Quantum Mechanics

Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential
3. Hydrogen Atom

Free Particle

Time-independent Schrodinger equation

$$\widehat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x)=E\cdot\psi(x)$$

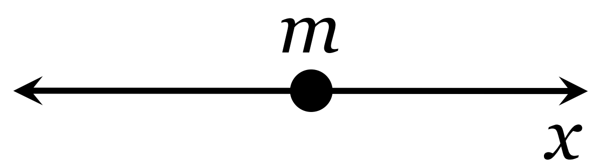
For a free particle *V(x)*=0

There are no external forces acting

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\cdot\psi(x)$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$



Second-order linear differential equation

Let us assume

$$\psi(x) = A\sin kx + B\cos kx$$

Trial Solution

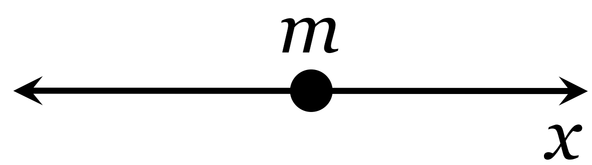
$$\psi(x) = A\sin kx + B\cos kx$$

$$\frac{\partial}{dx}\psi(x) = \frac{\partial}{dx}\left(A\sin kx + B\cos kx\right) = k\left(A\cos kx - B\sin kx\right)$$

$$\frac{\partial^2}{dx^2}\psi(x) = -k^2\left(A\sin kx + B\cos kx\right) = -k^2\psi(x)$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$



Second-order linear differential equation

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Trial Solution

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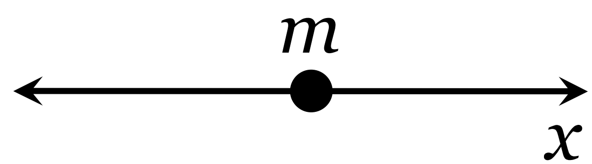
Free Particle

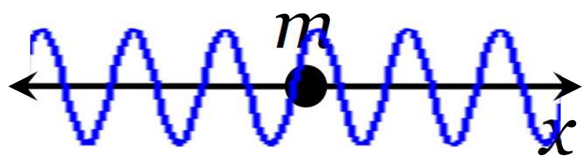


$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$

$$\frac{\hbar^2}{2m}k^2\psi(x) = E\cdot\psi(x) \quad\Rightarrow\quad E = \frac{\hbar^2 k^2}{2m} \quad\Rightarrow\quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$



de Broglie wave

$$\frac{\hbar^2}{2m}k^2\psi(x) = E\cdot\psi(x) \quad \Rightarrow \quad E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \pm\frac{\sqrt{2mE}}{\hbar}$$

$$E = \frac{\hbar^2 k^2}{2m}$$

There are no restrictions on k

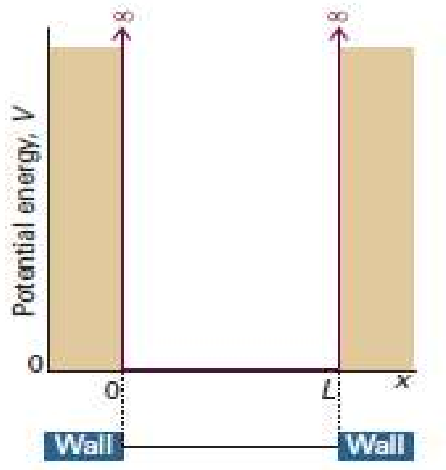
E can have any value

Energies of free particles are continuous

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

No Quantization **All energies are allowed**

Particle in 1-D Square-Well Potential



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E \cdot \psi(x)$$

For regions in the space $x < 0$ and $x > \mathrm{L} \Rightarrow V = \infty$

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{2m}{\hbar^2}(V - E)\cdot\psi(x) = \infty \cdot \psi(x)$$

Normalization condition not satisfied $\Rightarrow$

$\psi(x<0)=0$ and $\psi(x>L)=0$

Particle in 1-D Square-Well Potential

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+V(x)\psi(x)=E\cdot\psi(x)$$

For regions in the space $0 \le x \le L \Rightarrow V = 0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\cdot\psi(x)$$

This equation is similar to free particle Schrodinger
However, boundary conditions are present

Let is assume

$$\psi(x)=A\sin kx+B\cos kx$$ Trial Solution

$$E=\frac{\hbar^2k^2}{2m}$$ Energy

Particle in 1-D Square-Well Potential

$$\psi(x) = A\sin kx + B\cos kx$$

Boundary Condition $\quad x = 0 \quad \Rightarrow \quad \psi(x) = 0$

$$\psi(x) = A\sin kx \qquad \because \cos 0 = 1$$

Boundary Condition $\quad x = L \quad \Rightarrow \quad \psi(L) = 0$

$$\psi(L) = 0 \quad \Rightarrow \quad A\sin kL = 0 \quad \Rightarrow \quad A = 0 \quad \text{or} \quad \sin kL = 0$$

But the wavefunction *ψ(x)* CANNOT be ZERO everywhere

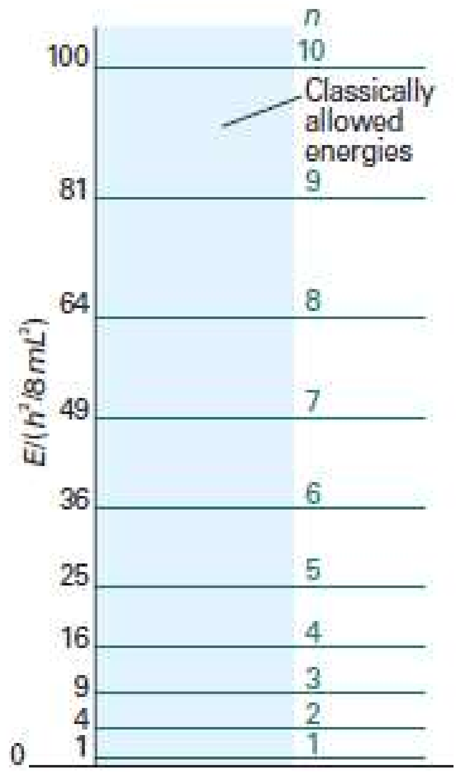
$\sin kL = 0 \quad \Rightarrow \quad kL = n\pi \quad$ n=1,2,3,4...

Wavefunction is $\quad \psi(x) = A\sin kx$

Particle in 1-D Square-Well Potential

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and } k = \frac{n\pi}{L}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad n=1,2,3,4\ldots$$



Energy is no longer continues but has discrete values; Quantization of energy

Energy separation increases with increasing values of *n*

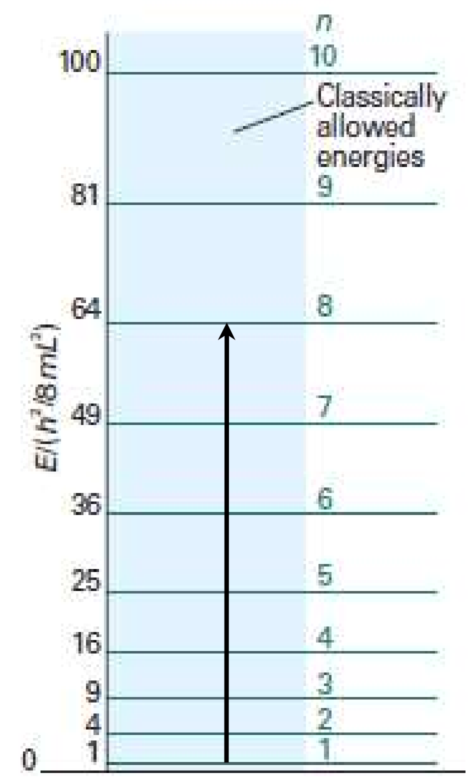
The lowest allowed energy level is for *n=1*

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} \quad \text{has a non zero value} \Rightarrow \text{Zero Point Energy}$$

Particle in 1-D Square-Well Potential: Spectroscopy

$$h\nu = \Delta E = E_f - E_i = \frac{n_f^2 h^2}{8mL^2} - \frac{n_f^2 h^2}{8mL^2} = \left(n_f^2 - n_i^2\right)\frac{h^2}{8mL^2}$$

Larger the box, smaller the energy of $h\nu$



Particle in 1-D Square-Well Potential

Wavefunction $\psi(x) = A\sin kx = A\sin\frac{n\pi}{L}x$

Normalization $\int_0^L \psi^*(x)\cdot\psi(x)\cdot dx = A^2\int_0^L \sin^2\frac{n\pi}{L}x\cdot dx = 1$

$$A = \sqrt{\frac{2}{L}} \qquad \psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$

Homework
Evaluate the above integral

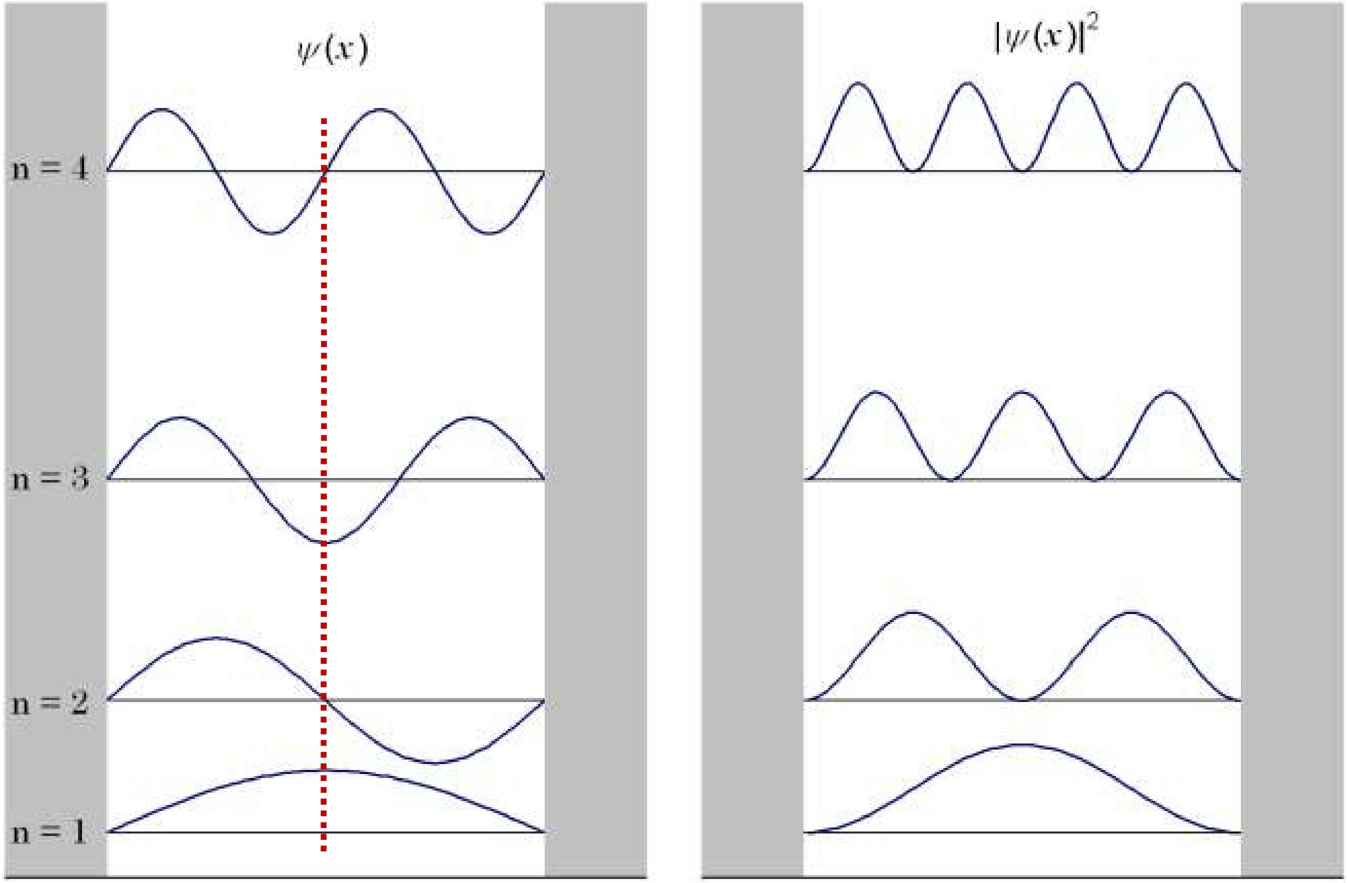
Particle in 1-D Square-Well Potential: Spectroscopy

Wavefunction $$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

n=1,3.. (odd)
Symmetric
(even function)

n=2,4.. (even)
Anti-Symmetric
(odd function)

Number of Nodes
(zero crossings) = n-1



Expectation values

$$\langle x \rangle = \int \psi^* \cdot x \cdot \psi \cdot dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot x \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot dx$$

$$= \frac{2}{L} \int_0^L x \cdot \sin^2 \frac{n\pi}{L} x \cdot dx$$

$$= \frac{L}{2}$$

Homework Verify!

Expectation values

$$\langle p_x \rangle = \int \psi^* \cdot \left(-i\hbar \frac{\partial}{\partial x} \right) \cdot \psi \cdot dx$$

$$= -i\hbar \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot \frac{\partial}{\partial x} \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot dx$$

$$= \frac{-2i\hbar n\pi}{L^2} \int_0^L \sin \frac{n\pi}{L} x \cdot \cos \frac{n\pi}{L} x \cdot dx$$

$$= 0$$

Homework
Verify!

Particle in 2-D Square-Well Potential

Hamiltonian $$\widehat{H} = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar}{2m}\frac{\partial^2}{\partial y^2} = \widehat{H}_x + \widehat{H}_y$$

$$\widehat{H} \cdot \psi(x,y) = E_n \cdot \psi(x,y)$$

Let us assume that

$$\psi(x,y) = \psi(x) \cdot \psi(y)$$

Particle in 2-D Square-Well Potential

$$\widehat{H} \cdot \psi(x,y) = \widehat{H} \cdot \left(\psi(x) \cdot \psi(y)\right)$$

$$= \left[\widehat{H}_x + \widehat{H}_y\right]\left(\psi(x) \cdot \psi(y)\right)$$

$$= \psi(y) \cdot \widehat{H}_x \cdot \psi(x) + \psi(x) \cdot \widehat{H}_y \cdot \psi(y)$$

$$= \psi(y) \cdot E_x \cdot \psi(x) + \psi(x) \cdot E_y \cdot \psi(y)$$

$$= E_x \cdot \psi(x) \cdot \psi(y) + E_y \cdot \psi(x) \cdot \psi(y)$$

$$= \left(E_x + E_y\right) \cdot \left(\psi(x) \cdot \psi(y)\right)$$

$$= \left(E_x + E_y\right) \cdot \left(\psi(x,y)\right)$$

Particle in 2-D Square-Well Potential

Hamiltonian $$\widehat{H} = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar}{2m}\frac{\partial^2}{\partial y^2} = \widehat{H}_x + \widehat{H}_y$$

$$\widehat{H} \cdot \psi(x,y) = E_n \cdot \psi(x,y)$$

$$\psi(x,y) = \psi(x) \cdot \psi(y)$$

$$E_n = E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$\boldsymbol{\psi}$ is a product of the eigenfunctions of the parts of $\hat{\boldsymbol{H}}$

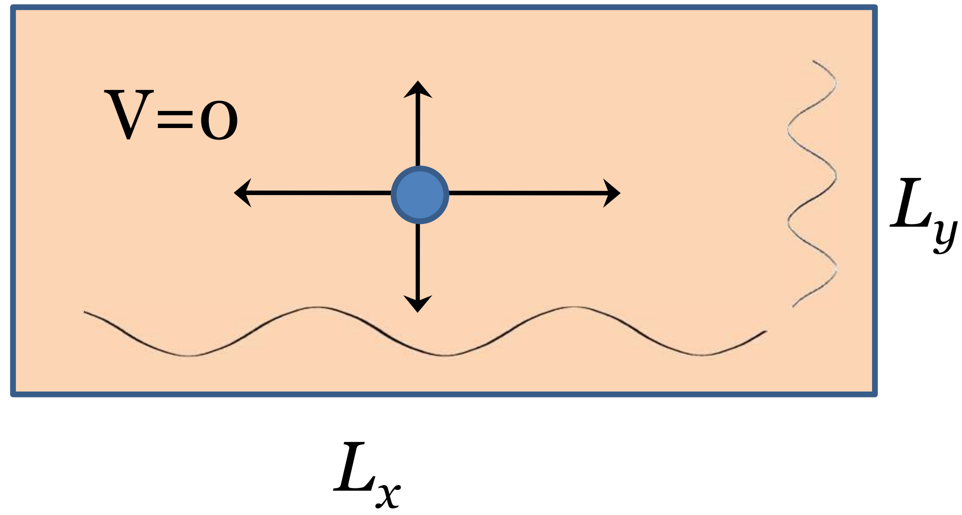
$\boldsymbol{E}$ is sum of the eigenvalues of the parts of $\hat{\boldsymbol{H}}$

Particle in 2-D Square-Well Potential

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$

$$= \sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$

$$= \frac{2}{\sqrt{L_x L_y}}\sin\frac{n\pi}{L_x}x\cdot\sin\frac{n\pi}{L_y}y$$



$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2}$$

$$= \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \quad n_x, n_y = 1,2,3,4\ldots$$