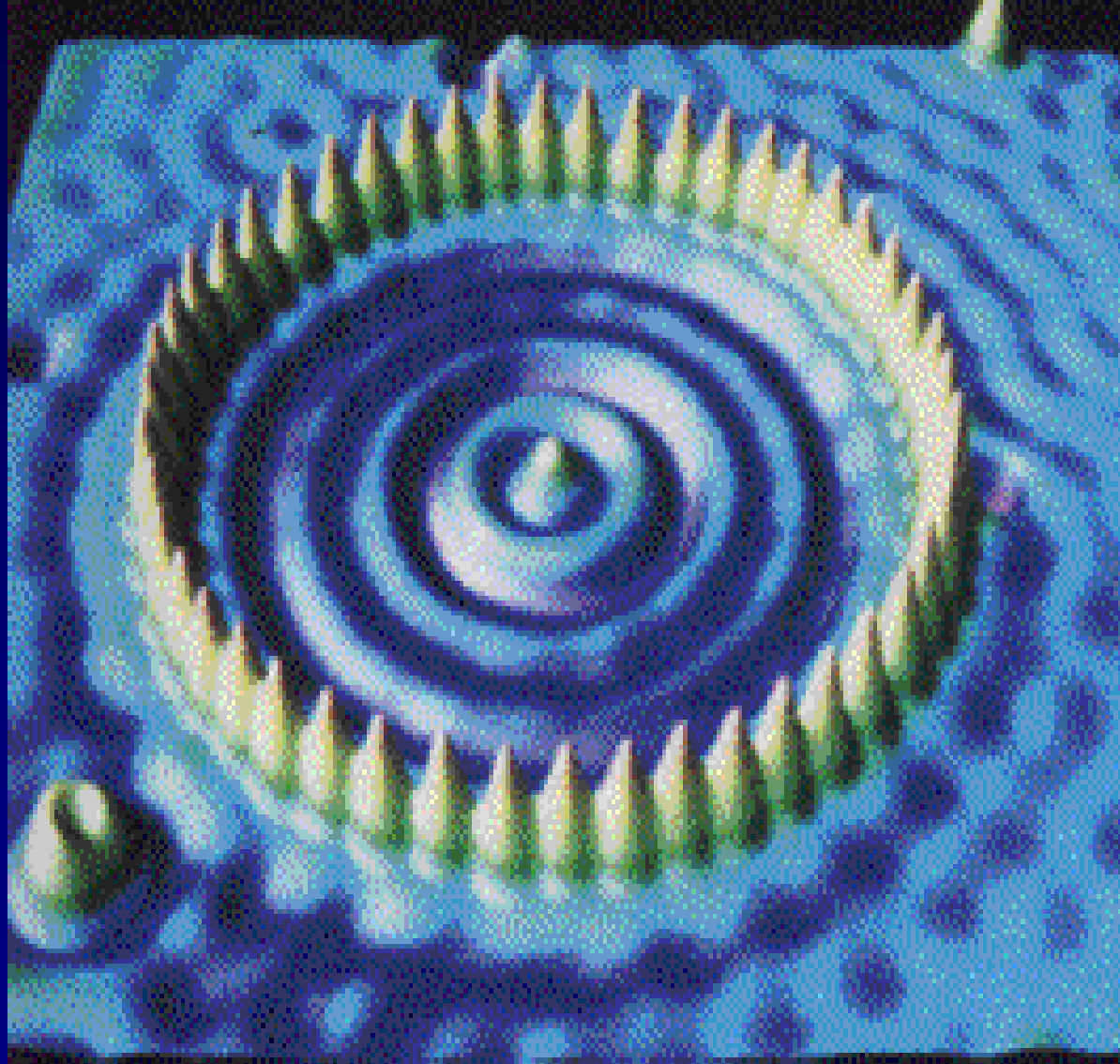


# Lecture 10: The Schrödinger Equation



# Overview

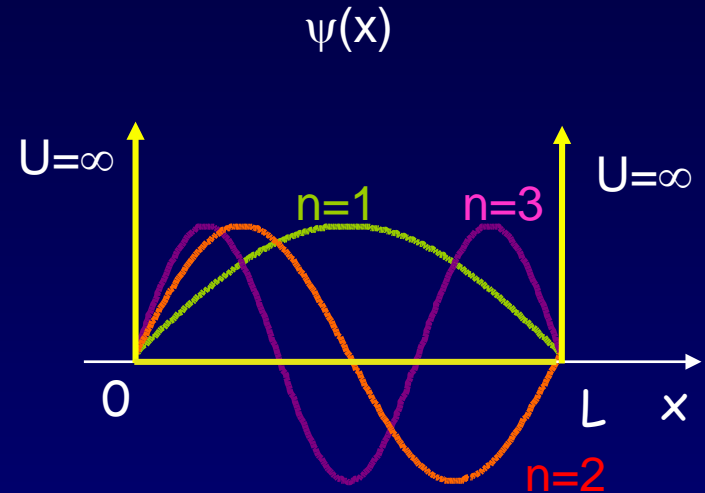
Probability distributions

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:

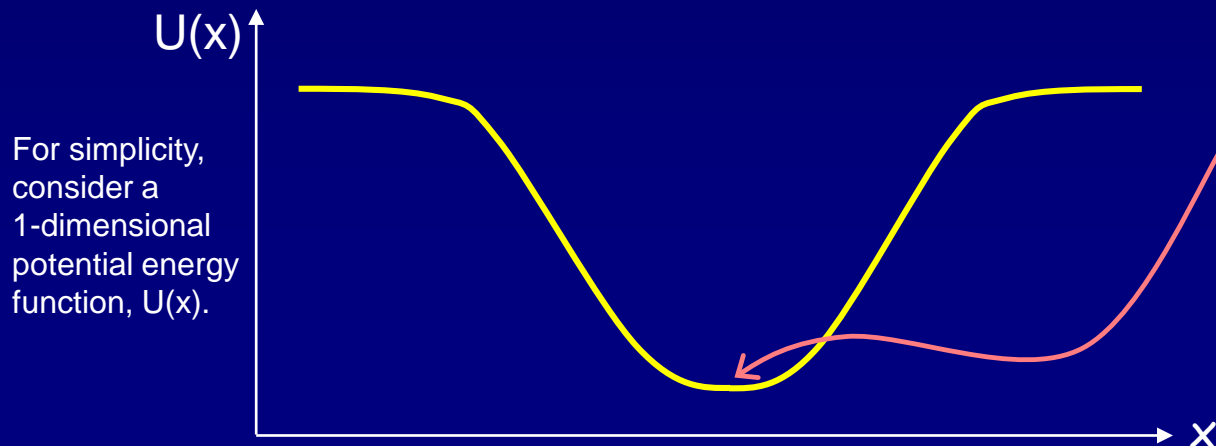
Electron in the coulomb potential produced by the nucleus

Electron in a molecule

Electron in a solid crystal

Electron in a nanostructure 'quantum dot'

Proton in the nuclear potential inside the nucleus

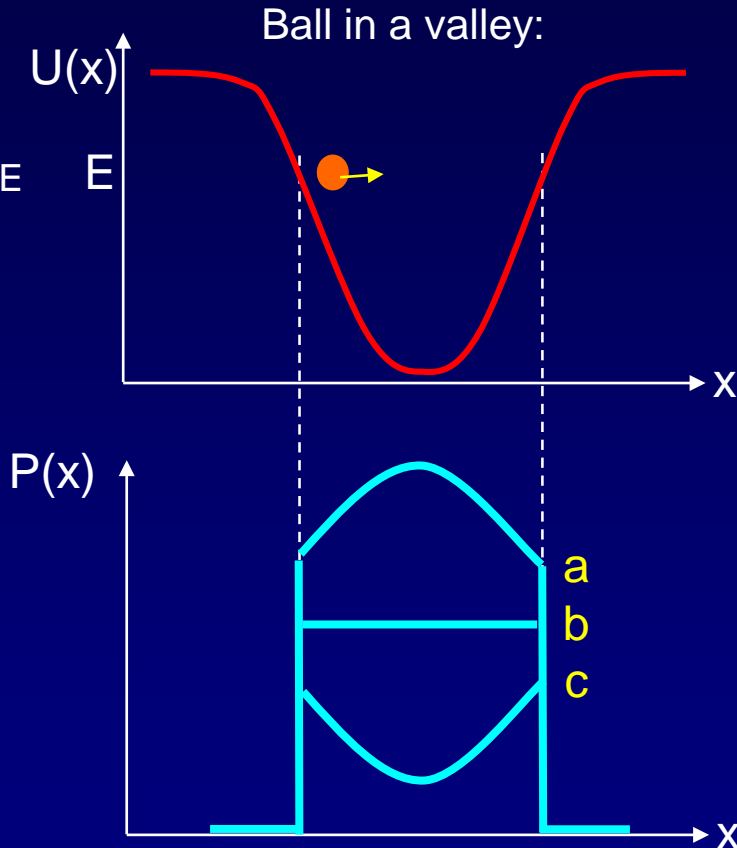
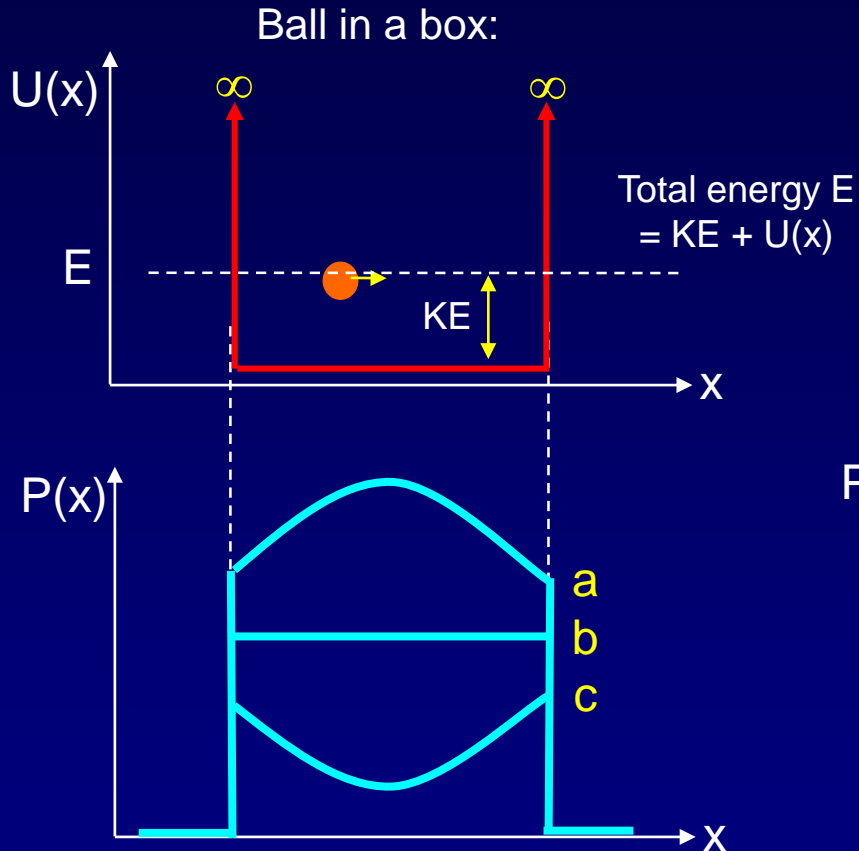


Classically, a particle in the lowest energy state would sit right at the bottom of the well. In QM this is not possible. (Why?)



# 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  $p = h/\lambda = \hbar k$ .

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

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)

$$\underbrace{\frac{d^2 E(x)}{dx^2}}_{\text{momentum term}} = \underbrace{\frac{1}{v^2} \frac{d^2 E(x)}{dx^2}}_{\text{frequency term}}$$

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

$$E(x, t) = E_0 \cos(kx - \omega t) \quad \text{This is known solution}$$

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:

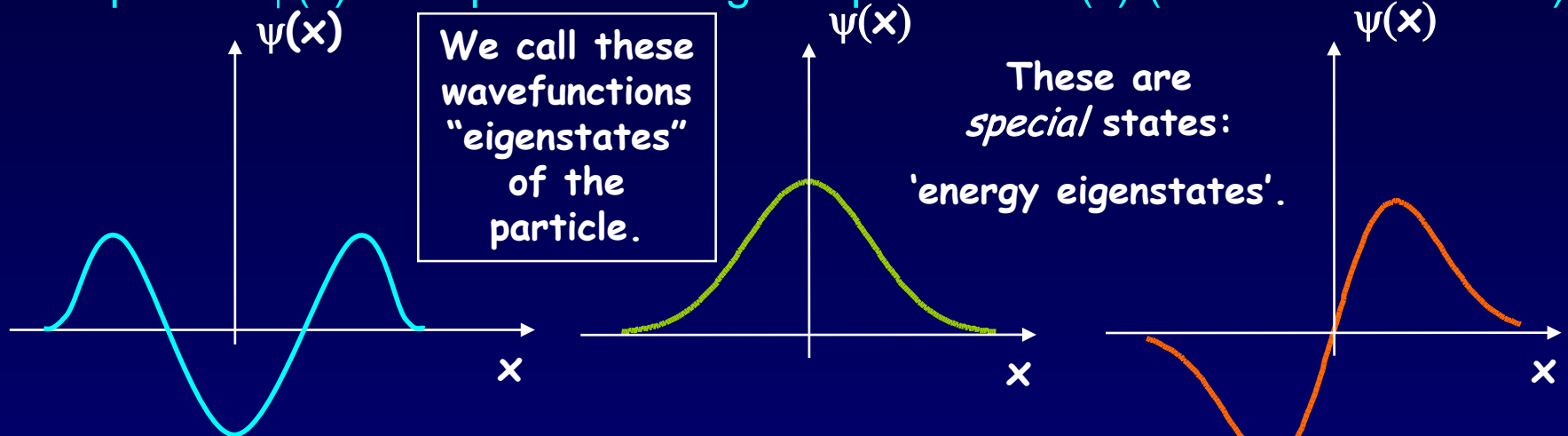
$$k^2 = \omega^2/v^2 \quad \text{or} \quad \hbar^2 k^2 = \hbar^2 \omega^2/v^2 \quad \text{or} \quad \text{momentum}^2 = \text{Energy}^2/v^2$$

That is a known fact about constant velocity waves!

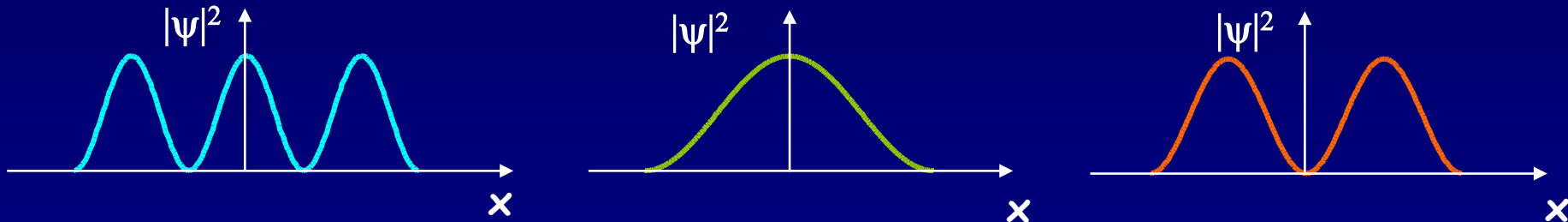
# Particle Wavefunctions: Examples

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  $x$ .

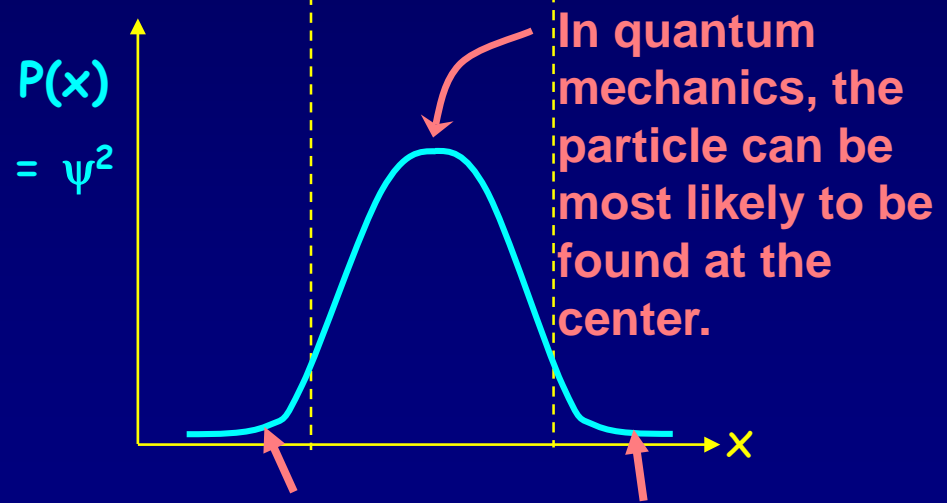
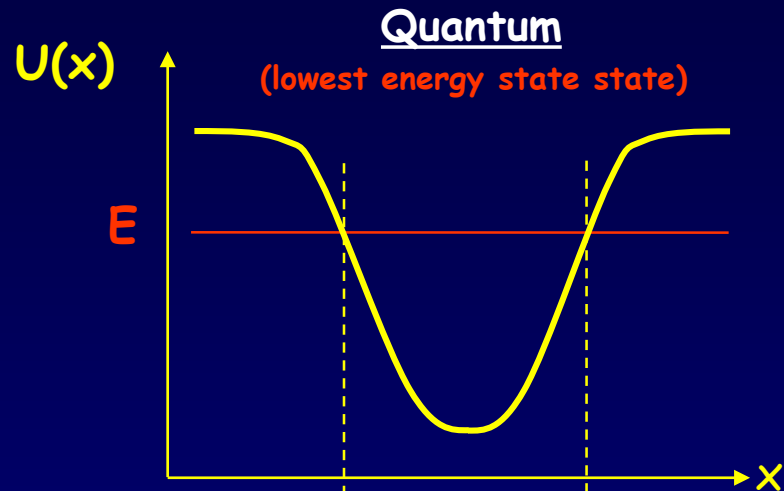
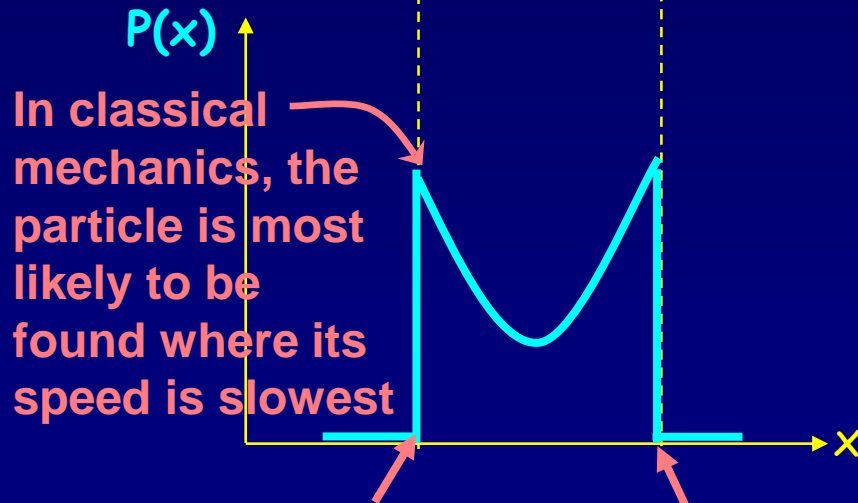
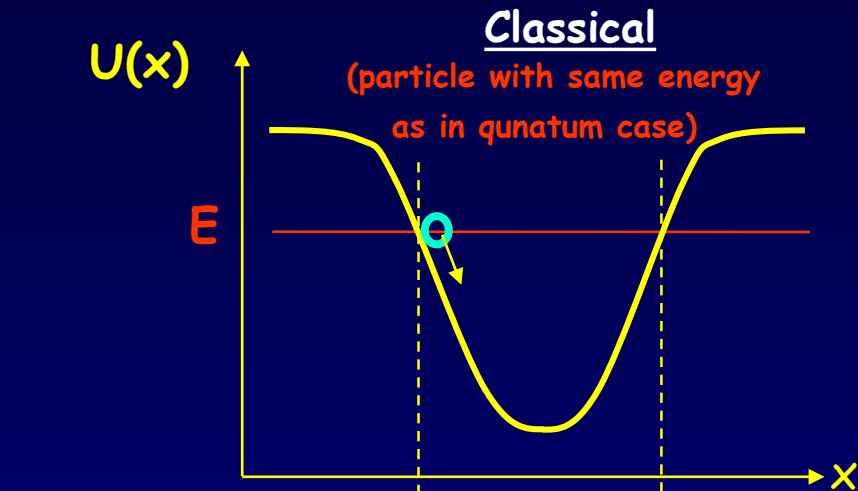
-- like the uncertainty that a particle went through slit 1 or slit 2.

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





# 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)  $e^{-ax}$

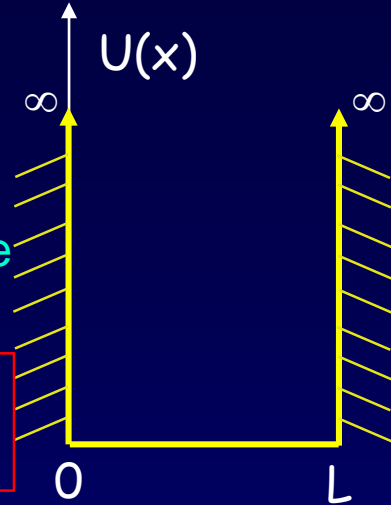
Most of the wave functions in P214 will be sinusoidal or exponential.

# 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.

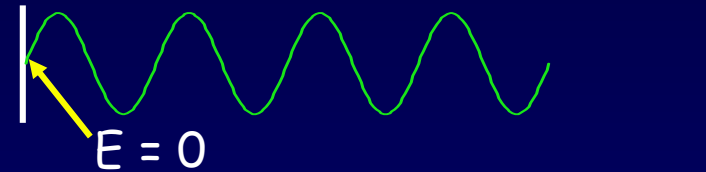
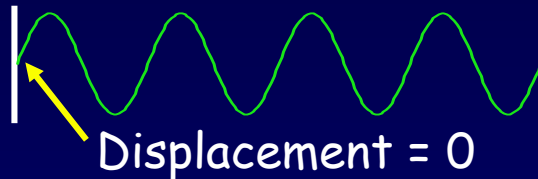
The wavelength is determined by the condition that it **"fits in the box."**

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.

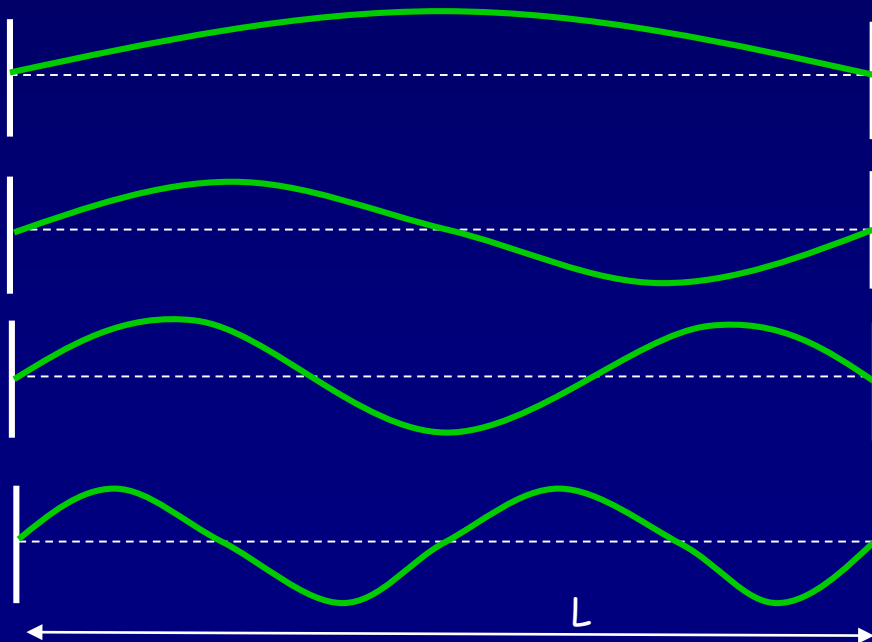
In a quantum box, the wave is the probability amplitude  $\psi(x)$  and the square  $|\psi(x)|^2$  is the probability of finding the electron near point  $x$ . The discrete set of allowed wavelengths results in a discrete set of allowed energies that the particle can have.

# 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



- 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

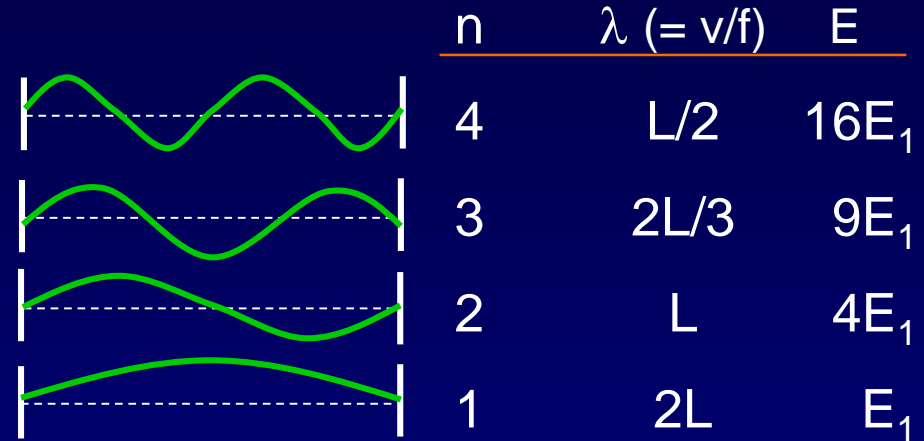
The discrete  $E_n$  are known as “energy eigenvalues”:

$$n\lambda_n = 2L$$

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

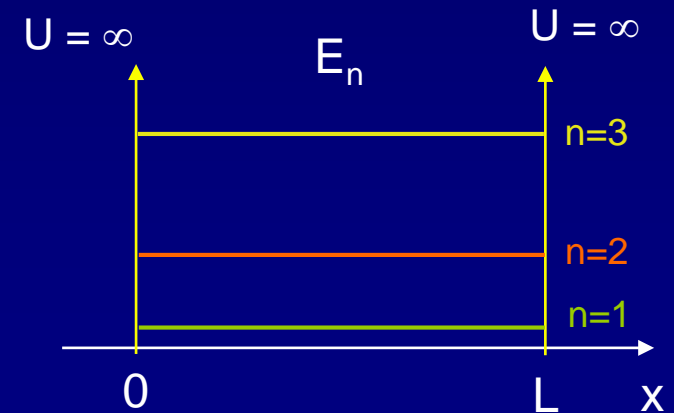
electron  
↓

$E_n = E_1 n^2$  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?)

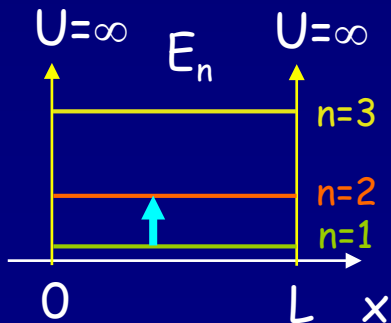


# Quantum Wire Example

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)

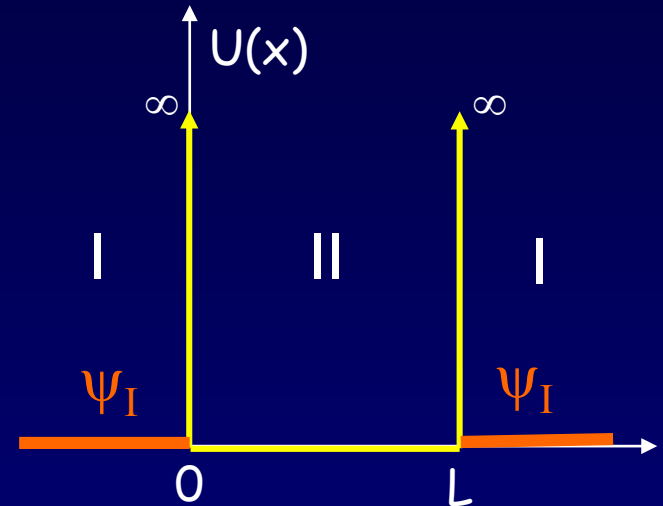
Regions 1 and 3 are identical, so we really only need to deal with two distinct regions, (I) outside, and (II) inside the well

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:

$$\psi_I(x) = 0$$



$U = 0$  for  $0 < x < L$

$U = \infty$  everywhere else

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

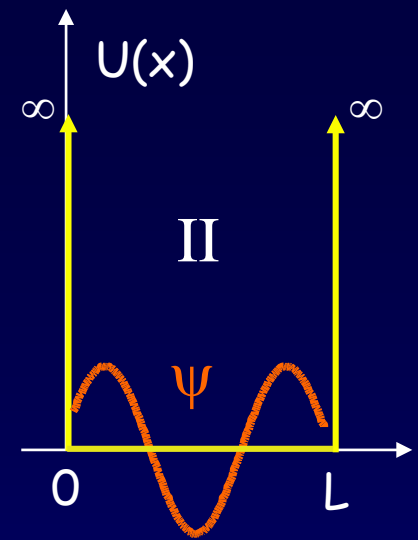
Note: The infinite well is an idealization.  
There are no infinitely high and sharp barriers.

# 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.

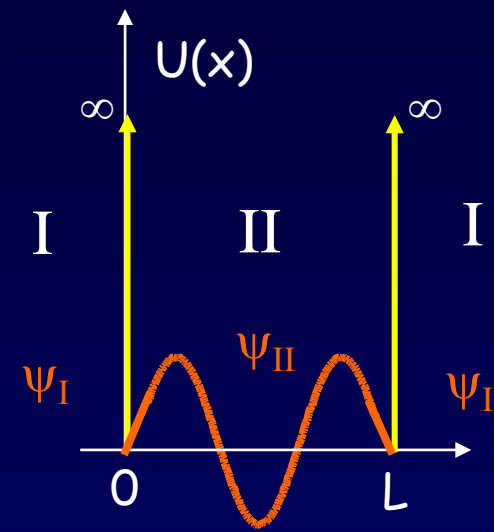
# Particle in a Box (3)

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 ( $x = L$ ).

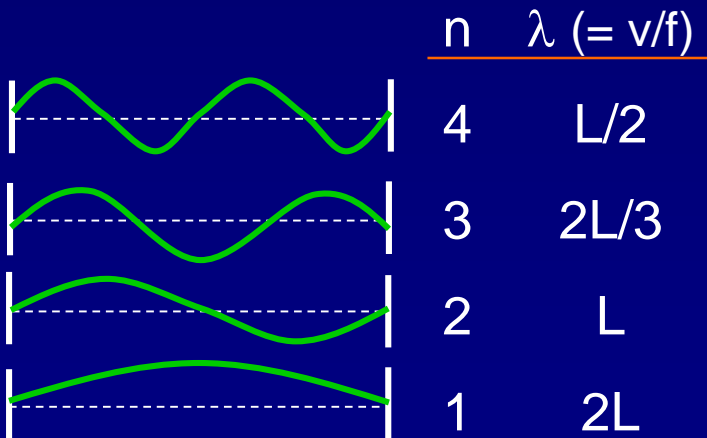
At  $x = L$ :  $\psi_I(L) = \psi_{II}(L)$

$$\Rightarrow 0 = B_1 \sin(kL)$$

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:

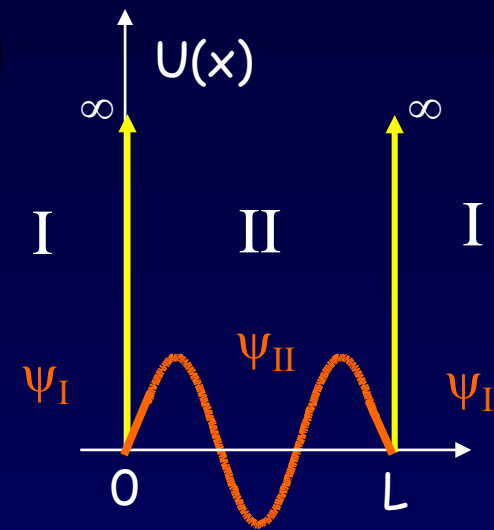
$$E = \frac{h^2}{2m\lambda^2}$$



$$E_n = E_1 n^2$$

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)