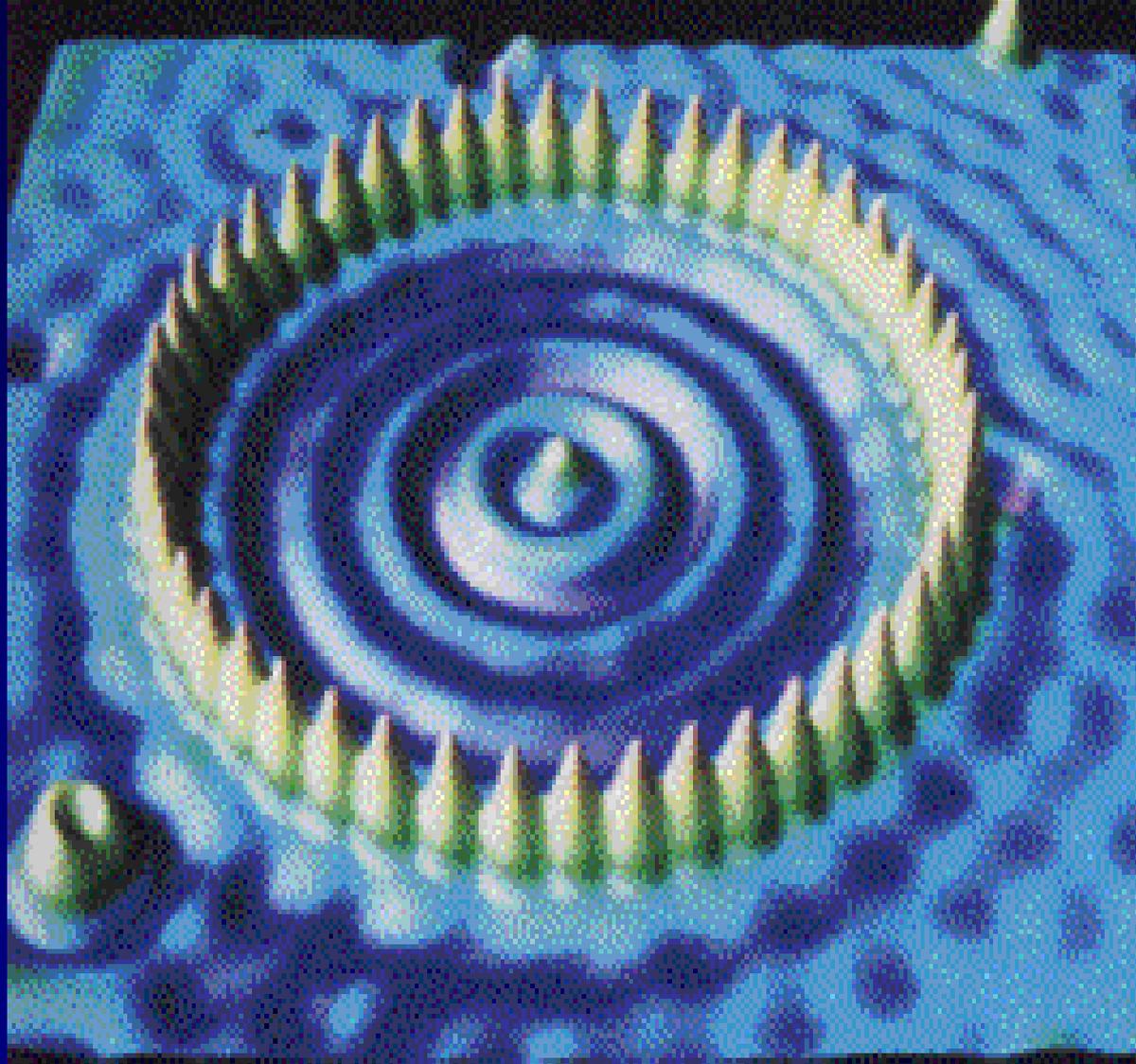


# Lecture 10: The Schrödinger Equation



# Overview

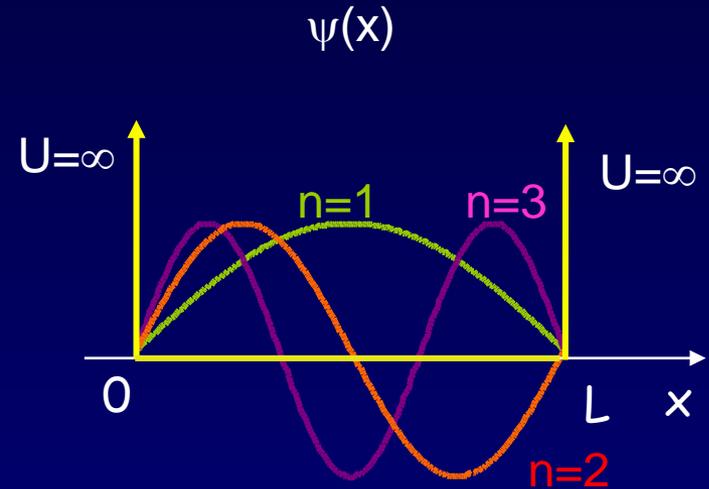
Probability distributions

Schrödinger's Equation

Particle in a "Box"

Matter waves in an infinite square well

Quantized energy levels



Nice descriptions in the text – Chapter 40

Good web site for animations <http://www.falstad.com/qm1d/>

# Matter Waves - Quantitative

Having established that matter acts *qualitatively* like a wave, **we want to be able to make precise *quantitative* predictions**, under given conditions. Usually the conditions are specified by giving a potential energy  $U(x,y,z)$  in which the particle is located.

Examples:

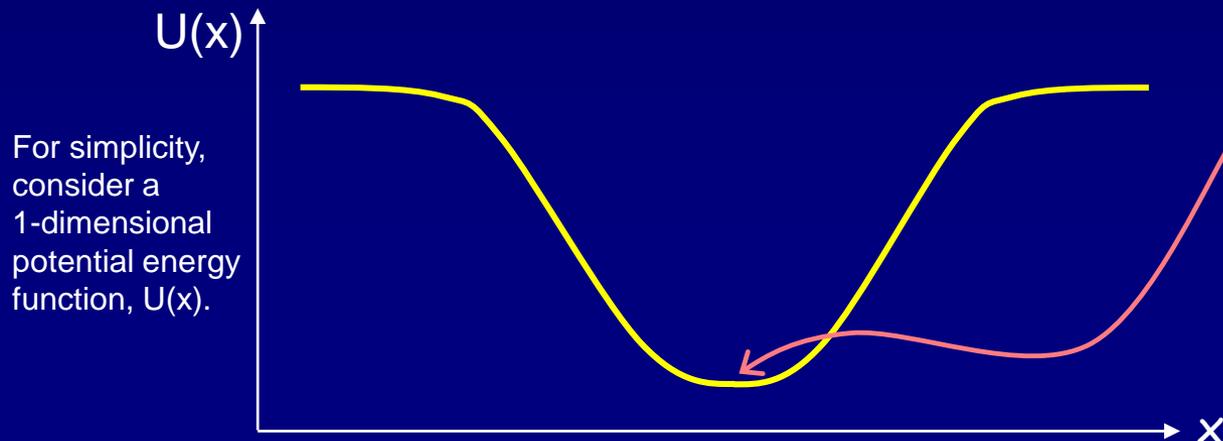
Electron in the coulomb potential produced by the nucleus

Electron in a molecule

Electron in a solid crystal

Electron in a nanostructure 'quantum dot'

Proton in the nuclear potential inside the nucleus

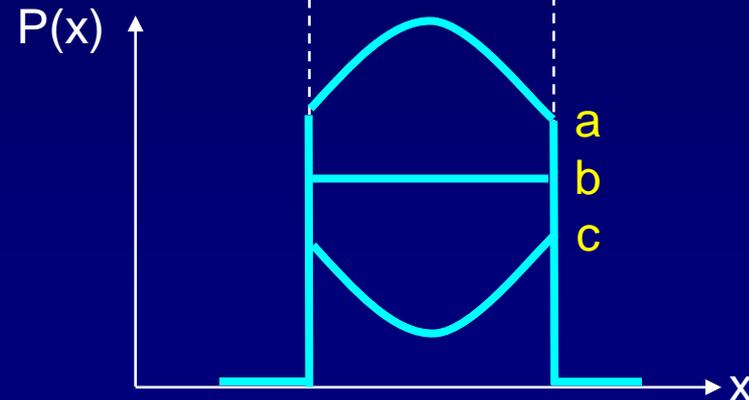
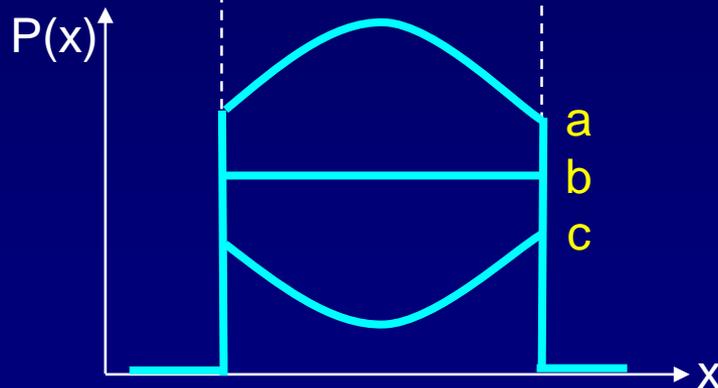
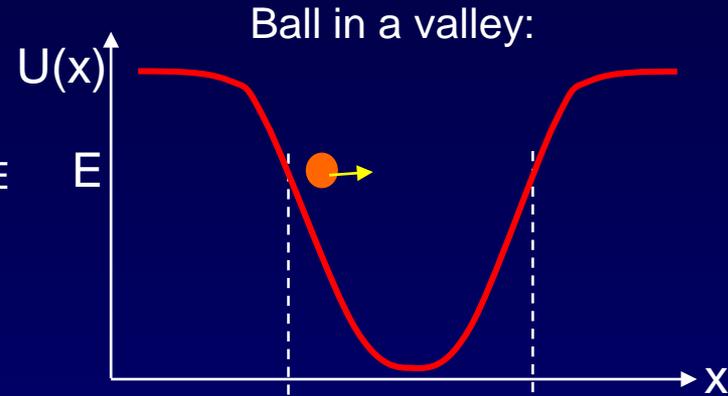
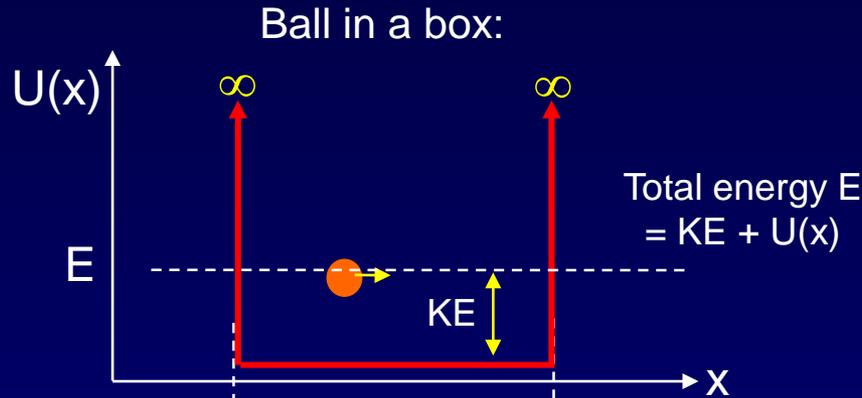


Classically, a particle in the lowest energy state would sit right at the bottom of the well. In QM this is not possible. (Why?)



# Act 1: Classical probability distributions

Start a classical (large) object moving in a potential well (two are shown here). At some random time later, what is the probability of finding it near position  $x$ ?



HINT: Think about speed vs position.

# The Schrödinger Equation (SEQ)

In 1926, Erwin Schrödinger proposed an equation that described the time- and space-dependence of the wave function for matter waves (*i.e.*, electrons, protons,...)

There are two important forms for the SEQ.

First we will focus on a very important special case of the SEQ, the time-independent SEQ. Also simplify to 1-dimension:  $\psi(x,y,z) \rightarrow \psi(x)$ .

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

This special case applies when the particle has a definite total energy ( $E$  in the equation). We'll consider the more general case ( $E$  has a probability distribution), and also 2D and 3D motion, later.

QM entities don't always have a definite energy.

Time does not appear in the equation. Therefore,  $\psi(x,y,z)$  is a standing wave, because the probability density,  $|\psi(x)|^2$ , is not a function of time. We call  $\psi(x,y,z)$  a "stationary state".

Notation:  
Distinguish  $\Psi(x,y,z,t)$  from  $\psi(x,y,z)$ .

The second form is the time-dependent SEQ. More on this later.

# Time-Independent SEQ

What does the time-independent SEQ represent?

It's actually not so puzzling...it's just an expression of a familiar result:

Kinetic Energy (KE) + Potential Energy (PE) = Total Energy (E)

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

KE term                      PE term                      Total E term

Can we understand the KE term? Consider a particle with a definite momentum. Its wave function is:  $\psi(x) \propto \cos(kx)$ , where  $p = h/\lambda = \hbar k$ .

$$\frac{d\psi}{dx} = -k \sin(kx) \quad \Rightarrow \quad \frac{d^2\psi}{dx^2} = -k^2 \cos(kx) = -\frac{p^2}{\hbar^2} \psi(x)$$

So, the first term in the SEQ is  $(p^2/2m)\psi$ . SEQ says

Total energy equals sum of potential energy and kinetic energy

Note that the KE of the particle depends on the curvature ( $d^2\psi/dx^2$ ) of the wave function. This is sometimes useful when analyzing a problem.



# Interpreting the SEQ

Another example where each term in a different wave equation has a meaning, and the DE itself contains a physical fact that is known to be true:

Classical waves with constant velocities (light waves, water waves, sound waves)

$$\frac{d^2 E(x)}{dx^2} = \frac{1}{v^2} \frac{d^2 E(x)}{dx^2}$$

momentum term

frequency term

What does this represent? To find out, plug a known solution into it:

$$E(x, t) = E_0 \cos(kx - \omega t)$$

This is known solution

LHS of WE is:  $-k^2 E(x, t)$ , while RHS is:  $-\omega^2/v^2 E(x, t)$

Cancel out the wave functions on both sides and get:

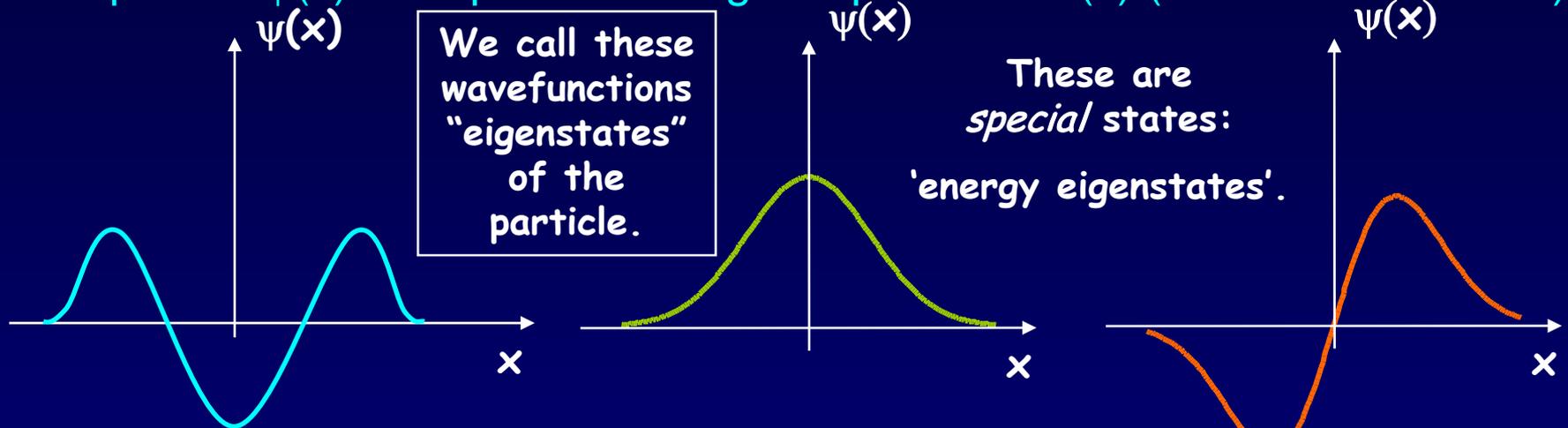
$$k^2 = \omega^2/v^2 \quad \text{or} \quad \hbar^2 k^2 = \hbar^2 \omega^2/v^2 \quad \text{or} \quad \text{momentum}^2 = \text{Energy}^2/v^2$$

That is a known fact about constant velocity waves!

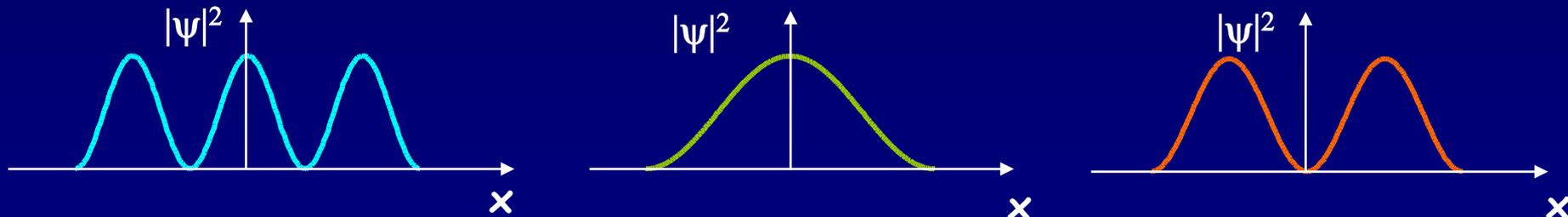
# Particle Wavefunctions: Examples

What do the solutions to the SEQ look like for general  $U(x)$ ?

Examples of  $\psi(x)$  for a particle in a given potential  $U(x)$  (but with different  $E$ ):



The corresponding probability distributions  $|\psi(x)|^2$  of these states are:



Key point: Particle cannot be associated with a specific location  $x$ .

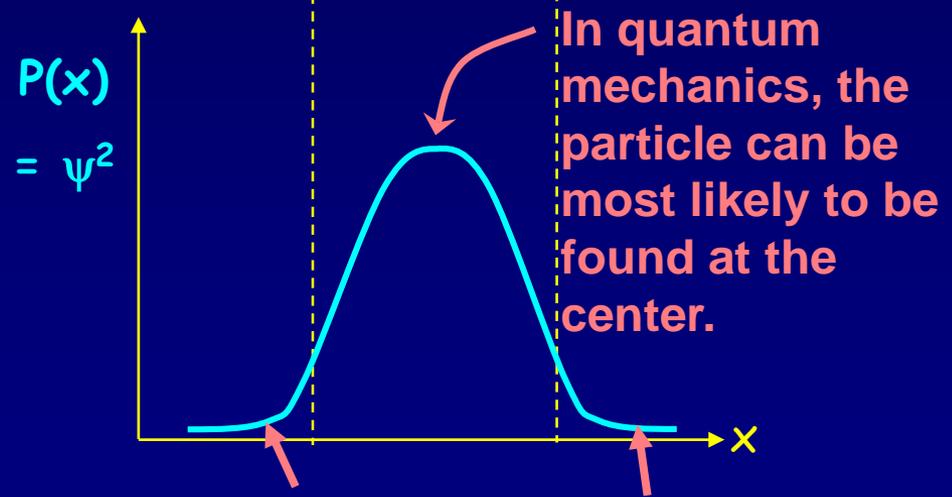
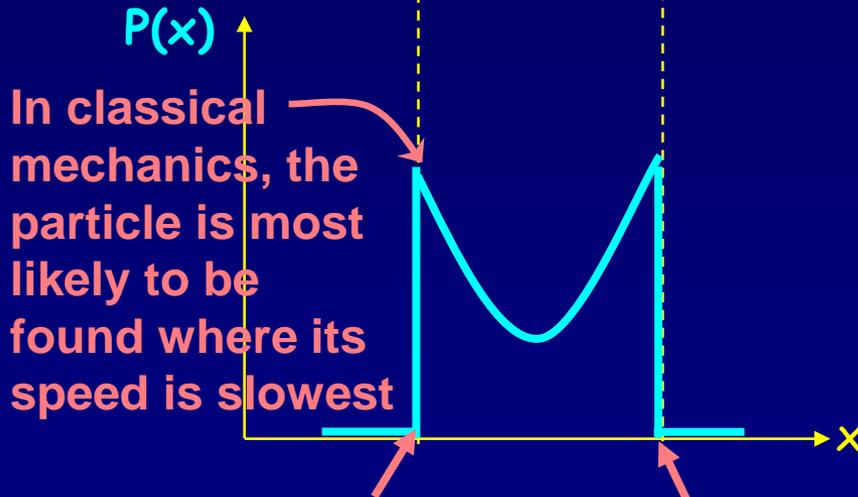
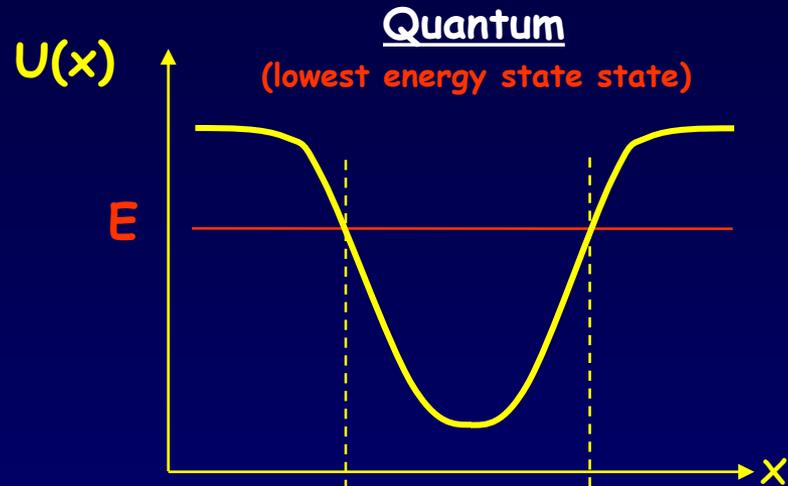
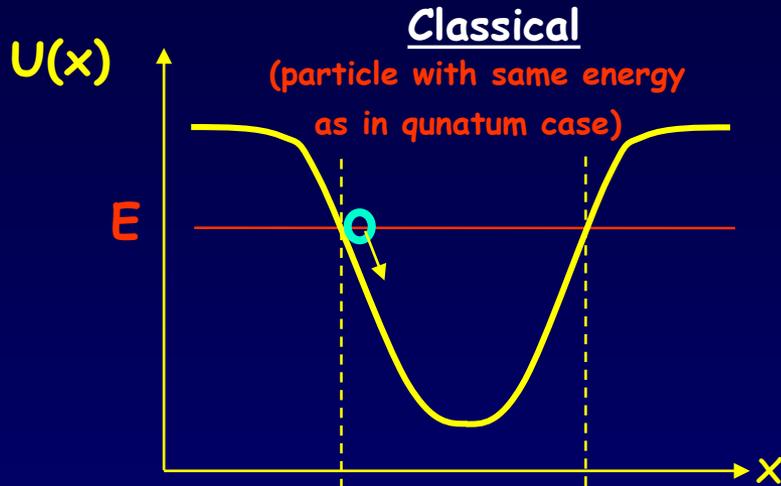
-- like the uncertainty that a particle went through slit 1 or slit 2.

Question: Which corresponds to the lowest/highest kinetic energy?

The particle kinetic energy is proportional to the *curvature* of the wave function.

# Probability distribution

## Difference between classical and quantum cases



In classical mechanics, the particle moves back and forth coming to rest at each "turning point"

In quantum mechanics, the particle can also be found where it is "forbidden" in classical mechanics.



# Solutions to the time-independent SEQ

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

Notice that if  $U(x) = \text{constant}$ , this equation has the simple form:

$$\frac{d^2 \psi}{dx^2} = C\psi(x)$$

where  $C = \frac{2m}{\hbar^2}(U - E)$  is a constant that might be positive or negative.

For positive  $C$  (i.e.,  $U > E$ ), what is the form of the solution?

- a)  $\sin kx$       b)  $\cos kx$       c)  $e^{ax}$       d)  $e^{-ax}$

For negative  $C$  ( $U < E$ ) what is the form of the solution?

- a)  $\sin kx$       b)  $\cos kx$       c)  $e^{ax}$       d)  $e^{-ax}$

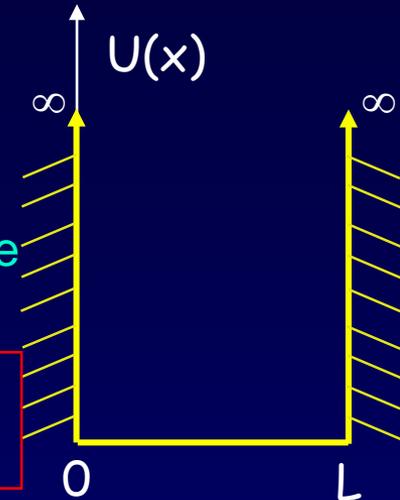
Most of the wave functions in P214 will be sinusoidal or exponential.

# Example: "Particle in a Box"

As a specific important example, consider a quantum particle confined to a region,  $0 < x < L$ , by infinite potential walls. We call this a "one-dimensional (1D) box".

$$U = 0 \text{ for } 0 < x < L$$

$$U = \infty \text{ everywhere else}$$



We already know the form of  $\psi$  when  $U = 0$ :  $\sin(kx)$  or  $\cos(kx)$ . However, we can constrain  $\psi$  more than this.

The waves have exactly the same form as standing waves on a string, sound waves in a pipe, etc.

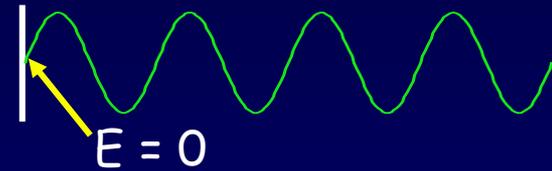
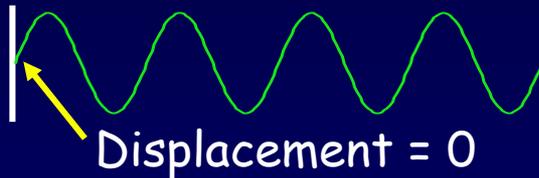
The wavelength is determined by the condition that it **"fits in the box."**

On a string the wave is a displacement  $y(x)$  and the square is the intensity, etc. The discrete set of allowed wavelengths results in a discrete set of tones that the string can produce.

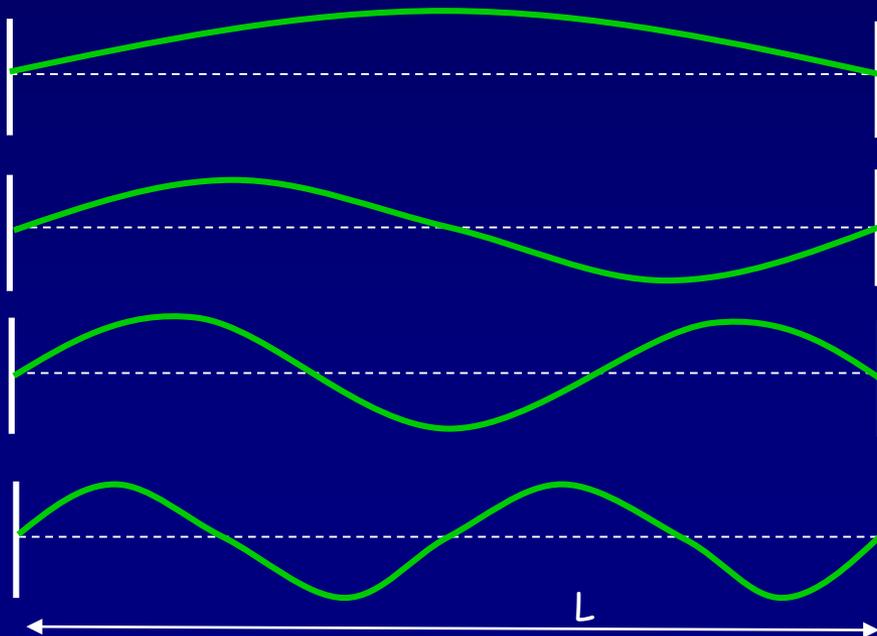
In a quantum box, the wave is the probability amplitude  $\psi(x)$  and the square  $|\psi(x)|^2$  is the probability of finding the electron near point  $x$ . The discrete set of allowed wavelengths results in a discrete set of allowed energies that the particle can have.

# Boundary conditions → Standing waves

- A standing wave is the solution for a wave confined to a region
- Boundary condition: Constraints on a wave where the potential changes
  - Displacement = 0 for wave on string
  - $E = 0$  at surface of a conductor



- If *both* ends are constrained (e.g., for a cavity of length  $L$ ), then only certain wavelengths  $\lambda$  are possible:



$n$	$\lambda$	$f$
1	$2L$	$v/2L$
2	$L$	$v/L$
3	$2L/3$	$3v/2L$
4	$L/2$	$2v/L$
$n$	$2L/n$	$nv/2L$

For waves on a string,  $v$  is fixed

$$n\lambda_n = 2L$$

$$\lambda_n = 2L/n$$

$n = 1, 2, 3 \dots$   
'mode index'



# The Energy is Quantized Due to Confinement by the Potential

The discrete  $E_n$  are known as “energy eigenvalues”:

$$n\lambda_n = 2L$$

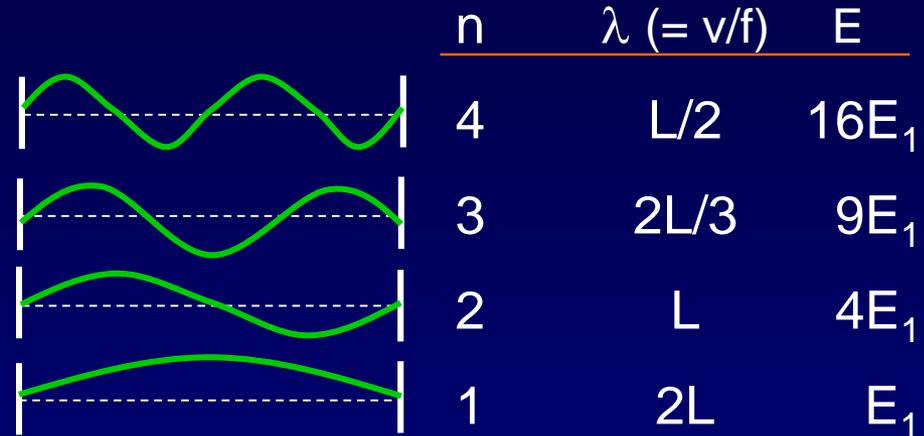
$$E_n = \frac{p^2}{2m} = \frac{h^2}{2m\lambda_n^2} = \frac{1.505 \text{ eV} \cdot \text{nm}^2}{\lambda_n^2}$$

electron

$E_n = E_1 n^2$

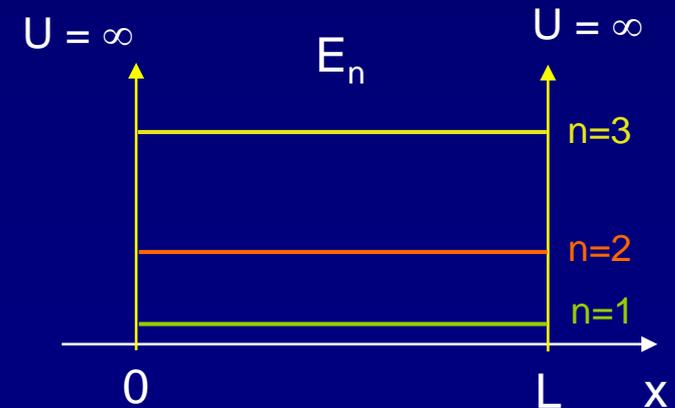
where

$E_1 \equiv \frac{h^2}{8mL^2}$



Important features:

- Discrete energy levels.
- $E_1 \neq 0$  ← an example of the uncertainty principle
- Standing wave ( $\pm p$  for a given E)
- $n = 0$  is not allowed. (why?)

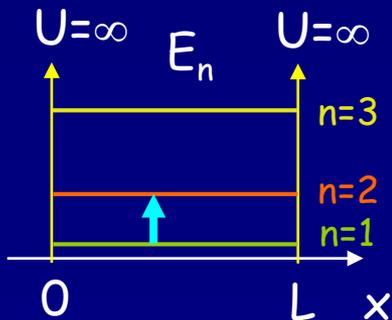


# Quantum Wire Example

An electron is trapped in a “quantum wire” that is  $L = 4$  nm long. Assume that the potential seen by the electron is approximately that of an **infinite square well**.

1: Calculate the ground (lowest) state energy of the electron.

2: What photon energy is required to excite the trapped electron to the next available energy level (*i.e.*,  $n = 2$ )?



The idea here is that the photon is absorbed by the electron, which gains all of the photon's energy (similar to the photoelectric effect).

# Boundary conditions

We can solve the SEQ wherever we know  $U(x)$ . However, in many problems, including the 1D box,  $U(x)$  has different functional forms in different regions. In our box problem, there are three regions:

1:  $x < 0$

2:  $0 < x < L$

3:  $x > L$

$\psi(x)$  will have different functional forms in the different regions.

We must make sure that  $\psi(x)$  satisfies the constraints (e.g., continuity) at the boundaries between these regions.

The extra conditions that  $\psi$  must satisfy are called “boundary conditions”. They appear in many problems.



# Particle in a Box (1)

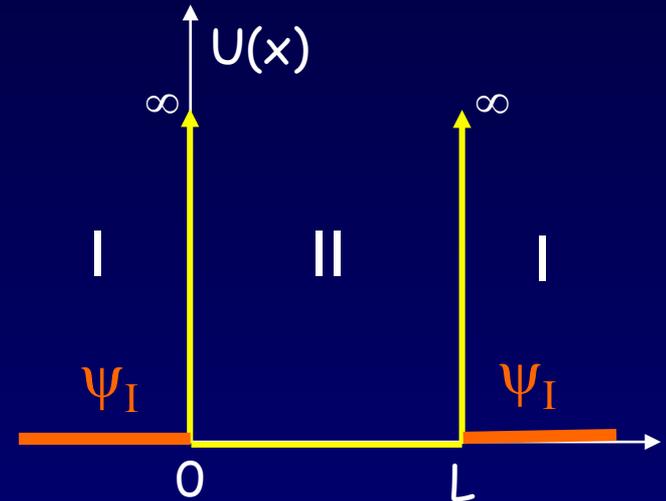
Regions 1 and 3 are identical, so we really only need to deal with two distinct regions, (I) outside, and (II) inside the well

Region I: When  $U = \infty$ , what is  $\psi(x)$ ?

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

For  $U = \infty$ , the SEQ can only be satisfied if:

$$\psi_I(x) = 0$$



$$U = 0 \text{ for } 0 < x < L$$

$$U = \infty \text{ everywhere else}$$

Otherwise, the energy would have to be infinite, to cancel  $U$ .

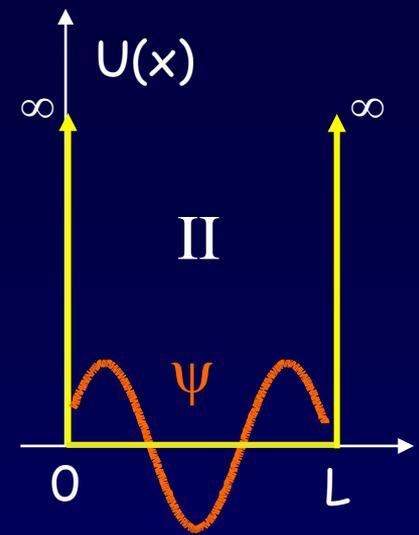
Note: The infinite well is an idealization.  
There are no infinitely high and sharp barriers.

# Particle in a Box (2)

Region II: When  $U = 0$ , what is  $\psi(x)$ ?

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

$$\frac{d^2 \psi(x)}{dx^2} = - \left( \frac{2mE}{\hbar^2} \right) \psi(x)$$



The general solution is a superposition of sin and cos:

$$\psi(x) = B_1 \sin kx + B_2 \cos kx \quad \text{where, } k = \frac{2\pi}{\lambda}$$

Remember that  $k$  and  $E$  are related:

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

because  $U = 0$

$B_1$  and  $B_2$  are coefficients to be determined by the boundary conditions.

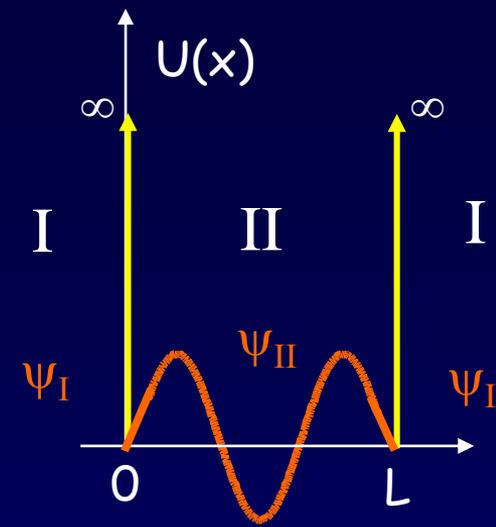
# Particle in a Box (3)

Now, let's worry about the boundary conditions.

Match  $\psi$  at the left boundary ( $x = 0$ ).

Region I:  $\psi_I(x) = 0$

Region II:  $\psi_{II}(x) = B_1 \sin kx + B_2 \cos kx$



Recall: The wave function  $\psi(x)$  must be continuous at all boundaries.

Therefore, at  $x = 0$ :

$$\psi_I(0) = \psi_{II}(0)$$

$$\Rightarrow 0 = B_1 \sin(0) + B_2 \cos(0)$$

$$0 = B_2$$

because  $\cos(0) = 1$  and  $\sin(0) = 0$

This “boundary condition” requires that there be no  $\cos(kx)$  term!



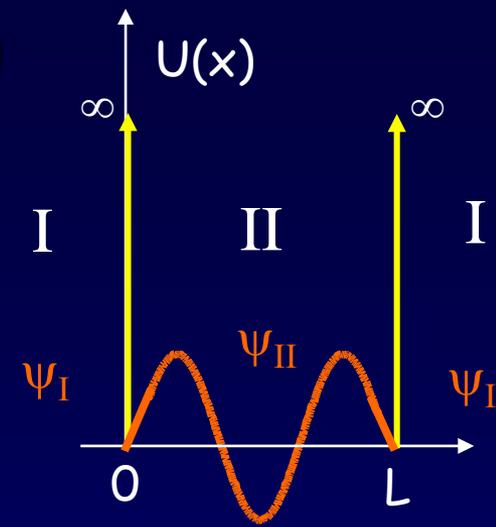
# Particle in a Box (4)

Now, match  $\psi$  at the right boundary ( $x = L$ ).

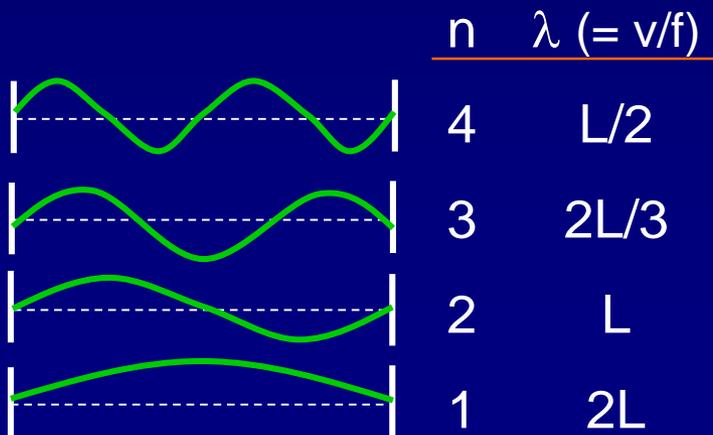
At  $x = L$ :  $\psi_I(L) = \psi_{II}(L)$   
 $\Rightarrow 0 = B_1 \sin(kL)$

This constraint requires  $k$  to have special values:

$$k_n = \frac{n\pi}{L} \quad n = 1, 2, \dots \quad \text{Using } k = \frac{2\pi}{\lambda}, \text{ we find: } n\lambda_n = 2L$$



This is the same condition we found for confined waves, e.g., waves on a string, EM waves in a laser cavity, etc.:



For matter waves, the wavelength is related to the particle energy:

$$E = h^2/2m\lambda^2$$



$$E_n = E_1 n^2$$

where

$$E_1 \equiv \frac{h^2}{8mL^2}$$

# Next Lectures

“Normalizing” the wavefunction

General properties of bound-state wavefunctions

Finite-depth square well potential (more realistic)