General solution of TDSE

Recall that we wrote the general solution of the TDSE as

$$\Psi_n(x,t) = \sum_{n=1}^{\infty} \underbrace{c_n}_{\text{complex coefficients}} \; \phi_n(x) \; e^{-i\frac{E_n}{\hbar}t}$$

For the infinite potential box we thus have

$$\Psi_n(x,t) = \sum_{n=1}^{\infty} c_n \; \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \; e^{-i\left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right)\frac{t}{\hbar}}$$

How to estimate c_n ?

General solution of TDSE

So, if we are given any $\Psi(x,0)$ we can write it in terms of the $\phi_n(x)$

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) = \sum_{n=1}^{\infty} c_n \ \phi_n(x)$$

How to we calculate the coefficients c_n?

Let us perform $\displaystyle\int_0^L \phi_m^*(x) \ \Psi(x,0) \ dx$

$$\int_0^L \phi_m^*(x) \ \Psi(x,0) \ dx = \sum_{n=1}^{\infty} \int_0^L \phi_m^*(x) \ c_n \phi_n(x) \ dx$$

General solution of TDSE

$$\int_0^L \phi_m^*(x)\ \Psi(x,0)\ dx = \sum_{n=1}^{\infty} \int_0^L \phi_m^*(x)\ c_n \phi_n(x)\ dx$$

$$= \sum_{n=1}^{\infty} c_n\ \underbrace{\int_0^L \phi_m^*(x)\ \phi_n(x)\ dx}_{\delta_{m,n}} = c_m$$

Thus, given a $\Psi(x,0)$, we can find the coefficients c_n as

$$c_n = \int_0^L \phi_n^*(x)\ \Psi(x,0)\ dx$$

Normalisation of General Solution

Is $\Psi(x,0)$ normalised ?

We need to check whether $\displaystyle\int_0^L |\Psi(x,0)|^2 \, dx = 1$

For that, first we need to write $\Psi^*(x,0)$.

$$\Psi^*(x,0) = \sum_{n=1}^{\infty} c_n^* \phi_n^*(x)$$

Here c_n^* and $\phi_n^*(x)$ are the complex conjugates of c_n and $\phi_n(x)$.

$$|\Psi(x,0)|^2 = \Psi^*(x,0)\Psi(x,0) = \sum_{n,m=1}^{\infty} c_m^* \phi_m^*(x) \; c_n \phi_n(x)$$

Normalisation of General Solution

So $$\int_0^L |\Psi(x,0)|^2 \, dx = 1$$

$$\Longrightarrow \sum_{n,m=1}^{\infty} \int_0^L c_m^* \phi_m^*(x) \; c_n \phi_n(x) dx = 1$$

$$\Longrightarrow \sum_{n,m=1}^{\infty} c_m^* c_n \int_0^L \phi_m^*(x) \; \phi_n(x) dx = 1$$

$$\Longrightarrow \sum_{n,m=1}^{\infty} c_m^* c_n \delta_{m,n} = 1 \quad \Longrightarrow \sum_{n,m=1}^{\infty} c_n^* c_n = \sum_{n,m=1}^{\infty} |c_n|^2 = 1$$

So the normalization of $\Psi(x,0)$ requires the sum of the modulus-squared of the coefficients to add to unity.

Normalisation of General Solution

So $$\int_0^L |\Psi(x,0)|^2 \, dx = 1$$

$$\implies \sum_{n,m=1}^{\infty} \int_0^L c_m^* \phi_m^*(x) \; c_n \phi_n(x) dx = 1$$

$$\implies \sum_{n,m=1}^{\infty} c_m^* c_n \int_0^L \phi_m^*(x) \; \phi_n(x) dx = 1$$

$$\implies \sum_{n,m=1}^{\infty} c_m^* c_n \delta_{m,n} = 1 \quad \implies \sum_{n,m=1}^{\infty} c_n^* c_n = \sum_{n,m=1}^{\infty} |c_n|^2 = 1$$

$|c_n|^2$ is the probability of measuring the energy E_n in the general state $\Psi(x,0)$.

Energy of General Solution

$$\hat{H}\Psi(x,0) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\Psi(x,0)$$

Will this give some $E\ \Psi(x,0)$?

$$\hat{H}\Psi(x,0) = \sum_{n=1}^{\infty} c_n \hat{H}\phi_n(x)$$

$$= \sum_{n=1}^{\infty} c_n E_n \phi_n(x) \neq E \sum_{n=1}^{\infty} c_n \phi_n(x)$$

$\Psi(x,0)$ is not a stationary state, i.e. it is not a solution of the TISE

Average Energy of General Solution

(Assuming $\Psi(x,0)$ is normalised)

$$\langle \hat{H} \rangle = \bar{E} = \int_0^L \Psi^*(x,0)\ \hat{H}\ \Psi(x,0)dx$$

$$= \int_0^L \left(\sum_{m=1}^{\infty} c_m^* \phi_m^*(x)\ \sum_{n=1}^{\infty} c_n \hat{H}\ \phi_n(x) \right) dx$$

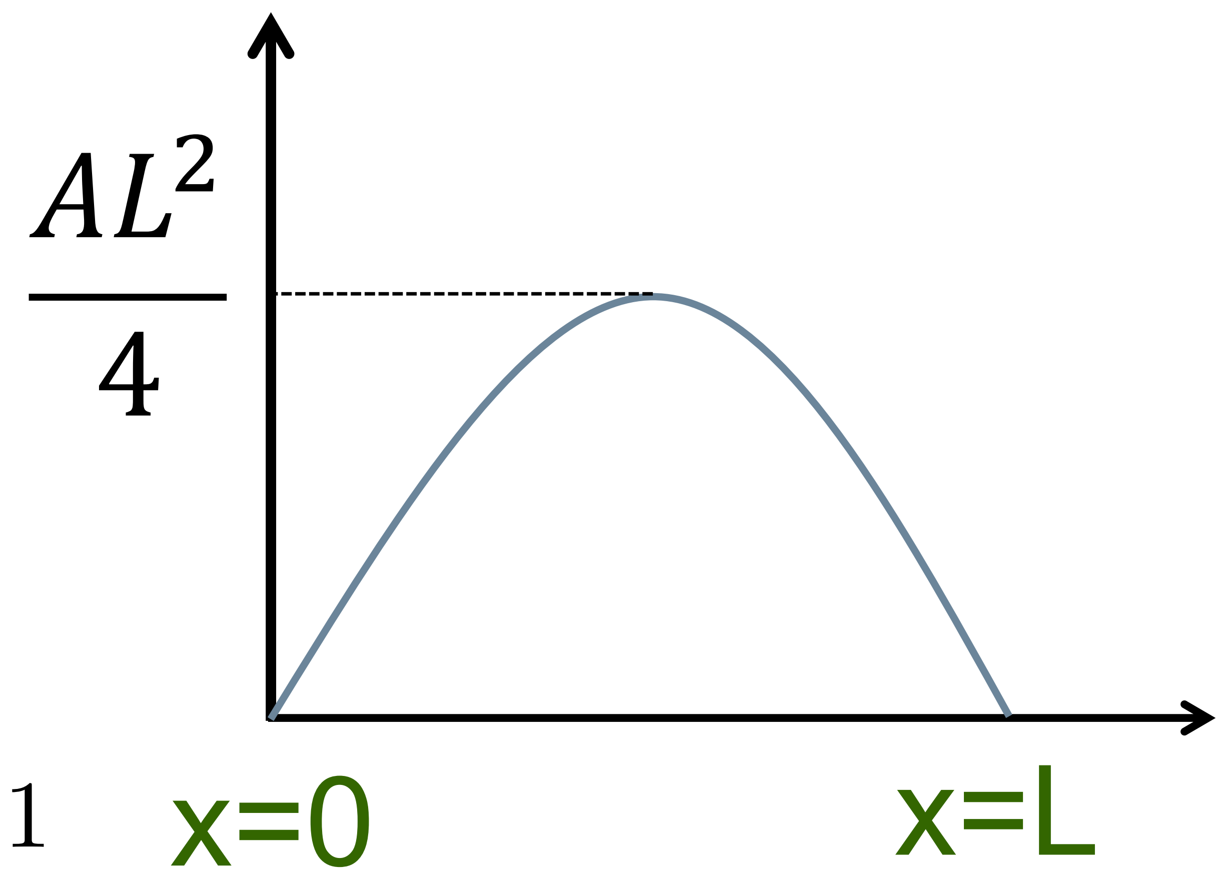
$$= \sum_{m,n=1}^{\infty} c_m^* c_n\ E_n \int_0^L \phi_m^*(x)\ \phi_n(x)dx$$

$$= \sum_{m,n=1}^{\infty} c_m^* c_n E_n \delta_{m,n} \quad = \sum_{n=1}^{\infty} |c_n|^2 E_n$$

Example 1:

Consider $\Psi(x) = A\ x(L-x)$ for $0 \leq x \leq L$ as an arbitrary state

of a particle in a 1D rigid box.



1. Find *A* by normalisation

$$\int_0^L |\Psi(x)|^2\ dx = 1$$

$$\Longrightarrow |A|^2 \int_0^L x^2 (L-x)^2\ dx = 1$$

$$\Longrightarrow A = \sqrt{\frac{30}{L^5}}$$

Example 1:

2. How to write $\Psi(x,t)$

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

And we know how to find c_n

$$c_n = \int_0^L \phi_n^*(x)\Psi(x,0)\ dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \sqrt{\frac{30}{L^5}} x(L-x)\ dx$$

$$= 0\ \forall \text{ even } n$$

$$= \frac{8\sqrt{15}}{(n\pi)^3}\ \forall \text{ odd } n$$

Example 1:

2. How to write $\Psi(x,t)$

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

$$\Psi(x,t) = \sqrt{\frac{30}{L}} \left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^3} \sin\left(\frac{n\pi}{L}x\right) e^{-i\left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right)\frac{t}{\hbar}}$$

Note that: $c_n \propto n^{-3}$

$\Psi(x,t)$ is $\phi_1(x)$ added to (1/27) $\phi_3(x)$ added to (1/125) $\phi_5(x)$

and so on... $\Psi(x,t)$ should mostly have the characteristics of $\phi_1(x)$

Example 1:

3. What is the energy of the particle in the state $\Psi(x,t)$

$$\bar{E} = \sum_{n=1}^{\infty} |c_n|^2 E_n = \sum_{n=1,3,5,..}^{\infty} \left[\frac{8\sqrt{15}}{(n\pi)^3}\right]^2 \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{5\hbar^2}{mL^2}$$

Note that $\bar{E}$ is almost same as E_1

4. What is the probability of measuring the energy E_1

$$|c_1|^2 = \left[\frac{8\sqrt{15}}{(\pi)^3}\right]^2$$

Example 2:

Assume:

$$\Psi(x,0) = \sqrt{\frac{2}{5L}}\sin\left(\frac{\pi}{L}x\right) + \sqrt{\frac{8}{5L}}\sin\left(\frac{4\pi}{L}x\right)$$

1. Normalise the above given wave-function

We can re-write the above function as

$$\Psi(x,0) = \sqrt{\frac{1}{5}}\phi_1(x) + \frac{2}{\sqrt{5}}\phi_4(x)$$

It is easy to see that $\displaystyle\sum_{n=1}^{\infty}|c_n|^2 = \frac{1}{5} + \frac{4}{5} = 1$

So Ψ (x, 0) is normalized.

Example 2:

2. Average value of Energy

$$\bar{E} = \sum_{n=1}^{\infty} |c_n|^2 \; E_n = \frac{1}{5} \; E_1 + \frac{4}{5} \; E_4$$

$$= \frac{1}{5} \; \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) + \frac{4}{5} \; \left(\frac{16\pi^2 \hbar^2}{2mL^2} \right) = 6.5 \; \left(\frac{\pi^2 \hbar^2}{mL^2} \right)$$

3. If no measurement is performed, what is the state of the particle at time t?

$$\Psi(x,t) = \sqrt{\frac{1}{5}} \phi_1(x) e^{-i \frac{E_1}{\hbar} t} + \frac{2}{\sqrt{5}} \phi_4(x) e^{-i \frac{E_4}{\hbar} t}$$

Example 2:

4. If a measurement is performed such that the value of energy is measured to be E_4, what is the state of the particle at time *t* after the measurement?

$$\Psi(x,t) = \phi_4(x)\ e^{-i\frac{E_4}{\hbar}t}$$

Show that, in the case of particle in a box

$$\Delta x \Delta p_x = \hbar \sqrt{\frac{(n^2\pi^2 - 6)}{12}}$$

Exercise:

- ✦ Determine the energy levels of a particle in a box using de Broglie equation.
- ✦ Show that zero point energy is the consequence of the uncertainty principle.
- ✦ An electron confined in a box go dimension of 0.5 nm. Estimate lowest energy level and the energy difference between the second and first level.