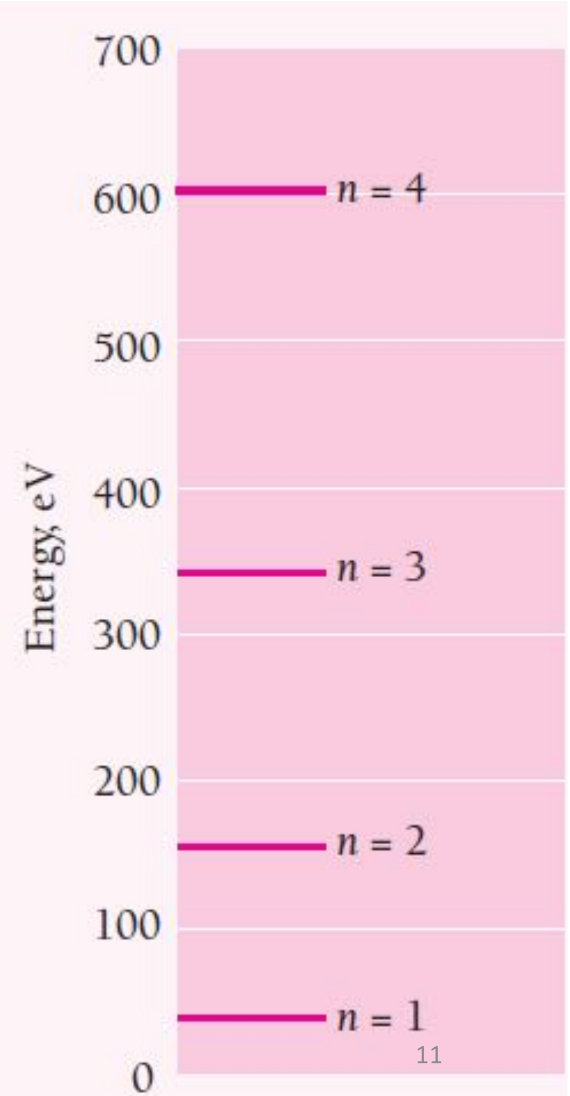
Here, m=9.1 x 10^{-31} kg and L = 0.10 nm = 1.0 x10^{-10} m, so that the permitted electron energies are:

$$E_n = \frac{(n^2)(6.63\times10^{-31}J.s)^2}{(8)(9.1\times10^{-31}\,kg)(1.0\times10^{-10}m)^2}$$

$$= 6.0\times10^{-18}n^2$$

$$= 38n^2\ eV$$

The minimum energy, the electron can have is 38 eV, corresponding to n =1. The sequence of energy levels continues with E_2 =152 eV, E_3 =342 eV, E_4 =608 eV, and so on.



Wave Functions of a particle in a box

The wave functions of a particle in a box whose energies are E_n are, from Eq. 5 with B=0,

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x$$

Substituting eq. 5 for E_n gives

$$\psi_n = A \sin \frac{n\pi x}{L} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

for the eigenfunctions corresponding to the energy eigenvalues, E_n.

These eigen functions meet all the requirements we discussed earlier such as ψ_n *are finite, single valued function of x; and* ψ_n *and* $d\psi_n/dx$ *are continuous.*

Furthermore, the integral of $|\psi|^2$ over all space is finite, as by integrating $|\psi|^2 dx$ from $x = 0$ to $x = L$.

$$\int_{-\infty}^{\infty} |\psi|^2 dx = \int_{o}^{L} |\psi|^2 dx$$

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

By trigonometric identity

$$sin^2\theta = \frac{1}{2}(1 - cos2\theta)$$

$$= \frac{A^2}{2}\left[\int_0^L dx - \int_0^L cos\left(\frac{2n\pi x}{L}\right) dx\right]$$

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

$$= A^2\left(\frac{L}{2}\right)$$

$|\psi_n|^2$ must be normalizable, that is

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

which gives,

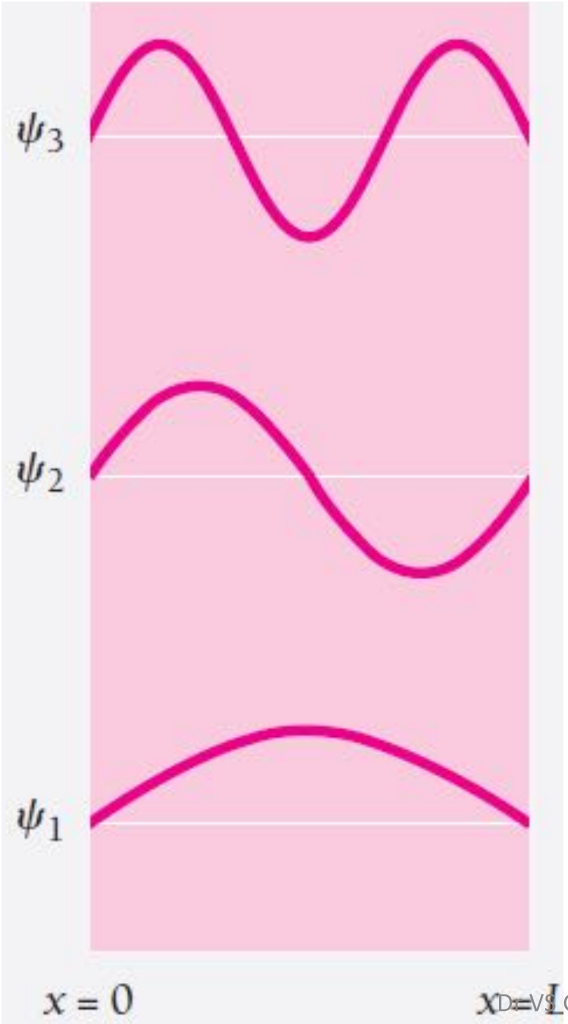
$$A^2\left(\frac{L}{2}\right) = 1$$

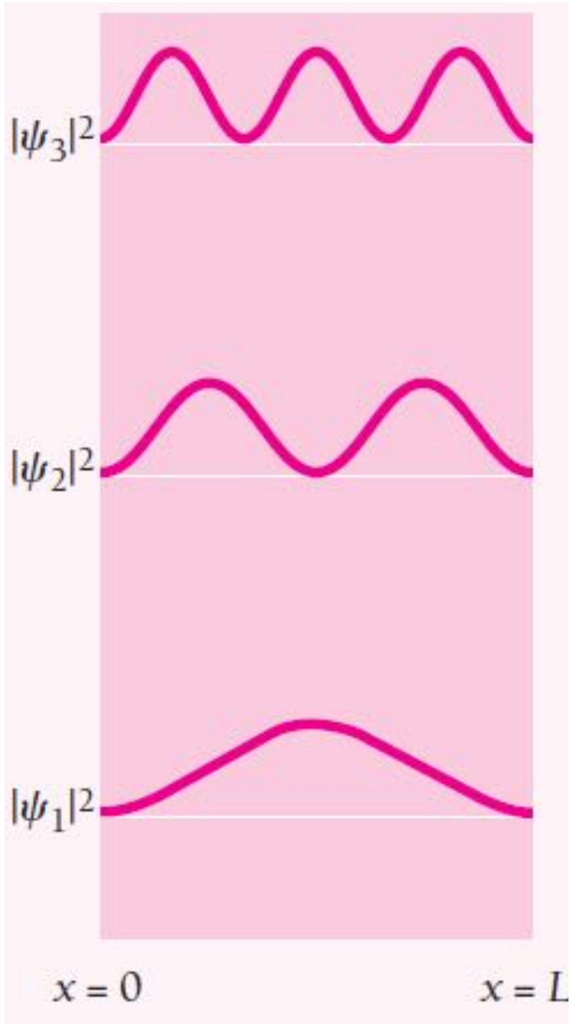
$$A = \sqrt{\frac{2}{L}}$$

Therefore, the normalized wave functions of the particle are:

$$\boxed{\psi_n = \sqrt{\frac{2}{L}} sin \frac{n\pi x}{L}}$$ n=1,2,3…

Wave functions and Probability densities of a particle confined in a box with infinitely hard walls





Problem: Find the probability that a particle trapped in a box L wide can be found between 0.45L and 0.55 L for the ground and first states.

Solution:

$$P_{x_1, x_2} = \int_{x_1}^{x_2} |\psi|^2 dx$$

$$= \frac{2}{L} \int_{x_1}^{x_2} sin^2 \left(\frac{n\pi x}{L}\right) dx$$

$$= \left[\frac{x}{L} - \left(\frac{1}{2n\pi}\right) sin \frac{2n\pi x}{L}\right]_{x_1}^{x_2}$$

Here x_1 =0.45L and x_2 =0.55L. For the ground state, which corresponds to n =1, we have,

$$P_{x_1, x_2} = 0.198 = 19.8 \, percent.$$

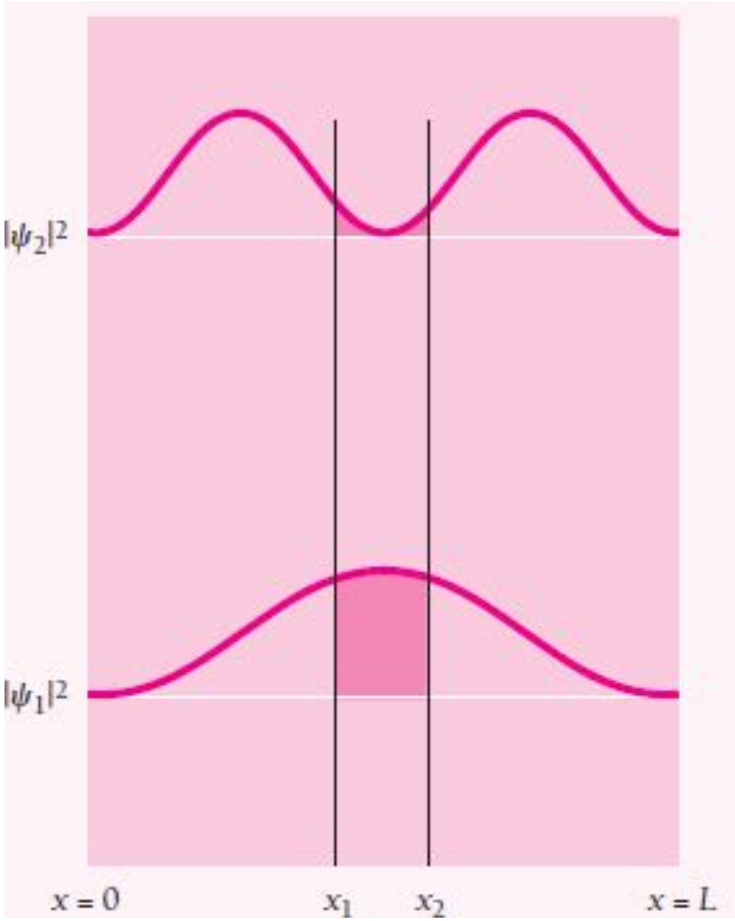
This is about twice the classical probability.

For the first excited state, which corresponds to n =2, we have

$$P_{x_1, x_2} = 0.0065 = 0.65\, percent$$

This low figure is consistent with the probability density of

$$|\psi|^2 = 0\ at\ x = 0.5L$$



The Probability of finding a particle in the box between x_1=0.45L and x_2=0.55L is equal to the area under the $|\psi|^2$ curves between these limits

Problem: Find the expectation value $\langle x \rangle$ of the position of a particle in a box L wide.

Solution:

The expectation value of x is $\langle x \rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx = \frac{2}{L}\int_0^L x\, sin^2\left(\frac{n\pi x}{L}\right) dx$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\, sin(2n\pi x/L)}{4n\pi/L} - \frac{cos(2n\pi x/L)}{8(n\pi/L)^2}\right]_0^L$$

Since $\sin n\pi = 0, \cos 2n\pi = 1, and \cos 0 = 1$, for all the values of n, the expectation value of x is

$$\langle x \rangle = \frac{2}{L}\left(\frac{L^2}{4}\right) = \frac{L}{2}$$

This means that the average position of the particle is the middle of the box

Problem: Find the momentum of a particle trapped in a one dimensional box.

Solution: The momentum operator can be written as,

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx$$

$$= \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi \, dx$$

The wave function associated to the particle trapped in a one dimensional box is given by

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

and $$\frac{d\psi}{dx} = \sqrt{\frac{2}{L}} \frac{n\pi}{L} sin \frac{n\pi x}{L}$$

After putting the values, we get

$$\langle p \rangle = \frac{\hbar}{i}\frac{2}{L}\frac{n\pi}{L}\int_0^L \sin\frac{n\pi x}{L}\ cos\frac{n\pi x}{L}dx$$

We note that $$\int \sin ax \cos ax dx = \frac{1}{2a}\sin^2 ax$$ where, a=nπ$/L$

Therefore, $$\langle p \rangle = \frac{\hbar}{iL}\left[sin^2\frac{n\pi x}{L}\ \right]_0^L = 0$$

Since, $Sin^2 0\ =\ \sin^2 n\pi = 0, \quad n = 1, 2, 3 \ldots\ldots$

The expectation value<p> of the particles momentum is zero

Momentum eigenvalues and eigenfunctions for a trapped particle

At first glance the previous conclusion regarding momentum of a trapped particle seems strange.

We know, $E = \frac{p^2}{2m}$, so we would anticipate that, the momentum eigenvalues for trapped particle:

$$p_n = \pm\sqrt{2mE_n} = \pm\frac{n\pi\hbar}{L} \qquad \text{......................}1$$

Momentum eigenvalues for trapped particle

The $\pm$ sign provides the explanation: The particle is moving back and forth, and so its *average* momentum for any value of *n* is

$$p_{avg} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

which is the expectation value

According to Eq. 1 there should be two momentum eigen functions for every energy eigen function, corresponding to the two possible directions of motion.

To find the eigenvalues of a quantum-mechanical operator, $\hat{p}$,we start from the eigenvalue equation:

$$\hat{p}\psi_n = p_n\psi_n \qquad \text{.......................2}$$

where each p_n is a real number.

Equation 2 holds only when the wave functions ψ_n are eigenfunctions of the momentum operator, $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$.

We can see at once that the energy eigenfunctions, $\psi_n = \sqrt{\frac{2}{L}} sin \frac{n\pi x}{L}$ are not also momentum eigenfunctions, because

$$\hat{p}\psi_n = \frac{\hbar}{i}\frac{d}{dx}\left(\sqrt{\frac{2}{L}} sin \frac{n\pi x}{L}\right) = \frac{\hbar}{i}\frac{n\pi}{L}\sqrt{\frac{2}{L}} cos \frac{n\pi x}{L} \neq p_n\psi_n$$

To find the correct momentum eigenfunctions, we note that

$$sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i}e^{i\theta} - \frac{1}{2i}e^{-i\theta}$$

Hence each energy eigenfunction can be expressed as a linear combination of the two wave functions, ψ_n^+ and ψ_n^- given as

$$\psi_n^+ = \frac{1}{2i}\sqrt{\frac{2}{L}}\,e^{in\pi x/L} \qquad \text{.......................3}$$

Momentum eigenfunctions

$$\psi_n^- = \frac{1}{2i}\sqrt{\frac{2}{L}}\,e^{-in\pi x/L} \qquad \text{.......................4}$$

Eq. 3 and eq. 4 represents momentum eigenfunctions for a trapped particle

Inserting the first of these wave functions in the eigenvalue equation, Eq. 2, we have

$$\hat{p}\psi_n^+ = p_n^+\psi_n^+$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi_n^+ = \frac{\hbar}{i}\frac{1}{2i}\sqrt{\frac{2}{L}}\frac{in\pi}{L}e^{in\pi x/L} = \frac{n\pi\hbar}{L}\psi_n^+ = p_n^+\psi_n^+$$

So that

$$p_n^+ = +\frac{n\pi\hbar}{L} \qquad \text{......................5}$$

Similarly the wave function ψ_n^- leads to the momentum eigenvalues

$$p_n^- = -\frac{n\pi\hbar}{L} \qquad \text{......................6}$$

Conclusion: ψ_n^+ and ψ_n^- are indeed the momentum eigenfunctions for a particle in a box, and Eq. 1 correctly states the corresponding momentum eigenvalues.

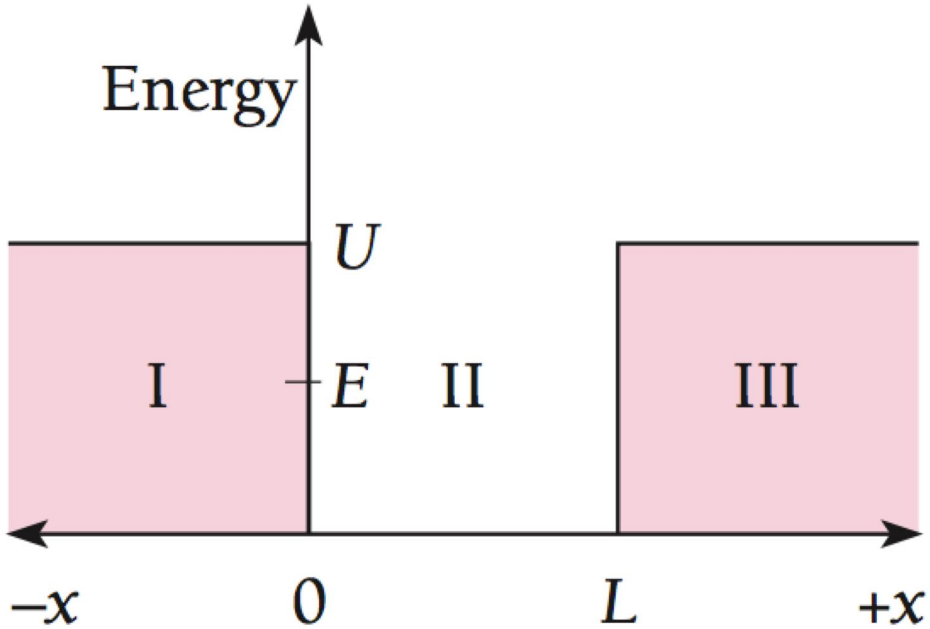
Potential energies are never infinite in the real world and the box with infinitely hard walls has no physical counterpart.

Potential wells with barriers of finite height certainly do exist.

What are the wave functions and energy levels of a particle trapped in such a well?

Finite potential well

Consider a potential well with square corners that is U high and L wide. Let the energy E of the trapped particle be less the height U of the barriers.



Outside the well

In regions I and III Schrodinger’s steady-state equation is

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E-U)\Psi = 0 \ldots\ldots\ldots\ldots\ldots(1)$$

which we can rewrite in the more convenient form

$$\frac{d^2\Psi}{dx^2} - a^2\Psi = 0 \ldots\ldots\ldots\ldots\ldots\ldots(2) \quad x < 0 \; and \; x > L$$

where $$a = \frac{\sqrt{2m(U-E)}}{\hbar}$$

The solutions to equation (2) are real exponentials:

$$\Psi_I = Ce^{ax} + De^{-ax}$$

$$\Psi_{III} = Fe^{ax} + Ge^{-ax}$$

Both Ψ_I and Ψ_{III} must be finite everywhere.

Since $e^{-ax} \to \infty \; as \; x \to -\infty$ & $e^{ax} \to \infty \; as \; x \to \infty$

the coefficients D and F must therefore be 0. Hence we have,

$$\Psi_I = Ce^{ax} \ldots\ldots\ldots\ldots(3)$$

$$\Psi_{III} = Ge^{-ax} \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

These **wave functions decrease exponentially inside the barriers** at the sides of the well.

Within the well: Schrodinger's equations is the same as

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}E\Psi = 0 \ldots\ldots\ldots\ldots(5)$$

and its solution is again

$$\Psi_{II} = A\sin\frac{\sqrt{2mE}}{\hbar}\,x + B\cos\frac{\sqrt{2mE}}{\hbar}\,x \ldots\ldots\ldots(6)$$

Boundary conditions:

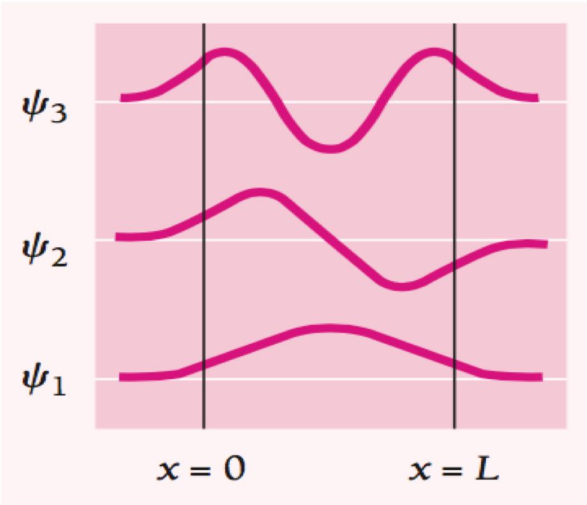
At $x = 0$: $\Psi_{II} = C$
At $x = L$: $\Psi_{II} = G$

so both the sine and cosine solutions of equation (6) are possible. For either solution, both Ψ and $\frac{d\Psi}{dx}$ must be continuous at $x = 0\ and\ x = L$:

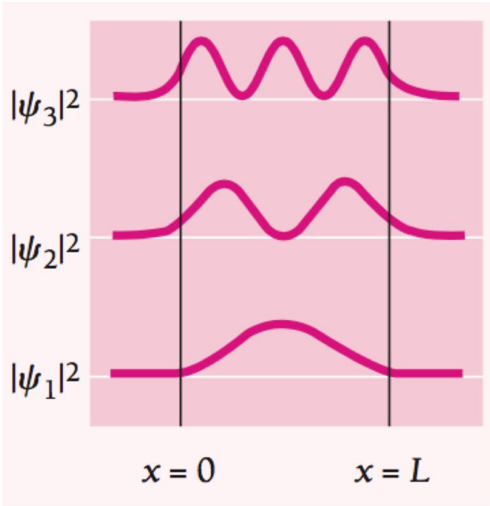
- When these boundary conditions are taken into account, the result is that **exact matching only occurs for certain specific values E_n** of the particle energy.

- Because the wavelengths that fit into the well are longer than for an infinite well of the same width, the corresponding particle momenta are lower (as $\lambda = \frac{h}{p}$). Hence **the energy levels E_n are lower for each n than they are for a particle in an infinite well**.

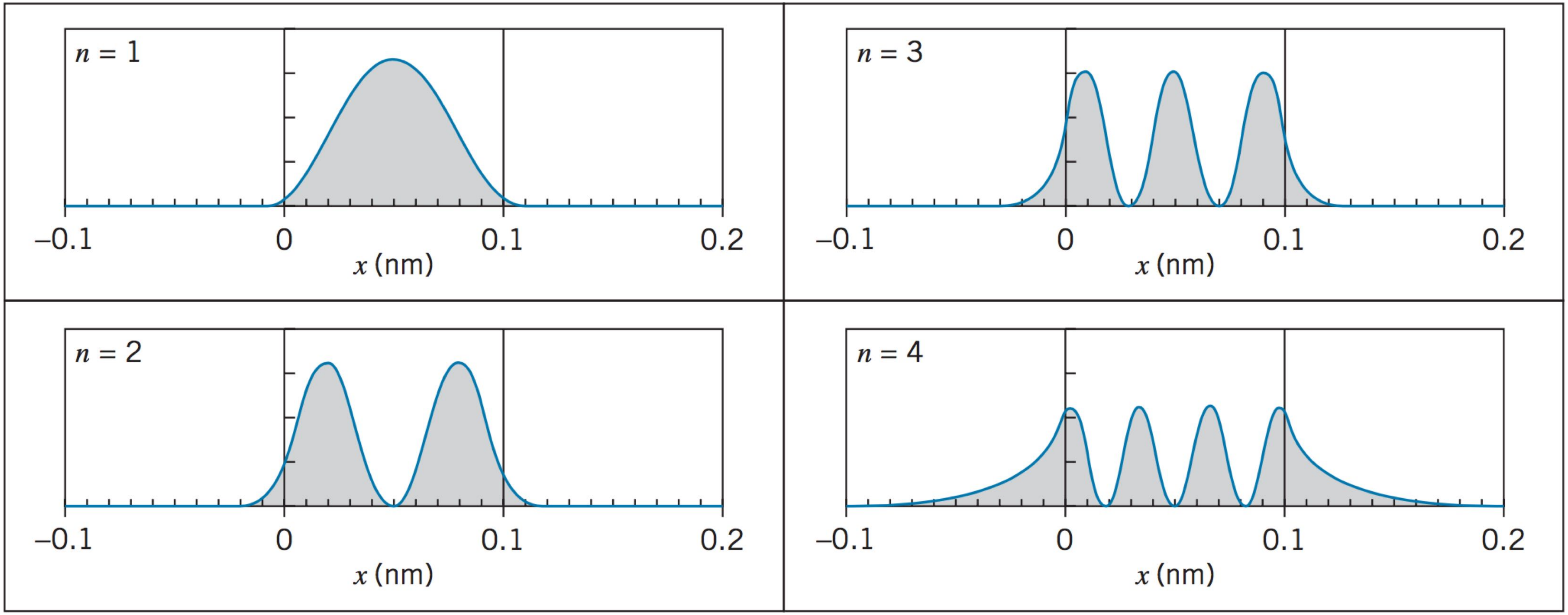
Wave functions

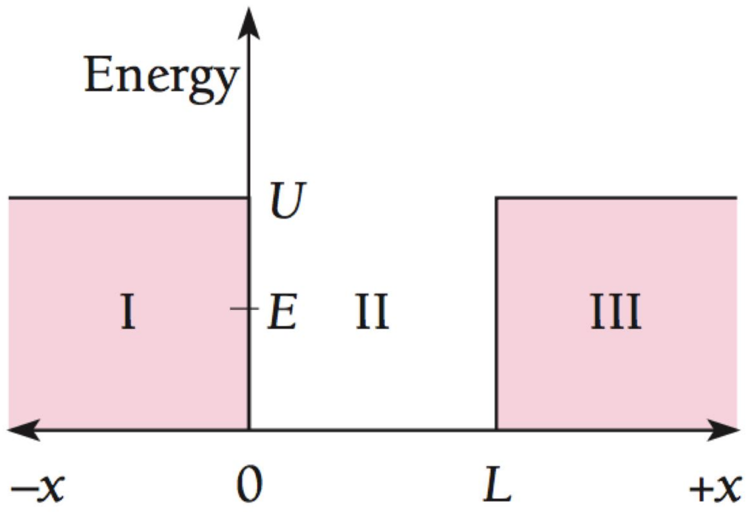


probability densities



The penetration distance increases as we go up in energy





According to **classical mechanics**, when the particle strikes the sides of the well, it bounces off without entering regions I and III.

In **quantum mechanics**, the particle also bounces back and forth, but now it has a certain **probability of penetrating into regions I and III even though E < U.**

"The wave function penetrates the walls, which lowers the energy levels"

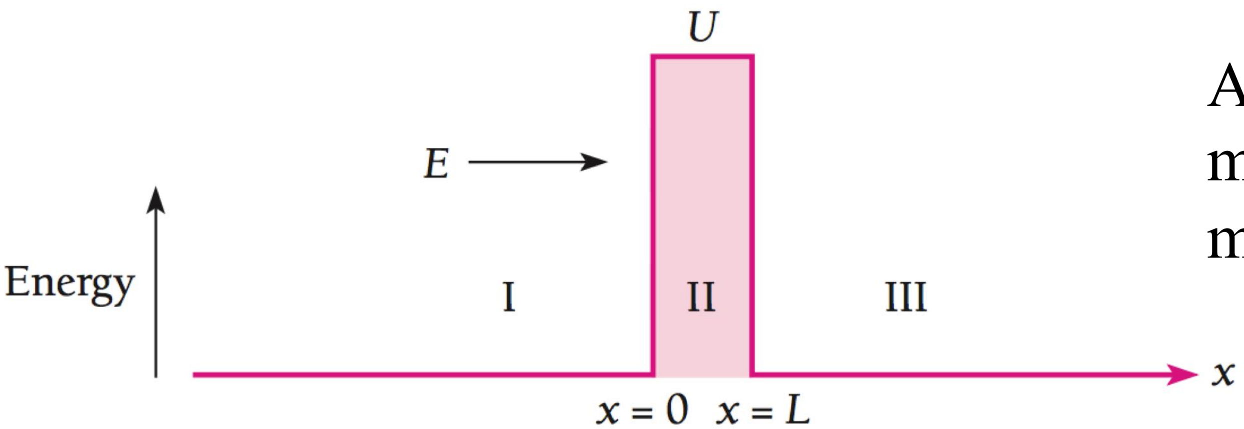
Even though the walls of the well are of finite height, they are assumed to be infinitely thick. As a result, the particle was trapped forever even though it could penetrate the walls.

What if the height & width of the barrier are finite?

Tunnel effect

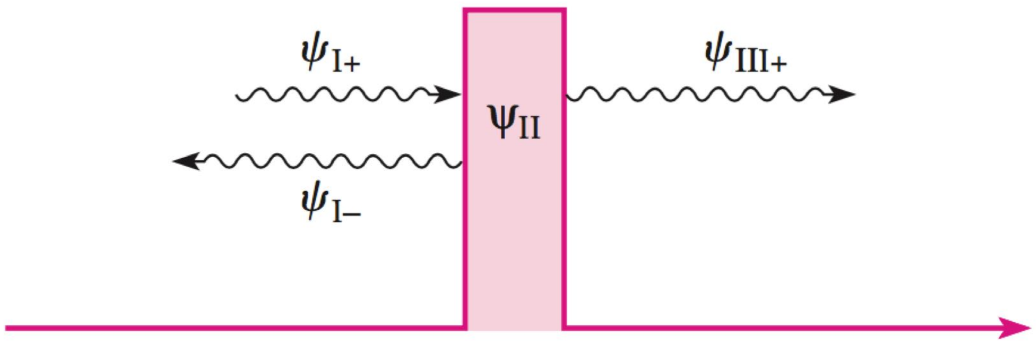
Let us consider a beam of identical particles all of which have the kinetic energy E. The beam is incident from the left on a potential barrier of height U and width L. The energy of every particle E < U again, but here the barrier has a finite width. On both sides of the barrier U=0, which means that no forces act on the particles there.

When a particle of energy E < U approaches a potential barrier….



According to classical mechanics, the particle must be reflected

According to quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted.



The particle has a finite chance of penetrating the barrier—This is called **barrier penetration or quantum mechanical tunneling**

<u>The following wavefunctions represent:</u>

Ψ_{I+}: incoming particles moving to the right
Ψ_{I-}: the reflected particles moving to the left
Ψ_{III}:transmitted particles moving to the right
Ψ_{II}: particles inside the barrier, some of which end up in region III while others return to region I.

Outside the barrier in regions I and III Schrodinger's equation for the particle takes the forms:

$$\frac{d^2\Psi_I}{dx^2} + \frac{2m}{\hbar^2} E\Psi_I = 0$$

$$\frac{d^2\Psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E\Psi_{III} = 0$$

The solutions to these equations that are appropriate here are

$$\Psi_I = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\Psi_{III} = Fe^{ik_1x} + Ge^{-ik_1x}$$

The wave number of de Broglie waves that represent the particles outside the barrier:

$$k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$$ "wave number outside barrier"

$$\Psi_{I+} = Ae^{ik_1 x}$$ "incoming wave"

The flux of particles that arrive at the barrier S = number of particles/sec

So, $$S = |\Psi_{I+}|^2 v_{I+}.$$

(v_{I+}: group velocity of the incoming waves = particle velocity)

At $x = 0$, the incident wave strikes the barrier and is partially reflected, with

$$\Psi_{I-} = Be^{-ik_1 x}$$ “reflected wave”

$$\Psi_I = \Psi_{I+} + \Psi_{I-}$$

On the far side of the barrier (x>L) there can only be a transmitted wave travelling in the +x direction at the velocity v_{III+} since region III contains nothing that could reflect the wave. Hence G=0:

$$\Psi_{III} = \Psi_{III+} = Fe^{ik_1 x}$$ “Transmitted wave”

In region II Schrodinger's equation for the particles is

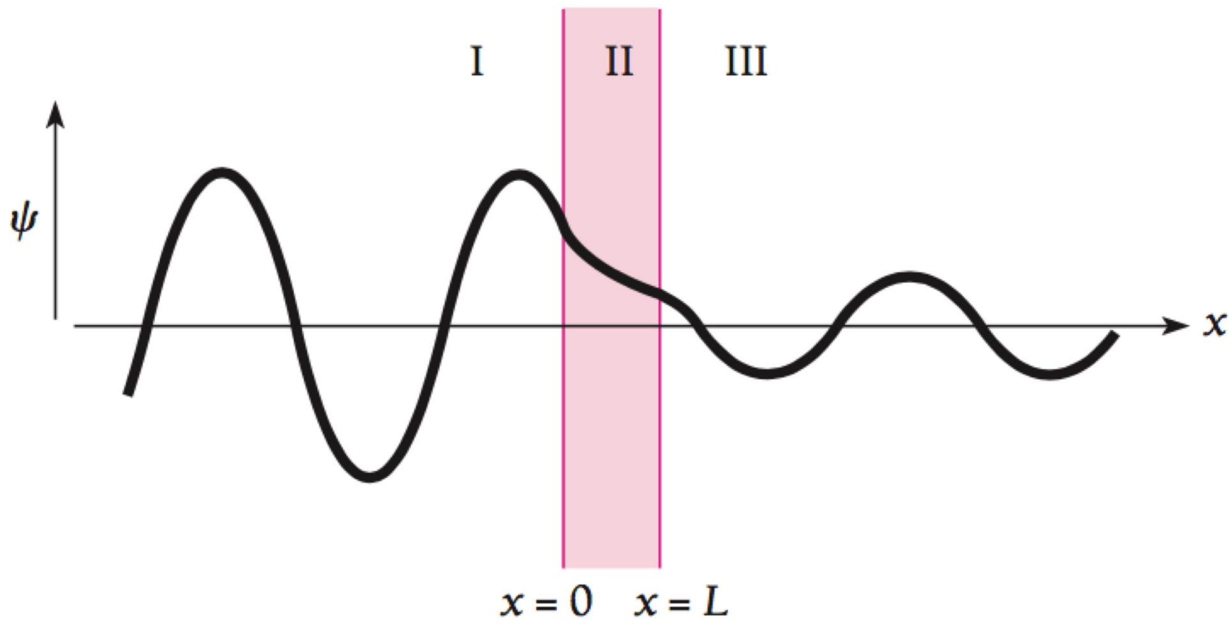
$$\frac{d^2\Psi_{II}}{dx^2} + \frac{2m}{\hbar^2}(E - U)\Psi_{II} = \frac{d^2\Psi_{II}}{dx^2} - \frac{2m}{\hbar^2}(U - E)\Psi_{II} = 0$$

Since U > E the solution is

$$\Psi_{II} = Ce^{-k_2x} + De^{k_2x}$$ "wave function inside the barrier"

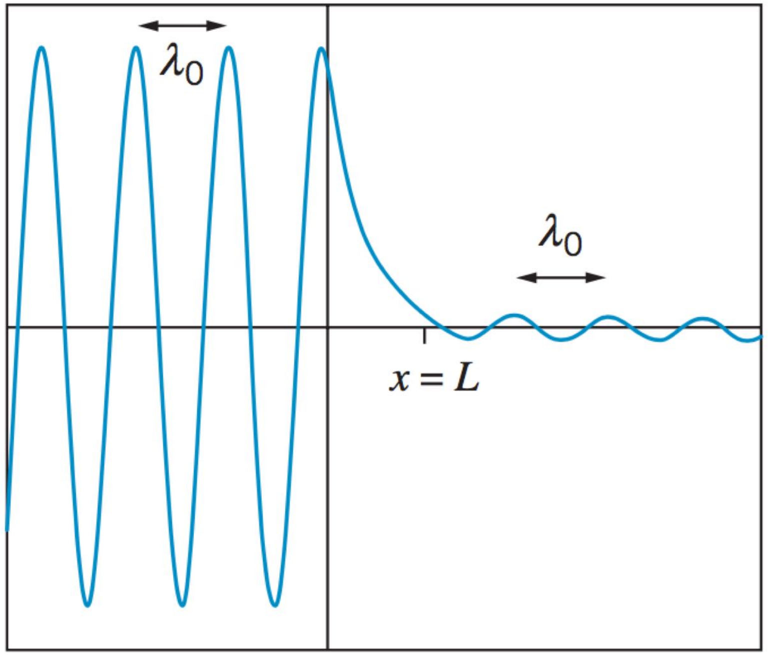
$$k_2 = \frac{\sqrt{2m(U-E)}}{\hbar}$$ "wave number inside the barrier"

Since the exponents are real quantities, ***Ψ_{II}* does not oscillate and therefore does not represent a moving particle.** However, the probability density $|\Psi_{II}|^2$ is not zero, so there is a finite probability of finding a particle within the barrier.



At each wall of the barrier, the wave functions inside and outside it must match up perfectly, which means that they must have the same values and slopes there.

Real part of the wave function



The wavelength λ_0 is the same on both sides of the barrier, but the amplitude beyond the barrier is much less than the original amplitude

Transmission Probability

The transmission probability T for a particle to pass through the barrier is equal to the fraction of the incident beam that succeed in tunneling through the barrier.

$$T = \frac{flux\ of\ particles\ that\ emerges\ from\ the\ barrier}{flux\ that\ arrives\ at\ it}$$

$$= \frac{|\Psi_{III+}|^2 v_{III+}}{|\Psi_{I+}|^2 v_{I+}} = \frac{FF^* v_{III+}}{AA^* v_{I+}}.$$

"Transmission probability"

Classically: T=0

(because a particle with E < U cannot exist inside the barrier)

Is transmission possible quantum mechanically?

Boundary conditions:

At $x = 0$: $\Psi_I = \Psi_{II}$; $\frac{d\Psi_I}{dx} = \frac{d\Psi_{II}}{dx}$

At $x = L$ $\Psi_{II} = \Psi_{III}$; $\frac{d\Psi_{II}}{dx} = \frac{d\Psi_{III}}{dx}$

Substituting for Ψ_I, Ψ_{II} and Ψ_{III},

$$A + B = C + D$$

$$ik_1 A - ik_1 B = -k_2 C + k_2 D$$

$$Ce^{-k_2 L} + De^{k_2 L} = Fe^{ik_1 L}$$

$$-k_2 Ce^{-k_2 L} + k_2 De^{k_2 L} = ik_1 Fe^{ik_1 L}$$

Solving the above equations for A/F and applying the following approximations:

(i)If potential barrier U is high relative to E, then : $k_2/k_1 > k_1/k_2$

(ii) If the barrier is wide enough, then : $k_2 L \gg 1$

$$\frac{A}{F} = \left(\frac{1}{2} + \frac{ik_2}{4k_1}\right) e^{(ik_1+k_2)L}$$

Substituting A/F and its conjugate $(A/F)^*$, $\quad T = \left(\frac{AA^*}{FF^*}\right)^{-1}$

Approximate Transmission probability $\quad \boldsymbol{T = e^{-2k_2L}}$

"A particle without the energy to pass over a potential barrier may still tunnel through it"

Conclusion:

- ✓ The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it.

- ✓ The higher the barrier & the wider it is, the less chance that the particle can get through.

Problem: Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50nm wide. (a) Find their respective transmission probabilities. (b) How are these affected if the barrier is doubled in width?

Solution:

Given : L = 0.5 nm=5.0x $10^{-10}m$, U= 10.0 eV

(a) For the 1.0 eV electrons, the approximate transmission probability is

$$T_1 = e^{-2k_2L}$$

$$k_2 = \frac{\sqrt{2m(U-E)}}{\hbar}$$

$$= \frac{\sqrt{2\times 9.1\times 10^{-31}(10-1)\times 1.602\times 10^{-19}}}{1.054\times 10^{-34}}$$

$$= \frac{1.6198999\times 10^{-24}kg.J}{1.054\times 10^{-34}\ \mathrm{J\ s}} = 1.5369\times 10^{10}m$$

$$\boldsymbol{T_1 = e^{-2k_2L} = e^{-16} = 1.1\times 10^{-7}}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average.

For the 2.0 eV electrons a similar calculation gives

$$T_2 = 2.4\times10^{-7}$$ (twice as likely to tunnel through the barrier)

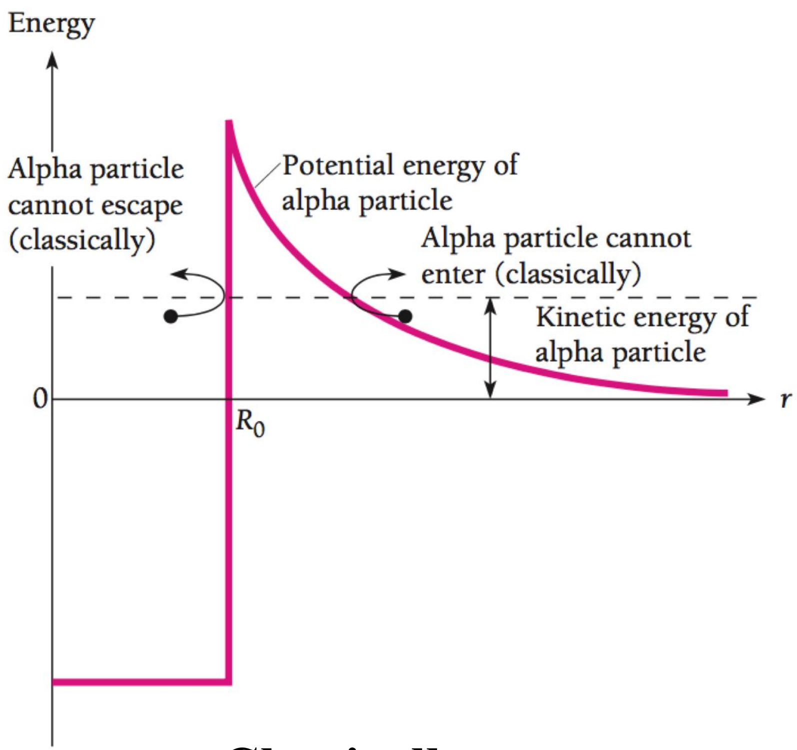
(b) If the barrier is double in width to 1.0 nm, the transmission probabilities become:

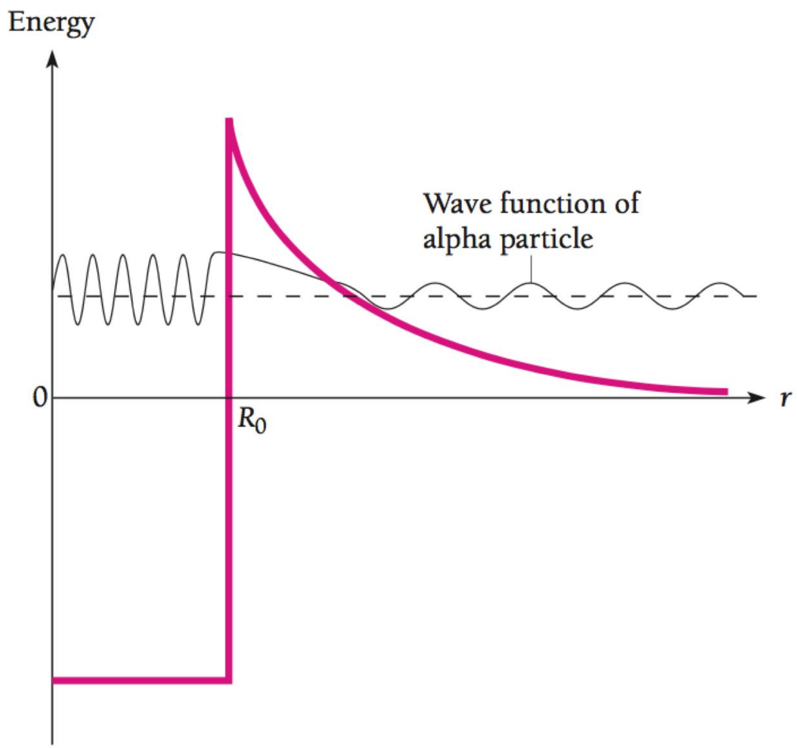
$$T_1' = 1.3\times10^{-14}, \qquad T_2' = 5.1\times10^{-14}$$

Evidently T is more sensitive to the width of the barrier than to the particle energy here.

Example of Tunneling: Alpha Decay

Kinetic energy of alpha particle < height of the potential barrier





Classically

Alpha particle cannot enter or leave the nucleus

Quantum mechanically

Alpha particle can tunnel through the barrier

Harmonic Oscillator

Its energy levels are evenly spaced

- Another situation that can be analyzed using the Schrodinger equation is the **one-dimensional simple harmonic oscillator.**
- **Harmonic oscillation or motion** takes place when a system of some kind vibrates about an equilibrium configuration.
- **The condition for harmonic oscillation** is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed.
- The inertia of the masses involved causes them to overshoot equilibrium, and the system oscillates indefinitely if no energy is lost.

- In the simple harmonic motion, an object of mass *m* attached to a spring of force constant *k*.

- According to Hooks law, the spring exerts a restoring force, F, on the object as

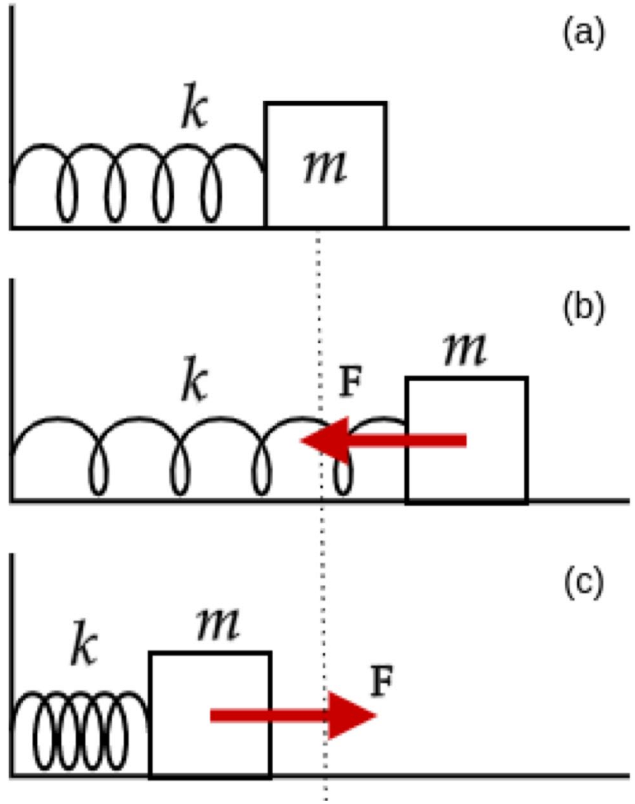
$$F = -kx \ldots\ldots\ldots\ldots\ldots 1$$

where x is the displacement from its equilibrium position.

- Acc. to second law of motion,

$$F = ma$$

$$or, \; F = m\, d^2x/dt^2 \ldots\ldots\ldots\ldots\ldots 2$$



After combining eq.1 and 2, we have,

$$-kx = m\frac{d^2x}{dt^2}$$

or,

$$\boldsymbol{m\frac{d^2x}{dt^2} + \frac{k}{m}x = 0} \quad \ldots\ldots\ldots\ldots 3$$

Harmonic oscillator

This is the differential equation of a harmonic oscillator classically.

The solution of eq.3 can be written as.

$$x = A\cos(2\pi\nu t + \phi) \quad ....4$$

where, $$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad ....5$$

- This is the *frequency of the harmonic oscillators* and A is their *amplitude.*
- ϕ is the *phase angle* which depends upon what *x* is at the time t=0 and on direction of motion then.
- All oscillations are simple harmonic in character when their amplitudes are sufficiently small.

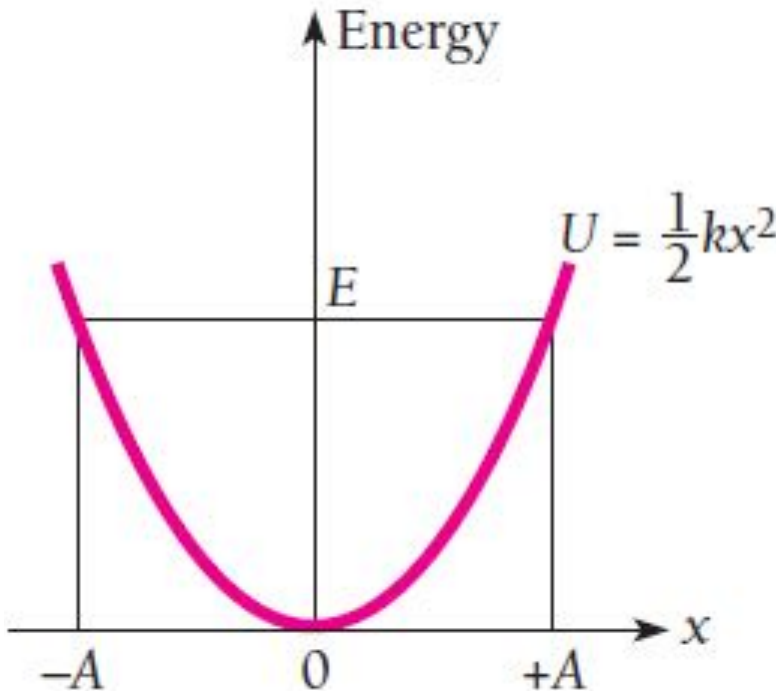
The potential energy of a harmonic oscillator

The potential-energy function $U(x)$ that corresponds to a Hooke's law force can be found by calculating the work needed to bring a particle from x=0 to x =x against such a force:

$$U(x) = -\int_0^x F(x)dx = k\int_0^x x\,dx = \frac{1}{2}kx^2$$

...............6

The potential energy of a harmonic oscillator is proportional to x^2 , where x is the displacement from the equilibrium position.



The curve of $U(x)$ versus x is a parabola.

If the energy of the oscillator is E, the particle vibrates back and forth between x=+A and x=-A, where E and A are related by

$$E = \frac{1}{2}kA^2$$

The amplitude A of the motion is determined by the total energy E of the oscillator, which classically can have any value.

Before further calculation, we can anticipate **three quantum mechanical modifications** to this classical picture:

1. The allowed energies will not form a continuous spectrum but a discrete spectrum of certain specific values only.

2. The lowest allowed energy will not be E=0, but will be some definite minimum energy $E=E_0$

3. There will be a certain probability that particle can penetrate the potential well. It is in and go beyond limits of $+A$ and $-A$.

The *Schrödinger Equation* for the harmonic oscillators having $U(x) = \frac{1}{2}kx^2$ is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \qquad \ldots\ldots\ldots\ldots\ldots 7$$

For simplicity , we introduce the dimensionless quantities y and α such that

$$y = \left(\frac{1}{\hbar}\sqrt{km}\right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}}\,x \qquad \ldots\ldots\ldots\ldots\ldots 8$$

$$\alpha = \frac{2E}{\hbar}\sqrt{\frac{m}{k}} = \frac{2E}{h\nu} \qquad \ldots\ldots\ldots\ldots\ldots 9$$

where ν is the classical frequency of the oscillation given by Eq. 5.

In making these substitutions, what we have done is change the units in which x and E are expressed from meters and joules, respectively, to dimensionless units.

In terms of y and α, Schrödinger's equation becomes,

$$\frac{d^2\psi}{dx^2} + (\alpha - y^2)\psi = 0 \qquad \text{...............10}$$

The solutions to this equation that are acceptable here are limited by the condition that $\psi \to 0$ as $y \to \infty$ in order that

$$\int_{-\infty}^{\infty} |\psi|^2 \, dy = 1$$

Otherwise the wave function cannot represent an actual particle.

The mathematical properties of Eq. 10 are such that this condition will be fulfilled only when,

$$\alpha = 2n + 1$$ where, n=0,1,2,3…

Since $\alpha=2E/h\nu$ acc. to eq. 9, the energy levels of a harmonic oscillators whose classical frequency of oscillation ν is are given by the formula

$$E_n = \left(n + \frac{1}{2}\right) h\nu \qquad \ldots\ldots\ldots\ldots\ldots 11$$

Energy levels of harmonic oscillator

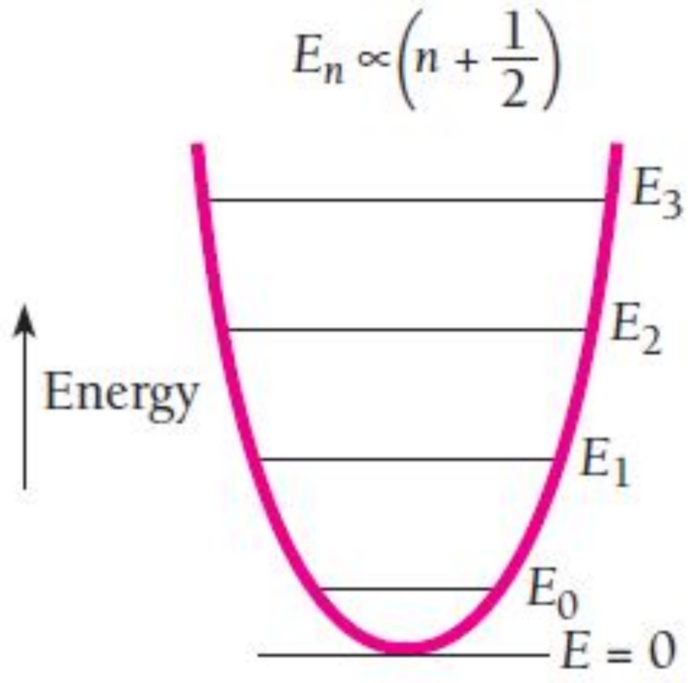
The energy of a harmonic oscillator is thus quantized in steps of hν.

When n=0,

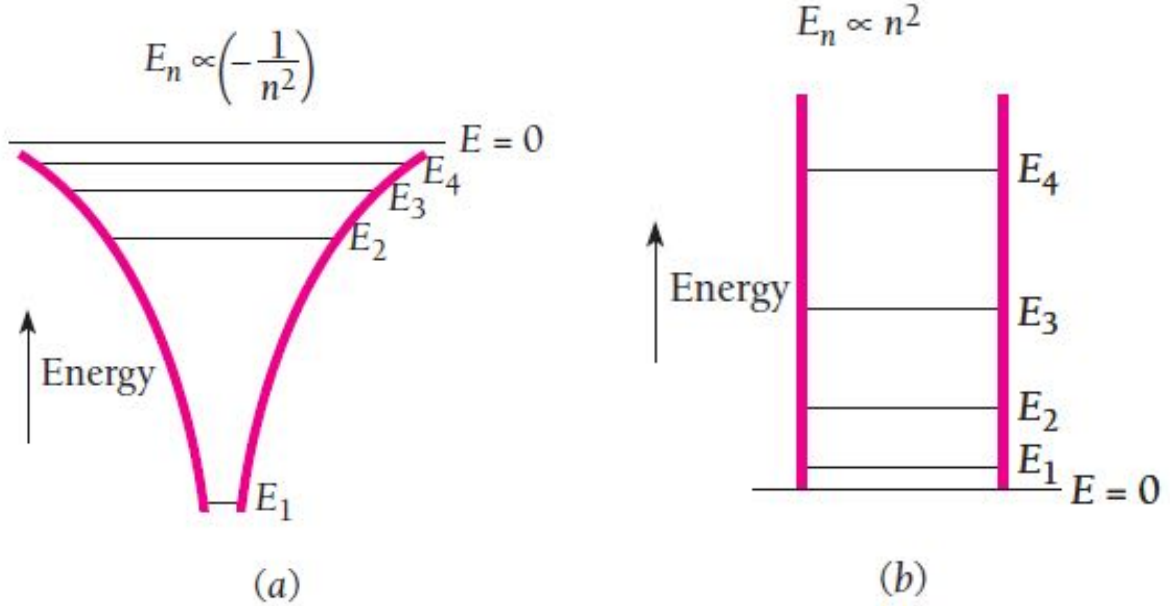
$$E_0 = \frac{1}{2} h\nu \qquad \ldots\ldots\ldots\ldots\ldots 12$$

Zero-point energy

which is the lowest value the energy of the oscillator can have. This value is called the **zero-point energy** because a harmonic oscillator in equilibrium with its surroundings would approach an energy of $E = E_0$ and not $E= 0$ as the temperature approaches 0 K.



Energies levels of a harmonic Oscillators



Potential wells and energy levels of (*a*) a hydrogen atom, (*b*) a particle in a box, and (*c*) a harmonic oscillator.

The spacing of the energy levels is constant only for the harmonic oscillator.

Wave functions

- For each choice of parameter α_n there is a different wave function Ψ_n.

- Each function consists of a polynomial H_n(y) (called a **Hermite polynomial**)

in either odd or even powers of y, the exponential factor $e^{-y^2/2}$, and a numerical coefficient which is needed for Ψ_n to meet

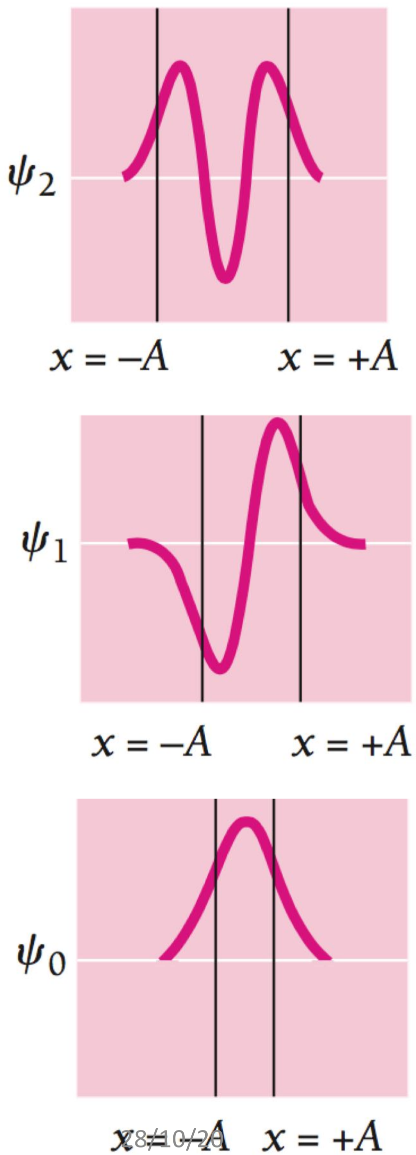
$$\int_{-\infty}^{\infty} |\Psi_n|^2 \, dy = 1, \quad n = 0, 1, 2, \ldots.$$ (**normalization condition)**

The general formula for the $n^{\,th}$ wave function is

$$\Psi_n = \left(\frac{2mv}{\hbar}\right)^{1/4} (2^n \, n!)^{-1/2} \, H_n(y) e^{-y^2/2}$$ **"Harmonic oscillator"**

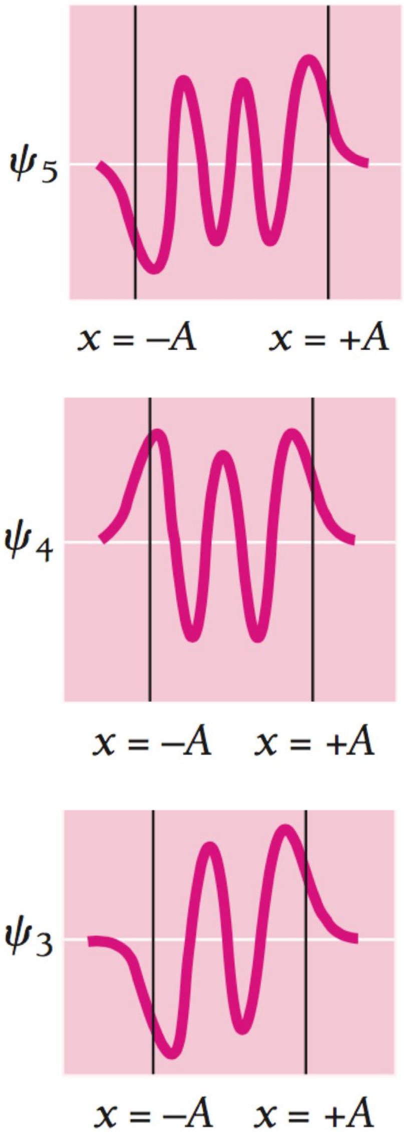
The first six Hermite polynomials $H_n(y)$

n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}h\nu$
1	$2y$	3	$\frac{3}{2}h\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}h\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}h\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}h\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}h\nu$



<u>The first six harmonic oscillator wave functions.</u>

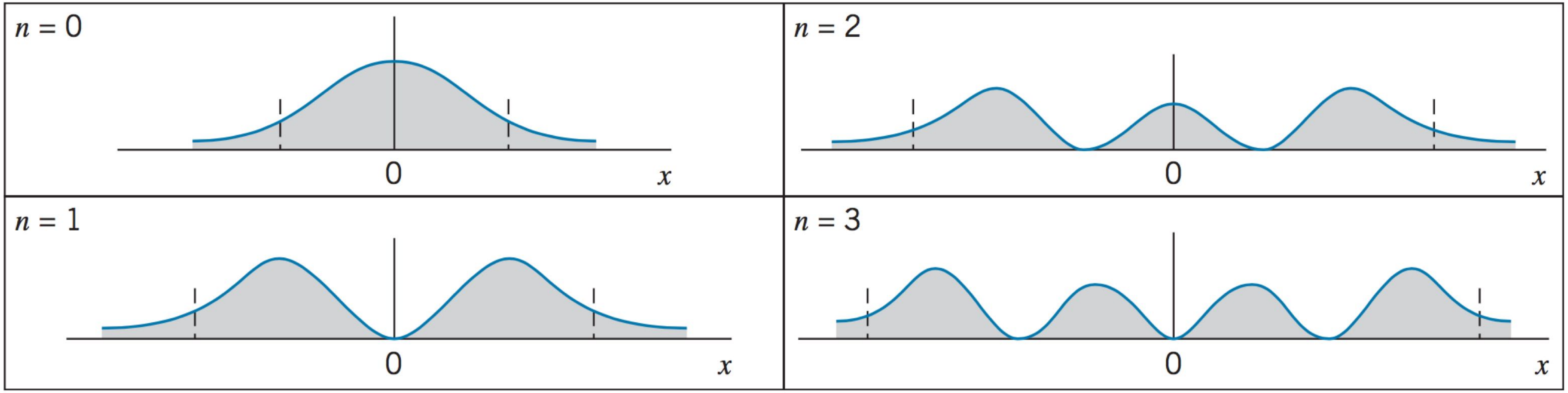
The vertical lines show the limits –A and +A between which a classical oscillator with the same energy would vibrate.



The first six harmonic oscillator wave functions.

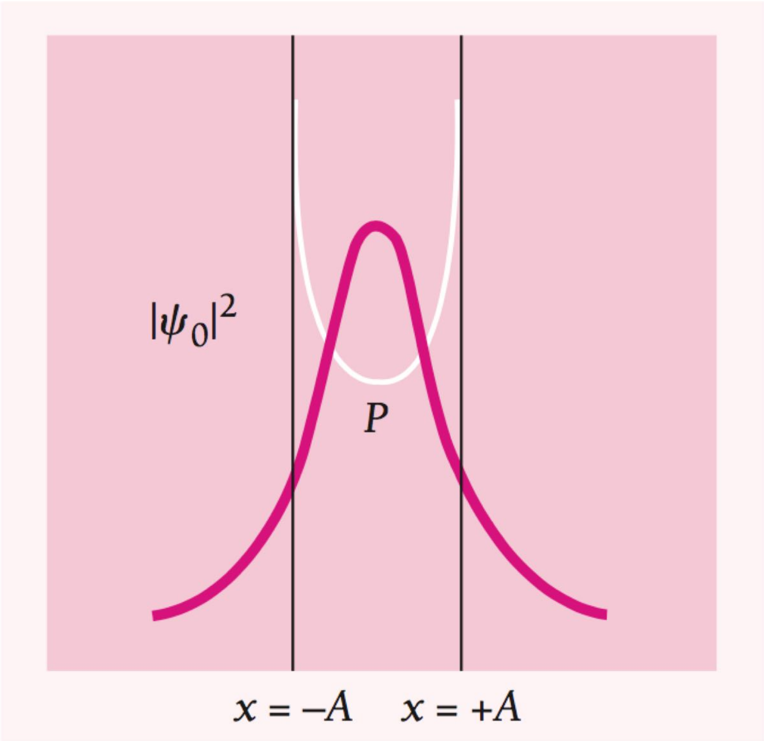
- For every energy level, the range to which a particle oscillating classically with the same total energy E_n would be confined is indicated.
- Evidently the particle is able to penetrate into classically forbidden regions, with an exponentially decreasing probability.

Probability densities for the simple harmonic oscillator

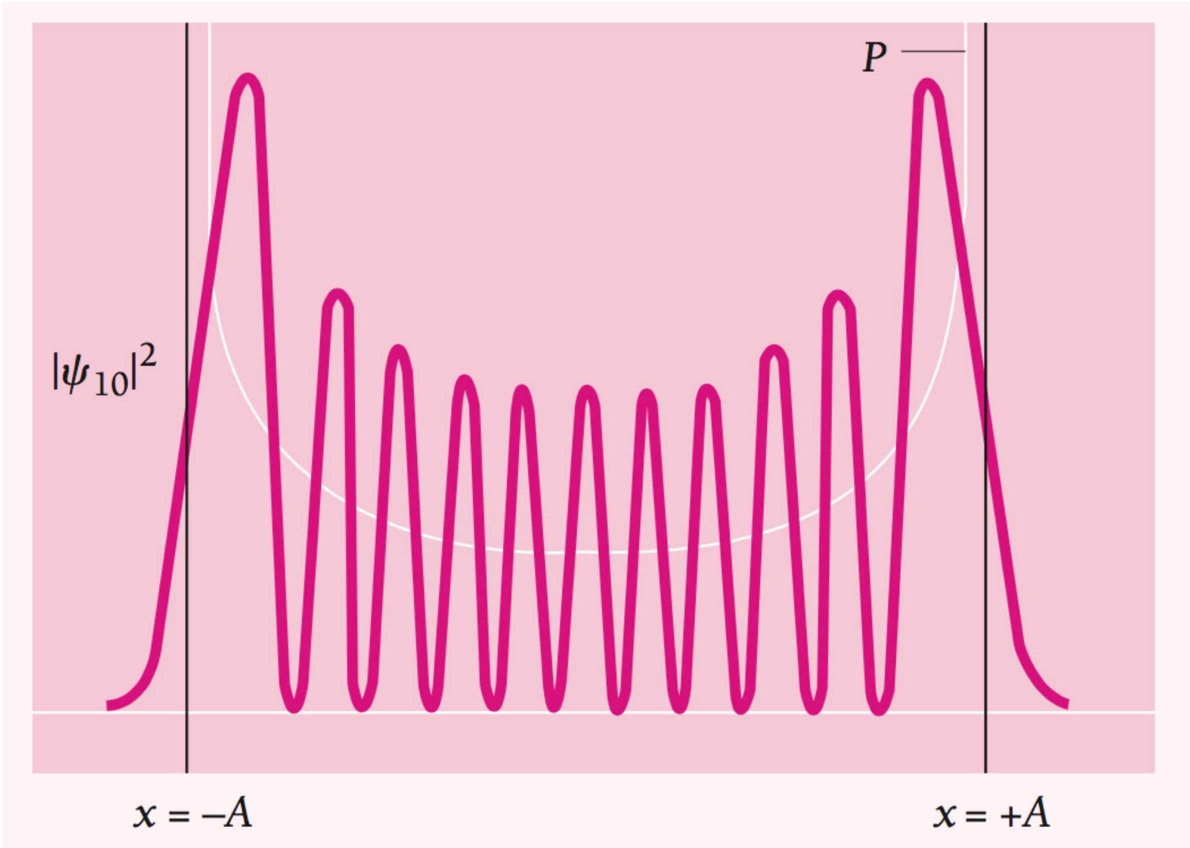


The distance between the classical turning points (marked by the short vertical lines) increases with energy.

Probability densities of a quantum-mechanical oscillator (pink) and that of a classical HO with the same energies (white)



$n = 0$



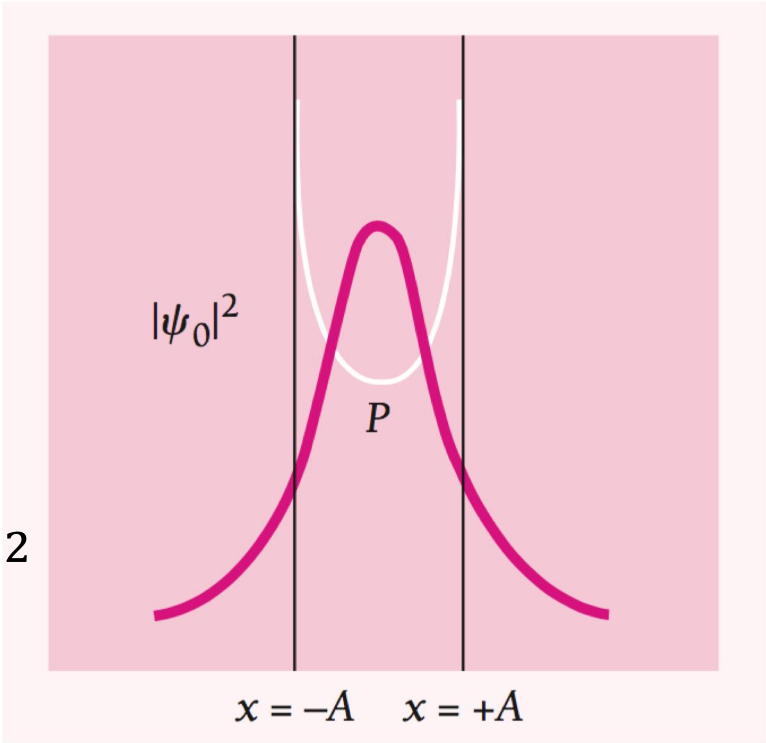
$n = 10$

For classical oscillator:

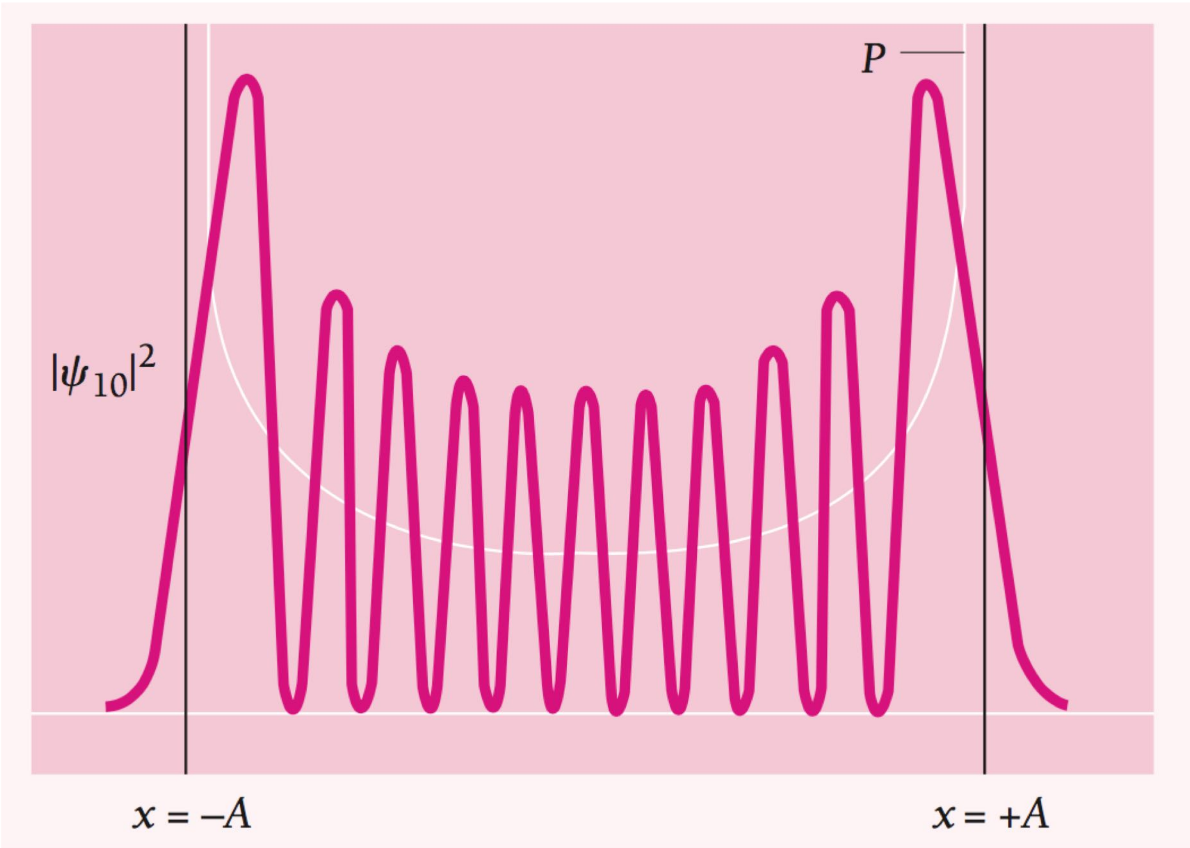
The probability P of finding the particle at a given position is greatest at the endpoints of its motion, where it moves slowly and least near the equilibrium position ($x = 0$), where it moves rapidly.

For Quantum mechanical oscillator:

Exactly the opposite behavior occurs when a quantum-mechanical oscillator is in its lowest energy state of $n = 0$. The probability density $|\Psi_0|^2$ has its maximum value at $x = 0$ and drops off on either side of this position. However this disagreement becomes less and less marked with Increasing n.



$n = 0$



From the graph of $\boldsymbol{n = 10}$, it is clear that $|\Psi_0|^2$ when averaged over x has approximately the general character of the classical probability P.

$\boldsymbol{n = 10}$

The exponential "tails" of $|\Psi_0|^2$ beyond $x = \pm A$ also decrease in magnitude with increasing n.

Thus the classical and quantum pictures begin to resemble each other more and more the larger the value of n, in agreement with the correspondence principle, although they are very different for small n.

Find the expectation value $< x >$ for the first two states of a harmonic oscillator.

Solution:

The general formula for $< x >$ is

$$< x >= \int_{-\infty}^{\infty} x \, |\Psi|^2 \, dx$$

In calculations such as this it is easier to begin with y in place of x and afterward change to x.

Consider the wave function:

$$\Psi_n = \left(\frac{2m\nu}{\hbar}\right)^{1/4} (2^n \, n!)^{-1/2} \, H_n(y) e^{-y^2/2}$$

From the tables:

$$\Psi_0 = \left(\frac{2m\nu}{\hbar}\right)^{1/4} e^{-y^2/2}.$$

$$\Psi_1 = \left(\frac{2m\nu}{\hbar}\right)^{1/4} \left(\frac{1}{2}\right)^{1/2} (2y)\, e^{-y^2/2}$$

The values of $< x >$:

For n=0 : $\int_{-\infty}^{\infty} y|\Psi_0|^2 dy = \int_{-\infty}^{\infty} y\, e^{-y^2} dy = -\left[\frac{1}{2} e^{-y^2}\right] = 0$

For n=1 : $\int_{-\infty}^{\infty} y|\Psi_1|^2 dy = \int_{-\infty}^{\infty} y^3\, e^{-y^2} dy = -\left[\left(\frac{1}{4} + \frac{y^2}{2}\right) e^{-y^2}\right] = 0$

The expectation value $< x >$ is therefore 0 in both cases.

In fact, **$< x >$=0 for all states of a harmonic oscillator**, which could be predicted since $x = 0$ is the equilibrium position of the oscillator, where its potential energy is a minimum.