Lecture 25

Schrödinger equation for a particle in a box

The time-dependent Schrödinger equation (TDSE) is given by

$$-\frac{\hbar^2}{2m}\nabla^2 \Psi(x,y,z,t) + V(x,y,z,t)\Psi = i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t)$$

If $V(x,y,z,t) = V(x,y,z)$ (does not depend on time),

we can use the separation of variables technique & suppose a solution of the following form:

$$\Psi(x,y,z,t) = \psi(x,y,z)\, T(t)$$

Plug into TDSE & note that

$$\nabla^2 \Psi = \nabla^2[\psi T] = T \nabla^2 \psi$$

$$\frac{\partial}{\partial t} \Psi = \frac{\partial}{\partial t}[\psi T] = \psi \frac{\partial T}{\partial t}$$

- This is what is meant by separation of variables for a partial diff. eq. That is, $T(t)$ is treated like a constant w.r.t. ∇^2 & ψ is treated like a constant w.r.t. $\frac{\partial}{\partial t}$.
- then the TDSE becomes

$$-T \frac{\hbar^2}{2m} \nabla^2 \psi + V \psi T = i\hbar \psi \frac{\partial T}{\partial t}$$

Divide by $T\psi$ to get

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + V = i\hbar\,\frac{\frac{\partial T}{\partial t}}{T}$$

Consider that $\psi = \psi(\vec{r})$, for $\vec{r} = (x, y, z)$

$T = T(t)$, $V = V(\vec{r})$.

So then the above equation has the form

$$f(\vec{r}) = g(t) \qquad \forall \vec{r}, t$$

The only way that this can hold for all $\vec{r}$ independent of t & for all t independent of $\vec{r}$ is if

$$f(\vec{r}) = g(t) = \text{const. independent of } \vec{r} \text{ or } t$$

Since V has units of potential energy, we write

$$\frac{-\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + V = \frac{i\hbar\frac{\partial T}{\partial t}}{T} = E$$

where E is the separation constant w/ units of energy.

The TDSE separates into

$$\frac{-\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + V = E \qquad \text{(time-independent SE)}$$

$$\frac{i\hbar\frac{\partial T}{\partial t}}{T} = E$$

Solve the second one 1st:

$$\Rightarrow \quad i\hbar\frac{\partial T}{\partial t} = ET$$

$$\Rightarrow \quad \frac{dT}{T} = \frac{-iE}{\hbar}\,dt$$

$$\Leftrightarrow \quad \ln T = \frac{-iEt}{\hbar} + c$$

$$\Leftrightarrow \quad T(t) = e^{-iEt/\hbar} e^{c}$$

$$= e^{-iEt/\hbar} \cdot A$$

For constant energy, time dependence has the following form:

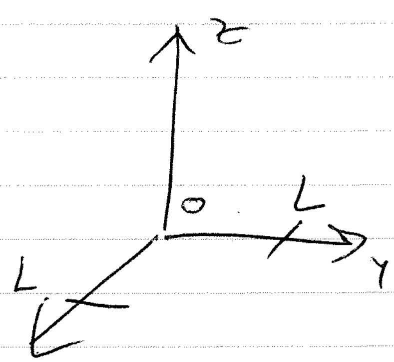
$$\Psi(\vec{r}, t) = \psi_E(\vec{r})\, e^{-iEt/\hbar}$$

where $\psi_E(\vec{r})$ solves the TISE.

Example: 2D particle in a box

$$V(x,y,z) = V(x,y)$$

$$= \begin{cases} 0 : & 0 \le x, y, \le L \\ \infty : & x > L \text{ or } y > L \end{cases}$$



Suppose separation of variables again

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

Plug in to TDSE for $0 \le x, y \le L$

TISE: $-\frac{\hbar^2}{2m}\nabla^2\psi + \cancel{V\psi}^{\,0 \text{ in box}} = E\psi$

$$\Rightarrow \nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0$$

(Helmholtz Eq.)

note that $\frac{2m}{\hbar^2}E$ has units of $\left[\frac{1}{L^2}\right]$

$$\Rightarrow k^2 \equiv \frac{2m}{\hbar^2}E \Rightarrow k = \frac{1}{\text{Length}} = \text{wave number}$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$\Rightarrow \nabla^2\psi + k^2\psi = 0$$

take $\psi(x,y) = X(x)\,Y(y)$

$$\Rightarrow \quad \nabla^2 \psi = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right] \psi$$

$$= \quad X''Y + XY''$$

$\Rightarrow$ TISE becomes

$$X''Y + XY'' + k^2 XY = 0$$

Divide by XY to get

$$\frac{X''}{X} + \frac{Y''}{Y} + k^2 = 0$$

Once again, this can hold iff

$$\frac{X''}{X} = -k_x^2 = \text{const.}$$

$$\frac{Y''}{Y} = -k_y^2 = \text{const.}$$

& $-k_x^2 - k_y^2 + k^2 = 0$

$$k^2 = k_x^2 + k_y^2 = \frac{2mE}{\hbar^2}$$ (called dispersion relation)

So then $X'' + k_x^2 X = 0$

$$Y'' + k_y^2 Y = 0$$

this is a simple harmonic oscillator for both degrees of freedom.

$$X(x) = A \sin k_x x + B \cos k_x x$$

$$Y(y) = C \sin k_y y + D \cos k_y y$$

Now apply boundary conditions

$$\psi(x,y) = X(x)\,Y(y)\Big|_{x=0,\ y=0} = 0$$

$\Rightarrow X(0) = 0 \Rightarrow B\cos(k_x \cdot 0) = 0 \Rightarrow B \cdot 1 = 0$
$\Rightarrow B = 0$

similarly, $Y(0) = 0 \Rightarrow D = 0$

$$\Rightarrow \quad X(x) = A \sin k_x x$$

$$Y(y) = C \sin k_y y$$

Apply other boundary condition

$$X(L) = A \sin(k_x L) = 0$$

$$\Rightarrow k_x L = n\pi \text{ for } n \in \{1, 2, 3, \dots\}$$

$$Y(L) = C \sin(k_y L) = 0$$

$$\Rightarrow k_y L = m\pi \text{ for } m \in \{1, 2, \dots\}$$

Quantization condition:

$$k_x = n\pi / L \ \& \ k_y = m\pi / L$$

$$\Rightarrow \quad k^2 = k_x^2 + k_y^2 = \left(\frac{n\pi}{L}\right)^2 + \left(\frac{m\pi}{L}\right)^2$$

$$= \frac{2m}{\hbar^2} E_{n,m}$$

$$\Rightarrow E_{n,m} = \frac{\hbar^2}{2m}\left[\left(\frac{n\pi}{L}\right)^2 + \left(\frac{m\pi}{L}\right)^2\right]$$

$$= \frac{\hbar^2 \pi^2}{2mL^2}\left(n^2 + m^2\right) \quad \text{for}$$

$$n, m \in \{1, 2, \ldots\}$$

So then

$$\psi(x,y) = \underbrace{A \cdot C}_{\text{normalization constant}} \cdot \sin\left(\frac{n\pi}{L}x\right) \cdot \sin\left(\frac{m\pi}{L}y\right)$$

To find it, note that we should have

$$\int_0^L \int_0^L dx\, dy\, |\psi(x,y)|^2 = 1$$

set N = normalization constant.

Then

$$1 = L^2 N^2 \int_0^L \int_0^L \frac{dx}{L} \frac{dy}{L} \sin^2\left(\frac{n\pi x}{L}\right) \sin^2\left(\frac{m\pi x}{L}\right)$$

define $\xi = \frac{x}{L}$ $\quad \zeta = \frac{y}{L}$

$$\Rightarrow \quad 1 = L^2 N^2 \left[\int_0^1 d\xi \, \sin^2(n\pi\xi) \right] \cdot \left[\int_0^1 d\zeta \, \sin^2(m\pi\zeta) \right]$$

each integral is equal to 1/2

$$\Rightarrow \quad 1 = \frac{L^2 N^2}{4}$$

$$\Rightarrow \quad N = \frac{2}{L}$$

$$\Rightarrow \quad \psi_{n,m}(x,y) = \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi}{L} y\right)$$

this is the normalized solution to the particle in a box time-independent Schrödinger equation.

→ general solution to TDSE is

$$\Psi_{n,m}(x,y,t) = \frac{2}{L}\sin\left(\frac{n\pi x}{L}\right)\cdot\sin\left(\frac{m\pi y}{L}\right) \cdot e^{-iE_{n,m}t/\hbar}$$

where $E_{n,m}$ is given above.

Then the general time-dependent solution is

$$\Psi(x,y,t) = \frac{2}{L}\sum_{n,m=1}^{\infty} c_{n,m}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi y}{L}\right) \cdot e^{-iE_{n,m}t/\hbar}$$

Suppose now that we add one additional boundary condition for time dependence.

For example, suppose we initially release the particle from the center of the box

@ $x = y = L/2$. The solution is no longer a standing wave solution.

- use the fact that

$$\delta(x-x') = \frac{2}{L}\sum_{n=1}^{\infty} \sin\left(\frac{n\pi x'}{L}\right) \cdot \sin\left(\frac{n\pi x}{L}\right)$$

$$\Rightarrow \delta\left(x-\frac{L}{2}\right) = \frac{2}{L}\sum_{n=1}^{\infty} \sin\left(\frac{n\pi}{2}\right) \sin\left(\frac{n\pi x}{L}\right)$$

$$\delta\left(y-\frac{L}{2}\right) = \frac{2}{L}\sum_{m=1}^{\infty} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{m\pi x}{L}\right)$$

Demand that

$$\Psi(x,y,0) = \delta\left(x-\frac{L}{2}\right) \cdot \delta\left(y-\frac{L}{2}\right)$$

$$\Rightarrow \frac{2}{L}\sum_{n \neq m=1}^{\infty} C_{n,m} \sin\left(\frac{n\pi}{L}x\right) \sin\left(\frac{m\pi y}{L}\right)$$

$$= \frac{4}{L^2}\sum_{n,m=1}^{\infty} \sin\left(\frac{n\pi}{2}\right) \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right)$$

Comparing like terms gives

$$c_{n,m} = \frac{2}{L} \sin\left(\frac{n\pi}{2}\right) \sin\left(\frac{m\pi}{2}\right)$$

$$\Rightarrow \Psi(x,y,t)$$

$$= \frac{4}{L^2} \sum_{n,m=1}^{\infty} \sin\left(\frac{n\pi}{2}\right) \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{2}\right) e^{-\frac{iE_{n,m}t}{\hbar}}$$