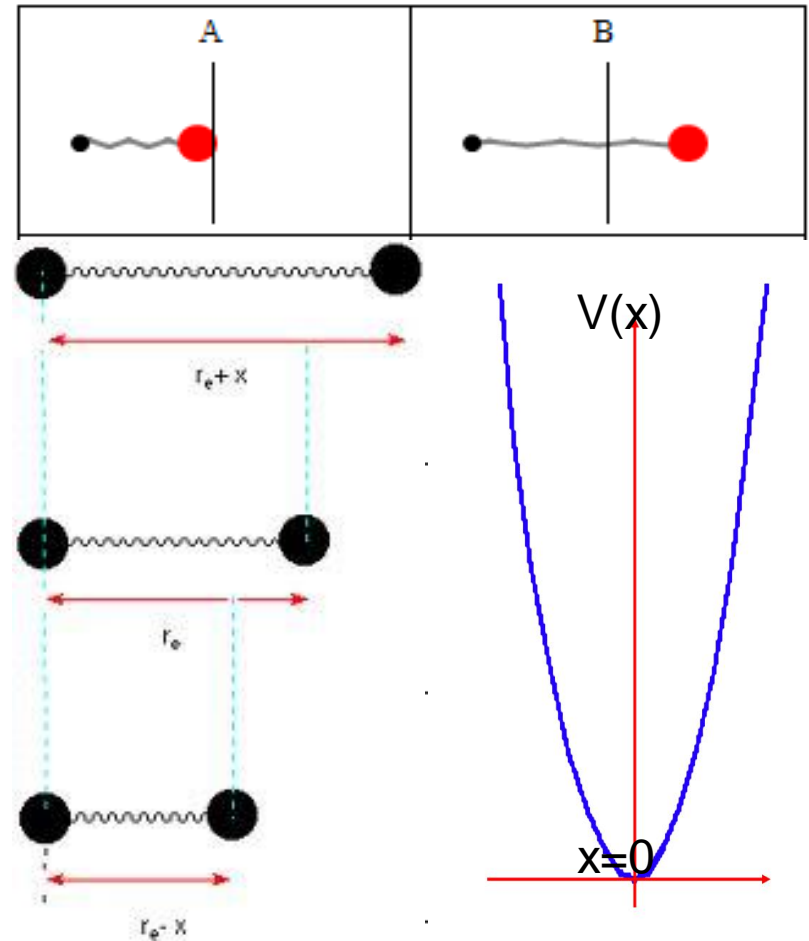
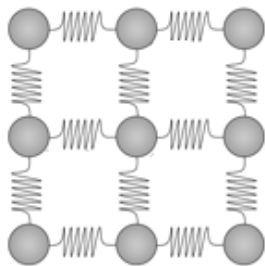


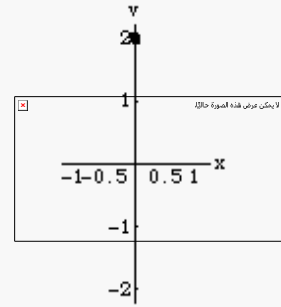
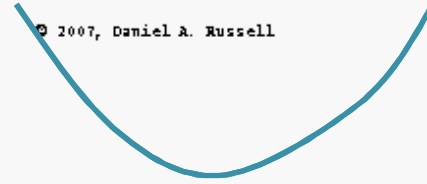
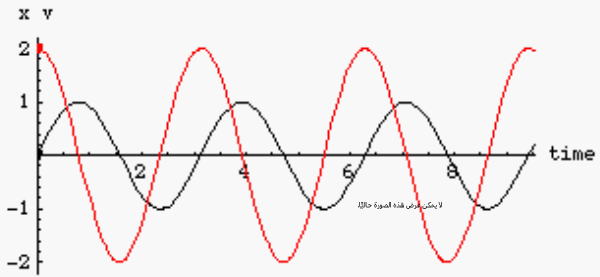
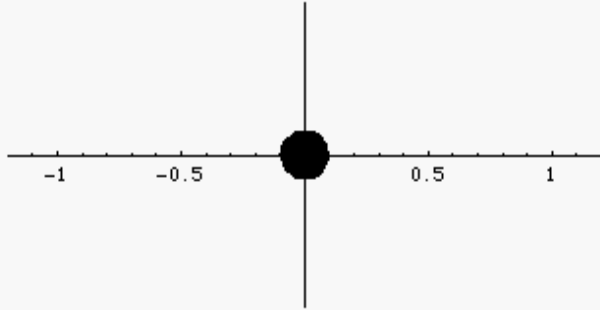
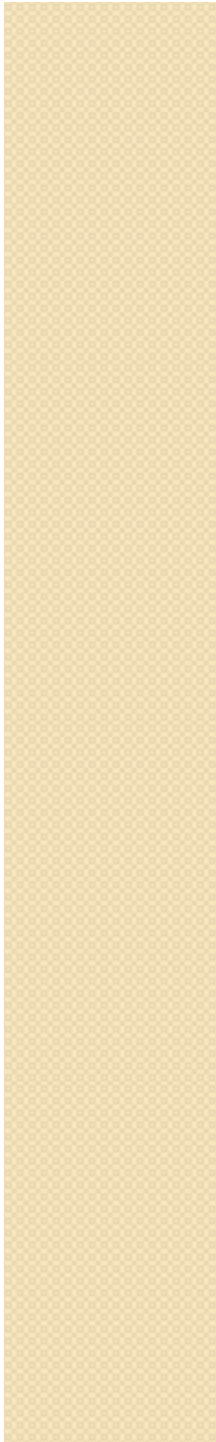
The quantum Harmonic Oscillator

Useful approximation for:

- Vibration of a diatomic molecule
- Vibrations of a polyatomic molecule of N atoms.

-Vibrations of a crystal lattice





Potential Energy for Harmonic Oscillator

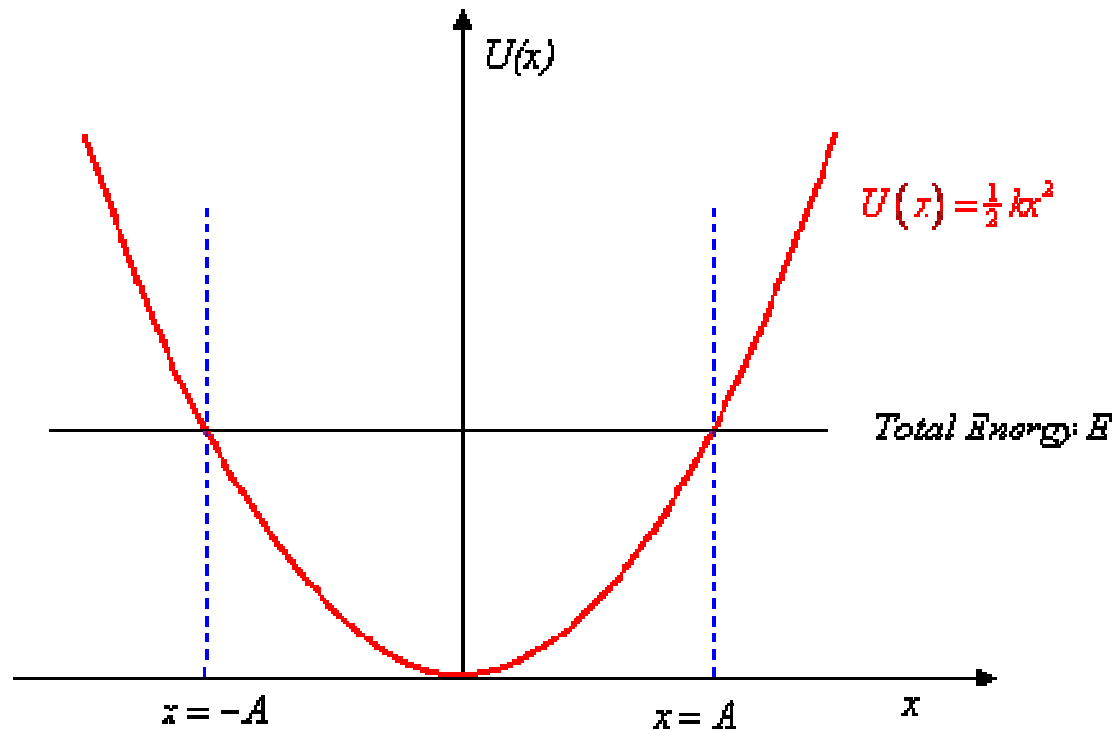
$$F = -\nabla V(x, y, z)$$

$$F = -\frac{dV(x)}{dx}$$

$$V(x) = -\int F \cdot dx = -\int (-kx) dx$$

$$V(x) = \frac{1}{2} kx^2 = \frac{1}{2} m\omega^2 x^2$$

- The oscillator has total energy equal to kinetic energy + potential energy.
- when the oscillator is at A , it is momentarily at rest, so has no kinetic energy



Potential Energy $U(x)$ for a Simple Harmonic Oscillator.

For **total** energy E , the oscillator swings back and forth between $x = -A$ and $x = +A$.

Classical Description of the problem: Classical prediction

$$F = -kx$$

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

$$\frac{d^2 x}{dt^2} = -\left(\frac{k}{m}\right)x$$

$$\frac{d^2 x}{dt^2} + \omega^2 x = 0$$

$$\omega = \sqrt{\frac{k}{m}}$$

The solution is $x = A \sin(\omega t) + B \cos(\omega t)$

By applying the boundary condition:

At $t=0$, $x=a$ and $v=0$

We get

$$x = a \cos(\omega t)$$

Where a is the amplitude

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

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

$$a = \sqrt{\frac{2E}{k}}$$

$$v^2 = \left(\frac{2E}{m}\right) - \left(\frac{k}{m}\right)x^2$$

$$v^2 = \left(\frac{k}{m}\right)(a^2 - x^2)$$

$$v = \pm\omega\sqrt{a^2 - x^2}$$

Let the probability of finding the particle in narrow region of length Δx at a position x and Δt to be the time required for the particle to cross Δx . Since the particle crosses Δx twice during each oscillation, we have

$$P(x)\Delta x = 2\Delta t / T$$

T is the periodic time

$$P(x) = \frac{2}{|v|T}$$


$$P(x) = \frac{1}{\pi\sqrt{a^2 - x^2}}$$

The function $P(x)$ is the classical probability density (probability per unit length). We need to compare it with the corresponding quantum mechanical probability density.

Classical (approximation) mechanics or quantum mechanics

To decide if we used classical (approximation) mechanics or quantum mechanics we calculate de Broglie wavelength and compare it with an important linear dimension in the problem (in this problem the amplitude of the oscillation). **If the de Broglie wavelength is negligibly small compare to the other then classical mechanics is safely be used.**

In the quantum-mechanics description of particle motion, **the concept of a particle trajectory is completely lost.** We can not know the particle position and momentum simultaneously this fundamental limitation is formalized in the Heisenberg uncertainty relation. In the case of quantum harmonic motion **we must stop visualizing a particle oscillation about a mean position and concentrate on the wave function.** The wave function corresponding to a particular state tells us all that can be known about the behaviour of the particle in that particular state.



The Schrodinger equation for a simple harmonic oscillator

The one-dimensional wave function $\Psi(x,t)$ is time dependent and satisfy the time-dependent Schrodinger equation. For a stationary state of definite energy E the wave function takes the form.

$$\Psi(x,t) = \Psi(x)e^{-i(E/\hbar)t}$$

Here we are concerned with stationary states, so we will concentrate on determining the spatial wave function $\Psi(x)$ which satisfy the time-independent Schrodinger equation and the corresponding value of E.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} kx^2 \psi(x) = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{mk}{\hbar^2} x^2 \right) \psi(x) = 0$$

$$-\infty < x < \infty$$

$$\text{assume } \begin{cases} \alpha^2 = \frac{mk}{\hbar^2} \\ \lambda = \frac{2mE}{\hbar^2 \alpha} \end{cases}$$

Change the variables

$$x \rightarrow \frac{y}{\sqrt{\alpha}}$$

$$-\infty < y < \infty$$

$$dx \rightarrow \frac{dy}{\sqrt{\alpha}}$$

$$\psi(x) \rightarrow \psi(y)$$

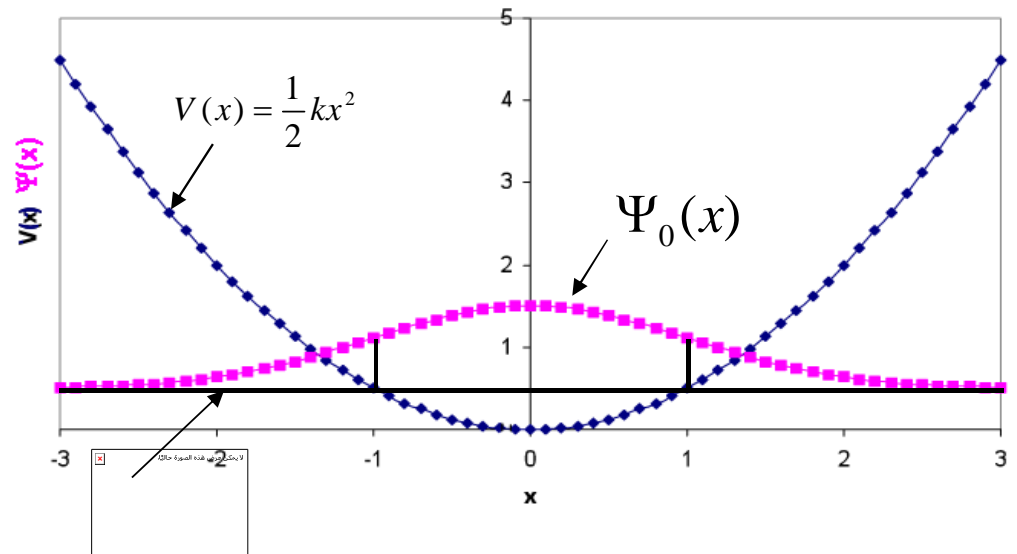
We arrive to

$$\frac{d^2\psi(y)}{dy^2} + (\lambda - y^2)\psi(y) = 0$$

The energy eigenfunctions

The harmonic oscillator potential has no rigid boundary but it does go to infinity at infinite distance from the origin. The boundary condition is that the allowed wave functions approach zero as x approaches $+\infty$ or $-\infty$. You may think that “*this condition is easy to arrange with any value of the total energy E , since the solution to any second-order differential equation contains two arbitrary constants*”. This is not so. One of the two constants fixes the **overall normalization** of the wave function and the remaining constant and the value of E are used to satisfy the two boundary conditions. There are an infinite number of discrete values of E which we label $E_1, E_2, E_3, \dots, E_n$, and to each of these there is a corresponding allowed wavefunction $\psi_1, \psi_2, \psi_3, \dots, \psi_n$.

If E is varied, even infinitesimally, from any one of the allowed values, then the wave function will diverge to infinity as x approaches $+\infty$ or $-\infty$. The allowed values of E are called **eigenvalues** of total energy and the corresponding wavefunctions are **eigenfunctions** of total energy.



For any given energy E , there will be a region of space where the potential energy is less than the total energy, this is called classically allowed region. In this region we expect the wave function to have properties similar to the standing waves inside a one-dimensional box (**the number of nodes of the wave function increase with increasing energy**). In the region of large x where the particle energy is much less than the potential energy (**classically forbidden region**) we expect a solution of exponential form. $\text{Exp}(-dx)$ is not a correct form because it does not go to zero as x goes to $-\infty$.

$$\psi(y) = Af(y)e^{-y^2/2}$$

$$A[f''(y) - 2yf'(y) - f(y) + y^2 f(y)]e^{-y^2/2} + (\lambda - y^2)Af(y)e^{-y^2/2} = 0$$

Divided by $Ae^{-y^2/2}$ and arrange we get

$$f''(y) - 2yf'(y) + (\lambda - 1)f(y) = 0$$

Compare the above equation with the Hermite differential equation

$$H_n''(y) - 2yH_n'(y) + 2nH_n(y) = 0$$

The solution of the Hermite differential equation is Hermite polynomials

If we choose $(\lambda - 1) = 2n$

$$\lambda = 2n + 1$$

Then

$$f(y) \equiv H_n(y)$$

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

$$H_0(y) = 1$$

$$H_1(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

$$\psi_n(y) = AH_n(y)e^{-y^2/2}$$

$$y = \sqrt{\alpha}x$$

$$\psi_n(x) = AH_n(\sqrt{\alpha}x)e^{-\alpha x^2/2}$$

To determine the constant A we normalize the wave function taking into account the relation

$$\int_{-\infty}^{\infty} H_n(y)H_m(y)e^{-y^2} dy = 2^n n! \sqrt{\pi} \delta_{nm}$$

$$A = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2}$$

$$\psi_n(x) = \left(\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} H_n(\sqrt{\alpha}x) e^{-\alpha x^2/2}$$

Table 7.2: The Harmonic Oscillator Wavefunctions

$$\psi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1 = \sqrt{2} \left(\frac{\alpha}{\pi} \right)^{1/4} \alpha^{1/2} x e^{-\alpha x^2/2}$$

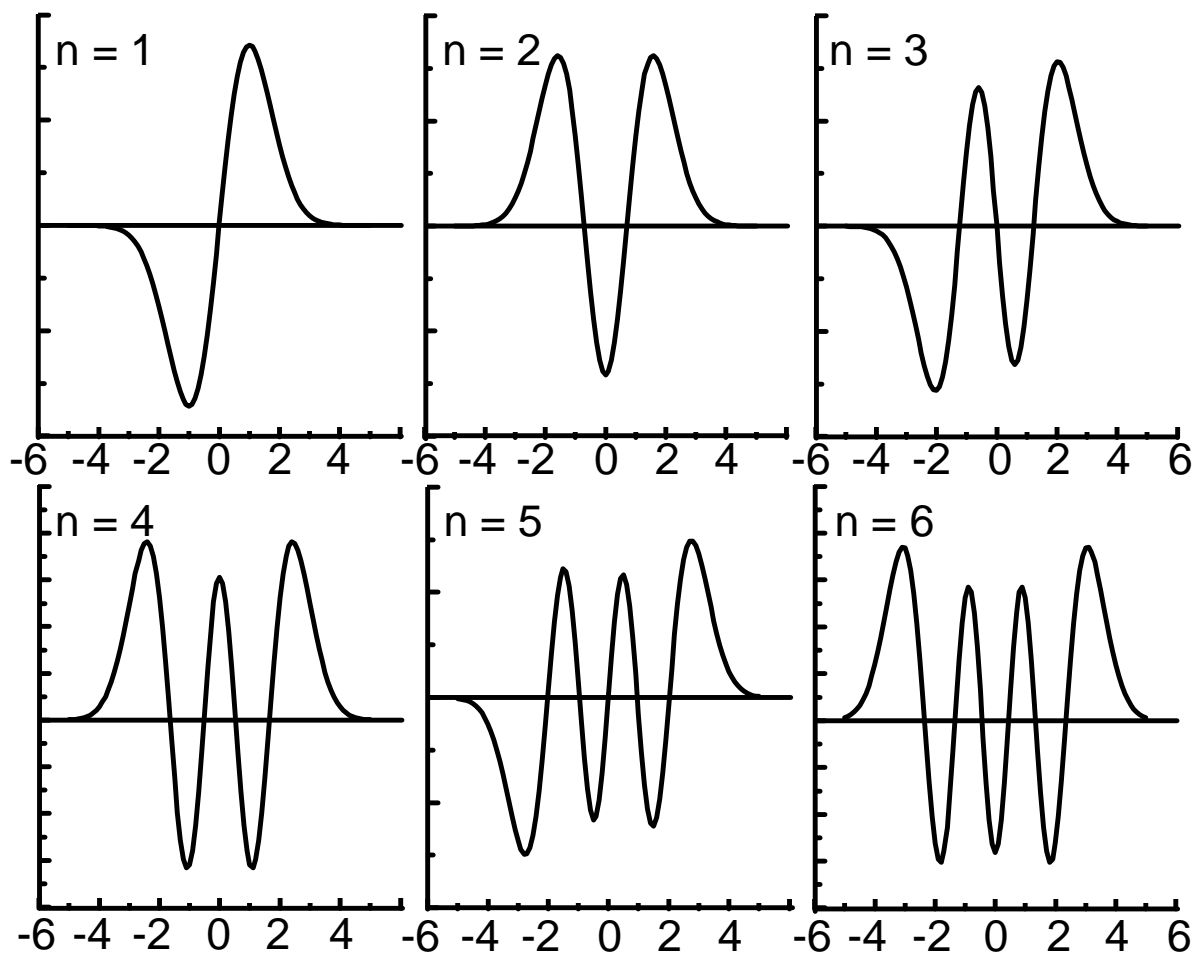
$$\psi_2 = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

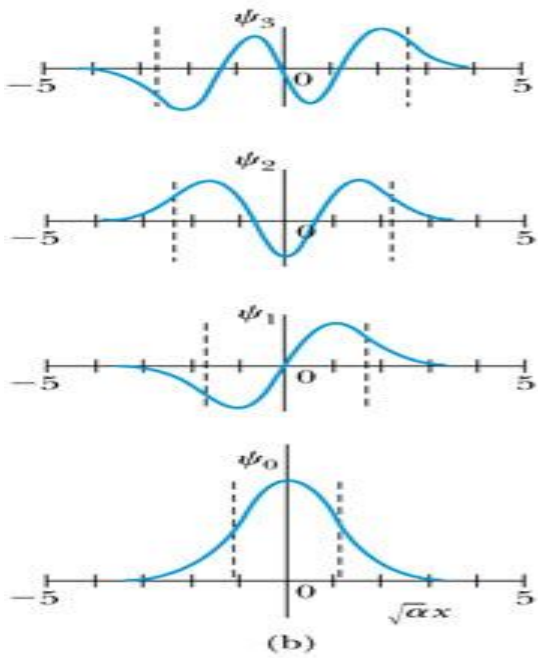
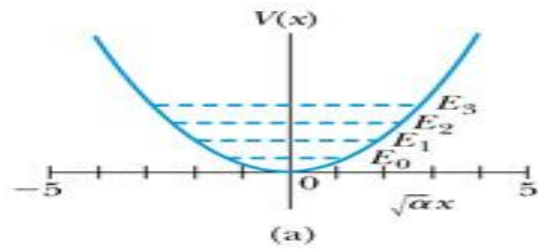
$$\psi_3 = \sqrt{3} \left(\frac{\alpha}{\pi} \right)^{1/4} (2\alpha^{3/2} x^3/3 - \alpha^{1/2} x) e^{-\alpha x^2/2}$$

$$\psi_4 = \frac{1}{\sqrt{6}} \left(\frac{\alpha}{\pi} \right)^{1/4} (2\alpha^2 x^4 - 6\alpha x^2 + 3/2) e^{-\alpha x^2/2}$$

$$\psi_5 = \frac{1}{\sqrt{15}} \left(\frac{\alpha}{\pi} \right)^{1/4} (2\alpha^{5/2} x^5 - 10\alpha^{3/2} x^3 + 15\alpha^{1/2} x/2) e^{-\alpha x^2/2}$$

$$\psi_\nu = \left(\frac{1}{2^\nu \nu!} \right)^{1/2} \left(\frac{\alpha}{\pi} \right)^{1/4} H_\nu(\alpha^{1/2} x) e^{-\alpha x^2/2}, \quad \alpha = \mu\omega/\hbar$$





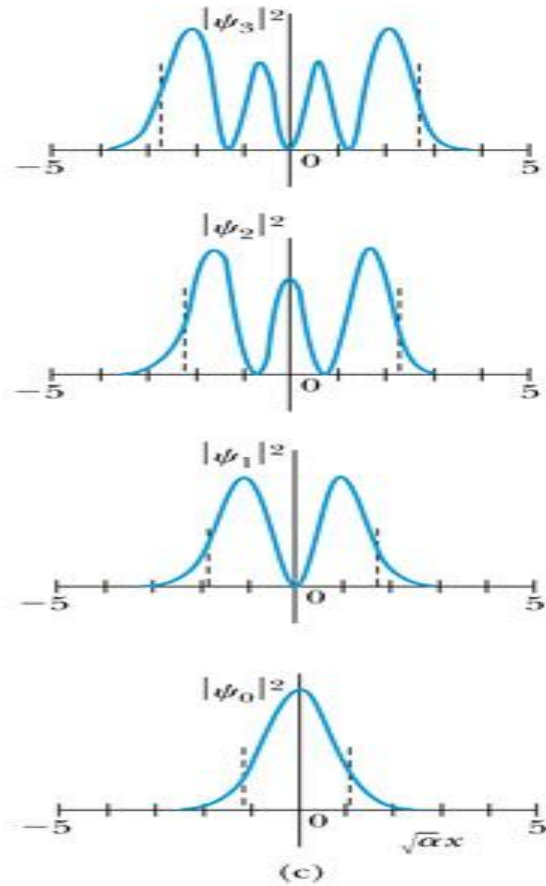
Wave functions

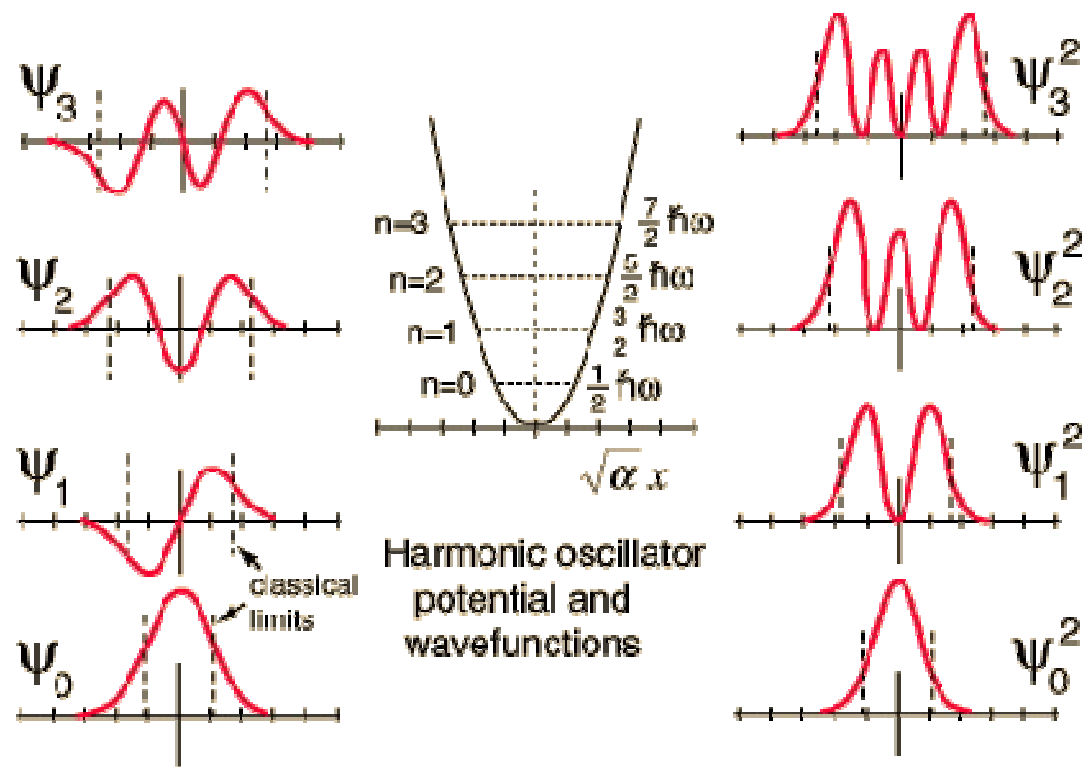
$$\psi_3(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}} (\sqrt{\alpha}x) (2\alpha x^2 - 3) e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} x e^{-\alpha x^2/2}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$





- The number of nodes increase with energy.
- The falling exponential with argument proportional to square of x insure that the wave functions go smoothly to zero as x go to $+\infty$ or $-\infty$.
- Each wave function has a definite symmetry, it is either an odd or even function of x (for even n the wave function is even and for odd n the wave function is odd). This property follow from the nature of the potential function. $U(x)=U(-x)$ i.e the potential symmetry about $x=0$. This means that any physical observable must also be symmetric about $x=0$, including the stationary state probability density function.
- The eigenfunctions spread out in space as the energy increases.

The energy eigenvalues

$$\lambda = (2n + 1) = \frac{2mE}{\hbar^2 \alpha}$$

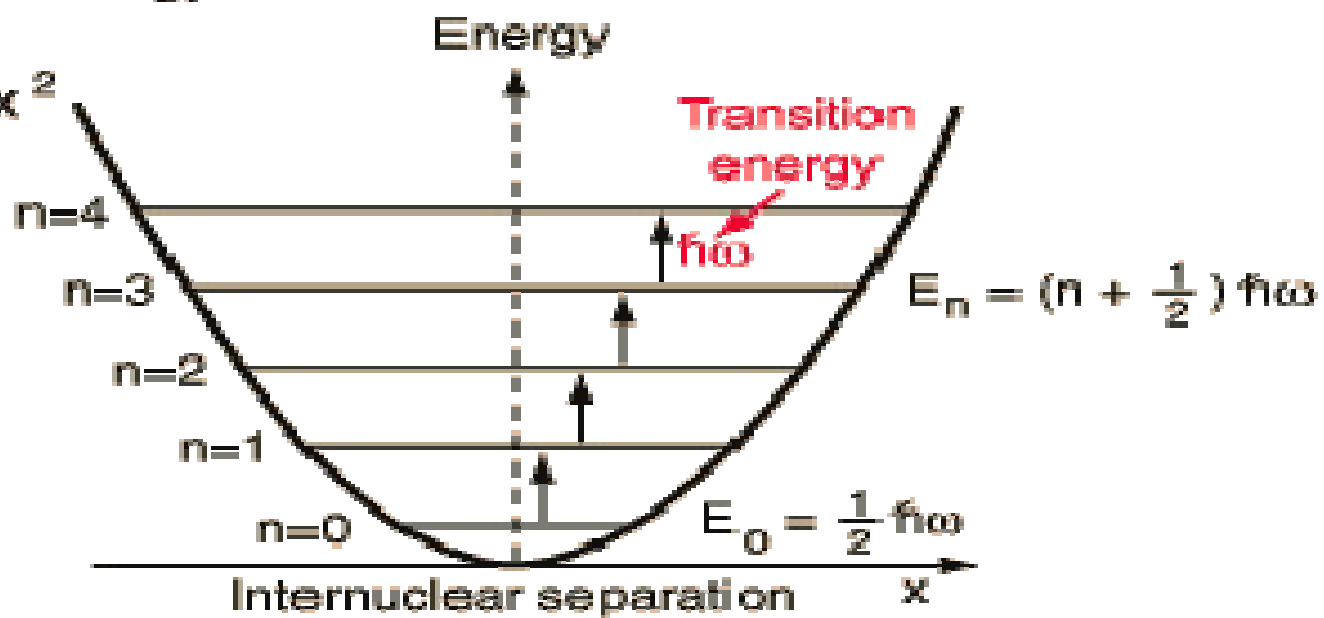
$$\alpha = \sqrt{\frac{mk}{\hbar^2}} = \frac{m}{\hbar} \omega$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$E_n = \left(n + \frac{1}{2}\right) \omega \hbar$$

Potential energy
of form

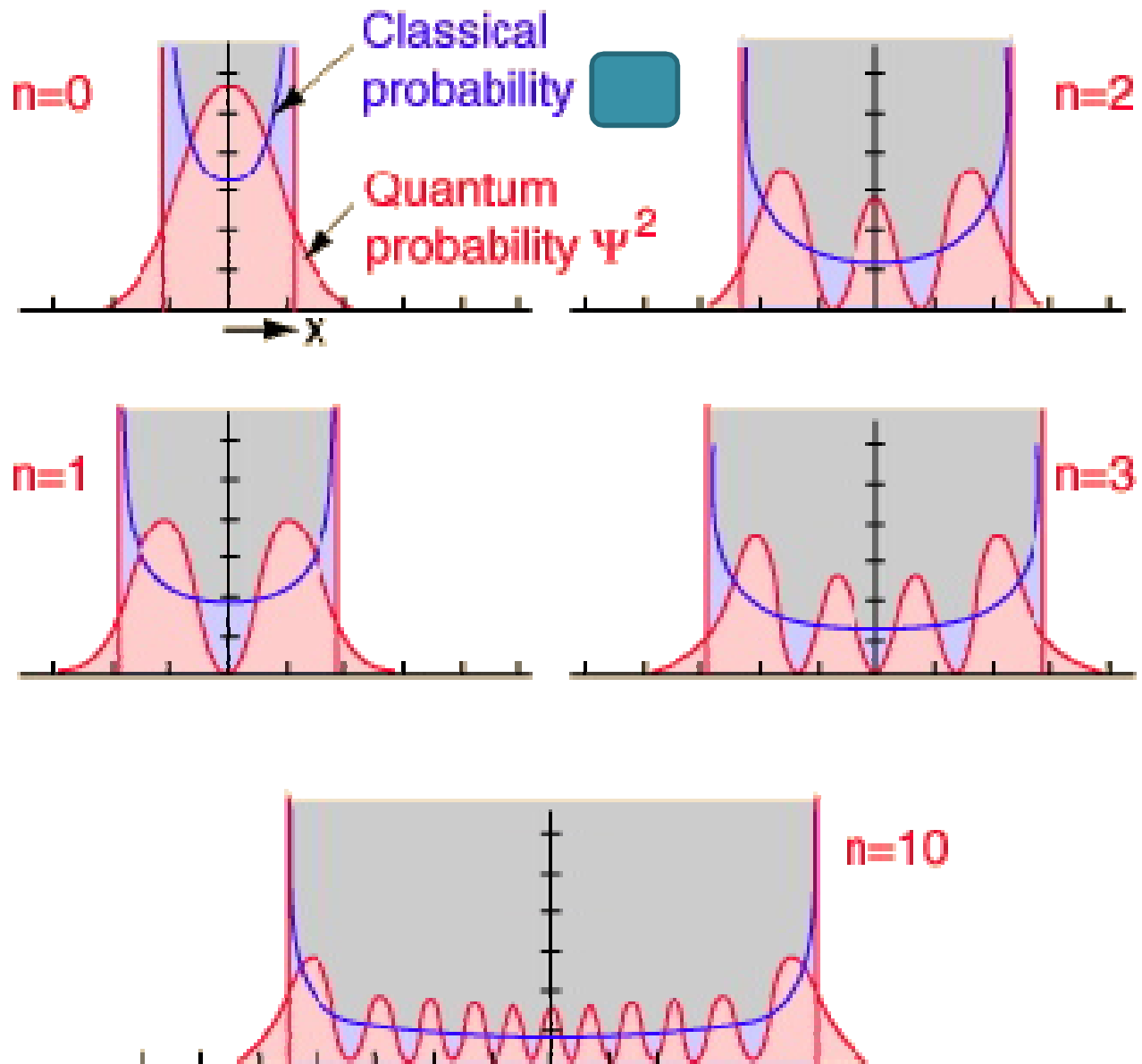
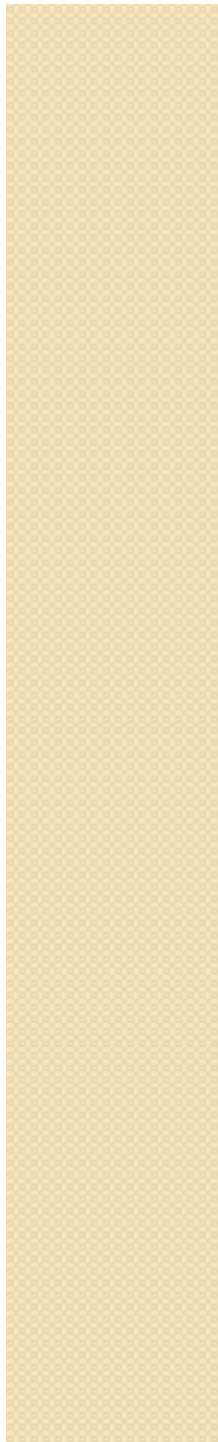
$$\frac{1}{2} kx^2$$



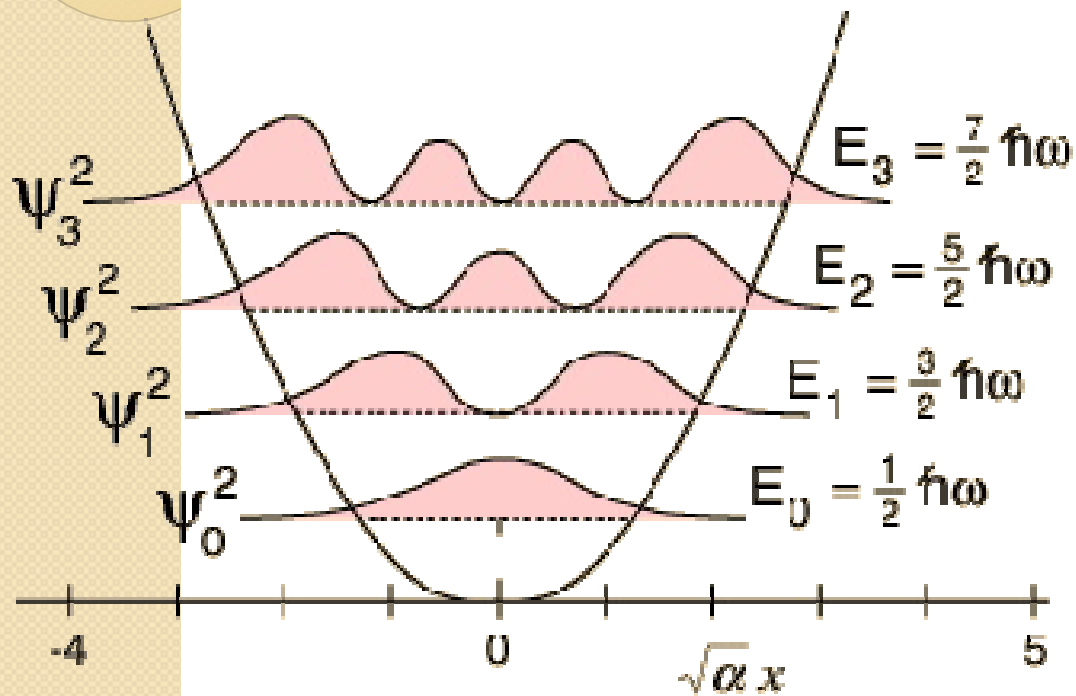
Probability densities and comparison with classical prediction

$$\frac{\Delta E}{E_n} = \frac{\omega \hbar}{(n + 1/2)\omega \hbar} \rightarrow 0, \text{ as } n \rightarrow \infty$$

An important prediction of quantum mechanics is the so-called **zero point energy**. When the quantum number $n=0$, the total energy is $E_0 = \frac{1}{2}\omega \hbar$ and this is the smallest possible value of the total energy of any harmonic oscillator. This effect is a purely quantum effect it has no parallel in classical mechanics, which allows energies arbitrarily close to zero.



Probability Distributions for the Quantum Oscillator (ψ^2_{vib})



there is a finite probability that the oscillator will be found outside the "potential well" indicated by the smooth curve. This is forbidden in classical physics.

Useful integral

$$\int_{-\infty}^{\infty} x^n e^{-\alpha x^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots |n-1| \pi^{1/2}}{2^{n/2} \alpha^{(n+1)/2}}, n = 0, 2, 4, \dots$$

Useful matrix elements of the infinite Box

$$\langle m|x|n \rangle = a \cdot \begin{cases} 1/2 & m = n \\ 0 & m \neq n, m \pm n = \text{even} \\ -\frac{8mn}{\pi^2 [m^2 - n^2]^2} & m \neq n, m \pm n = \text{odd} \end{cases}$$

The general time-dependent solution to Schrodinger equation for the infinite Box

Since any combination of solutions to a linear differential equation is itself a solution, the general solution to the time dependent Schrodinger equation is given by

$$\Psi(x, t) = \sum_n c_n e^{-i\omega_n t} \psi_n(x)$$

If we know the form of the solution at time $t=0$, then we can determine The coefficients from the relation

$$\int \psi_m^*(x) \Psi(x, 0) dx = c_m e^{-i\omega_m(0)} = c_m$$