

# **Part-3**

## **T.I.S.E. in 2D and 3D**

## Now, let's take a quick look back...

**Schrödinger Equation :**  $\hat{E} \Psi(r, t) = \hat{H} \Psi(r, t)$

**- in 3D and time:**  $i\hbar \frac{\partial \Psi(r, t)}{\partial t} = V(r, t) \Psi(r, t) - \frac{\hbar^2}{2m} \nabla^2 \Psi(r, t)$

**- in 1D and time:**  $i\hbar \frac{\partial \Psi(x, t)}{\partial t} = V(x, t) \Psi(x, t) - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2}$

**General solution :**  $\Psi(x, t) = \psi(x) \phi(t) = \psi(x) e^{-i\omega t} = \psi(x) e^{-iEt/\hbar}$   
 $\Psi(x, t)$  is called wave function,  $\psi(x)$  is called eigen function.

**Schrödinger Equation,**

**- time independent & 1D:**  
 (when  $V$  doesnot explicitly  
 depends on time)

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

$$\Rightarrow \frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + [E - V(x)] \psi(x) = 0$$

- You have done the problem of particle in a box in 1D, let's look at the problem in multi dimensions.
- This is the same slide as slide-3, just to recap...

## S.T.I.E in 2D :

Schrödinger Equation in 3D and time :

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

Schrödinger time independent equation (S.T.I.E.) in 3D :

$$E \Psi(r, t) = V(r, t) \Psi(r, t) - \frac{\hbar^2}{2m} \nabla^2 \Psi(r, t)$$

$$\Rightarrow E \psi(r) = V(r) \psi(r) - \frac{\hbar^2}{2m} \nabla^2 \psi(r)$$

**Schrödinger time independent equation (S.T.I.E.) in 2D :**

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

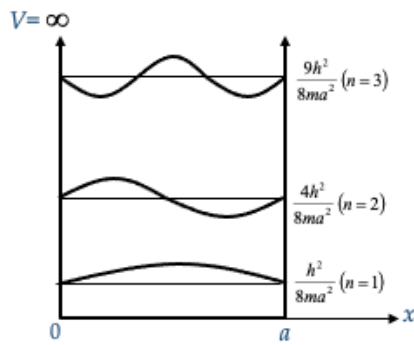
$$\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} \right] + [E - V(x, y)] \psi(x, y) = 0$$

In 2D, by conservation of energy,  $E = V(x, y) + \frac{p_x^2 + p_y^2}{2m}$

- Here we see how we write the TISE in 2D, just by considering x and y coordinates for instance. Note the potential is a function of x and y and the total energy = potential + kinetic, where we have two momentum components  $p_x$  and  $p_y$ . Hence the matter wave in this scenario has a 2D shape, with two wavelength components, one along x and the other along y (some representative schematics are at the end of this problem – slide 35).
- Similarly in a 3D case, the particle will have three components  $p_x$ ,  $p_y$  and  $p_z$ , hence three wavelengths one along each coordinate axis. The total kinetic energy of the particle will therefore be  $(p_x^2 + p_y^2 + p_z^2)/2m$ .

## Same old problem: Particle in a infinite potential well

### 1D



$$\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + [E - V(x)] \psi(x) = 0$$

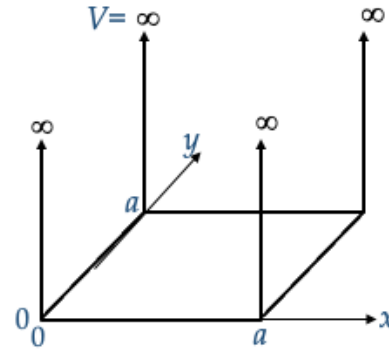
$$\psi(x) = A \sin(kx) + B \cos(kx), \quad k = \sqrt{2mE}/\hbar$$

Possible solutions are :  $\sin(ka) = 0$  or  $\cos(ka) = 0$

$$\text{i.e. } ka = n\pi \Rightarrow k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} \Rightarrow E = \frac{n^2 \hbar^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}$$

i.e. discrete energy levels, with quantum number 'n'

### 2D



**Aim:** to find out the eigen function and eigen values (energy states) of the particle.

▪ **define potential :**

$$V(x, y) = \begin{cases} 0 & \text{if } 0 < x, y < a \\ \infty & \text{elsewhere} \end{cases}$$

▪ **write down T.I.S.E :**

$$\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} \right] + [E - V(x, y)] \psi(x, y) = 0$$

- 1D problem is easy to visualize, like a wave along a string.
- However we can think 2D infinite potential well as a ball is free to move on a plane having borders. 3D potential well is similar to an air molecule in a box.
- For 2D and 3D cases, the dimensions along each dimension can be similar, or diff.
- On the left, we have the recap of the 1D case you have done already.
- On the right, we apply the same recipe, as we have been using so far, to solve the problem.
- Here, for simplicity, we start with assuming a square well, i.e. same length on both axes, and we will see a very interesting concept – called “degeneracy”. We will then follow that for a rectangular well and we will see how we ‘lift’ the degeneracy by having a non-symmetrical system.

- **define general expression for the eigen function :**

Assuming,  $x$  and  $y$  are independent variables in  $\psi(x, y)$ , we can separate out as

$$\psi(x, y) = f(x)g(y),$$

$$\text{where } f(x) = A \sin(k_x x) + B \cos(k_x x),$$

$$g(y) = C \sin(k_y y) + D \cos(k_y y) \quad \text{where } k^2 = k_x^2 + k_y^2 = 2mE/\hbar^2$$

- **apply boundary conditions :**

Since it is an infinite potential well, there is zero probability of finding the particle outside the box, as we did in the 1D case,  $\psi(x, y)$  must vanish outside the well.

$$\checkmark \quad \psi(x, y)|_{x=0} = 0 \quad \Rightarrow f(x)g(y)|_{x=0} = 0 \quad \Rightarrow f(x)|_{x=0} = 0 \quad \Rightarrow B = 0$$

$$\checkmark \quad \psi(x, y)|_{y=0} = 0 \quad \Rightarrow f(x)g(y)|_{y=0} = 0 \quad \Rightarrow g(y)|_{y=0} = 0 \quad \Rightarrow D = 0$$

$$\checkmark \quad \psi(x, y)|_{x=a} = 0 \quad \Rightarrow f(x)g(y)|_{x=a} = 0 \quad \Rightarrow f(x)|_{x=a} = 0 \quad \Rightarrow \sin(k_x a) = 0$$

$$\Rightarrow k_x a = n_x \pi, \text{ where } n_x = 1, 2, 3, \dots$$

$$\checkmark \quad \psi(x, y)|_{y=a} = 0 \quad \Rightarrow f(x)g(y)|_{y=a} = 0 \quad \Rightarrow g(y)|_{y=a} = 0 \quad \Rightarrow \sin(k_y a) = 0$$

$$\Rightarrow k_y a = n_y \pi, \text{ where } n_y = 1, 2, 3, \dots$$

- **Some more algebra (normalisation) :**

$$\psi(x, y) = f(x)g(y) = A \sin(k_x x) C \sin(k_y y) = A' \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right)$$

- Now, recalling the 1D case, the matter wave is confined by the boundaries (as the potential at the boundary is infinity, there is no penetration of the wave beyond the boundary). So only possible waves are those who have nodes at the boundary.
- Hence only discrete wavelengths are possible, defined by the width of the box, i.e. box width multiple times the half wavelengths  
for instance, when we say  $k_x (= \frac{2\pi}{\lambda_x}) = \frac{n_x \pi}{a} \Rightarrow \lambda_x = \frac{2a}{n_x}$ , or,  $a = n_x \frac{\lambda_x}{2}$
- Note, the quantum numbers cannot be zero, that would mean zero wavelength, an invalid solution. The ground state, i.e. the lowest energy state would be for  $(n_x, n_y) = (1, 1)$  – largest possible wavelength ( $\Rightarrow$  minimum possible momentum) in both axes.
- If wavelengths are discrete, so as their momentum, and hence the energy. That's why the formula.

Same situation happens in 2D and 3D.

- For 2D, the wave function is like a surface wave, like the waves we create on water. If we assume the coordinates are mutually exclusive, using separation of variable, we can separate the dependencies and hence the each function will have nodes at their respective boundary. Hence, the boundary conditions.
- Due to the boundary conditions, we get the possible values for  $k_x$  and  $k_y$ , which can be used to define the eigenfunction  $\psi(x, y)$ .

Now, normalising the eigen function over 2D space, we can find the constant  $A'$

$$\begin{aligned} \iint_{-\infty}^{\infty} |\psi(x, y)|^2 dx dy &= 1 \\ \Rightarrow A'^2 \int_{-\infty}^{\infty} \sin^2\left(\frac{n_x \pi}{a} x\right) dx \int_{-\infty}^{\infty} \sin^2\left(\frac{n_y \pi}{a} y\right) dy &= 1 \\ \Rightarrow A'^2 \int_0^a \sin^2\left(\frac{n_x \pi}{a} x\right) dx \int_0^a \sin^2\left(\frac{n_y \pi}{a} y\right) dy &= 1 \\ \Rightarrow A' &= 2/a \end{aligned}$$

- Hence, the eigen function for this particle, trapped in a 2D infinite potential well, is :

$$\psi(x, y) = \frac{2}{a} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right)$$

- and, can also find the eigen states...

$$\begin{aligned} k^2 &= k_x^2 + k_y^2 = \frac{2mE}{\hbar^2} \\ \Rightarrow E &= \frac{\hbar^2}{2m} (k_x^2 + k_y^2) = \frac{\hbar^2}{2m} \left( \frac{n_x^2 \pi^2}{a^2} + \frac{n_y^2 \pi^2}{a^2} \right) \\ \Rightarrow E &= \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2) \end{aligned}$$

To compare with 1D case:

$$E_{(1D)} = \frac{\hbar^2}{8ma^2} n^2$$

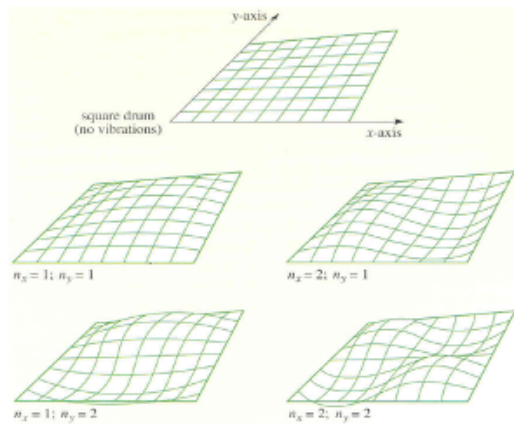
- Moving forward, we can normalize the wavefunction, as we know that the the particle is definitely inside the potential well. This will give us the normalization constant, and we can then get the full expression of the wavefunction. As you can see, the wavefunction depend strongly on the dimension of the well.
- We can also calculate the energy of the particle, and we see a very similar expression as we had for 1D. We will have discrete energy levels, that depends on the size of the box. Only difference is that we will have two quantum numbers in this case, each one representing the ‘mode’ of the wave in its axis.
- For instance, if  $n_x = 2$  and  $n_y = 3$ , we wave has 3 nodes along x axis and 4 nodes along y axis. And the energy (eigen value) of the particle will be  $E = \frac{\hbar^2}{8ma^2} (4 + 9) = \frac{13 \hbar^2}{8ma^2}$  and we the eigen function for this particle is  $\psi_{2,3}(x, y) = \frac{2}{a} \sin\left(\frac{2\pi}{a} x\right) \sin\left(\frac{3\pi}{a} y\right)$
- Now, what if  $n_x = 3$  and  $n_y = 2$ ? The particle will have the same energy  $\frac{13 \hbar^2}{8ma^2}$ , but a different eigen function  $\psi_{3,2}(x, y)$ .

- i.e. diff eigen states for the same eigen value – its called “degeneracy” – a very important concept in quantum mechanics.



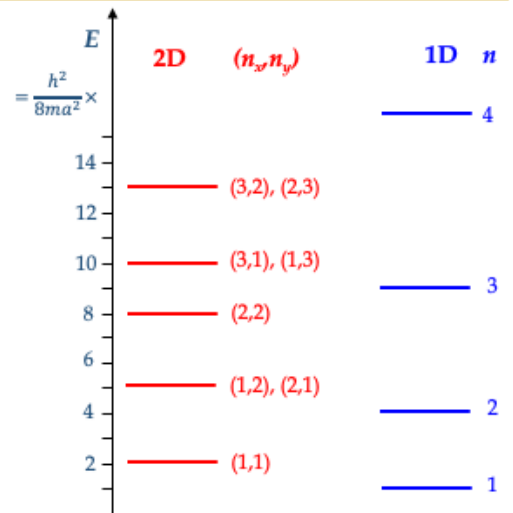
■ now, what does it mean?

- The energy of the particle is quantised, as in case of the 1D model, but slightly different way.
- Note that for some of the energy levels in 2D case is associated with two eigenstates.
- Just because there is only one energy level does not mean the eigenstates are the same (see below)



You can have different modes of vibrations associated to same energy.

i.e. can have completely different behaviour that nonetheless have same total energy.



In physics, the word that characterise this phenomena is called

**Degeneracy.**

And the eigen functions corresponding to the same eigen value (total energy,  $E$ ) are called **degenerate states**.

- In the plot on right, we see that for the 2D square-well case, we have several energy states represented by two eigenstates, we call these as ‘degenerate eigen states’. For instance,  $\psi_{2,3}$  and  $\psi_{3,2}$ . Also note the difference in energies of different allowed energy states between 1D and 2D cases, for a given ‘ $a$ ’. We have significantly more number of energy levels.
- On the left you see how one can represent different eigen states based on their quantum numbers, i.e. no of nodes.
- Now the question comes to mind, what is the origin of this degeneracy? The simplest answer is the symmetry – as the dimensions are equal on both axes, and there is no preferred choice for the particle to define which one is x axis or y axis,  $\psi_{1,2}$  and  $\psi_{2,1}$  have the exactly same pair of wavelengths, hence momentum.
- Then you may ask, what if the size of the well were not the same along the X and y axis, i.e. if we break the symmetry of the problem?

I will leave the derivation for you to try, but in a logical way, you will say that the eigen function along x and y will have different wavelengths even for the same quantum number :  $\lambda_x = \frac{2a}{n_x}$ ,  $\lambda_y = \frac{2b}{n_y}$  (or if you prefer thinking in terms of k,  $k_x = \frac{n_x\pi}{a}$  and  $k_y = \frac{n_y\pi}{b}$ ), where a and b are the size of the box along x and y axes.

- Hence the wavefunction in this case will be

$$\psi_{n_x, n_y}(x, y) = \frac{2}{\sqrt{ab}} \sin\left(\frac{n_x\pi}{a} x\right) \sin\left(\frac{n_y\pi}{b} y\right)$$

And the energy will be

$$E_{n_x, n_y} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right)$$

And you can now immediately realize that  $E_{2,3} \neq E_{3,2}$  if  $a \neq b \Rightarrow$  no degeneracy (or we say the degeneracy is lifted). Hence  $\psi_{2,3}$  and  $\psi_{3,2}$  are non-degenerate states.

## Similar approach for Particle in a 3D potential well !!!

**T.I.S.E :**

$$\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right] + [E - V(x, y, z)] \psi(x, y, z) = 0$$

**Eigen function :**

$$\psi(x, y, z) = f(x)g(y)h(z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a}x\right) \sin\left(\frac{n_y \pi}{a}y\right) \sin\left(\frac{n_z \pi}{a}z\right)$$

**Eigen value :**

$$E = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

Note, the number of quantum numbers is related to the number of degrees of freedom of the system, which in turn increases the degeneracy.

**If we have a non-cubical box, i.e. of sides  $a, b$  &  $c$ , for instance,**

**Eigen function :**

$$\psi(x, y, z) = f(x)g(y)h(z) = \left(\frac{2\sqrt{2}}{\sqrt{abc}}\right) \sin\left(\frac{n_x \pi}{a}x\right) \sin\left(\frac{n_y \pi}{b}y\right) \sin\left(\frac{n_z \pi}{c}z\right)$$

**Eigen value :**

$$E = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

This is said to lift or raise the degeneracy of the levels (i.e. the degenerate eigenstates now have unique energies). This demonstrates that **degeneracy is strongly related to symmetry.**

- Now if you have got the 2D case completely, this would not be slightly difficult to understand and work out.
- Here we have 3 quantum numbers defining the mode of vibration along each axis, defining the eigen states and eigen values.
- Then if you have a symmetrical system, you will have some degree of degeneracy, otherwise not.
- The degree of degeneracy for a given energy level can be calculated by finding the possible sets of  $(n_x, n_y, n_z)$  that results the same eigen value.
- For instance, if  $a=1, b=1$  and  $c=2$ , you can have  $\psi_{123}$  and  $\psi_{213}$  degenerate states.
- If you were asked to make a table of energy levels, the ground state would be the one with  $n_x = n_y = n_z = 1$ . The energy levels above that will be 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> ... excited states. You can then also find out the degree of degeneracy for each level as mentioned in the point above. This is quite a typical problem asked in exams and assignments.

- The derivations for the 2D square-well is given in the slides. But the derivation for other cases are quite similar and you can check with the final final expressions given here. In case of any issues, let me know. Part or whole derivation can be asked in the assessment.