# Lecture 6
# Particle in a 3D Box & Harmonic Oscillator

We are solving Schrödinger equation for various simple model systems (with increasing complexity).

## Particle in a Three-Dimensional Box

For a 3D box:

$$V(x,y,z) = \begin{cases} 0 & \text{if } 0 < x < L_x, \;\; 0 < y < L_y, \text{ and } \;\; 0 < z < L_z \\ \infty & \text{otherwise} \end{cases}$$

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} \\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \\ &= -\frac{\hbar^2}{2m}\nabla^2 \end{aligned}$$

where, $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ is called the Laplace Operator or the Laplacian, which follows differential operator principles, such as: $\nabla^2 = \nabla.\nabla$ etc.

Schrödinger equation to solve is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$$

Boundary conditions for solving the above partial differential equation (PDE) are:

$$\begin{aligned} \psi(0,y,z) &= \psi(L_x,y,z) = 0 \\ \psi(x,0,z) &= \psi(x,L_y,z) = 0 \\ \psi(x,y,0) &= \psi(x,y,L_z) = 0 \end{aligned}$$

Like in the case of particle in 2D box, we use the method of separation of variables

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

So, we can apply the above boundary conditions and that the potential (which is zero here) is separable along the x, y, and z coordinates.
Using this separation of variables, it is straightforward to solve this problem, and we observe three quantum numbers arising (due to boundary conditions along the three directions).

$$\psi(x,y,z) \equiv \psi_{n_x,n_y,n_z}(x,y,z)$$

$$E_n = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{h^2}{8m}$$

The case of particle in 3D box has more degeneracies (maximum of 6) as compared to that of 2D box (maximum of 2) and none in case of 1D box.

To plot the wave function, one requires 4–dimensions. Thus, we will use contour surfaces to visualize these orbitals. Nodal planes will arise for the solutions of $\psi_{n_x,n_y,n_z}(x,y,z)$. We list below the various useful operators that correspond to their observables:

| Observable | | Operators | |
|---|---|---|---|
| Name | Symbol | Symbol | Operation |
| position | $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ | $\hat{\mathbf{r}}$ | multiply with $\mathbf{r}$ |
| momentum | $\mathbf{p}$ | $\hat{\mathbf{p}}$ | $-i\hbar\left(\frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k}\right)$ |
| kinetic energy | $T$ | $\hat{T}$ | $-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ |
| potential energy | $V(x,y,z)$ | $\hat{V}(x,y,z)$ | Multiply with $V(x,y,z)$ |
| total energy | $E = T + V(x,y,z)$ | $\hat{H}$ | $-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$ |
| angular momentum | $l_x = yp_z - zp_y$ | $\hat{L}_x$ | $-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ |
| | $l_y = zp_x - xp_z$ | $\hat{L}_y$ | $-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ |
| | $l_z = xp_y - yp_x$ | $\hat{L}_z$ | $-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ |

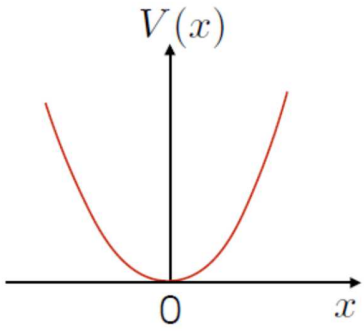
Many of the important principles of quantum mechanics are illustrated by the various particle-in-a-box systems that we have studied. It is the classic way of studying density of states in metals. Quantization, degeneracies, role of dimensionality, etc. are naturally seen in these systems.
We now move to other quantum systems that are exactly soluble. Let us take the case with the classical analog of Simple Harmonic Oscillator (SHO), where instead of the abrupt transitions of potential that is either zero or infinity (for particle in a box), more smooth potentials are going to be considered.

Simplest case: **The one-dimensional harmonic oscillator**

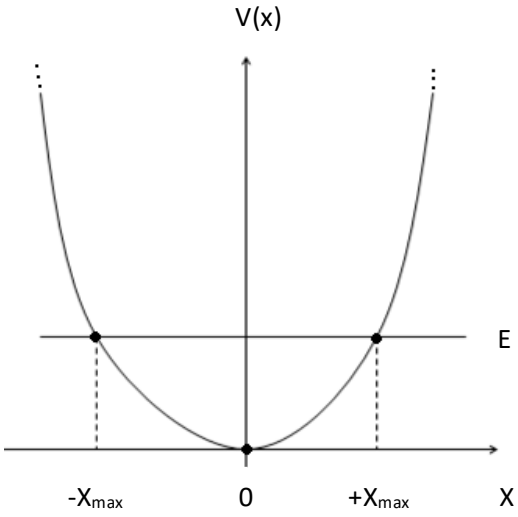
## Harmonic Oscillator

We consider the vibration of a particle of mass m which moves along $x$ and is attached to a wall by a spring of force constant $k$. The particle of mass 'm' oscillates around its equilibrium position at a frequency ω. For such a 1–D harmonic oscillator, the potential energy is given by

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




This potential is a parabola. Classical analog of such cases exists in Vibrating springs, pendulums, etc. Here we look at the quantum mechanical solution. The Hamiltonian operator for this system is given by $\hat{H} = \left[ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right]$, and the Schrödinger equation is given by $\left[ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right]\psi(x) = E\psi(x)$.




x : <u>displacement</u>

Parabola.

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

This is a confining potential as well. Thus, we expect discrete or quantized E levels in QM. One can solve the above differential equation using the power series method—but we will only look at the solutions instead of deriving them. The energy is quantized, as one would assume from the shape of the potential (that it confines the particle), one finds that acceptable of the above equation exist only when

$$E_n = \left( n + \frac{1}{2} \right)\hbar\omega, \qquad n = 0, 1, 2.....$$

and $\omega = \sqrt{\frac{k}{m}}$ = frequency of vibration.

The vibrational quantum number $n$ takes only non-negative integral values. Thus, the energy is quantized. The allowed energy levels are equally spaced. The zero-point energy is $\frac{1}{2}\hbar\omega$. Again, its existence is a consequence of the uncertainty principle. However, the potential is much smoother than particle in a box potential, as the $V(x) \longrightarrow \infty$, only when $x \longrightarrow \infty$, or $x \longrightarrow -\infty$. Thus, one would expect that $\psi(x) \longrightarrow 0$, only as $|x| \longrightarrow \infty$. The wave functions turn out to have the $e^{-\alpha^2x^2/2}H_n(\alpha x)$ where $H_n(\alpha x)$ is a function called Hermite polynomial. The exact solutions are:

$$\psi_n(x) = N_n H_n(\alpha x)\ e^{-\alpha^2x^2/2}, \quad \alpha = \left(\frac{mk}{\hbar^2}\right)^{1/4}, \quad N_n = \left(\frac{\alpha}{2^n n!\pi^{1/2}}\right)^{1/2}$$

The explicit forms of the lowest few $H_n(\alpha x)$ are:

| $n$ | $H_n(t)$ |
|---|---|
| 0 | 1 |
| 1 | $2t$ |
| 2 | $4t^2 - 2$ |
| 3 | $8t^3 - 12t$ |

Hermite polynomials: here t = $\alpha x$

This is one of the few cases where the Schrödinger equation $\hat{H}\Psi = E\Psi$ can be solved exactly.

The lowest wavefunction is:

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

As $\psi_n(x)$ for $n = 0$ is not zero, like for the particle in a box. Thus, we consider $n = 0$, unlike in the case of particle in a box. Thus $\psi_0(x)$ doesn't have any nodes, and $\psi_0(x) \to 0$ only when $x \to \infty$ and $x \to -\infty$. This is a Gaussian function (which is bell shaped), and centered at $x = 0$. For $n = 1$, $H_1(\alpha x) = 2\alpha x$, the wave function contains the product of $2\alpha x$ with a Gaussian (and has a different normalization constant):

$$\psi_1(x) = \left(\frac{\alpha}{2\pi^{1/2}}\right)^{1/2} 2\alpha x\, e^{-\alpha^2x^2/2} = \left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2} x e^{-\alpha^2x^2/2}$$

Clearly, $\psi_1(x)$ has a node at $x = 0$. Presence of nodes are determined by the Hermite polynomials, i.e. for $x = x_{\text{node}}$ for which $H_n(\alpha x_{\text{node}}) = 0$.

For a quantum number n, there will be n number of nodes. Since the wave functions go beyond the classical limit, thus tunneling takes place here. This is due to the "soft" nature of the potential (as compared to infinite wall potential like in particle in a box); note that the potential $V(x) \longrightarrow \infty$ as $|x| \longrightarrow \infty$.

The presence of Gaussian term in the wavefunction can be understood by considering the Hamiltonian for the problem at the limit $|x| \longrightarrow \infty$. In this limit:

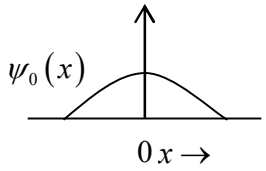
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = 0$$

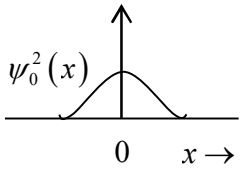
This is because the $x^2$ terms dominate the RHS of the equation with $|x| \to \infty$. For this equation, $\exp(\pm\alpha^2x^2)$ is a solution. However, $\exp(+\alpha x^2)$ has to be ignored in order to prevent wave function going to $\infty$ as $|x| \to \infty$. For the intermediate values of $x$, there should be a polynomial to describe the modulations in the wave function, and thus

$$\psi(x) = f(x)\ \exp(\pm\alpha^2x^2)$$

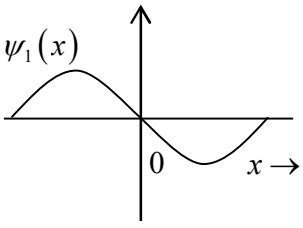
is a reasonable solution. On the other hand, $f(x)$ cannot exceed $\exp(\pm\alpha^2x^2)$ at large values of $x$. Thus the polynomial $f(x)$ has to be finite, and the quantum numbers control the order of the polynomial.

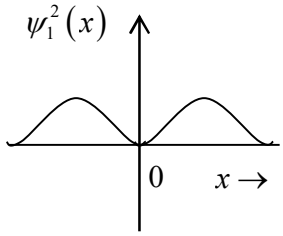
Now we can plot the wavefunctions:

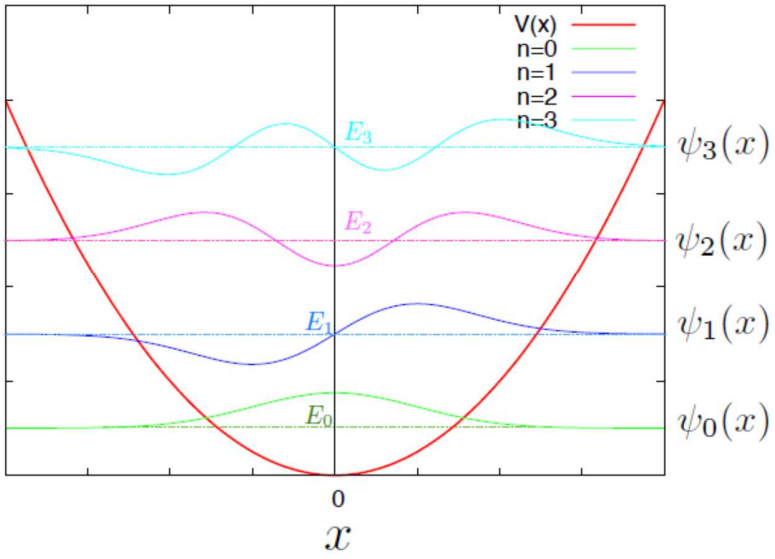



Note that, $\psi(x) \to 0$ as $x \to \pm\infty$






Wavefunctions and energy levels of a 1–D quantum mechanical simple harmonic oscillator

When a function $f$(x) follows: $f$(-x) = $f$(x), then the function is even and whereas, when it follows $f$(-x) = -$f$(x), then the function is an odd function. Thus, $e^{-\alpha^2 x^2/2}$ is an even function, while $H_n(\alpha x)$ is either even or odd function, depending on $n$.

If $f(x)$ is an odd function, then

$$\int_{-\infty}^{\infty} dx\, f(x) = 0$$

and for an even function,

$$\int_{-\infty}^{\infty} dx\, f(x) = 2\int_{0}^{\infty} dx\, f(x)$$

Thus,

$$< x >= \int_{-\infty}^{\infty} dx\, \psi_n(x)\, x\, \psi_n(x) = 0$$

as the integrand is odd: $\psi_n(x) \times \psi_n(x)$ is even for all $n$, and $x$ is odd. Now,

$$< p >= \int_{-\infty}^{\infty} dx\, \psi_n(x) \left(-i\hbar \frac{d}{dx}\right) \psi_n(x) = 0$$

as the integrand will be always odd: if $\psi_n$ is odd, then its derivative is even, and vice versa. The origin of odd/even symmetry can be considered as a result of the symmetry present in the Hamiltonian, especially because the kinetic energy and the potential energy terms are composed of $p^2$ and $x^2$ terms, respectively. Such symmetry can be also seen in the classical solution of the Harmonic oscillator.

Hermite polynomials follow the orthogonality condition:

$$\int_{-\infty}^{\infty} dt\, H_n(t) H_{n'}(t) \exp(-t^2) = 0 \quad \text{if } n \neq n'.$$

The normalization condition is

$$\int_{-\infty}^{\infty} dt\, H_n(t)^2 \exp(-t^2) = \pi^{1/2} 2^n n!$$

Hermit polynomials also show the recursion relationship

$$H_{n+1}(t) = 2tH_n(t) - 2nH_{n-1}(t)$$

Spacing of energy levels is Constant

$$\Delta E = E_{n+1} - E_n = \hbar\omega = h\nu \qquad (\omega = 2\pi\nu)$$