PH 112: Quantum Physics and Applications

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Week 04, Lectures 2 and 3: Particle in a 1-D box

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First Application: Free particle

- Free Particle

  Studied the simplest physical situation, an object that has no forces acting on it and thus has a constant potential energy everywhere!

- Solutions

  - Sin(k x) and Cos(k x) are solutions to Schrodinger equation. However, they are not eigenfunctions of momentum operator.

  - $\exp(\pm ikx)$ are solutions to Schrodinger equation and eigenfunctions of momentum operator.

- Properties of solutions

  1. Probability density is the same for all values of x.

  2. The free-particle wave functions are not normalizable.

Second Application: Particle in 1-D box

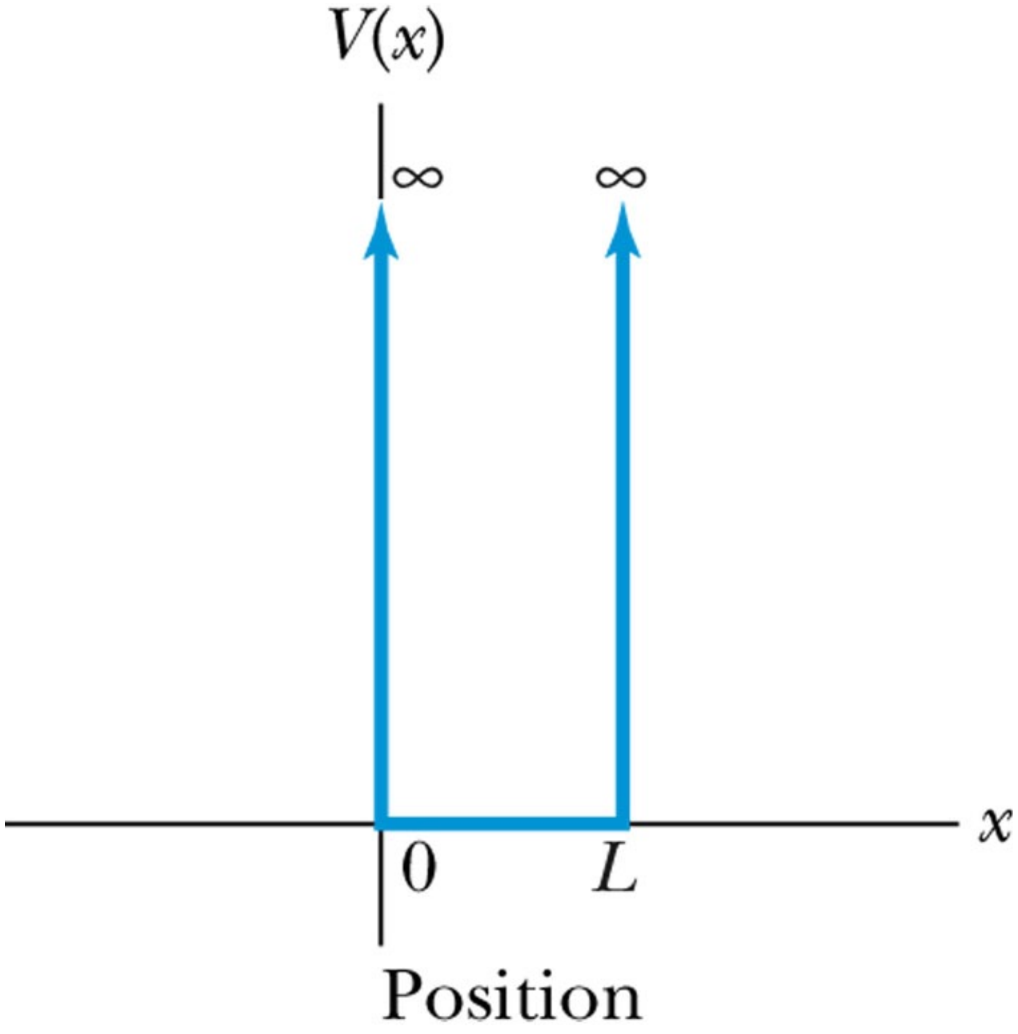
Infinite Square Well

- This is the simplest non-trivial application of the Schrodinger equation.

- Infinite well is an idealization. There are no infinitely high and sharp barriers.

- Interestingly, this also illustrates many of the fundamental concepts of quantum mechanics.

  Set up: A particle in this potential is completely free, except at the two ends, where an infinite force prevents it from escaping.



$$V(x) = \begin{cases} 0 & \text{if} \quad 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Infinite Square Well: Outside the well

- Time-independent Schrodinger equation $$-\frac{\hbar^2}{2m}\frac{d}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

- Infinite potential energy constitute an impenetrable barrier.
- Since the particle is confined inside the well, $\psi(x)$ outside the well vanishes:

$$\psi(x) = 0 \quad \text{for} \quad x < 0 \quad \text{and} \quad x > L$$

- Requirement that the wavefunction is continuous leads to

$$\psi(0) = 0 \quad \text{and} \quad \psi(L) = 0$$

- These constitute boundary conditions on the wavefunction within the box.

Infinite Square Well: Inside the well

- Inside the well: $V(x) = 0$
- Schrodinger equation is $\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0$ $\quad k^2 = \frac{2mE}{\hbar^2}$
- This is the equation of a simple harmonic oscillator in Mechanics with the following substitution $\psi(x) \to x(t)\,, \quad x \to t$
- Possible solutions are $$\psi(x) = \begin{cases} A\sin kx + B\cos kx \\ Ce^{ikx} + De^{-ikx} \end{cases}$$
- Unlike free particle, we can choose either one of the solutions!

Infinite Square Well: Non-trivial solutions

- Constants *A and B* are determined by the boundary conditions of $\psi(x)$
- Usually, both $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous. Since $V(x) \to \infty$, only $\psi(x)$ applies.
- First condition at *x = 0:* $\psi(0) = 0 \implies A\sin 0 + B\cos 0 = B = 0$
- Second condition at *x = L:* $\psi(L) = 0 \implies A\sin(kL) = 0$
- Two possibilities

$$\begin{array}{lll} A = 0 & \text{no particle} & \psi(x) \text{ vanishes everywhere} \\ A \neq 0 & \sin(kL) = 0 & kL = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \cdots \end{array}$$

Energy Eigen values

- *n = 0* also gives $\psi(x) = 0$ everywhere. No particle anywhere!

- Negative solutions do not give anything new! $\sin(-\theta) = -\sin(\theta)$

  Negative sign can be absorbed into *constant A.*

- Distinct solutions are $k_n = \frac{n\pi}{L} \quad \text{where} \quad n = 1, 2, \cdots$

- From the relation between *E and k*, we have

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = \frac{h^2}{8mL^2} n^2 \quad \text{where} \quad n = 1, 2, \cdots$$

Wave functions

- Wave functions corresponding to the energies E_n are

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad \text{where} \quad n = 1, 2, \cdots$$

- Quantum particle in the infinite square well can not have any energy. It has to be one of these special allowed values.
- Probability to find a particle in any other energy is zero!
- The occurrence of discrete or quantized energy levels is characteristic of a bound system.
- For the free particle, the absence of confinement allowed an energy continuum.
- In both cases, the number of energy levels is infinite.

Finding A

- We used two properties of Ψ to obtain the wave functions:
  - It should be single valued
  - It should be continuous everywhere.

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right) \quad \text{where} \quad n = 1, 2, \cdots$$

- We still have not used one more property of Ψ

$$\int_{-\infty}^{\infty} P(x)dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

- Normalization in this case becomes

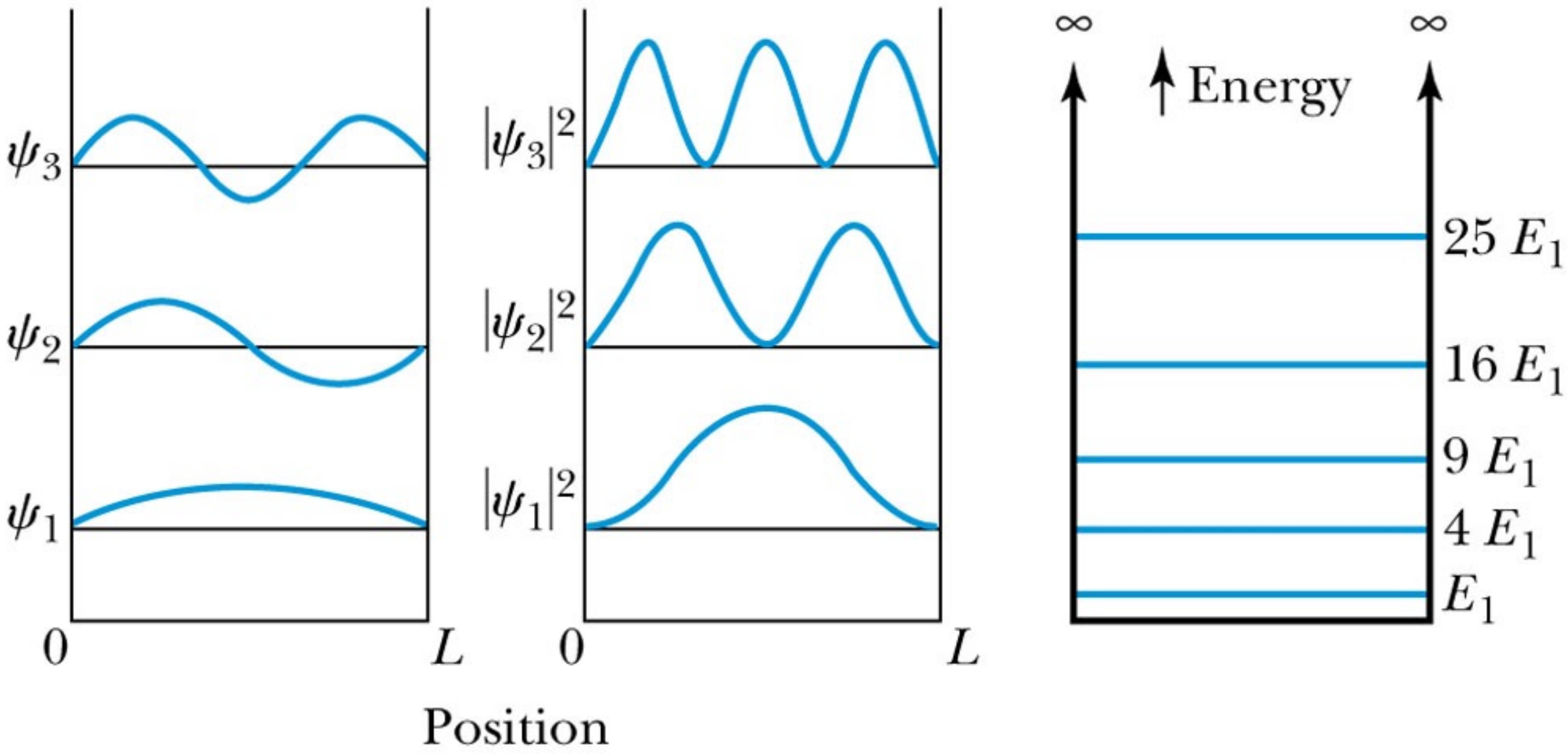
$$\int_0^L |\psi_n(x)|^2 dx = 1 \implies |A|^2 \int_0^L \sin^2(k_n x) = 1 \implies |A|^2 \frac{L}{2} = 1 \text{ or } |A| = \sqrt{\frac{2}{L}}$$

- Normalized wave-functions are

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \quad \text{where} \quad n = 1, 2, \cdots$$

Properties of the solutions

First few wave-functions and Energies

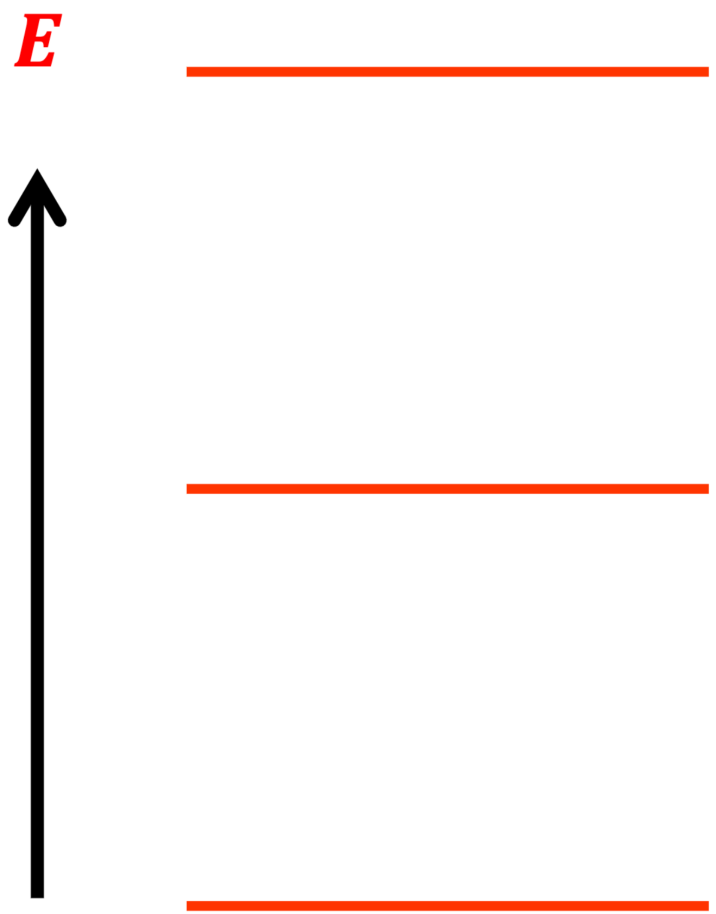


- For a classical particle bouncing back and forth in a well, the probability to find the particle is equally likely throughout the well.
- For a quantum particle in a stationary state, the probability distribution is not uniform. There are "nodes" where the probability is zero!

Energy eigen values are

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} = n^2 E_1$$

Properties of Energy Eigenvalues

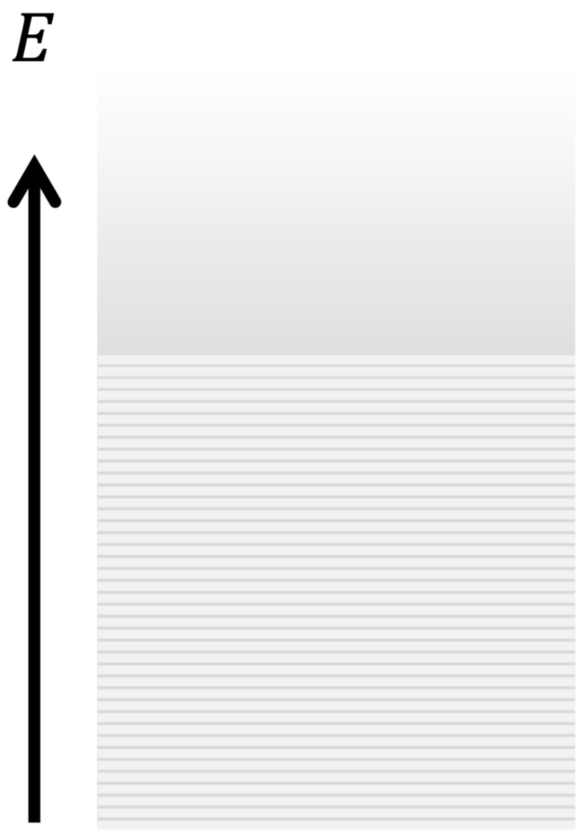


Electron in a box of $1\ \text{Å}$

$$E_1 = \frac{(6.63\times10^{-34})^2}{8(9.11\times10^{-31})(10^{-10})} = 37.6\ eV$$

An Iron ball of mass of 10 gm in a box of L = 10 cm

$$E_1 = \frac{(6.63\times10^{-34})^2}{8(0.01)\ (0.1)}$$
$$= \ 10^{-46}\ eV;$$
$$E_2, E_3 \simeq 10^{-46} eV$$



quasi-continuous!

Ground state and Heisenberg Uncertainty principle

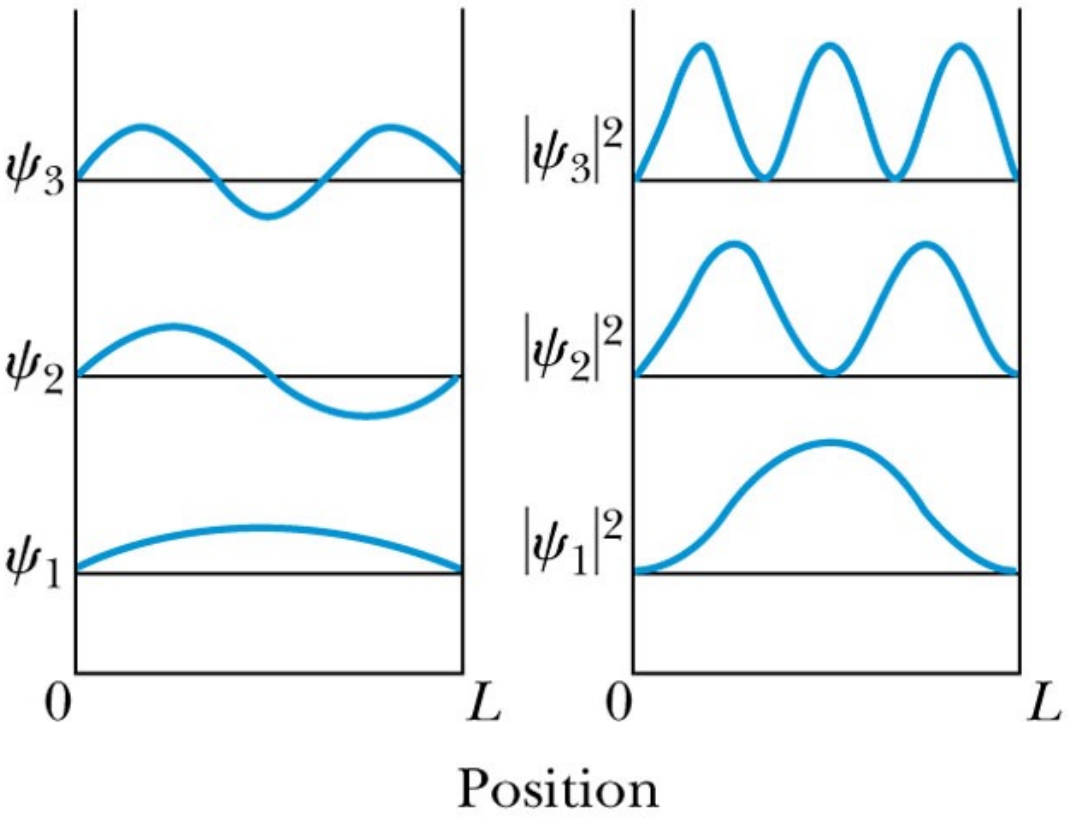
- The lowest energy bound state has non-zero energy (zero point energy).
- Since ground state energy is not zero, the kinetic energy and the momentum of a bound particle cannot be reduced to zero!
- Minimum value of momentum is

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} = \frac{p_{\min}^2}{2m} \implies p_{\min} = \frac{\pi\hbar}{L}$$

The particle cannot be at rest!

- Expressing this as an uncertainty in momentum, we have $\Delta p \sim \frac{\hbar}{L}$
- The uncertainty in the position is $\Delta x \sim L$
- Ground-state satisfies the HUP $\Delta x \Delta P \sim \hbar$

Understanding the nodes



- Like in classical waves (guitar), the wavefunctions are a superposition of left and right moving waves!

$$\Psi_n(x,t) \propto e^{i(k_n x - E_n t)} - e^{-i(k_n x + E_n t)}$$

- Nodes are caused by the interference of the left and right moving waves.
- Interference "does not remove" the particle, it just "pushes" the particle around.
- Due to interference of waves, a particle is more likely to be found in some regions and less likely to be found at the nodes.

Infinite Square Well: Few points

- Wavefunctions are alternating even and odd functions about the symmetry axis. Number of nodes in the n-th eigenfunction = (n-1).

- Wavefunctions are mutually orthogonal

$$\int_0^L dx\psi_i^*\psi_j = \frac{2}{L}\int_0^L dx \sin\frac{i\pi x}{L}\sin\frac{j\pi x}{L} = \delta_{ij}$$

- Wavefunction are NOT eigen-functions of Momentum operator

$$-i\hbar\frac{\partial}{\partial x}\sin(kx) = -i(\hbar k)\ \cos(kx) \Longrightarrow \hat{p}_x \sin(kx) \neq p_x \cos(kx)$$

- The particle in 1-D well does not have one unique momentum value.

Expectation Values

- Recall from probability the definition of mean

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \, x P(x)$$

- Expectation value of Position

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \, x |\Psi(x,t)|^2$$

- Expectation value of momentum

$$\langle p_x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x}\right) \Psi(x,t) dx}{\int_{-\infty}^{\infty} \phi^*(x) \phi(x) dx}$$

Evaluation <x> and <p> for n = 1

$$< x >= \int_0^L (\sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L}))x(\sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L}))dx$$

$$< x >= \frac{2}{L}\int_0^L x\sin^2(\frac{\pi x}{L})dx$$

Set $u = \frac{\pi x}{L}$

$$< x >= \frac{2}{L}\int_0^\pi (\frac{L}{\pi}u)\sin^2(u)(\frac{L}{\pi}du)$$

$$< x >= \frac{2L}{\pi^2}\int_0^\pi u\sin^2(u)du$$

$$< x >= \frac{2L}{\pi^2}(\frac{\pi^2}{4})$$

$$< x >= \frac{L}{2}$$

$$< p >= \int_0^L (\sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L}))(-i\hbar\frac{d}{dx}(\sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L}))dx$$

$$< p >= -i\hbar\frac{2}{L}\int_0^L \sin(\frac{\pi x}{L})(\frac{\pi}{L}\cos(\frac{\pi x}{L}))dx$$

$$< p >= -i\hbar 2\pi\int_0^L \sin(\frac{\pi x}{L})\cos(\frac{\pi x}{L})dx$$

$$< p >= -ih\int_0^\pi \sin(u)\cos(u)(\frac{L}{\pi}du)$$

$$< p >= -ih\frac{L}{\pi}\int_0^\pi \sin(u)\cos(u)du$$

$$< p >= -ih\frac{L}{\pi}\int_0^\pi \sin(u)\cos(u)du$$

$$< p >= -ih\frac{L}{\pi}(0)$$

$$< p >= 0$$

Superposition of states

Superposition of states

- Consider Schrodinger equation $$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)+V(x)\Psi(x,t)=\hbar\omega\Psi(x,t); \quad E=\hbar\omega$$
- If Ψ_1 and Ψ_2 are solutions with same energy E, then $\Psi=\Psi_1+\Psi_2$ is also a solution.
- If Ψ_1 and Ψ_2 are solutions with different energies E_1, E_2 :

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_{\omega_1}(x,t)+V(x)\Psi_{\omega_1}(x,t)=\hbar\omega_1\Psi_{\omega_1}(x,t)=i\hbar\frac{\partial}{\partial t}\Psi_{\omega_1}(x,t)$$
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_{\omega_2}(x,t)+V(x)\Psi_{\omega_2}(x,t)=\hbar\omega_2\Psi_{\omega_2}(x,t)=i\hbar\frac{\partial}{\partial t}\Psi_{\omega_2}(x,t)$$

- $\Psi=\Psi_{\omega_1}+\Psi_{\omega_2}$ is also a solution of TD Schrodinger equation.
- This holds for arbitrary superposition of states

$$\Psi(x,t)=\sum_{n=0}^{\infty}\Phi_{\omega_n}(x)e^{-i\omega_n t} \quad \rightarrow \quad \int_0^{\infty}\Phi(\omega,x)e^{-i\omega t}d\omega$$

Time evolution of superposed states: Example

- A wavefunction that is a sum of eigenfunctions with different energies are not eigenstate of the Hamiltonian.

- Eigenstates of the time-independent Schrodinger equation have a probability distribution that does not change with time

$$|\Psi(x,t)|^2 = |\psi(x)e^{-i\omega_n t}|^2 = |\psi(x)|^2 = |\Psi(x,0)|^2$$

Stationary states

- The probability distributions of superposed states depend on time.

Example: At time t = 0, the particle is in the superposition of the first two energy levels:

$$\Psi(x,0) = \frac{1}{\sqrt{2}}\left[\psi_1(x) + \psi_2(x)\right]$$

Aim: To determine how particle's state change with time. Find $\Psi(x,t), \text{ for } t > 0$

Time evolution of superposed states: Example

- Since potential is time-independent, we have

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left(e^{-i\omega_1 t}\psi_1(x) + e^{-i\omega_2 t}\psi_2(x)\right)$$

- We define: $\omega_n = \frac{E_n}{\hbar} = \frac{n^2\pi^2\hbar}{2mL^2}$ and $\omega_n = n^2\,\omega_1$

- Substituting the wavefunctions, we have

$$\Psi(x,t) = \frac{1}{\sqrt{L}}e^{-i\omega_1 t}\left(\sin\left(\frac{\pi x}{L}\right) + e^{-3i\omega_1 t}\sin\left(\frac{2\pi x}{L}\right)\right)$$

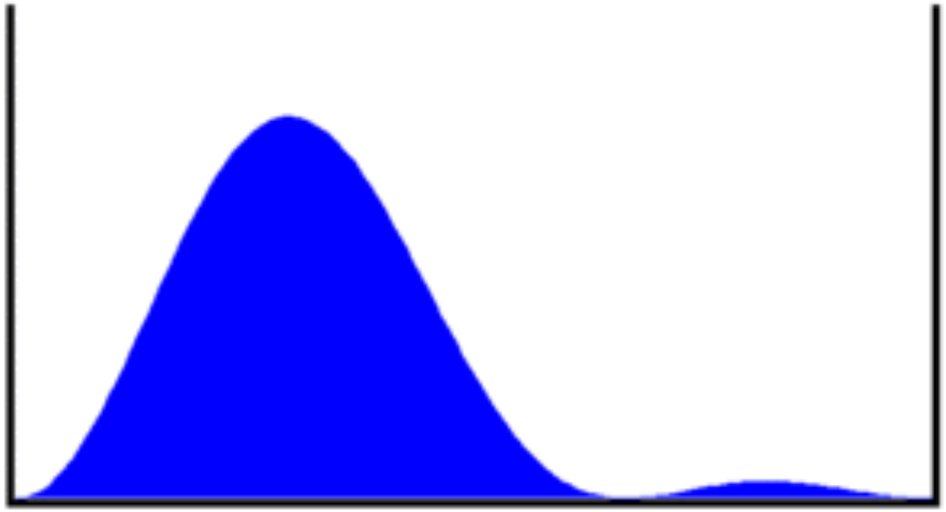
Time evolution of superposed states: Example

- Probability density

$$p(x,t) = \Psi^*(x,t)\Psi(x,t)$$
$$= \frac{1}{L}\left(\sin\left(\frac{\pi x}{L}\right) + e^{-3i\omega_1 t}\sin\left(\frac{2\pi x}{L}\right)\right)\left(\sin\left(\frac{\pi x}{L}\right) + e^{3i\omega_1 t}\sin\left(\frac{2\pi x}{L}\right)\right)$$
$$= \frac{1}{L}\left(\sin^2\left(\frac{\pi x}{L}\right) + \sin^2\left(\frac{2\pi x}{L}\right) + 2\cos(3\omega_1 t)\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\right) .$$

The most likely place to find the particle oscillates back and forth across the box.

This oscillation occurs at frequency $\omega_2 - \omega_1 = 3\omega_1$.



Time evolution of general superposed state

- General solution to the TD Schrodinger equation

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t/\hbar}$$

- Given an initial condition the coefficients c_n can be determined

$$c_n = \sqrt{\frac{2}{L}} \int_0^L dx \sin\left(\frac{n\pi x}{L}\right) \Psi(x,0)$$

Remember Fourier Series

- Starting with normalized $\psi(x,0)$, implies

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

- $|c_n|^2$ is equal to the probability of finding the particle energy to be E_n.

``Real life” application of particle in a box

Quantum Dots

- A quantum dot is a very small structure, e.g. a semiconductor nanocrystal embedded in another semiconductor material, which can confine electrons or other carriers in all three dimensions.

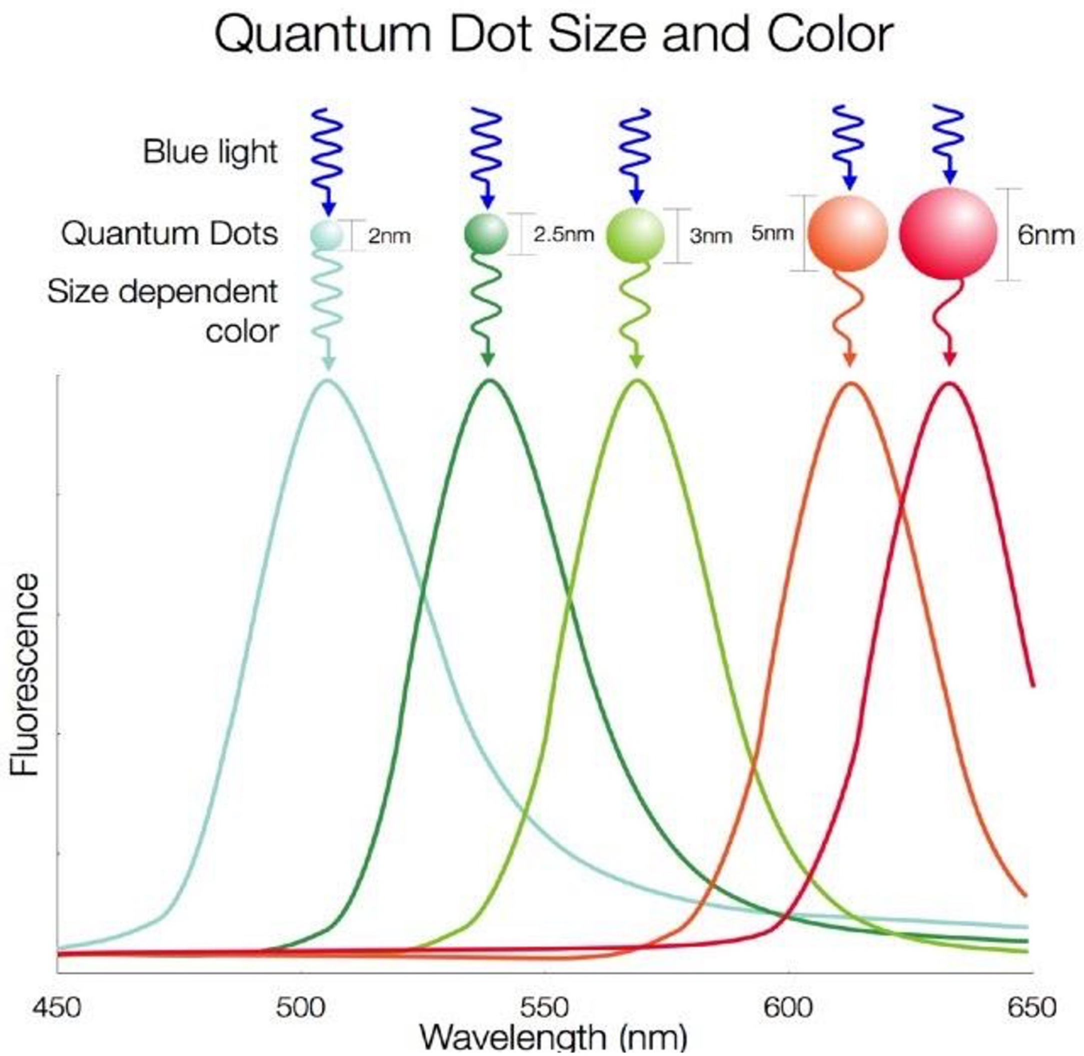
- The confinement of electron in all three dimensions is like particle in 3-D box!

- Like particle (atom) in a box, an ideal isolated quantum dot has discrete energy levels.

- Quantum dots can be considered as artificial atoms where the energy levels can be adjusted by design, e.g. by controlling the quantum dot dimensions or the material composition

- If the size of the quantum dot is small enough that the quantum confinement effects dominate (typically less than 10 nm), the electronic and optical properties are highly tunable.

Quantum Dots



Next generation display (TV) screens will use Quantum dots technology. Several advantages:

1. The color of light each quantum dot gives is very stable and pure.
2. Quantum dots can show precise colors while the light from LEDs get mixed with adjacent colors.
3. The 3 primary colors are more clearly distinguished in comparison to conventional TVs. Quantum dot display show a wide range of colors more accurately.

Credit: Nanosysinc.com

Summary

- Energy states of a quantum particle in a box are found by solving the time-independent Schrodinger equation.

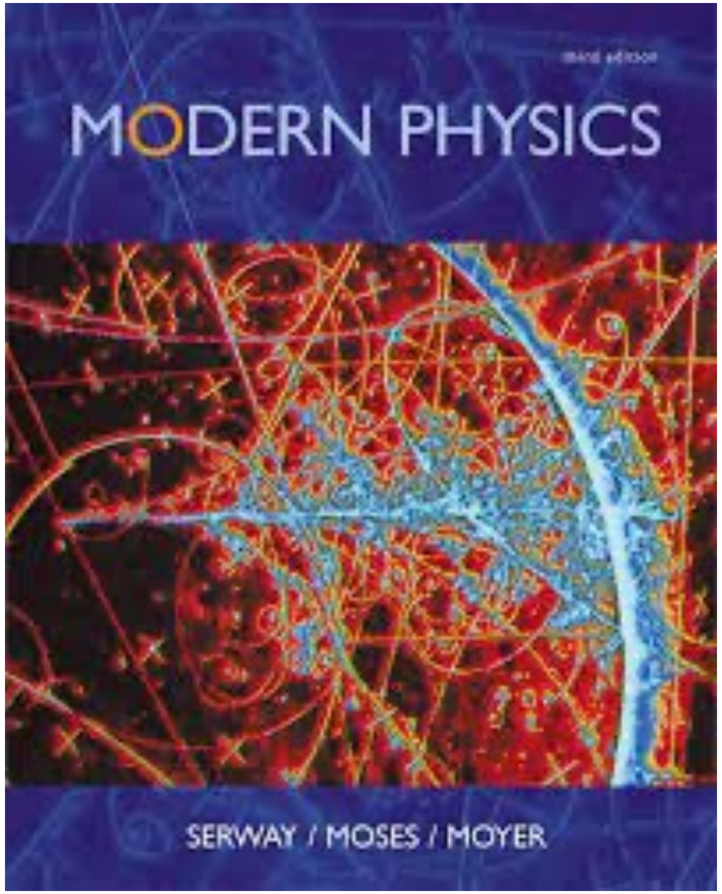
- To solve the time-independent Schrodinger equation and find the stationary states, we require that the wave function vanishes at the box wall.

- Energy states of a particle in a box are quantized and indexed by number *(n)*.

- The quantum picture differs significantly from the classical picture when a particle is in a low-energy state of a low quantum number.

Recommended Reading

Particle in a box section 6.4



What happens at the nodes of a wavefunction?

What happens at the node?

- Let x_0 be a node of the wavefunction ψ(x). We then have:

$$\psi(x_0) = 0. \text{ However, in general, } \frac{d\psi}{dx}(x = x_0) \neq 0; \frac{d^2\psi}{dx^2}(x = x_0) \neq 0$$

- What happens to $|\psi(x)|^2$ at $x = x_0$?

$$\frac{d}{dx}|\psi(x)|^2|_{x=x_0} = 2\psi(x_0)\psi'(x_0) = 0$$

$$\frac{d^2}{dx^2}|\psi(x)|^2|_{x=x_0} = 2\left(\psi'(x_0)^2 + \psi(x_0)\psi''(x_0)\right) = 2\psi'(x_0)^2 > 0$$

- ψ(x) is a local minimum of $[\psi(x)]^2$, as well as a zero of ψ(x) and of $[\psi(x)]^2$.

What happens at the node?

- Assume that the particle is confined in a region [-1,1].
- Consider a subinterval B_l = [$x_0 - l$, $x_0 + l$], with $0 \leq l \leq 1$, which contains the node x_0.
- Let us expand $[\psi(x)]^2$ in a Taylor series in B_l around x_0.
- From the earlier results, the expansion starts with a second-order term, i.e.

$$[\psi(x)]^2 = [\psi(x_0 + h)]^2 = \{d^2 [\psi(x)]^2 /dx^2 \}|_{x0} . h^2/2! = [\psi'(x_0)]^2 . h^2 ,$$

- Probability of finding the particle in B_l is (Probability -> 0 very fast)

$$P_l(h) = \int_{x_0-l}^{x_0+l} |\psi(x)|^2 dx = \frac{1}{2}\frac{d^2}{dx^2}|\Psi(x_0)|^2 \int_{-l}^{l} h^2 dh = \frac{1}{3}|\Psi'(x = x_0)|^2 h^3$$

What happens elsewhere?

- Let y be an ordinary point (not a node) in [- 1, 1].
- Consider a subinterval A_l = [y – *l*, y + *l*] contained in [- 1, 1].
- Probability of finding the particle in A_l is

$$P_l(y) = \frac{l}{L} = l < 1$$

- If we let *l* become smaller and smaller, P_l (x) tends to zero; however, it does so much more slowly than P_l (h) corresponding to a node x_0 of ψ(x).