Lecture Notes: January 9, Thurs, Lecture 2

Schrodinger Equation Expressions for a Particle in 1-D Infinite and 3-D Infinite Potential Wells

Objectives:

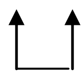
- Express Schrodinger Equations for a particle at bound states in 1D (x) and 3D (x, y, z) infinite wells. Describe quantized energy states and wave functions for infinite potential wells. Understand energy degeneracies.

………

We have the time-independent Schrodinger Equation:

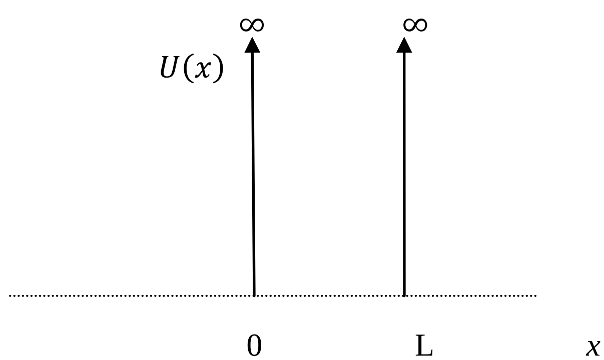
$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\,\psi(x) = \mathrm{E}\,\psi(x) \qquad \text{(e2.1)}$$

Bound States represent cases when a particle's wave function is limited to a finite region of space by the potential energy, $U(x)$. We will consider wave functions and energies three such cases:

- Infinite Well $where\ U(x)$ = 
- Finite Well $where\ U(x)$ = 

A Particle with E in a 1 Dimensional Infinite Well

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



Where $x \le 0$, wave functions CANNOT exist since the potential is infinity. → $\psi_{x\le 0}(x) = 0$
Where $x \ge L$, wave functions CANNOT exist since the potential is infinity → $\psi_{x\ge L}(x) = 0$
Where $0 < x < L$, put $U(x) = 0$ into the time-independent Schrodinger Equation (e2.1),

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = \mathrm{E}\,\psi(x) \qquad \text{(e2.2)}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\psi(x) = -\,k^2\,\psi(x) \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \text{(e2.3)}$$

Since the wave function has to be confined inside the infinite well, we can consider $\sin(kx)$ *or* $\cos(kx)$ that satisfy (e2.2) as $\psi_{0<x<L}(x)$.

BUT, since $\psi(x)$ needs to be continuous which means

- $\psi_{x\le 0}(x=0) = 0$ → We take only $\sin(kx)$ for $\psi_{0<x<L}(x)$ (drop $\cos(kx)$)
- $\psi_{x\ge L}(x=0) = 0$ → $\psi_{0<x<L}(x=L) = \sin(kL) = 0$ gives energy quantization rules

$$kL = \sqrt{\frac{2mE}{\hbar^2}}L = n\pi \qquad \text{where n =1, 2, 3, etc.} \qquad \text{(e2.4)}$$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad \text{Energy quantization} \quad \text{(e2.5)}$$

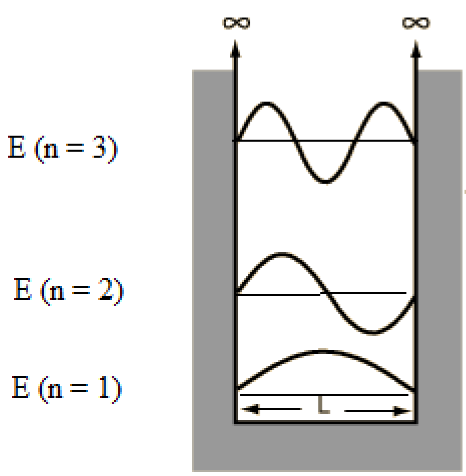
- Normalization

$$\psi_{0<x<L}(x) = A\sin(kx) = \mathrm{A}\sin(\frac{n\pi x}{L})$$

$$\int_0^L |\psi_{0<x<L}(x)|^2 = 1 = \mathrm{A}^2\int_0^L \sin\left(\frac{n\pi x}{L}\right)^2 dx = \mathrm{A}^2\frac{\mathrm{L}}{2} \rightarrow \mathrm{A} = \sqrt{\frac{2}{L}} \quad \text{(e2.6)}$$

THEREFORE,

- Wave function: $\psi_{0<x<L}(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$
- Energy $E = \frac{n^2\pi^2\hbar^2}{2mL^2}$



$$E\ (n=3) = 9\,\frac{\pi^2\hbar^2}{2mL^2}$$

$$E\ (n=2) = 4\,\frac{\pi^2\hbar^2}{2mL^2}$$

$$E\ (n=1) = 1\,\frac{\pi^2\hbar^2}{2mL^2}$$

Schrodinger Equation in three dimensions using (x, y, z) coordinates

$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \rightarrow \frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{x},t) + U(\vec{x})\Psi(\vec{x},t) = i\hbar\frac{\partial\Psi(\vec{x},t)}{\partial t}$

In (x, y, z) coordinates, $\vec{x} = (x, y, z)$, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The time-dependent Schrodinger Equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{x},t) + U(\vec{x})\Psi(\vec{x},t) = i\hbar\frac{\partial\Psi(\vec{x},t)}{\partial t} \qquad \text{(e2.7)}$$

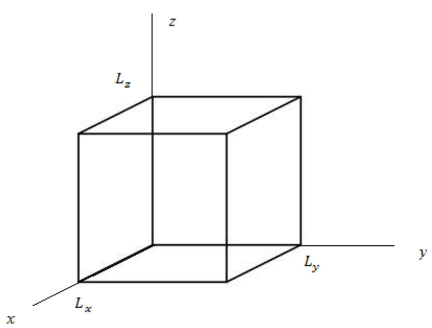
$$\text{Normalization: } \int |\Psi(\vec{x},t)|^2\, dV = 1$$

The time-independent Schrodinger Equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E\,\psi(\vec{x}) \qquad \text{(e2.8)}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = -\frac{2m}{\hbar^2}(E - U(x,y,z))\psi(x,y,z)$$

A particle with E in a 3 Dimensional Infinite Well



$$U(\vec{x}) = \begin{cases} 0 & 0 < x < L_x, 0 < y < L_y . 0 < z < L_z \\ \infty & otherwise \end{cases}$$

The 3D infinite well problem is an extension of the 1D infinite well problem in all three direcitons, because we can separate wave functions as

$$\psi(\vec{x}) = \psi(x,y,z) = F(x)G(y)H(z) \qquad \text{(e2.9)}$$

If we put (e2.9) into (e2.8), we get

$$\frac{1}{F(x)}\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)}\frac{\partial^2 G(y))}{\partial y^2} + \frac{1}{H(z)}\frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2} \qquad \text{(e2.10)}$$

$$\begin{cases} \frac{d\,F(x)}{dx^2} = C_x F(x) \rightarrow F(x) = A_x \sin\frac{n_x \pi x}{L_x} \\ \frac{d\,G(y)}{dy^2} = C_y G(y) \rightarrow G(y) = A_y \sin\frac{n_y \pi y}{L_y} \\ \frac{d\,H(z)}{dz^2} = C_z H(z) \rightarrow H(z) = A_z \sin\frac{n_z \pi z}{L_z} \end{cases} \qquad \text{(e2.11)}$$

Put (e2.11) into (e2.10)

$$-\frac{n_x^2\pi^2}{{L_x}^2}-\frac{n_y^2\pi^2}{{L_y}^2}-\frac{n_z^2\pi^2}{{L_z}^2}=-\frac{2mE}{\hbar^2} \rightarrow E_{(n_x,n_y,n_z)}=\left(\frac{n_x^2}{{L_x}^2}+\frac{n_y^2}{{L_y}^2}+\frac{n_z^2}{{L_z}^2}\right)\frac{\pi^2\hbar^2}{2m} \quad \text{(e2.12)}$$

→ Energy Quantized!

$$\psi\,(x,y,z) = F(x)G(y)H(z) = A\,\sin\frac{n_x\pi x}{L_x}\sin\frac{n_y\pi y}{L_y}\sin\frac{n_z\pi z}{L_z}$$

- Lowest Energy State is $(n_x\,,n_y,n_z\,) = (1,1,1)$
  - $E_{(1,1,1)} = \left(\frac{1^2}{{L_x}^2}+\frac{1^2}{{L_y}^2}+\frac{1^2}{{L_z}^2}\right)\frac{\pi^2\hbar^2}{2m}$
  - $\psi_{(1,1,1)} = A\,\sin\frac{\pi x}{L_x}\sin\frac{\pi y}{L_y}\sin\frac{\pi z}{L_z}$

Degeneracy occurs when different wave functions have the same energy.

When $L_x = L_y = L_z = L$

We can see that

- $E_{(1,1,1)} = (2^2 + 1^2 + 1^2)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 3\,(\frac{\pi^2\hbar^2}{2mL^2})$ → One wave function $\psi_{(1,1,1)} = A\,\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}$ (nondegenerate)
- $E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)} = (2^2 + 1^2 + 1^2)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6\,\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$

  → 3 wave functions $\begin{cases}\psi_{(2,1,1)} = A\,\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}\\ \psi_{(1,2,1)} = A\,\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{\pi z}{L}\\ \psi_{(1,1,2)} = A\,\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{2\pi z}{L}\end{cases}$

  (degenerate)

  Degeneracy = 3 (# of different wave functions that correspond to the same energy)

Consider an electron in a cubic 3D infinite well of 1 nm at the $E_{(2,1,1)}$ state

- Calculate the $E_{(2,1,1)}$ value
  - $E_{(2,1,1)} = 6\,\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = (2^2 + 1^2 + 1^2)\frac{\pi^2(1.055 \times 10^{-34}\ \text{J sec})^2}{2(9.11 \times 10^{-31}\text{kg})(10^{-9}\ \text{m})^2}$

    $= 3.62 \times 10^{-19}$ J $= 2.26$ eV (the same as $E_{(1,2,1)} = E_{(1,1,2)}$)

Where $\begin{cases} \text{electron mass } = 9.11 \times 10^{-31}\text{kg} \\ h = 1.055 \times 10^{-34} \text{ J sec} \\ L = 10^{-9} \text{ m} \end{cases}$ and 1 eV = 1.602 x 10^{-19} J

- Probability density
  - $|\psi_{(2,1,1)}|^2 = A^2 \left(\sin\frac{2\pi x}{L}\right)^2 \left(\sin\frac{\pi y}{L}\right)^2 \left(\sin\frac{\pi z}{L}\right)^2$

    Since the value of $(sin\theta)^2$ *is highest when* $\theta = \frac{1}{2}\pi, \frac{3}{2}\pi, etc.$, the probability density will be highest when $\begin{cases} x = \frac{L}{4}, \frac{3L}{4} \\ y = \frac{L}{2} \\ z = \frac{L}{2} \end{cases}$

Consider $L_x = L_y = L,\ L_z = .9\,L$ (that is, a slightly nonsymmetric box along the z axis)

- With the perfect symmetry ($L_x = L_y = L_z = L$), $E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)}$
- With the change in symmetry,
  - $E_{(1,1,1)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (1 + 1 + 1.23)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 3.23\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$
  - $E_{(2,1,1)} = E_{(1,2,1)} = \left(\frac{2^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (4 + 1 + 1.23)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6.23\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$
  - $E_{(1,1,2)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{2^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (1 + 1 + 4.92)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6.92\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$

- *Energy Split*