PH 101: Physics I

Module 3: Introduction to Quantum Mechanics

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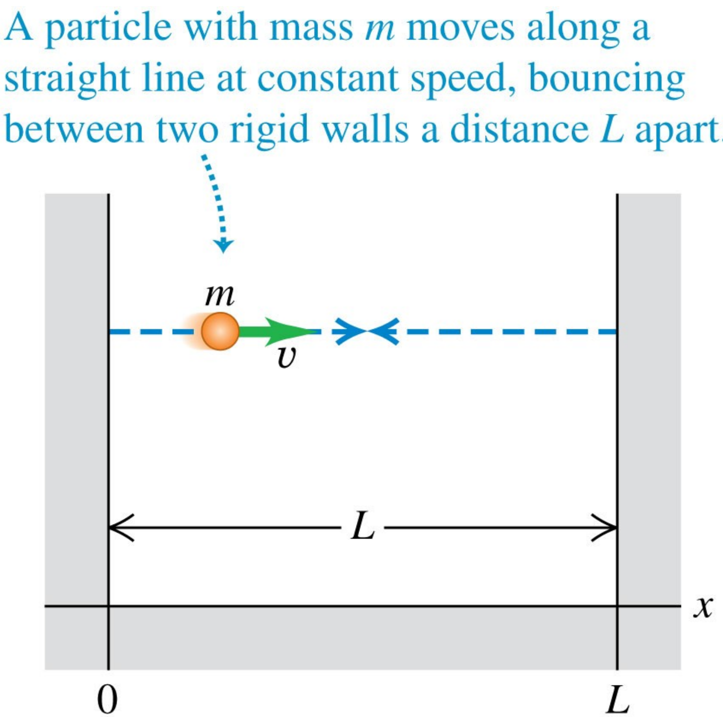
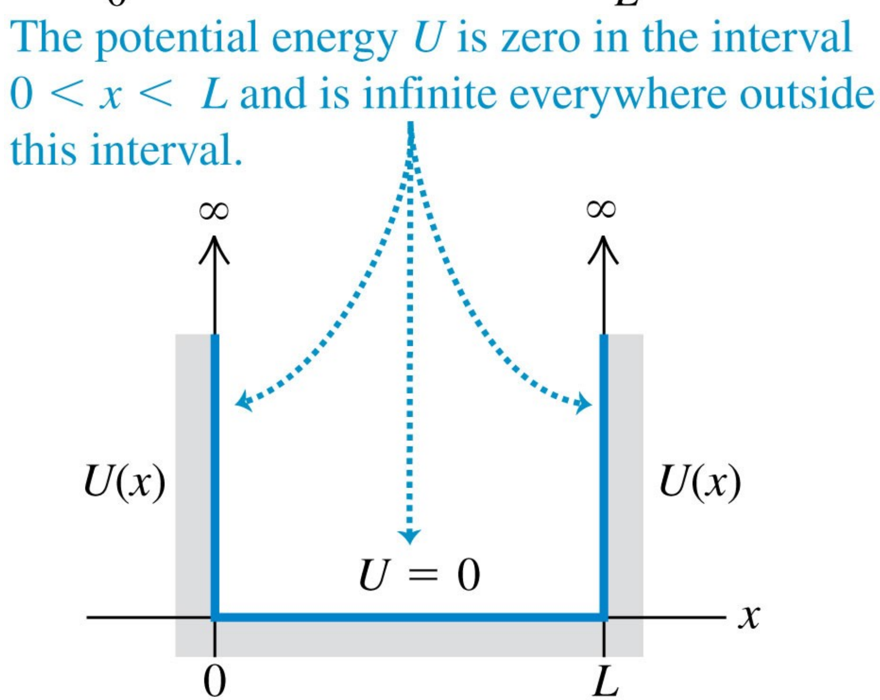
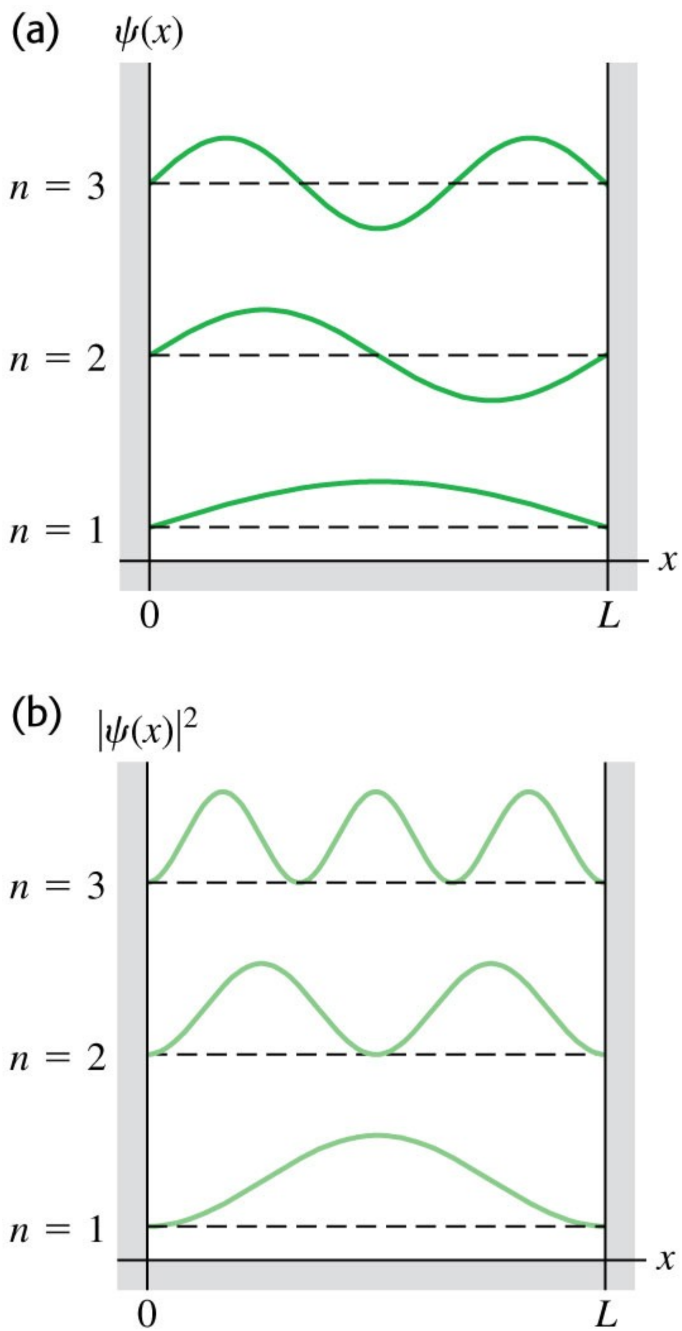
RECAP

Particle in an infinite well







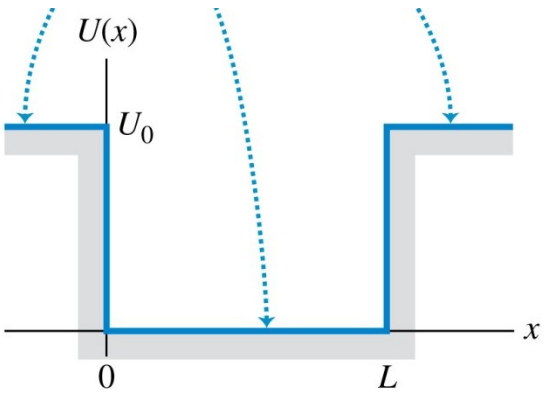
RECAP

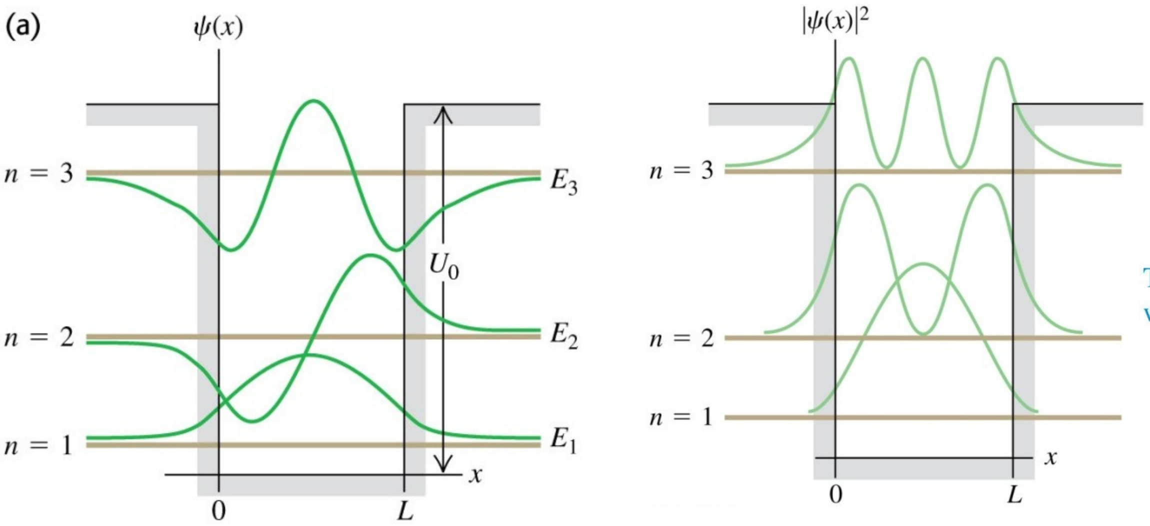
Particle in a finite well

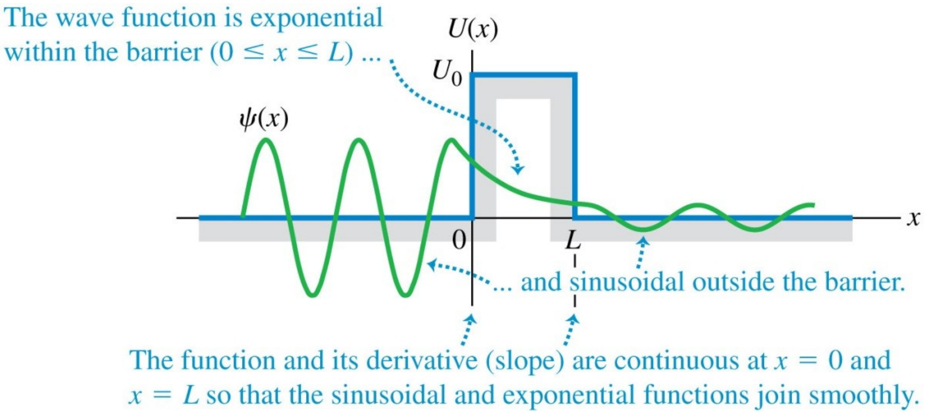
$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U_0\psi(x)=E\psi(x) \quad (\text{for } x<0)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x) \quad (\text{for } 0<x<L)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U_0\psi(x)=E\psi(x) \quad (\text{for } x>L)$$







RECAP

Time evolution in the Hilbert space

In Hilbert space a general function has the expansion in terms of the basis functions,

$$\psi(x) = c_1\,\varphi_1(x) + c_2\,\varphi_2(x) + \ldots\ldots \qquad [1]$$

and the coefficients are similarly given as,

$$c_j \equiv < \varphi_j\,|\psi > = \int_{-\infty}^{\infty} \varphi_j^*(x)\psi(x)\; dx$$

HW: Prove this by multiplying [1] above on both sides by $\varphi_j^*(x)$ and integrate with respect to x and use the orthogonality and normalization of the basis functions $\varphi_j(x)$.

Consider a general state f(x) is given for the particle in an infinite well. The function can be represented as the superposition of the eigen states given by

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right).$$

This represents **Fourier series** for f(x), and the fact that "any" function can be expanded in this way is sometimes called **Dirichlet's theorem**.
The coefficients c_n can be evaluated by Fourier's trick, which exploits the orthonormality of $\{\psi_n\}$ Multiply both sides of the above equation by $\psi_m(x)^*$ and integrate.

RECAP

Time evolution in the Hilbert space

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right).$$

$$\boxed{\int \psi_m(x)^* f(x)\,dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\,dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m.}$$

Thus the nth coefficient in the expansion of $f(x)$ is

$$c_n = \int \psi_n(x)^* f(x)\,dx.$$

Thus, the **stationary states** are given by

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

and the most general solution is $\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$

Above equation gives $\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$ $\quad c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)\,dx.$

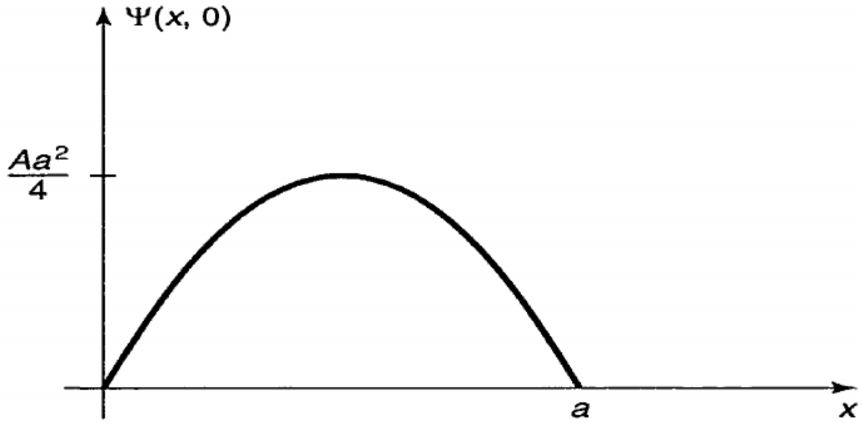
Given the initial wave function $\psi(x, 0)$, we first compute the expansion coefficients c_n, and then obtain $\psi(x, t)$.

Time evolution in the Hilbert space

Example: A particle in the infinite square well has the initial wave function

$$\Psi(x, 0) = Ax(a - x), \qquad (0 \leq x \leq a),$$

for some constant A . Outside the well, of course, $\psi = 0$. Plot $\psi(x, 0)$. Find $\psi(x, t)$.



Normalize the wave function,

$$1 = \int_0^a |\Psi(x, 0)|^2 \, dx = |A|^2 \int_0^a x^2 (a - x)^2 \, dx = |A|^2 \frac{a^5}{30},$$

$$A = \sqrt{\frac{30}{a^5}}.$$

Example Contd..

$$
\begin{aligned}
c_n &= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}}\, x(a-x)\, dx \\
&= \frac{2\sqrt{15}}{a^3}\left[a \int_0^a x \sin\left(\frac{n\pi}{a}x\right) dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right) dx\right] \\
&= \frac{2\sqrt{15}}{a^3}\left\{a\left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]\Big|_0^a\right. \\
&\quad \left. -\left[2\left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2 - 2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]\Big|_0^a\right\} \\
&= \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0)\right] \\
&= \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0) - \cos(n\pi)\right] \\
&= \begin{cases} 0, & \text{if } n \text{ is even,} \\ 8\sqrt{15}/(n\pi)^3, & \text{if } n \text{ is odd.} \end{cases}
\end{aligned}
$$

so that, $$\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5\ldots} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right) e^{-in^2\pi^2\hbar t/2ma^2}.$$

Example Contd..

Given $$\psi(x,t) = \sum_n c_n \psi_n(x,t)$$

What is the probability to find the system in the ground state at time t=0?

$$P_1 = |c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.9985550143640185$$

What is the probability to find the system in the second excited state?

$$P_3 = |c_3|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \frac{1}{3^6} = 0.00136976$$

Similarly,

$$P_5 = 0.0000639075, \quad P_7 = 8.48758 \times 10^{-6}$$

Harmonic Oscillator

Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be an object supported by a spring or floating in a liquid, a diatomic molecule, an atom in a crystal lattice.

The condition for harmonic motion 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.

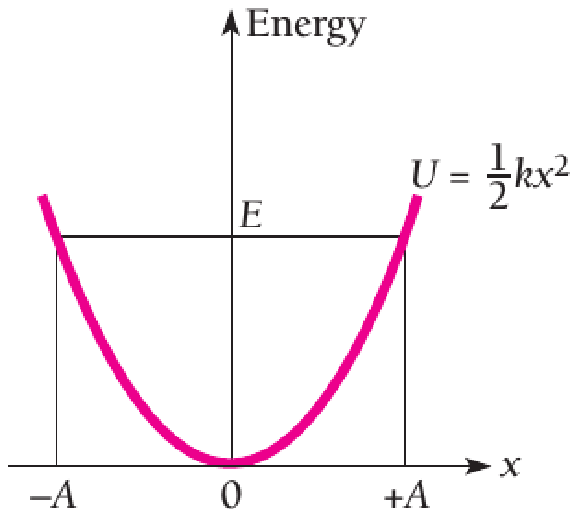
In the special case of simple harmonic motion, the restoring force F on a particle of mass m is linear; that is, F is proportional to the particle's displacement x from its equilibrium position and in the opposite direction.

Thus $$F = -kx$$

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

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

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



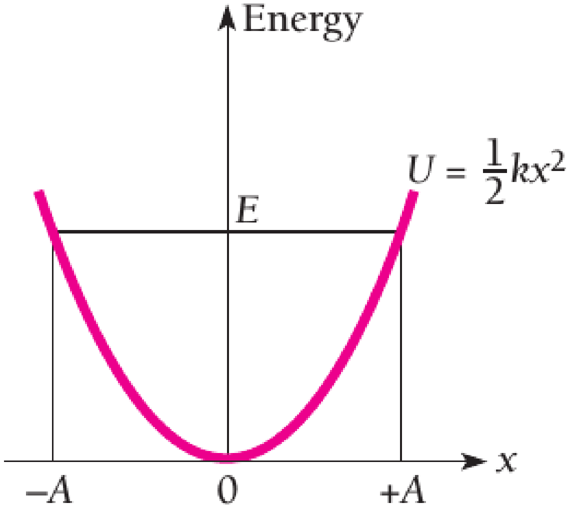
Quantum Harmonic Oscillator

$$\hat{E} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2.$$

$$\hat{E}\phi(x;n) = E_n\phi(x;n)$$

Time independent Schrodinger Equation for the Harmonic oscillator will have the form as

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi(x;n)}{\partial x^2} + \frac{1}{2}m\omega^2x^2\phi(x;n) = E_n\phi(x;n)$$



$$\alpha \equiv \sqrt{\frac{\hbar}{m\omega}} \qquad u \equiv \frac{x}{\alpha} \qquad \varepsilon = \frac{E}{\frac{\hbar\omega}{2}}$$

$$\frac{\partial^2\phi}{\partial u^2} = (u^2 - \varepsilon)\phi.$$

We need to find the solution of the above equation.

First, we apply asymptotic analysis: $\lim_{u\to\pm\infty}(u^2 - \varepsilon) \approx u^2$

So we have, $\lim_{u\to\pm\infty}\frac{\partial^2\phi}{\partial u^2} \approx u^2\phi.$

Harmonic Oscillator

We can consider the trial solution as $\phi(u) = \phi_0 e^{\frac{\alpha u^2}{2}}$

We find that $\frac{\partial \phi}{\partial u} = \alpha u \phi$ and $\frac{\partial^2 \phi}{\partial u^2} = (\alpha + \alpha^2 u^2)\phi \approx \alpha^2 u^2 \phi$

Comparing this to our differential equation, we see that we need

$\alpha^2 = 1$ $\alpha = \pm 1$

$$\boxed{\phi(u) = \phi_A e^{\frac{u^2}{2}} + \phi_B e^{-\frac{u^2}{2}}.}$$

The first part is not normalizable, though, so we do not want that. We keep only the second part and generalize the constant to a function of u that is relatively constant and well-behaved as $u \to \pm\infty$, so we say that

$$\phi(u) = s(u) e^{-\frac{u^2}{2}}$$

Substituting the above function in the Schroedinger eqaution we get

$$\frac{\partial^2 s}{\partial u^2} - 2u\frac{\partial s}{\partial u} + (\varepsilon - 1)\, s = 0.$$

Harmonic Oscillator

Before we solve this, we need to figure out the behavior of $s(u)$. We know that it should grow less rapidly than $e^{+\frac{u^2}{2}}$ as $u \to \pm\infty$. Also, there should be multiple solutions corresponding to discrete bound states. Finally, the nth solution should have n nodes.

Let's consider the solution in the form as series $$s(u) = \sum_{j=0}^{\infty} a_j u^j$$

Plugging this into the differential equation yields

$$\sum_{j=0}^{\infty}((j+1)(j+2)a_{j+2} - (2j+1-\varepsilon)a_j)u^j = 0.$$

Again, as this is true for *all* u, the overall coefficients must all be identically zero.

$$\boxed{a_{j+2} = \frac{2j+1-\varepsilon}{(j+1)(j+2)}a_j}$$

$$\lim_{j\to\infty} a_{j+2} \approx \frac{2j}{j^2}a_j \approx \frac{a_j}{\frac{j}{2}}$$

$$\boxed{a_j \approx \frac{C}{(\frac{j}{2})!}}$$

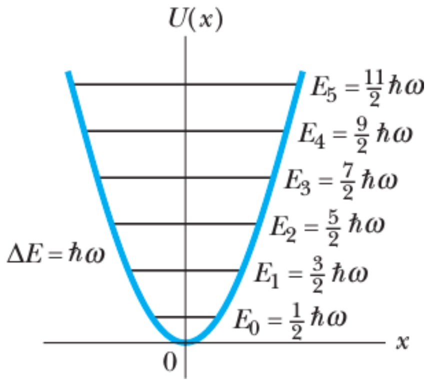
Harmonic Oscillator

$$s(u) \approx C \sum_j \frac{u^j}{\left(\frac{j}{2}\right)!} = C \sum_n \frac{u^{2n}}{n!} = Ce^{u^2}.$$

Unfortunately, this is exactly what we do not want, as plugging this into $\phi(u) = s(u)e^{-\frac{u^2}{2}}$ recovers the non-normalizable solution.

The only way out of this conundrum is that the series must be finite. In particular, let us suppose that that there exists some n such that when $j = n$, the numerator $2j + 1 - \varepsilon = 0$. Then all of the subsequent $a_j = 0$. Imposing that condition yields that $\varepsilon = 2n + 1$. But we know that $\varepsilon \equiv 2(\hbar\omega)^{-1}E$. Therefore, the energy eigenvalues are

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



Energy of Harmonic oscillators is quantized and it has zero point energy.

This suggest that 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.

Let us construct some solutions for this. For $n = 0$, we have $\varepsilon = 1$, so $a_2 = 0$, and we can impose that $a_1 = a_3 = a_5 = \ldots = 0$. This implies that $s(u) = a_0$, so

$$\phi(u; 0) = a_0 e^{-\frac{u^2}{2}}.$$

Harmonic Oscillator

For $n = 1$, we have $\varepsilon = 3$, so finding that $a_3 = 0$ and imposing $a_0 = a_2 = a_4 = \ldots = 0$ implies that $s(u) = a_1 u$, so

$$\phi(u;1) = a_1 u e^{-\frac{u^2}{2}}.$$

n	$\frac{2E_n}{\hbar\omega}$	$\phi(x;n)e^{+\frac{x^2}{2a^2}}$
0	1	N_0
1	3	$N_1 \cdot \left(\frac{2x}{a}\right)$
2	5	$N_2 \cdot \left(\frac{4x^2}{a^2} - 2\right)$
$\vdots$	$\vdots$	$\vdots$
n	$2n+1$	$N_n \mathcal{H}_n\left(\frac{x}{a}\right)$

$$N_n = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}}$$

$$\boxed{\phi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}2^n n!}\right)^{1/2} e^{-\xi^2/2} H_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\alpha x) e^{-\alpha^2 x^2/2}.}$$

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

Harmonic Oscillator

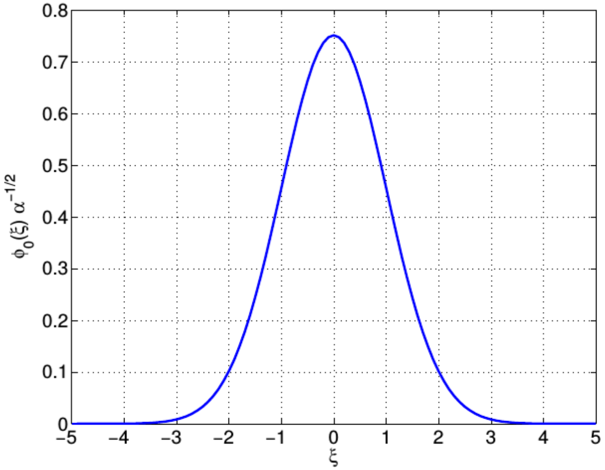
For ease of comparison between the classical and quantum results, let us calculate the classical probability $p(x)dx$ of finding the particle in the interval dx around x, when a random observation is carried out. This probability is equal to the fraction of the total time that the particle spends in this interval.

Denote the period of oscillation by $T_{\mathrm{osc}} = 2\pi/\omega$, this probability is given by

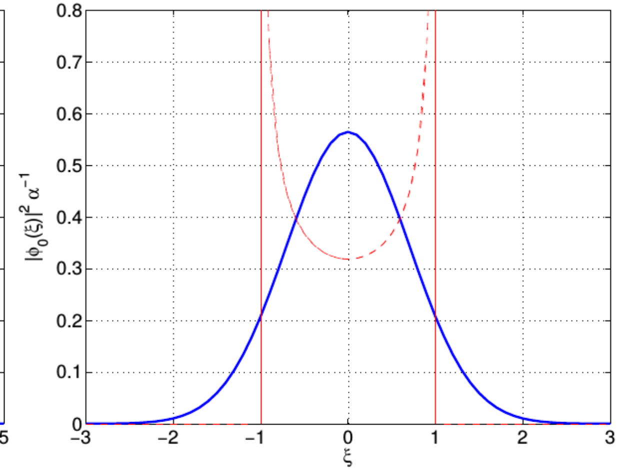
$$p(x)dx = \frac{1}{T_{\mathrm{osc}}}\frac{2dx}{v(x)} = \frac{\omega}{2\pi}\frac{2dx}{(-1)\omega X_0 \sin(\omega t - \phi)} = \frac{dx}{\pi\left(X_0^2 - x^2\right)^{1/2}}$$

Obviously, $p(x)dx$ is largest near the turning points, $x = \pm X_0$, where the speed of the classical particle vanishes.

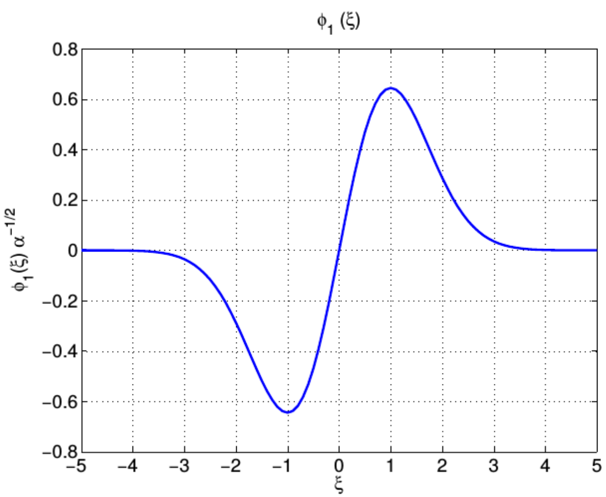
Harmonic Oscillator



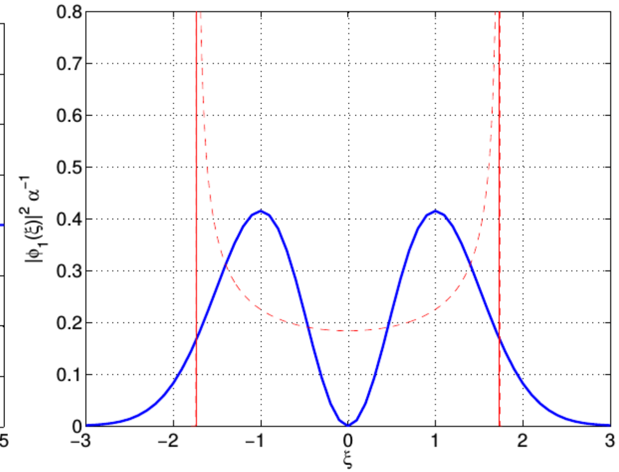
(a) $\phi_0(\xi)$



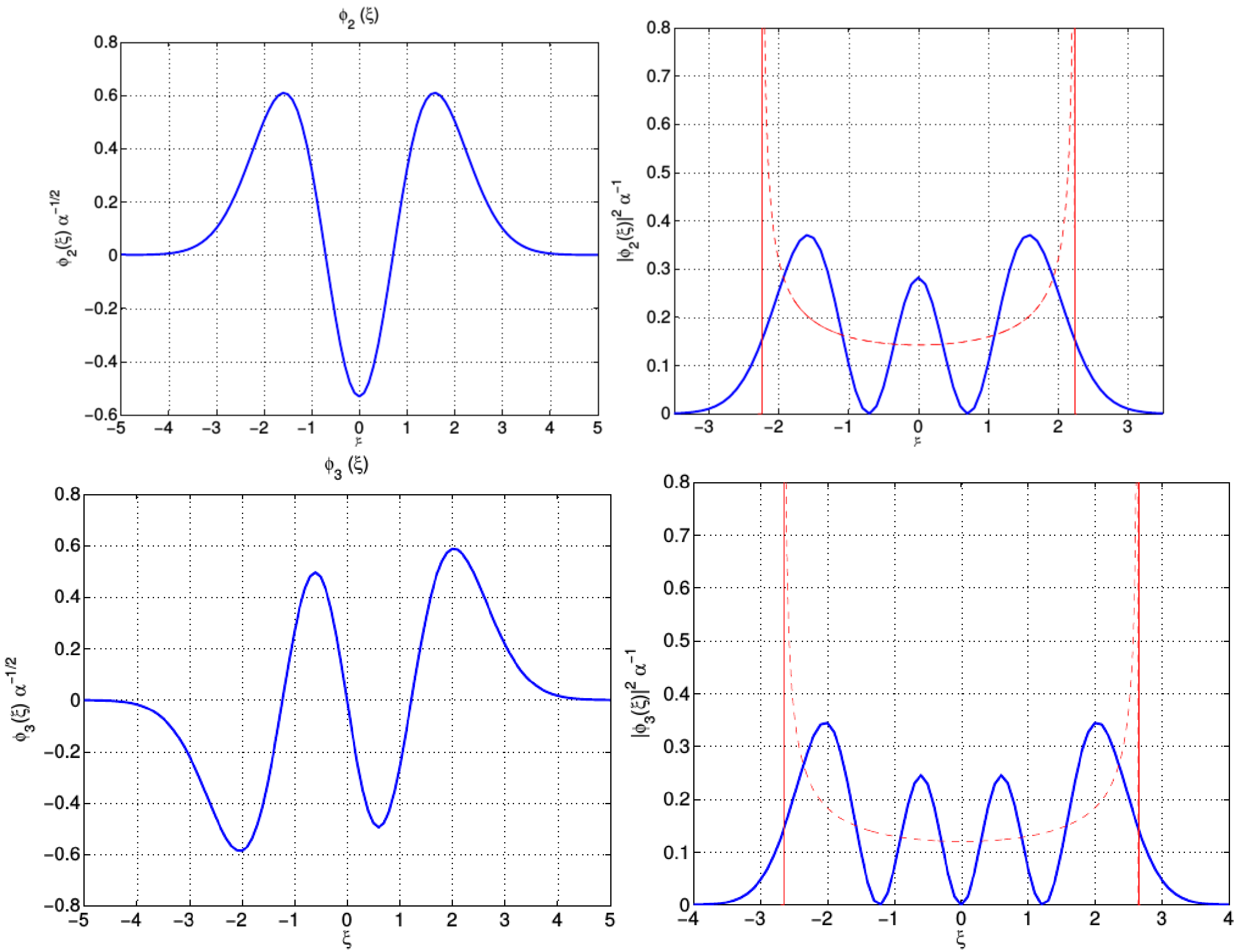
(b) $|\phi_0(\xi)|^2$



(c) $\phi_1(\xi)$



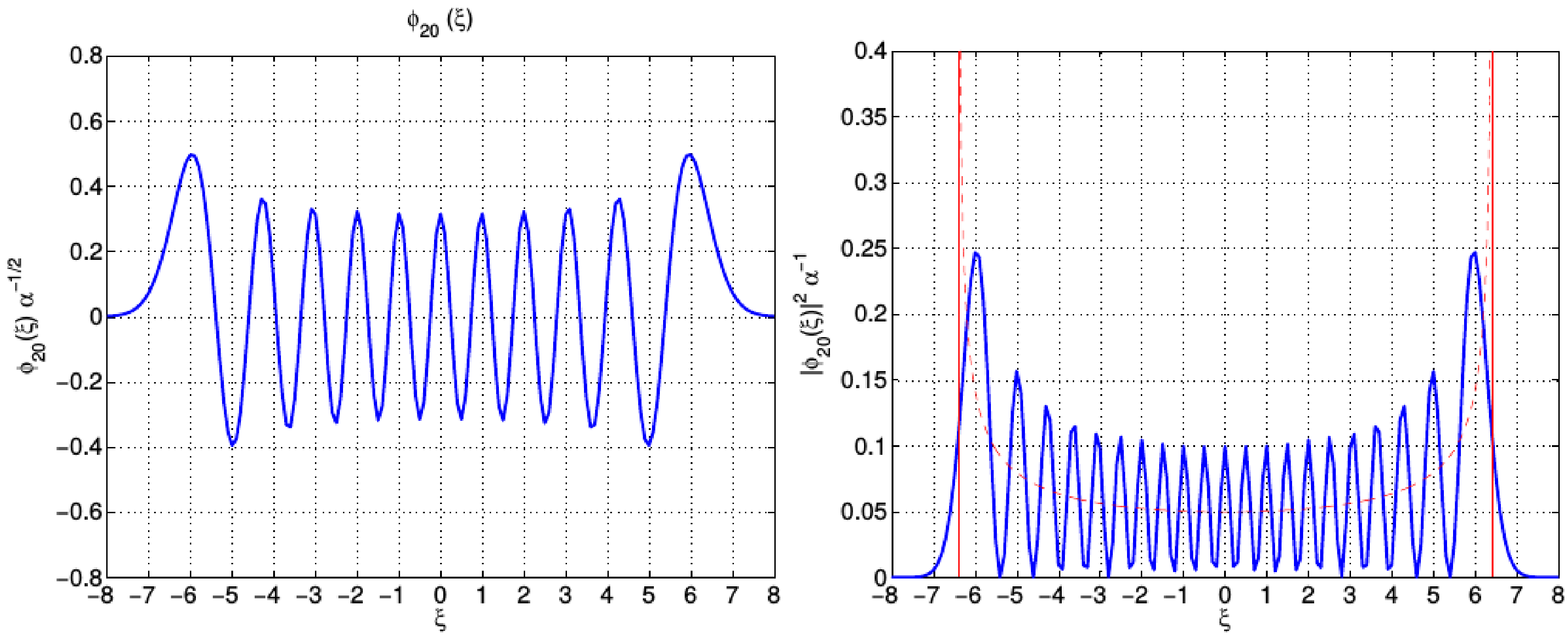
(d) $|\phi_1(\xi)|^2$



(c) $\phi_3(\xi)$ (d) $|\phi_3(\xi)|^2$

Quantum probability (blue line) and Classical probability (red dashed line).

Harmonic Oscillator

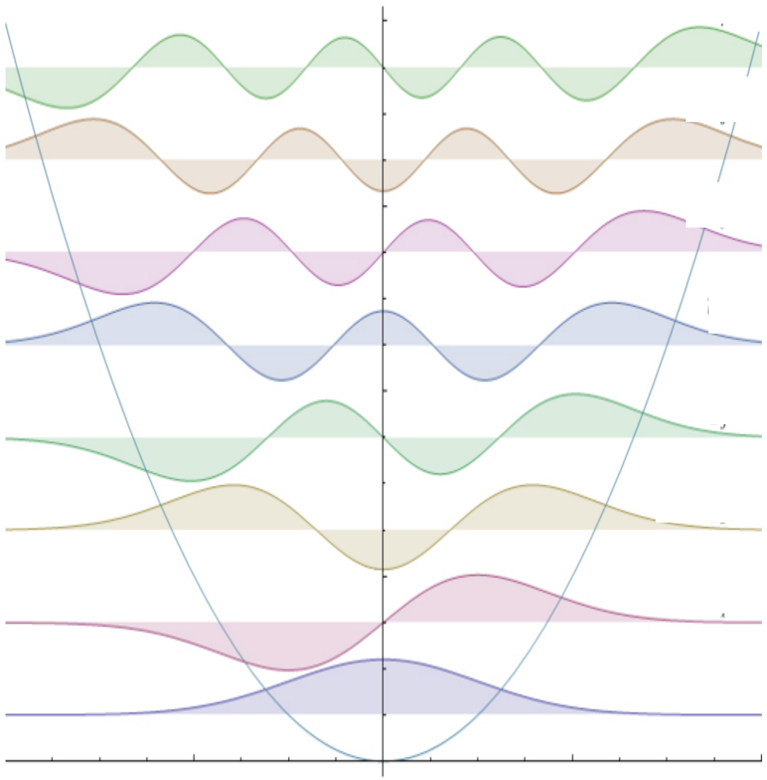


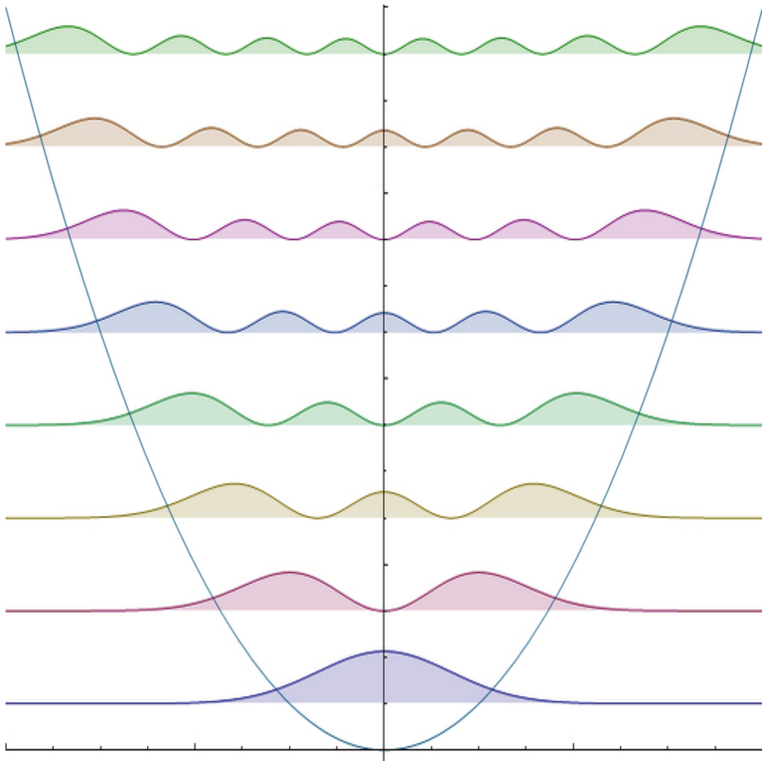
(e) $\phi_{20}(\xi)$ (f) $|\phi_{20}(\xi)|^2$

For large 'n' quantum probability (blue line) and classical probability (red dashed line) matches very well.

Also known as Bohr's correspondence principle.

Harmonic Oscillator





Eigen wave functions have definite parity as the potential is symmetric about x=0. Wave function corresponding to n=1,3,5,7,.... are even function while n=2,4,6,7,.. are odd function.

Example

Find the expectation value $\langle x \rangle$ for the first two states of a harmonic oscillator.

Solution:

The general formula for $\langle x \rangle$ is

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\psi|^2\,dx$$

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

$$\psi_0 = \left(\frac{2m\nu}{\hbar}\right)^{1/4} e^{-y^2/2}$$

$$\psi_1 = \left(\frac{2m\nu}{\hbar}\right)^{1/4}\left(\frac{1}{2}\right)^{1/2}(2y)\,e^{-y^2/2}$$

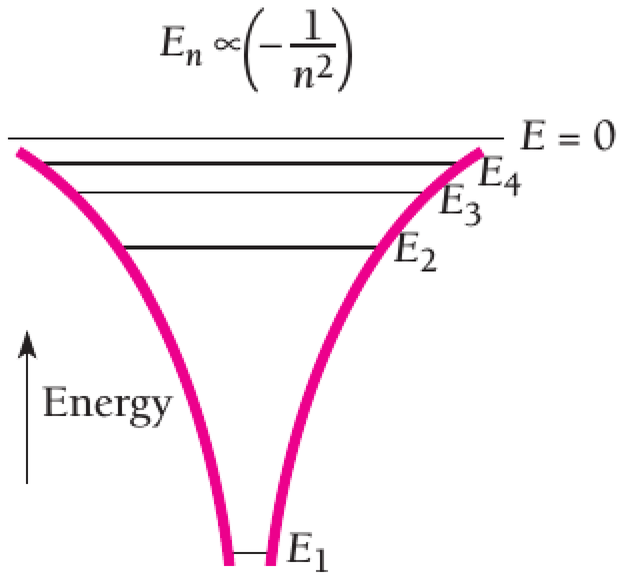
The values of $\langle x \rangle$ for $n = 0$ and $n = 1$ will respectively be proportional to the integrals

$$n = 0\colon \int_{-\infty}^{\infty} y|\psi_0|^2\,dy = \int_{-\infty}^{\infty} ye^{-y^2}\,dy = -\left[\frac{1}{2}e^{-y^2}\right]_{-\infty}^{\infty} = 0$$

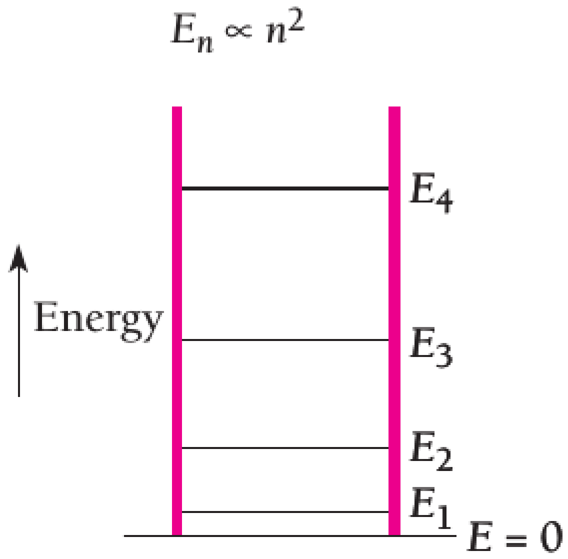
$$n = 1\colon \int_{-\infty}^{\infty} y|\psi_1|^2\,dy = \int_{-\infty}^{\infty} y^3e^{-y^2}\,dy = -\left[\left(\frac{1}{4} + \frac{y^2}{2}\right)e^{-y^2}\right]_{-\infty}^{\infty} = 0$$

The expectation value $\langle x \rangle$ is therefore 0 in both cases. In fact, $\langle x \rangle = 0$ 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.

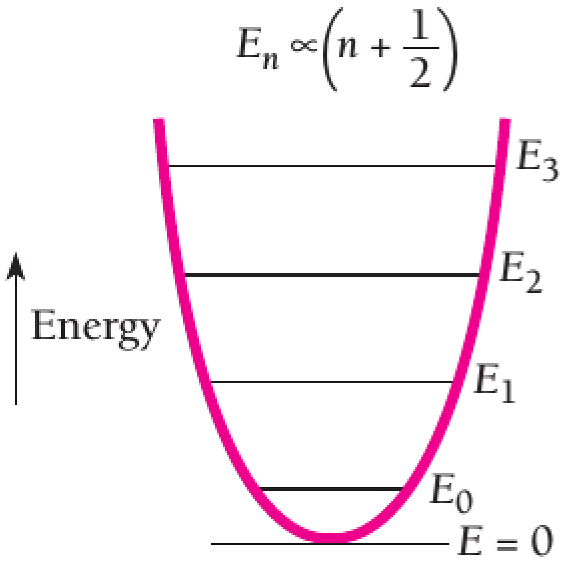
Comparison



Hydrogen Atom



Particle in a box



Harmonic oscillator