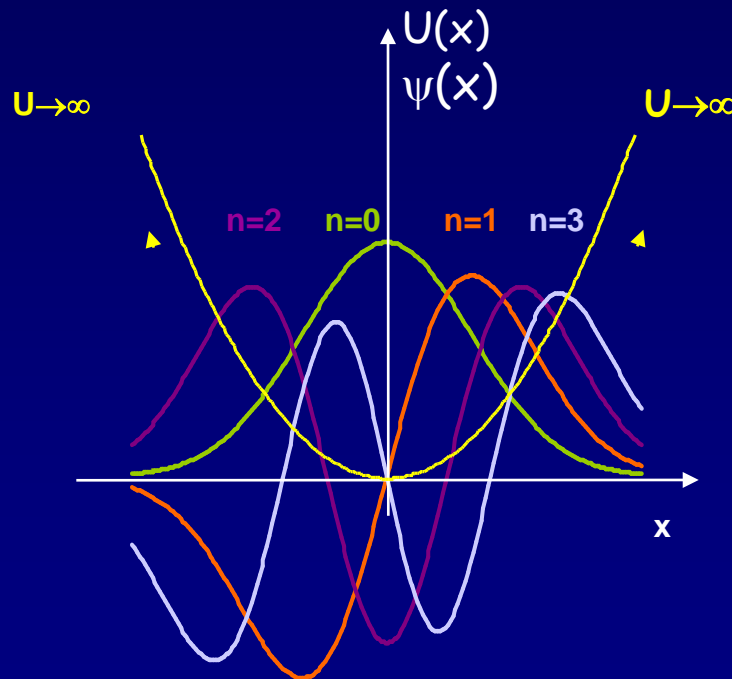# Lecture 12:
Particle in 1D boxes, Simple Harmonic Oscillators

This week and last week are critical for the course:

Week 3, Lectures 7-9:
- Light as Particles
- Particles as waves
- Probability
- Uncertainty Principle

Week 4, Lectures 10-12:
- Schrödinger Equation
- Particles in infinite wells, finite wells

Midterm Exam Monday, week 5
It will cover lectures 1-12 (but not SHOs).
Practice exams: Old exams are linked from the course web page.
Review   Sunday before Midterm: 3pm Loomis 141

Office hours: Sunday and Monday

Next week:
Homework 4 covers material in lecture 10 – due on Thur. after midterm.
        We strongly encourage you to look at the homework before the midterm!
Discussion: Covers material in lectures 10-12. There will be a quiz.

L10: 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: $\psi(x,y,z) \rightarrow \psi(x)$.

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

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".

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

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

Properties of Bound States

Several trends exhibited by the particle-in-box states are generic to bound state wave functions in any 1D potential (even complicated ones).
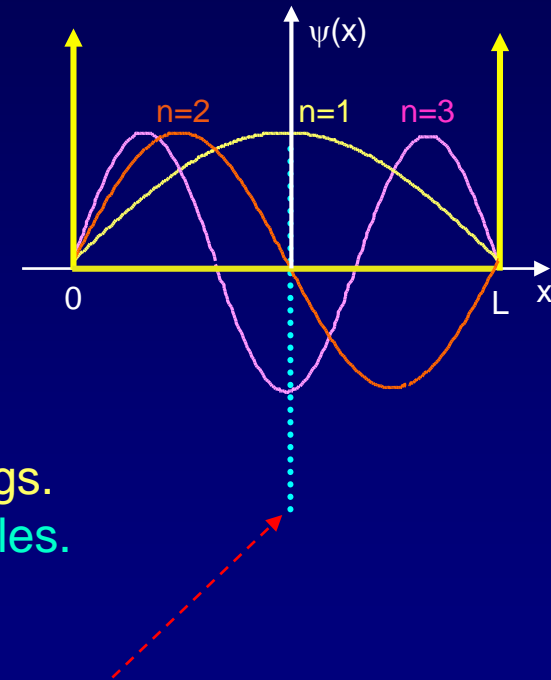
1: The overall curvature of the wave function increases with increasing kinetic energy.
$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = \frac{p^2}{2m}\psi(x) \text{ for a sine wave}$$

2: The lowest energy bound state always has finite kinetic energy -- called "zero-point" energy. Even the lowest energy bound state requires some wave function curvature (kinetic energy) to satisfy boundary conditions.

3: The nth wave function (eigenstate) has (n-1) zero-crossings. Larger n means larger E (and p), which means more wiggles.

4: If the potential U(x) has a center of symmetry (such as the center of the well above), the eigenstates will be, alternately, even and odd functions about that center of symmetry.
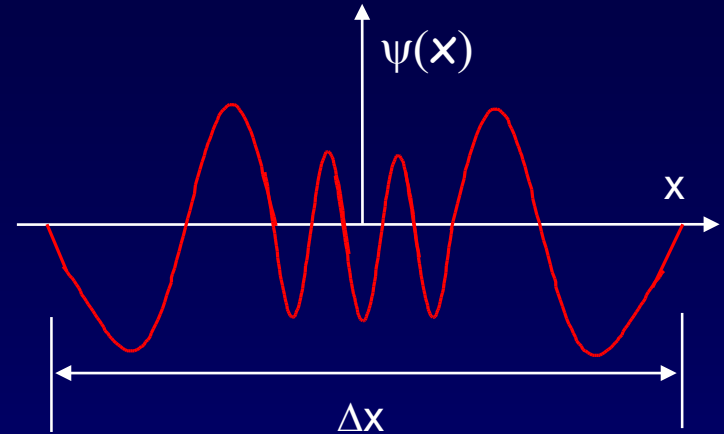
Act 1

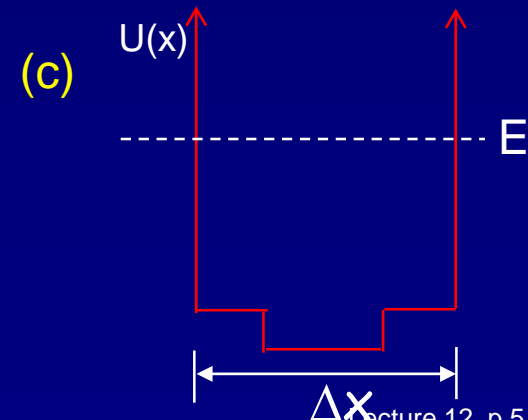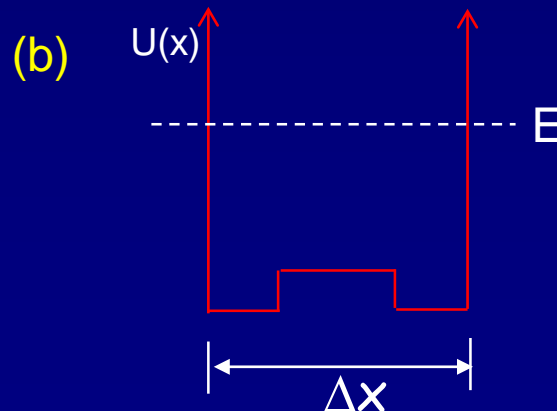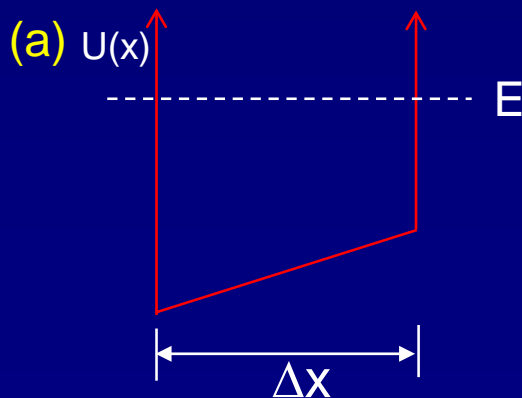The wave function below describes a quantum particle in a range Δx:

1. In what energy level is the particle?
   n =

   (a) 7   (b) 8   (c) 9

$\psi(x)$

x

Δx

2. What is the approximate shape of the potential U(x) in which this particle is confined?

(a) U(x)

E

Δx

(b) U(x)

E

Δx

(c) U(x)

E

Δx

Solution

The wave function below describes a quantum particle in a range Δx:

1. In what energy level is the particle?
   n =

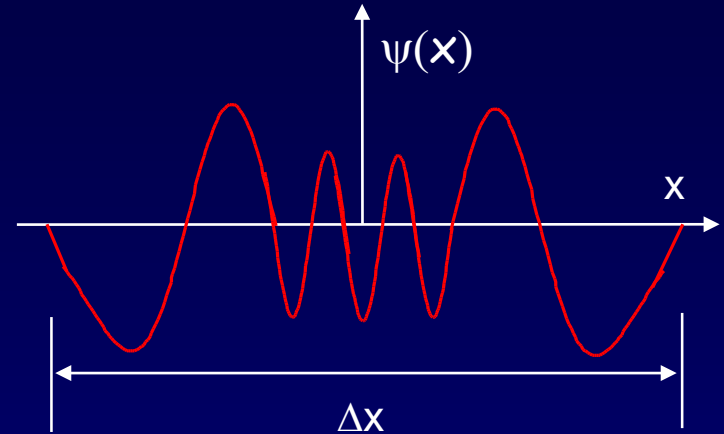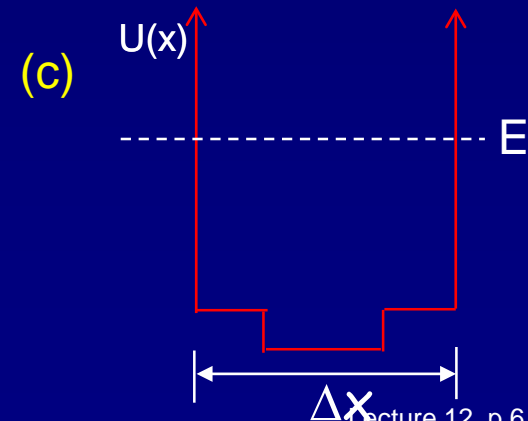   (a) 7   (b) 8   (c) 9

   Eight nodes.
   Don't count the boundary conditions.

$\psi(x)$

x

Δx

2. What is the approximate shape of the potential U(x) in which this particle is confined?

(a) U(x)   E Δx

(b) U(x)   E Δx

(c) U(x)   E Δx

Solution

The wave function below describes a quantum particle in a range Δx:

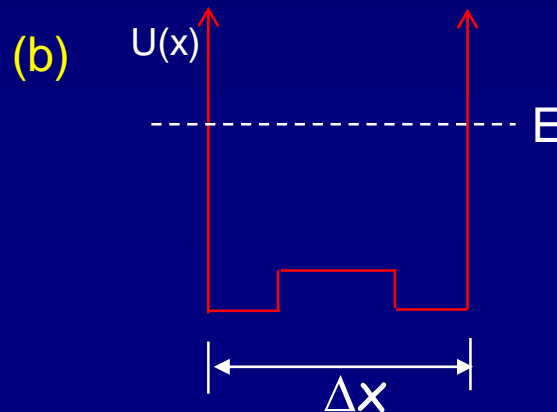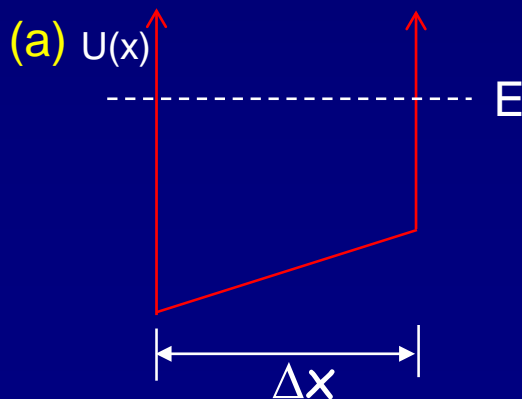1. In what energy level is the particle?
   n =

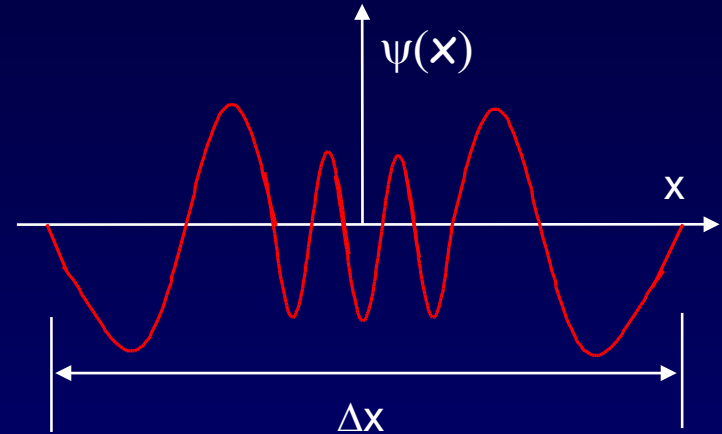   (a) 7   (b) 8   (c) 9

   Eight nodes.
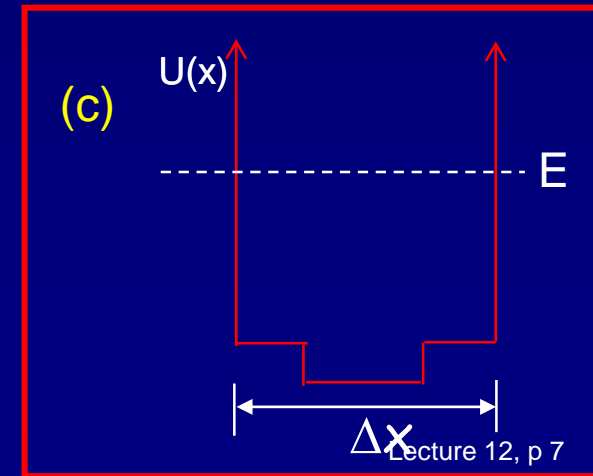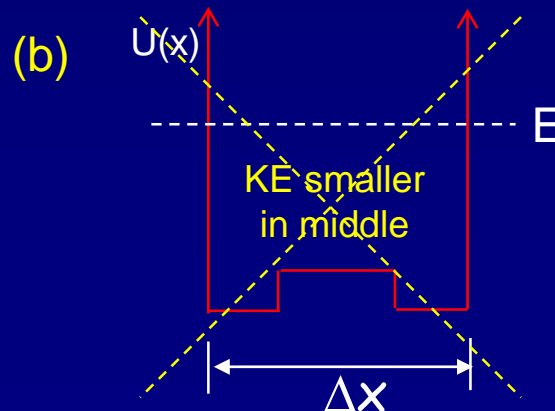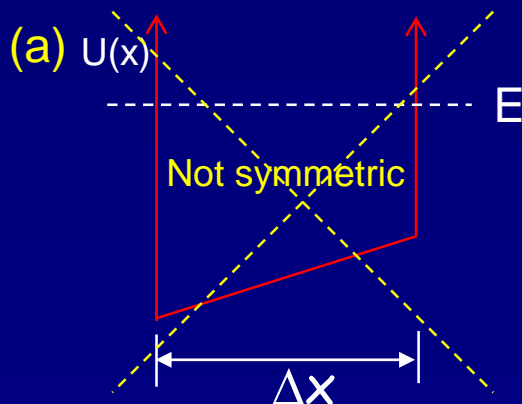   Don't count the boundary conditions.

ψ(x)

x

Δx

2. What is the approximate shape of the potential
   U(x) in which this particle is confined?   Wave function is symmetric.
   Wavelength is shorter in the middle.

(a) U(x)   (b) U(x)   (c) U(x)

E   E   E

Not symmetric   KE smaller
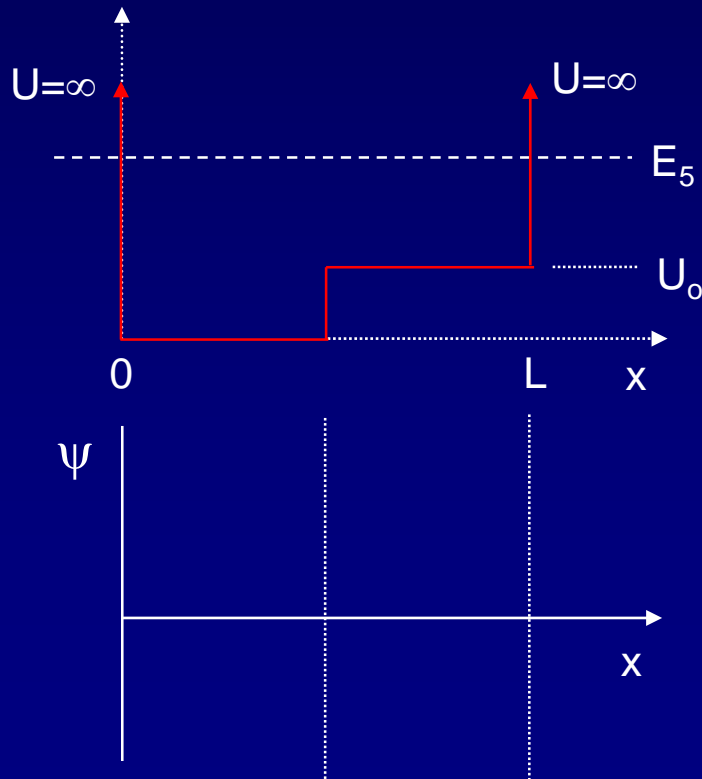   in middle

Δx   Δx   Δx

Bound State Properties: Example

Let's reinforce your intuition about the properties of bound state wave functions with this example:

Through nano-engineering, one can create a step in the potential seen by an electron trapped in a 1D structure, as shown below. You'd like to estimate the wave function for an electron in the 5th energy level of this potential, without solving the SEQ. The actual wavefunction depends strongly on the parameters U_o and L. Qualitatively sketch a possible 5th wave function:
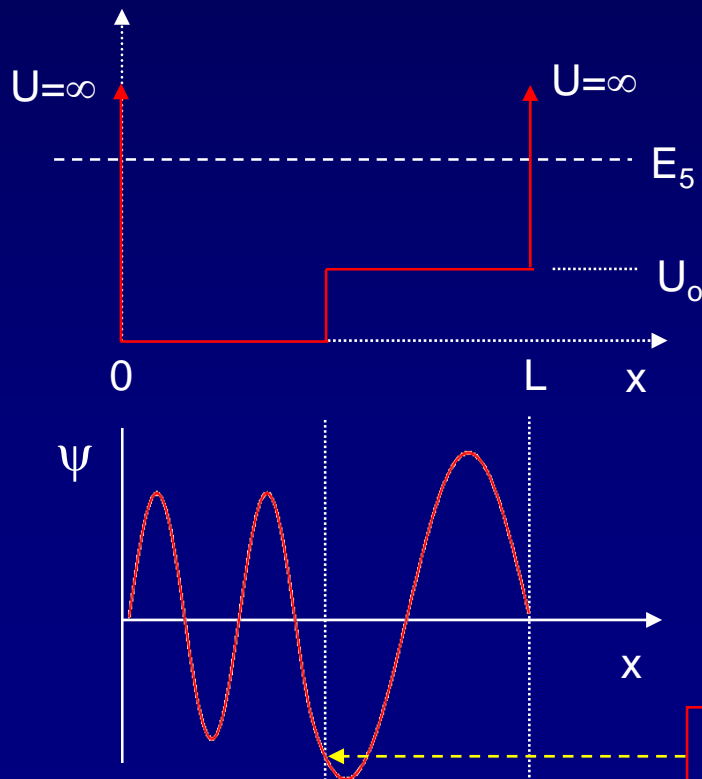

Consider these features of ψ:

1: 5th wave function has __ zero-crossings.

2: Wave function must go to zero at ____ and ____.

3: Kinetic energy is _____ on right side of well, so the curvature of ψ is _____ there.

Bound State Properties: Solution

Let's reinforce your intuition about the properties of bound state wave functions with this example:

Through nano-engineering, one can create a step in the potential seen by an electron trapped in a 1D structure, as shown below. You'd like to estimate the wave function for an electron in the 5th energy level of this potential, without solving the SEQ. The actual wavefunction depends strongly on the parameters U_o and L. Qualitatively sketch a possible 5th wave function:

$U=\infty$ $U=\infty$

E_5

U_o

0   L   x

ψ

x

ψ and $d\psi/dx$ must be continuous here.

Consider these features of ψ:

1: 5th wave function has _4_ zero-crossings.

2: Wave function must go to zero at $\underline{x = 0}$ and $\underline{x = L}$.

3: Kinetic energy is _lower_ on right side of well, so the curvature of ψ is _smaller_ there.
    The wavelength is longer.

Particle in Infinite Square Well Potential

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + U(x)\psi_n(x) = E_n\psi_n(x) \qquad \text{inside well}$$

$$\psi_n(x) \propto \sin(k_n x) = \sin\left(\frac{2\pi}{\lambda_n}x\right) = \sin\left(\frac{n\pi}{L}x\right) \qquad \text{for} \quad 0 \le x \le L$$
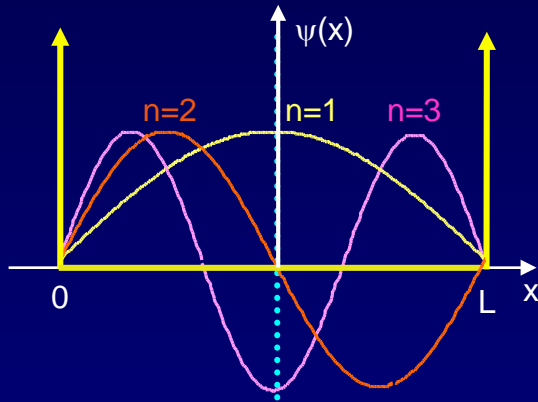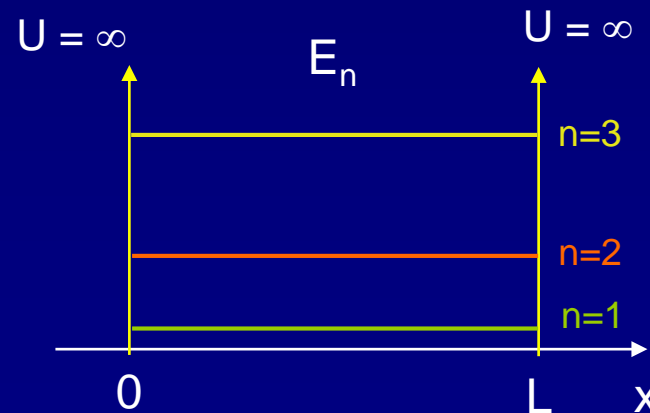
$$n\lambda_n = 2L$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \qquad \text{for} \quad 0 \le x \le L$$

The discrete E_n are known as "energy eigenvalues":

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

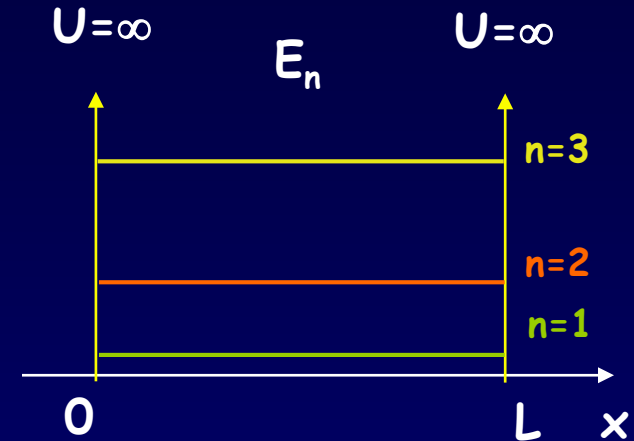$$\boxed{E_n = E_1 n^2} \quad \text{where} \quad \boxed{E_1 \equiv \frac{h^2}{8mL^2}}$$

Act 2

1. An electron is in a quantum "dot". If we decrease the size of the dot, the ground state energy of the electron will

   a) decrease

   b) increase

   c) stay the same

2. If we decrease the size of the dot, the difference between two energy levels (e.g., between $n = 7$ and 2) will

   a) decrease

   b) increase

   c) stay the same

Solution

1. An electron is in a quantum "dot". If we decrease the size of the dot, the ground state energy of the electron will
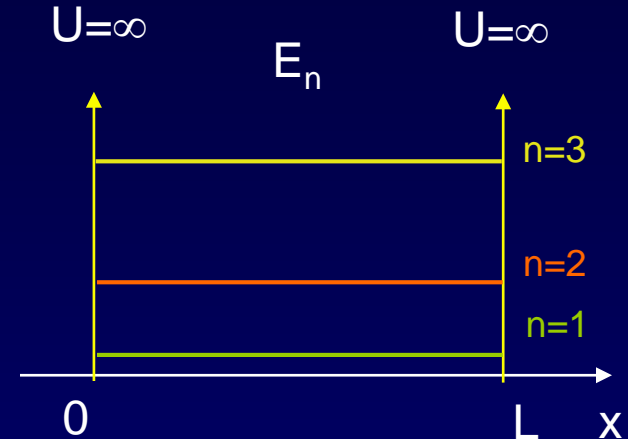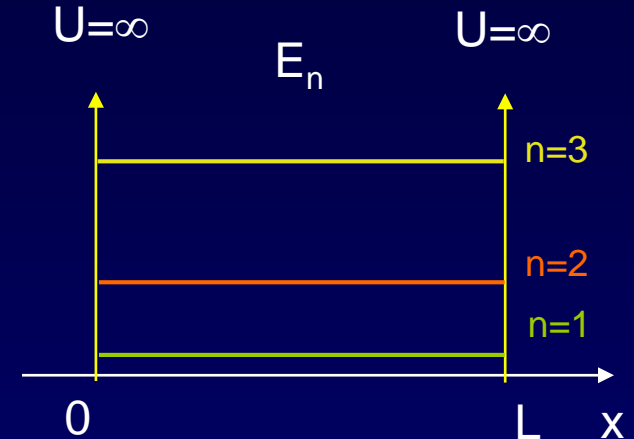
   a) decrease
   b) increase
   c) stay the same

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

The uncertainty principle, once again!

U=∞ E_n U=∞

n=3
n=2
n=1

0   L   x

2. If we decrease the size of the dot, the difference between two energy levels (e.g., between n = 7 and 2) will

   a) decrease
   b) increase
   c) stay the same

Solution

1. An electron is in a quantum "dot". If we decrease the size of the dot, the ground state energy of the electron will

    a) decrease

    b) increase

    c) stay the same

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

The uncertainty principle, once again!

$U=\infty$ E_n $U=\infty$

n=3

n=2

n=1

0   L   x

2. If we decrease the size of the dot, the difference between two energy levels (e.g., between n = 7 and 2) will

    a) decrease

    b) increase

    c) stay the same

$E_n = n^2 E_1$

$E_7 - E_2 = (49 - 4)E_1 = 45E_1$

Since E_1 increases, so does ΔE.

"Quantum Confinement" – size of material affects "intrinsic" properties

M. Nayfeh (UIUC) : Discrete uniform Si nanoparticles
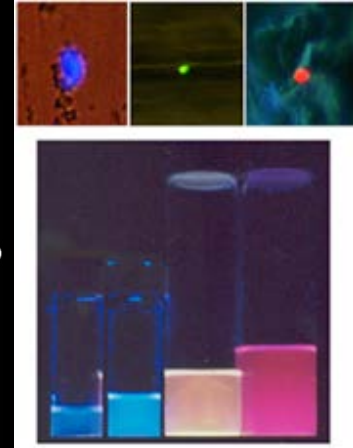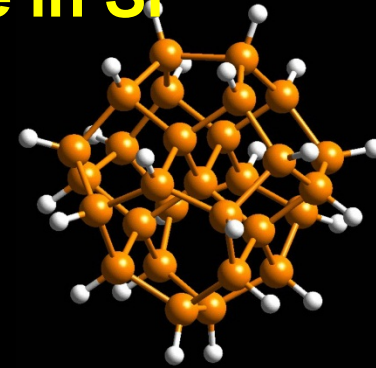
- **Transition from bulk to molecule-like in Si**

- A family of magic sizes of hydrogenated Si nanoparticles

- No magic sizes > 20 atoms for non-hydrogenated clusters

- Small clusters *glow*: color depends on size →

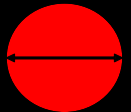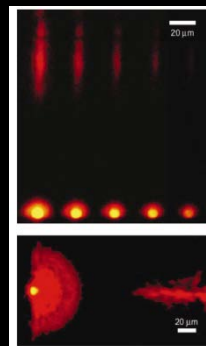- Used to create Si nanoparticle microscopic laser:
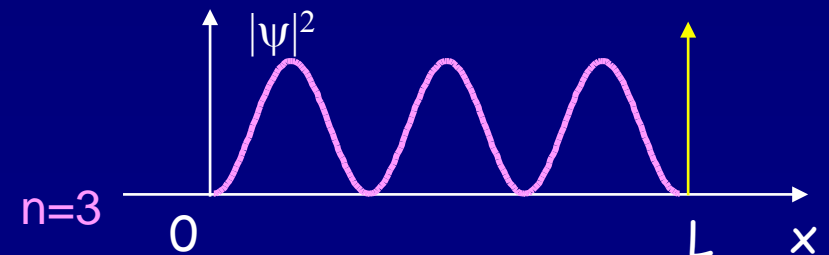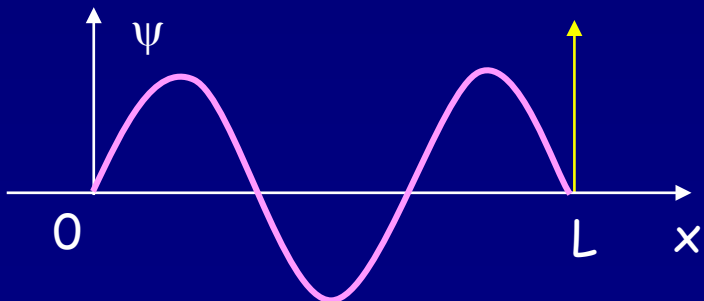
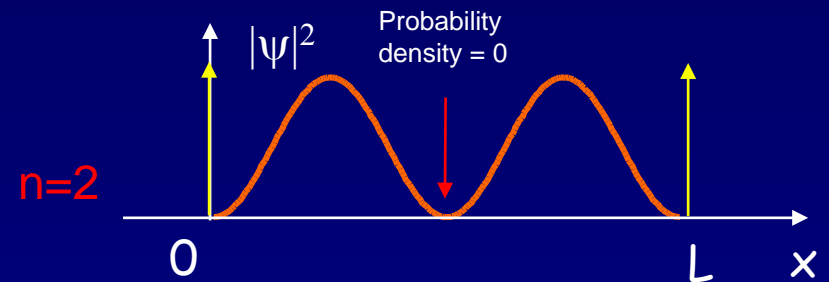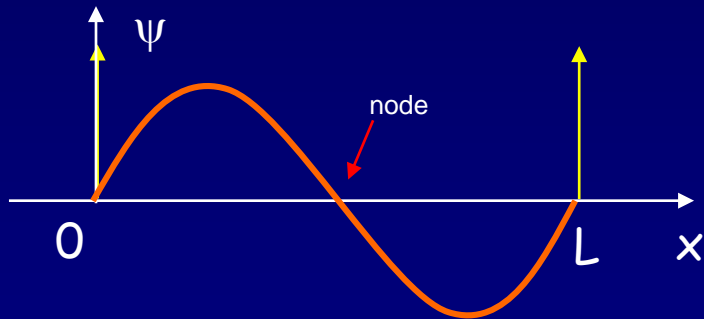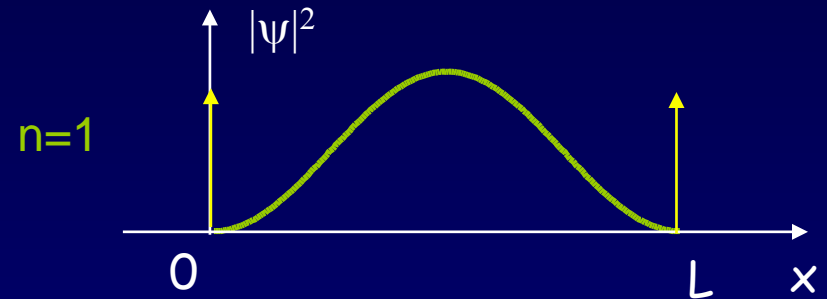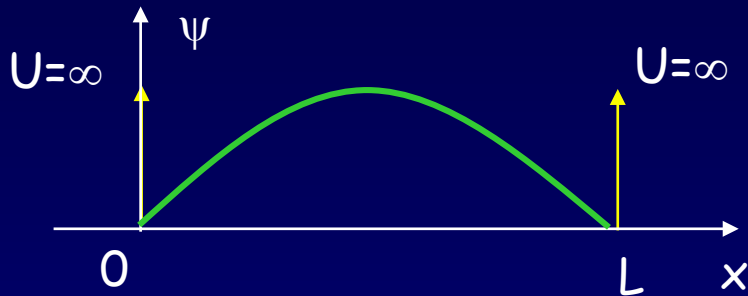| 1 nm	1.67 nm	2.15 nm	2.9 nm
Blue	Green	Yellow	Red

Probabilities

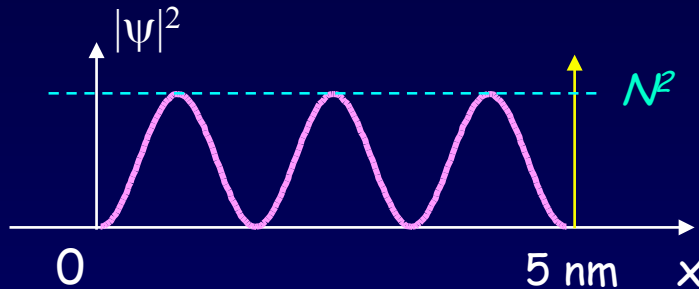Often what we measure in an experiment is the probability density, $|\psi(x)|^2$.

$$\psi_n(x) = N\sin\left(\frac{n\pi}{L}x\right)$$

Wavefunction =
Probability amplitude

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

Probability per
unit length
(in 1-dimension)

Probability Example

Consider an electron trapped in a 1D well with L = 5 nm. Suppose the electron is in the following state:
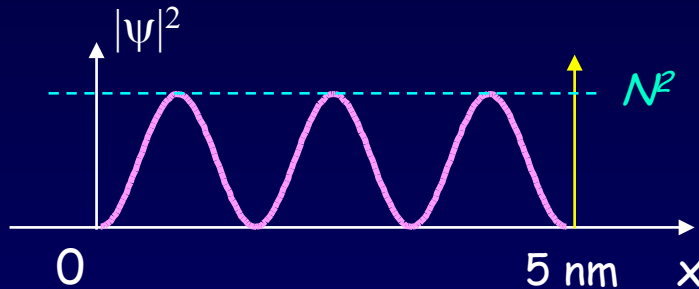

$$\left|\psi_n(x)\right|^2 = N^2 \sin^2\left(\frac{n\pi}{L}x\right)$$

a) What is the energy of the electron in this state (in eV)?

b) What is the value of the normalization factor squared N^2?

c) Estimate the probability of finding the electron within ±0.1 nm of the center of the well? (No integral required. Do it graphically.)

Solution

Consider an electron trapped in a 1D well with L = 5 nm. Suppose the electron is in the following state:

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

a) What is the energy of the electron in this state (in eV)?

$$n = 3, \qquad E_n = E_1 n^2 = \frac{1.505\ eV \cdot nm^2}{4(5nm)^2} 3^2 = 0.135\ \text{eV}$$

b) What is the value of the normalization factor squared N^2?

$$P_{tot} = 1 = N^2 \tfrac{L}{2} \Rightarrow N^2 = \tfrac{2}{L} = 0.4\ \text{nm}^{-1}$$

c) Estimate the probability of finding the electron within ±0.1 nm of the center of the well? (No integral required. Do it graphically.)

$$\text{Probability} = (\Delta x)\psi^2_{middle} \approx (0.2\ \text{nm})N^2 = 0.08 \qquad [(\sin(3\pi x/L))^2 \approx 1\ \text{for}\ x \approx L/2]$$

This works because the entire interval is very close to the middle peak.

Act 3

In the previous exercise, we found that the probability to find the electron within ±0.1 nm of the center of the well was ~8%.
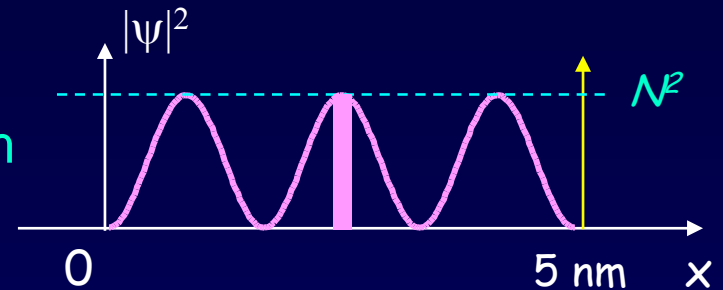
If the original energy of the particle was 0.135 eV, what is the likely new energy after we make the measurement (and find the particle in the center)?

      a) < 0.135 eV

      b) 0.135 eV

      c) > 0.135 eV

Solution

In the previous exercise, we found that the probability to find the electron within ±0.1 nm of the center of the well was ~8%.
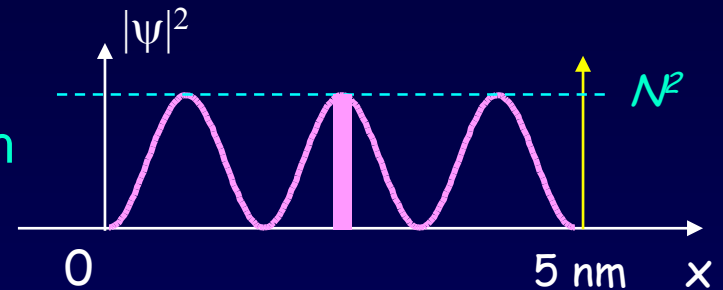

If the original energy of the particle was 0.135 eV, what is the likely new energy after we make the measurement (and find the particle in the center)?
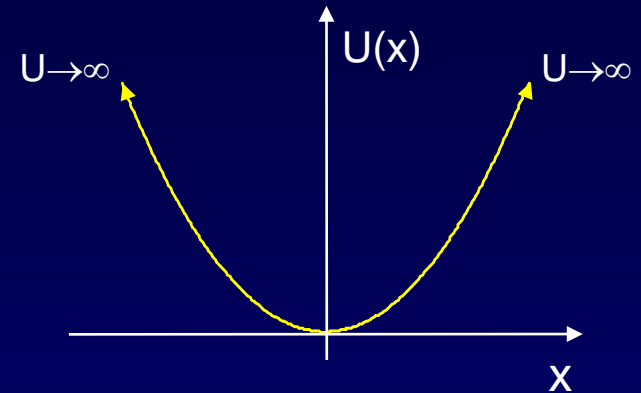
    a) < 0.135 eV

    b) 0.135 eV

    c) > 0.135 eV

We've greatly reduced the uncertainty in the location of the particle, and therefore greatly increased it's momentum uncertainty, and hence, it's likely energy.

Harmonic Oscillator Potential

Another very important potential is
the harmonic oscillator:

$$F = -\kappa x \qquad U(x) = -\int F \, dx = \int \kappa x \, dx$$

$$U(x) = \tfrac{1}{2} \kappa x^2 \qquad \omega = (\kappa/m)^{1/2}$$

Why is this potential so important?

- It accurately describes the potential for many systems. *E.g.*, sound waves in solids.

- It approximates the potential in almost every system for small departures from equilibrium. *E.g.*, chemical bonds.

To a good approximation,
everything is a harmonic oscillator.

Chemical bonding potential

Taylor expansion of U near minimum.
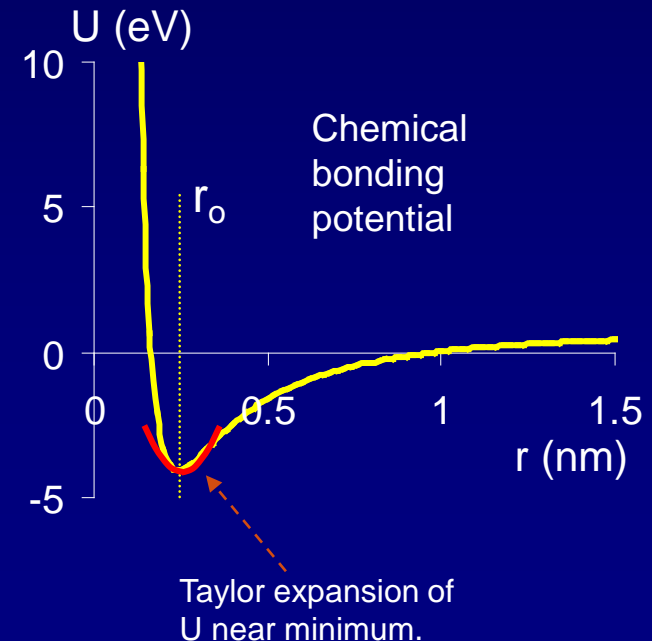
Harmonic Oscillator (2)

The differential equation that describes the HO is too difficult for us to solve here. Here are the important features of the solution.

The most important feature is that
the energy levels are equally spaced: $E_n = (n+1/2)\hbar\omega$.

ω is the classical oscillation frequency

The ground state (n = 0) does not have E = 0.
Another example of the uncertainty principle.

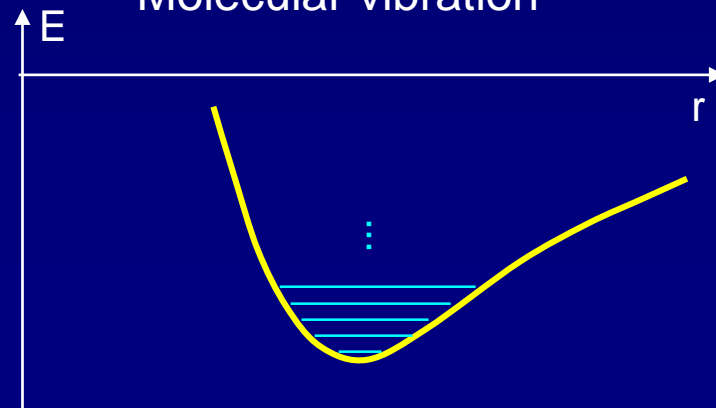Beware!! The numbering convention is not the same as for the square well.

Energy

n=3 ——— $\frac{7}{2}\hbar\omega$

n=2 ——— $\frac{5}{2}\hbar\omega$

n=1 ——— $\frac{3}{2}\hbar\omega$

n=0 ——— $\frac{1}{2}\hbar\omega$

Spacing between vibrational levels of molecules in atmospheric CO_2 and H_2O are in the infrared frequency range.

$$\Delta E = \hbar\omega = hf \sim 0.01 \text{ eV}$$

This is why they are important greenhouse gases.

Molecular vibration

E

r
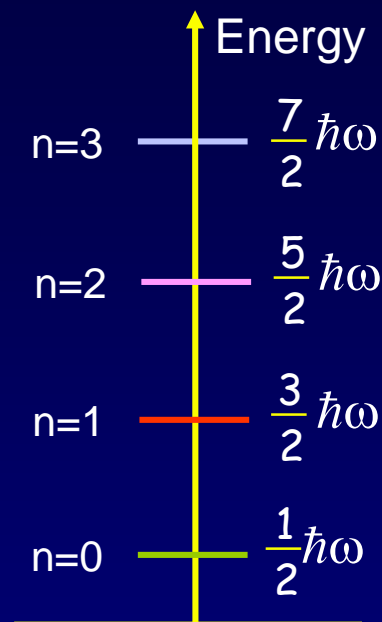
Harmonic Oscillator Wave Functions

To obtain the exact eigenstates and associated allowed energies for a particle in the HO potential, we would need to solve this SEQ:
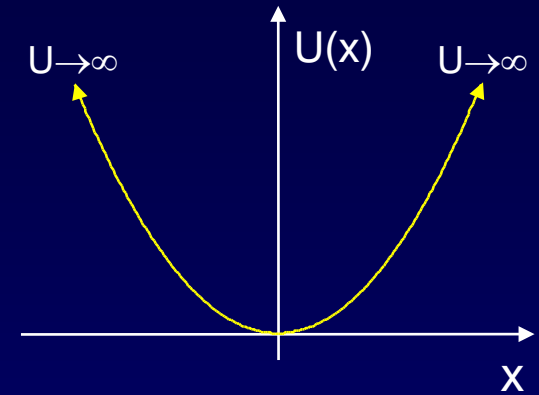
$$-\frac{\hbar^2}{2m}\frac{d^2\,\psi(x)}{dx^2} + \frac{1}{2}\kappa x^2 \psi(x) = E\psi(x)$$

This is solvable, but not here, not now …

However, we can get a good idea of what $\psi_n(x)$ looks like by applying our general rules.

The important features of the HO potential are:

- It's symmetrical about x = 0.
- It does not have a hard wall (doesn't go to ∞ at finite x).
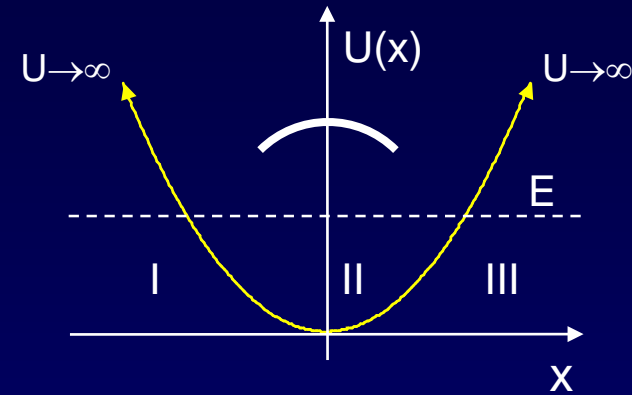
U→∞   U(x)   U→∞

x

HO Wave Functions (2)

Consider the state with energy E. There are two forbidden regions and one allowed region.

Applying our general rules, we can then say:

In region II E>U and SEQ tells us that the curvature of ψ(x) has the opposite sign as its value (curves *toward* the axis)

$$-\frac{\hbar^2}{2m}\frac{d^2\,\psi_n(x)}{dx^2} = \left(E_n - U(x)\right)\psi_n(x)$$

In regions I and III, just the opposite: E<U and there the curvature of ψ(x) has the same sign as its value (curves *away from* the axis)

$U \to \infty$ U(x) $U \to \infty$

E

I   II   III

X

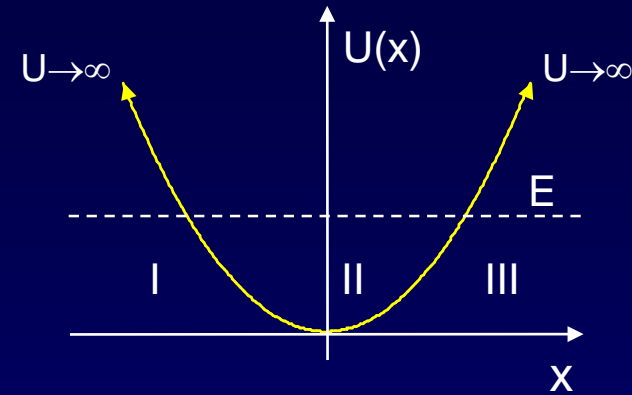$$\frac{d^2}{dt^2}x(t) = F\left(x(t)\right)$$

Some similarity to what you have to do to solve for a Newtonian trajectory, but it IS different!

HO Wave Functions (2)

Consider the state with energy E. There are two forbidden regions and one allowed region.

Applying our general rules, we can then say:

- $\psi(x)$ curves toward zero in region II and away from zero in regions I and III.
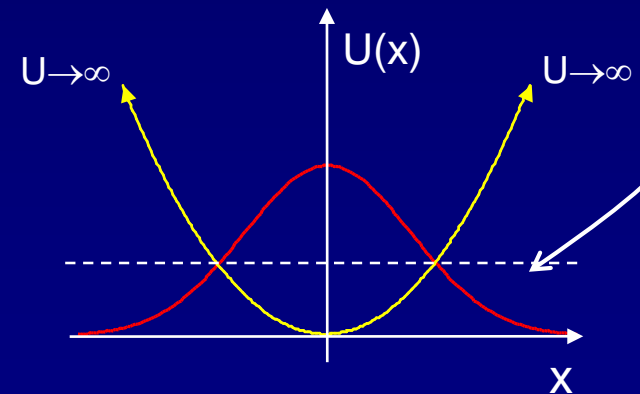
- $\psi(x)$ is either an even or odd function of x.

Let's consider the ground state:

- $\psi(x)$ has no nodes.

- $\psi(x)$ is an even function of x.

This wave function resembles the square well ground state. The exact functional form is different—a 'Gaussian'—but we won't need to know it in this course:

$$\psi_{n=0}(x) \propto e^{-x^2/2a^2} \qquad a^2 = \frac{\hbar}{\sqrt{m\kappa}}$$
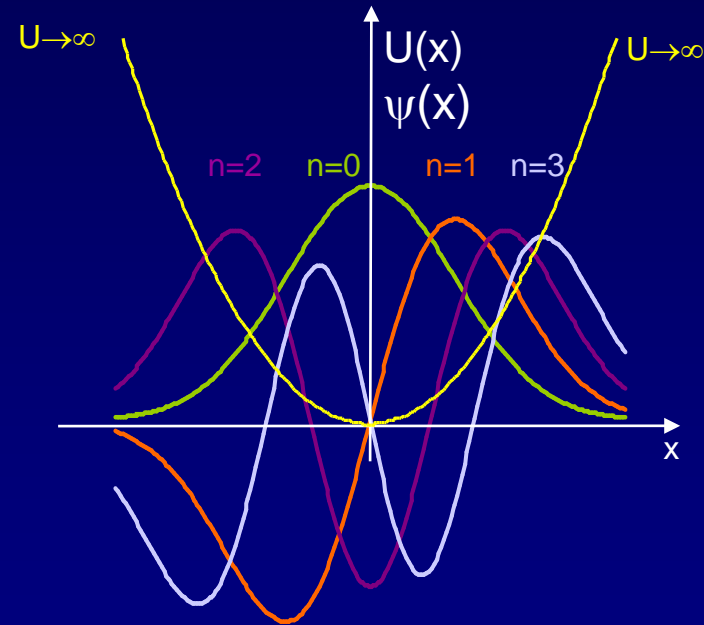
Can you see how this works here?

HO Wave Functions (3)

For the excited states, use these rules:

- Each successive excited state has one more node.
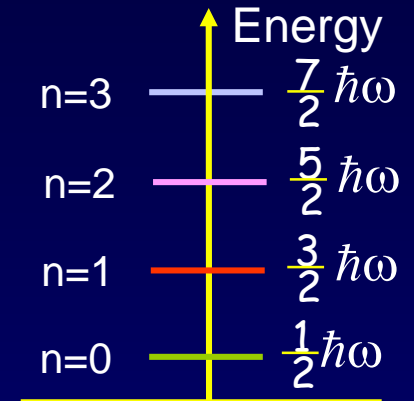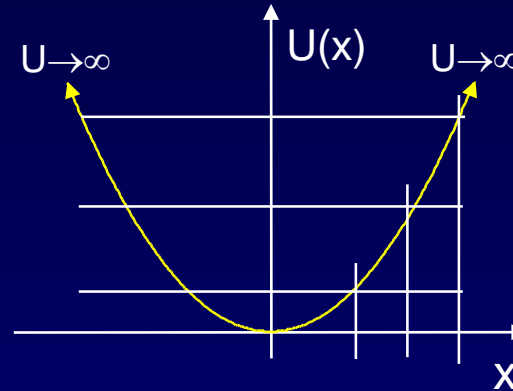- The wave functions alternate symmetry.

Unlike the square well, the allowed region gets wider as the energy increases, so the higher energy wave functions oscillate over a larger x range. (but that's a detail…)
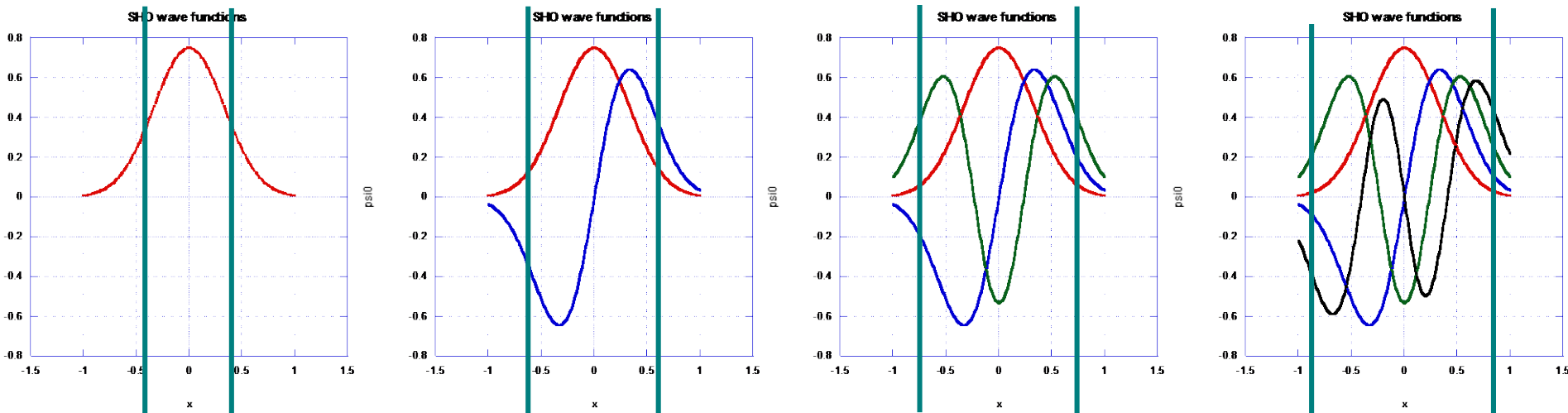
Take a look at how we can interpret the SHO wave functions

See how the curvature change works out

At the classical "turning points" the curvature changes

Green lines denote where the last energy level enters the forbidden region

Harmonic Oscillator Exercise

A particular laser emits at a wavelength $\lambda = 2.7$ μm. It operates by exciting hydrogen fluoride (HF) molecules between their ground and 1st excited vibrational levels. Estimate the ground state energy of the HF molecular vibrations.

Solution

A particular laser emits at a wavelength $\lambda = 2.7$ μm. It operates by exciting hydrogen fluoride (HF) molecules between their ground and 1st excited vibrational levels. Estimate the ground state energy of the HF molecular vibrations.

Recall:

$E_{photon} = hc/\lambda = (1240$ eV-nm$)/2.7\mu$m $= 0.46$ eV

and: (by energy conservation)

$E_{photon} = \Delta E = E_1 - E_0 = \hbar\omega = 2E_0$

Therefore,

$\boxed{E_0 = \frac{1}{2}\,\hbar\omega = 0.23 \text{ eV}}$

$\hbar\omega$

n=1

n=0

$\frac{1}{2}\hbar\omega$