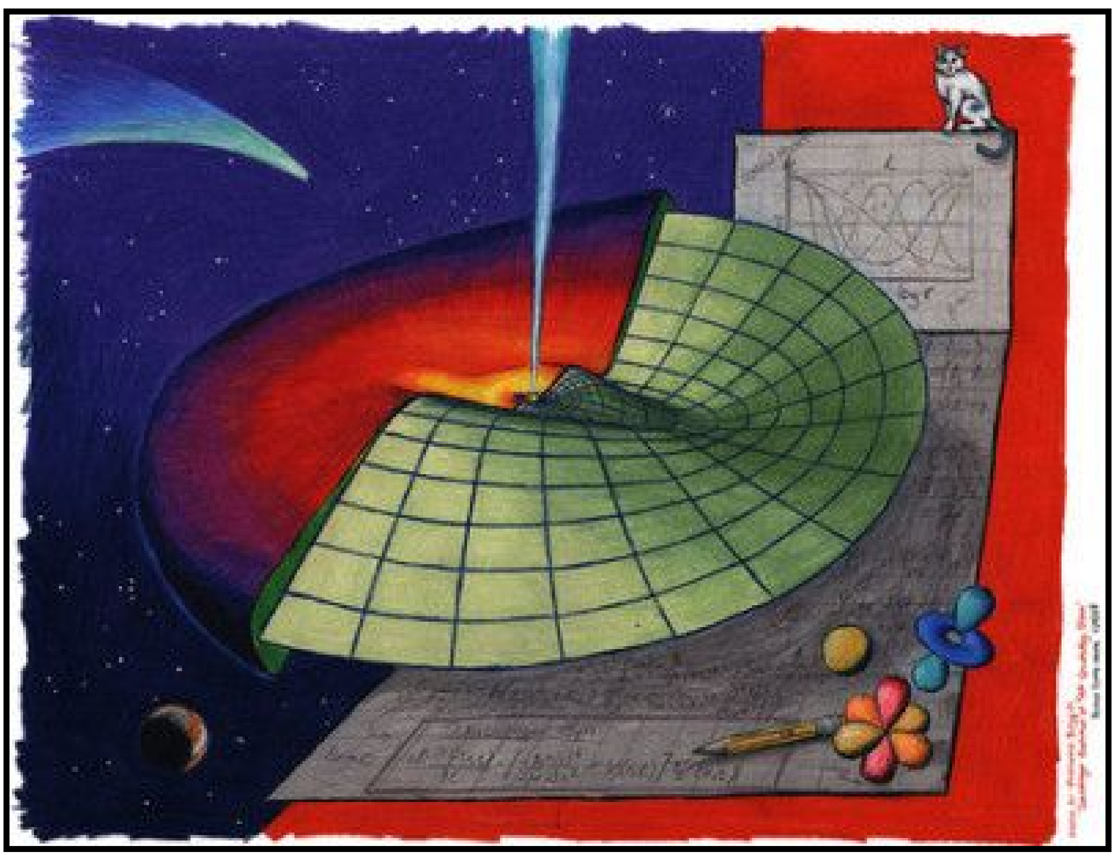
Quantum Mechanics

"If you think you understand quantum mechanics, you don't understand quantum mechanics."

-Richard Feynman



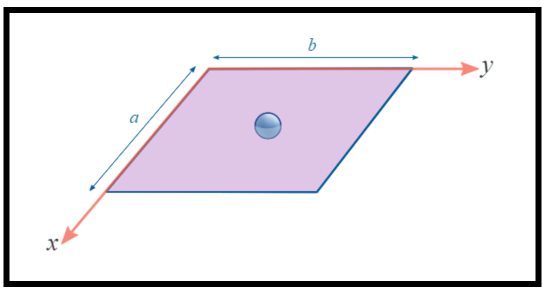
Mid-Term Evaluation

Project Report

<u>Engineering Physics Department</u>

<u>Quantum Mechanics</u>

<u>III Semester</u>



<u>‘Interpretation of a Particle in a 2D box’</u>

Submission By:

Pankaj Gupta-2K19/EP/064

Shivangi Singh-2K19/EP/091

Under the Guidance of:

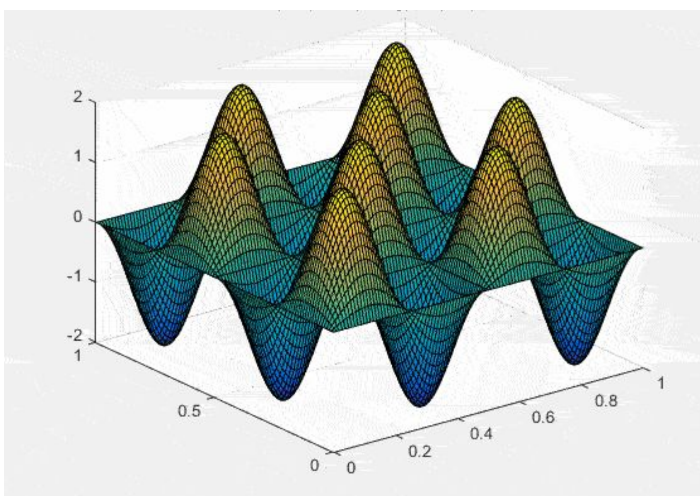
Prof. RK. Sinha

Dept.Of Applied Physics

Introduction

All strings make the same music, and support the same physics,because all strings have the same shape. The vibrational physics of a drumhead is, on the other hand, shape-dependent—whence *Mark Kac Famous question:"Can one hear the shape of a drum?"* Relatedly, all instances of the quantum mechanical "particle-in-a-box" problem are, in the one-dimensional case, scale equivalent to one another, but higher-dimensional instances of the same problem are (in general) inequivalent.

Though the one-dimensional box-problem yields quite readily to exact closed-form analysis—the simplest (but only the simplest!) aspects of which can be found in every quantum text—the higher-dimensional problem ($N \geq 2$) is in most of its aspects analytically intractable except in certain special cases

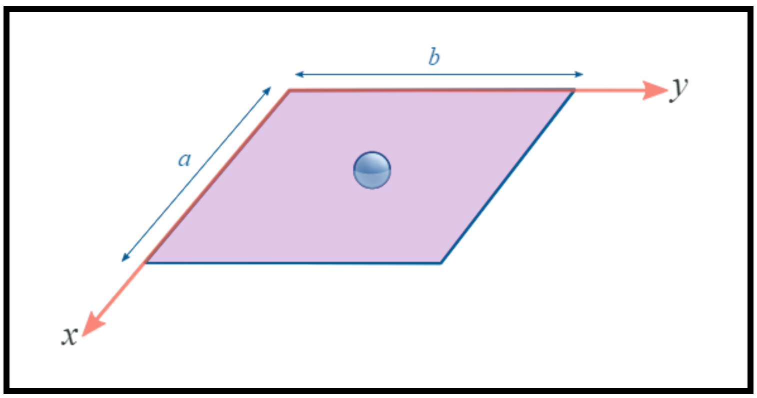


A Particle in a Two-Dimensional Square Box

The particle in a box problem is perhaps the most simple problem in quantum mechanics.

Likewise, a particle in a 2-D box also has a simple solution which is the product of the two 1-D boxes.

Let us now consider the Schrödinger Equation for an electron confined to a two dimensional box, $0<x<a$ and $0<y<b$.That is to say, within this rectangle the electron wavefunction behaves as a free particle ($V(x,y)=0$),but the walls are impenetrable so the wavefunction $\psi(x,y,t)=0$ at the walls.



** Internet Source:https://chem.libretexts.org/*

Figure 1 : A particle in a $a\times b$ 2-dimensional box with infinite height can only be found within the box

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Extending the (time-independent) Schrödinger equation for a one dimensional system.

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

(1)

to a two-dimensional system is not difficult.

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

(2)

Where:

$\hbar$	$\frac{h}{2\pi}$ (reduced Plank's constant)
h	Plank's constant (describes size of quanta in quantum mechanics)
m	mass of particle

Ψ	wave function (replaces the concept of trajectory in classical mechanics)
$V(x,y)$	potential energy of particle
E	total energy of particle

Equation (2) can be simplified for the particle in a 2D box since we know that V(x,y)=0 within the box and V(x,y)=∞ outside the box.

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

(3)

Since the Hamiltonian (i.e. left side of Equation 3) is the sum of two terms with independent (separate) variables, we try a product wavefunction like in the *Separation of Variables* approach used to separate time-dependence from the spatial dependence previously.

Within this approach we express the 2-D wavefunction as a product of two independent 1-D components.

$$\psi(x,y) = X(x)Y(y). \tag{4}$$

This ansatz separates Equation 3 into two independent one-dimensional Schrödinger equations.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 X(x)}{\partial x^2}\right) = \varepsilon_x X(x). \tag{5}$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 Y(y)}{\partial y^2}\right) = \varepsilon_y Y(y). \tag{6}$$

where the total energy of the particle is the sum of the energies from each one-dimensional Schrödinger equation.

$$E = \varepsilon_x + \varepsilon_y \tag{7}$$

The differential equations in Equations 5 and 6 are familiar as they were found for the particle in a 1-D box. They have the general solution.

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x) \tag{8}$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y) \tag{9}$$

Applying Boundary Conditions:

The general solutions in Equations 8 and 9 can be simplified to address boundary conditions dictated by the potential, i.e., $\psi(0,y)=0$ and $\psi(x,0)=0$. Therefore, $B_x=0$ and $B_y=0$.

Thus, we can combine Equations 8 , 9 , and 4 to construct the wavefunction $\psi(x,y)$ for a particle in a 2D box of the form

$$\psi(x,y) = N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) \tag{10}$$

We still need to satisfy the remaining boundary conditions $\psi(L,y)=0$ and $\psi(x,L)=0$

$$N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) = 0 \tag{11}$$

and

$$N \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right) = 0 \tag{12}$$

Equation 11 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L\right) = 0 \tag{13}$$

independent of the value of y , while equation 12 can be satisfied if

$$\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L\right) = 0 \tag{14}$$

independent of the value of x. These are the same conditions that we encountered for the one-dimensional box, hence we already know the $\sin$ function in each case can be zero in many places. In fact, these two conditions are satisfied if

$$\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}L = n_x\pi \tag{15}$$

and

$$\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}L = n_y\pi \tag{16}$$

which yield the allowed values of ε_x and ε_y as

$$\varepsilon_{n_x} = \frac{\hbar^2\pi^2}{2mL^2}n_x^2 \tag{17}$$

and

$$\varepsilon_{n_y} = \frac{\hbar^2\pi^2}{2mL^2}n_y^2 \tag{18}$$

We need two different integers n_x and n_y because the conditions are completely independent and can be satisfied by any two different (or similar) values of these integers. The allowed values of the total energy are now given by

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2) \tag{19}$$

Note that the allowed energies now depend on two integers nx and ny rather than one. These arise from the two independent boundary conditions in the x and y directions. As in the one-dimensional box, the values of nx and ny are both restricted to the natural numbers 1,2,3,... Note, therefore, that the ground state energy $E_{1,1}$ is

$$E_{1,1} = \frac{\hbar^2\pi^2}{mL^2} \tag{20}$$

is larger than for the one-dimensional box because of the contributions from kinetic energy in the x and y directions.
Once the conditions on ε_{nx} and ε_{ny} are substituted into Equation 10 , the wavefunctions become

$$\psi_{n_x,n_y}(x,y) = N\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right) \tag{21}$$

The constant N is now determined by the normalization condition

$$\int_0^L \int_0^L |\psi_{n_x,n_y}(x,y)|^2 dx\, dy = 1$$

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

$$N^2 \frac{L}{2} \cdot \frac{L}{2} = 1$$

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

so that the complete normalized 2D wavefunction is

$$\psi_{n_x,n_y}(x,y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \tag{22}$$

Probability Calculation:

The fact that the wavefunction $\psi n_x n_y(x,y)$ is a product of one-dimensional wavefunctions:

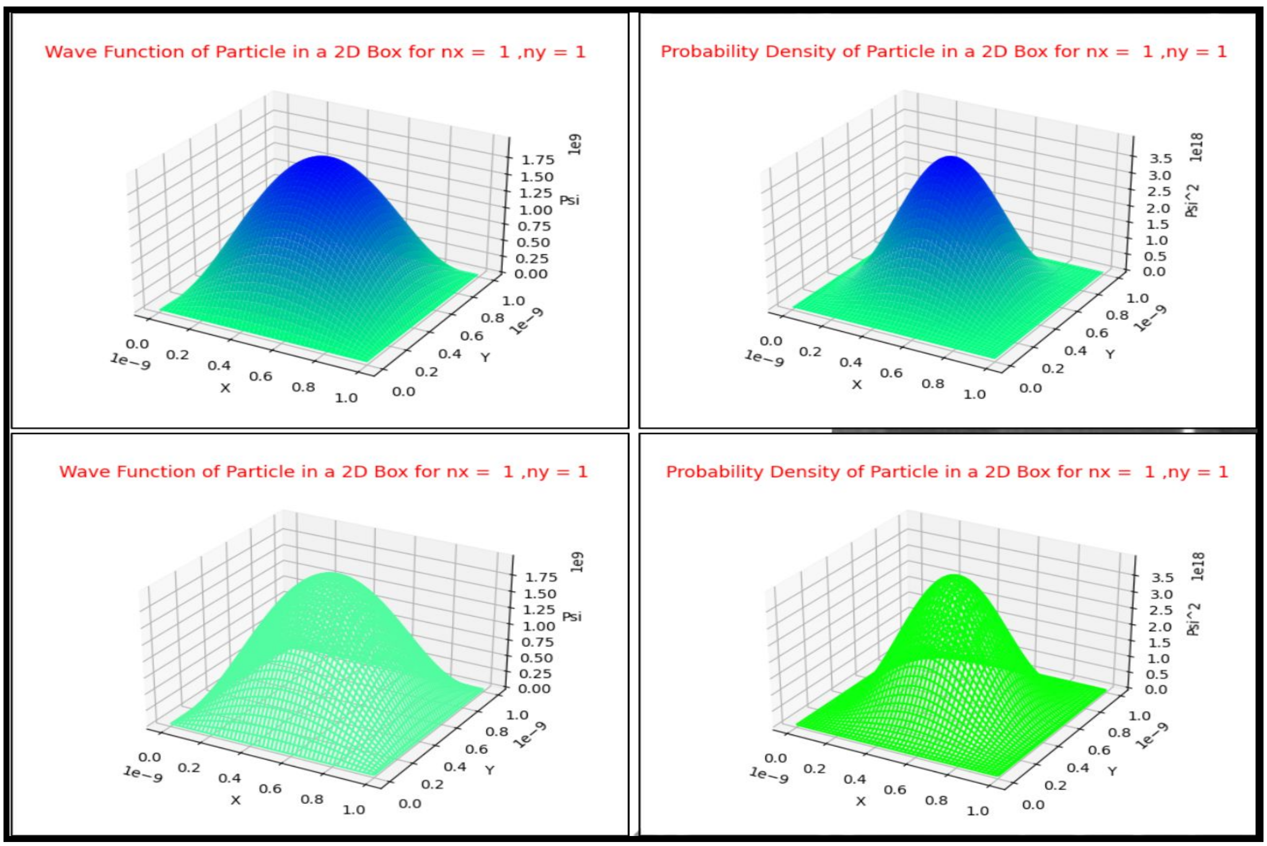
$$\psi_{n_x n_y}(x,y) = \psi_{n_x}(x)\psi_{n_y}(y) \tag{23}$$

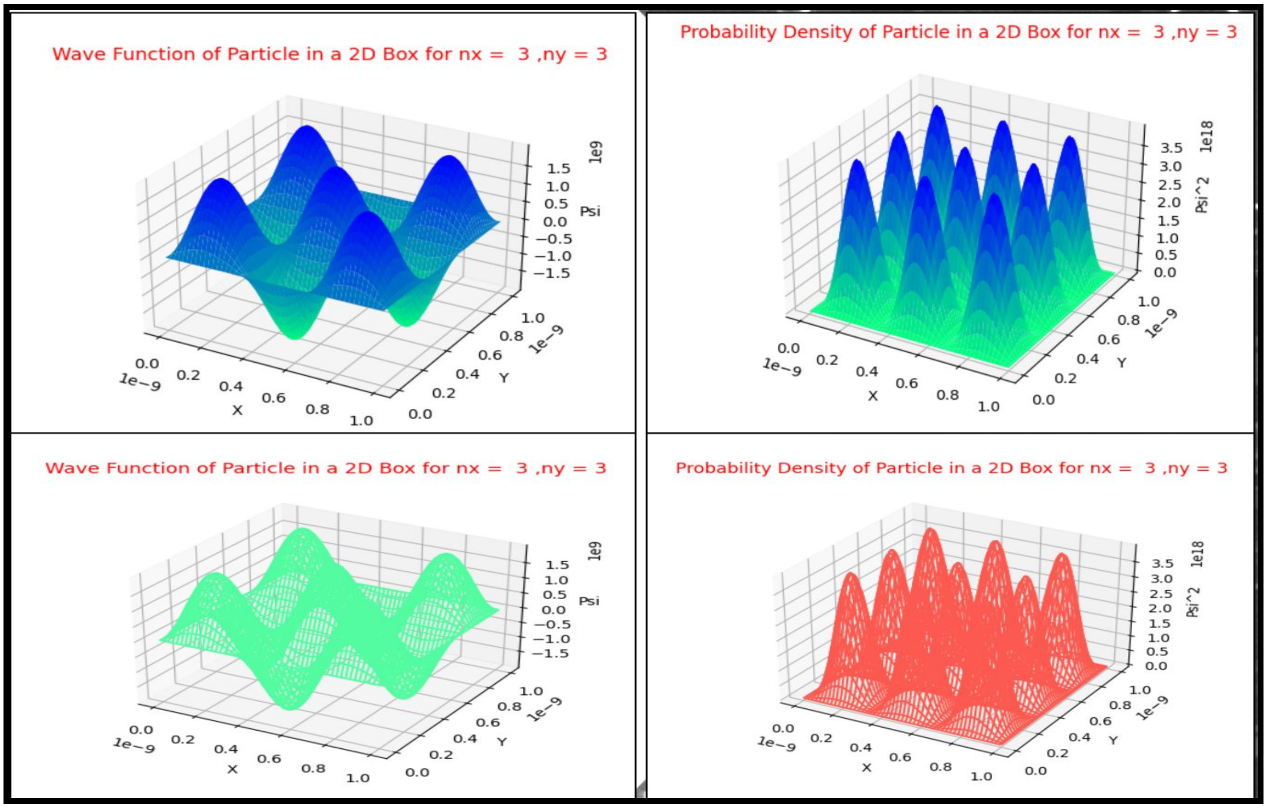
makes the calculation of probabilities rather easy. The probability that a measurement the particle's position will yield a value of $x \in [a,b]$ and $y \in [c,d]$ is

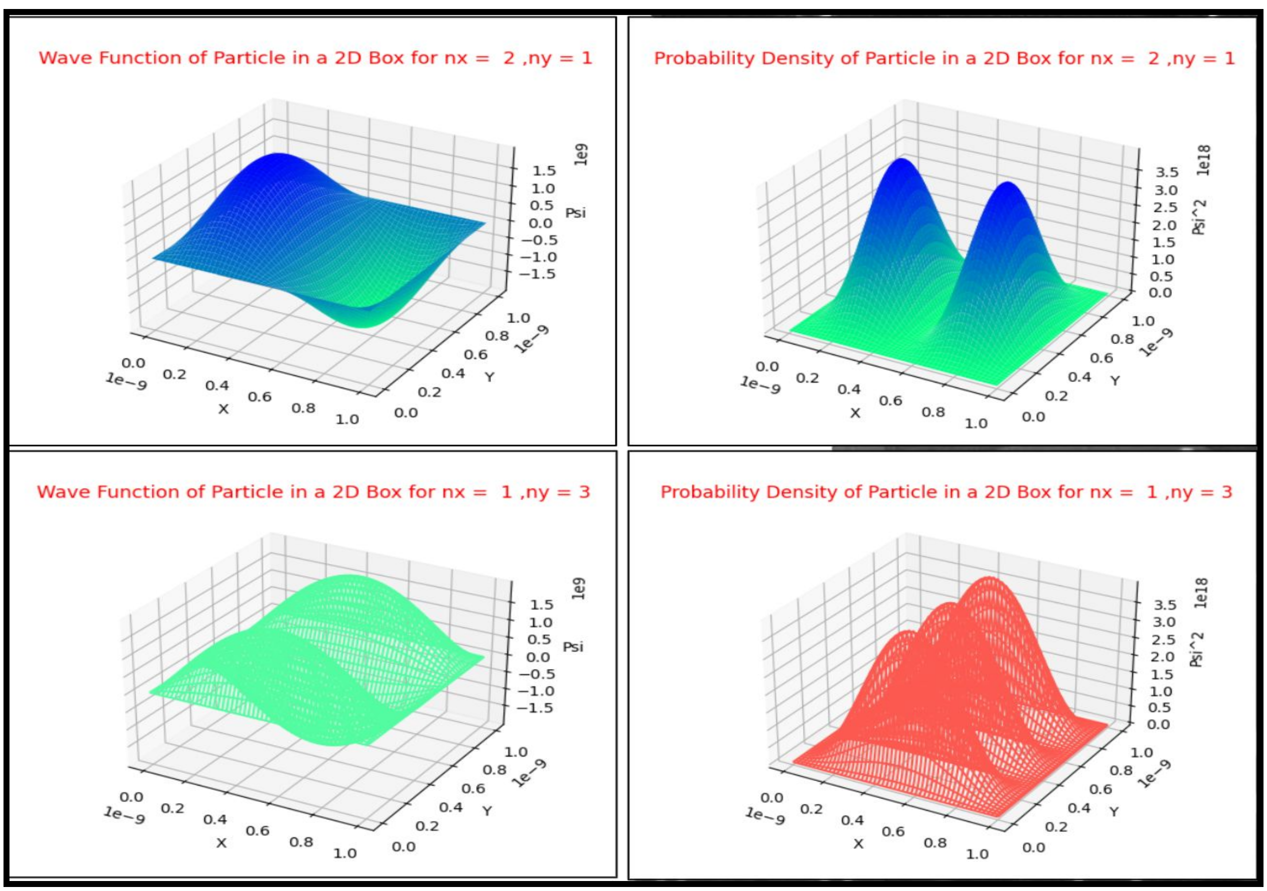
$$
\begin{aligned}
P(x \in [a,b] \; and \; y \in [c,d]) &= \int_a^b dx \int_c^d dy |\psi_{n_x n_y}(x,y)|^2 \\
&= \int_a^b dx \int_c^d dy \psi_{n_x}^2(x) \psi_{n_y}^2(y) \\
&= \left[\int_a^b \psi_{n_x}^2(x) dx \right] \left[\int_c^d \psi_{n_y}^2(y) dy \right]
\end{aligned}
$$

(24)

Various Preview of Code based Simulations :




Wave Function of Particle in a 2D Box for nx = 3 ,ny = 3
Psi
1e9
X
Y
1e−9
Probability Density of Particle in a 2D Box for nx = 3 ,ny = 3
Psi^2
1e18
X
Y
1e−9
Wave Function of Particle in a 2D Box for nx = 3 ,ny = 3
Psi
1e9
X
Y
1e−9
Probability Density of Particle in a 2D Box for nx = 3 ,ny = 3
Psi^2
1e18
X
Y
1e−9


Wave Function of Particle in a 2D Box for nx = 2 ,ny = 1
Psi
1e9
X
Y
1e−9
Probability Density of Particle in a 2D Box for nx = 2 ,ny = 1
Psi^2
1e18
X
Y
1e−9
Wave Function of Particle in a 2D Box for nx = 1 ,ny = 3
Psi
1e9
X
Y
1e−9
Probability Density of Particle in a 2D Box for nx = 1 ,ny = 3
Psi^2
1e18
X
Y
1e−9

Python Based Code For The Same Simulation :

Using VS Code Editor -

```
import numpy as np
import matplotlib.pyplot as plt
from mpl_toolkits.mplot3d import axes3d

n_x = int(input('Enter the principle Quantum Number ,nx : '))   #
principle quantum number nx
n_y = int(input('Enter the principle Quantum Number ,ny : '))   #
principle quantum number ny

Type_plot = input('Enter the type of plot you want - Surface,
Wireframe, Contour : ')

l = 10 ** -9 #length of the particle in the box, manually set in the
code

N = 100 # Meshsize
#set our 'x' and 'y' arrays
x,y = np.linspace(0,l,N),np.linspace(0,l,N)  #generate a(100)
linearly spaced array from 0 to 'l'

# 'l' is preset variable
N = (2/l) #normalization constant for  Particle in a 2d box

#Asin(kx) --> Asin(n(pi)x/l)
def psi_3d(a,b):
   # defination of our wave function that fits the limitations
   psi_3d = N*(np.sin((n_x * np.pi * a)/l) * np.sin((n_y * np.pi *
b)/l))
   return psi_3d

# Making our wavefunction in the Z-Axis
```

```
X,Y = np.meshgrid(x,y) #for 'x' and  'y' respectively, meshgrid sets
up a matrix for the two variables 'X' & 'Y' (capitals), 'x' and 'y'
are preset arrays

psi = np.array([psi_3d(x,y) for x,y in zip(np.ravel(X),np.ravel(Y))])
#ravel returns a continuous flattened array,
#zip() is on interator tuple which joins similar objects together,
#psi_3d(x,y) calls the def function, then sets the a,b values as x,y
values found in the Zip() brackets,
# this is all saved as an array in the variable 'Psi'

Psi = psi.reshape(X.shape) # Decreases the number of values in
'psi' from 10000 to 100 in comparison to 'X',
P_Density = Psi**2   # Probability Density
#X.shape looks at the shape (no. of values) in 'X' then .reshape
changes the shape of the array without changing it's data,
variable saved as 'Psi'

#Plot our 2d box onto a 3d plane
fig = plt.figure()
ax = fig.add_subplot(111,projection='3d') # generates a
different plot for each graph, includes the size of the graph,
makes dimension of the graph '3d'

if Type_plot == 'surface' or Type_plot == 'Surface' :
   ax.plot_surface(X, Y, Psi,cmap = plt.cm.winter_r) #includes
the variables required to plot graph (x,y,z) , plots 'X' vs 'Y'
vs 'A*Psi'
elif Type_plot == 'contour' or Type_plot == 'Contour' :
   ax.contourf(X, Y, Psi)
elif Type_plot == 'wireframe' or Type_plot == 'Wireframe' :
   ax.plot_wireframe(X, Y, Psi,color = 'xkcd:sea green' )
```

```python
#includes info of the curve

#labels our x,y,z axis
plt.xlabel('X')
plt.ylabel('Y')
ax.set_zlabel('Psi')
plt.title('Wave Function of Particle in a 2D Box for nx =
'+str(n_x)+' ,ny = '+str(n_y),color='red')
# gives the graph a title
plt.savefig('2D Box Wave function.png')

#Plot our 2d box onto a 3d plane
fig = plt.figure()
ax = fig.add_subplot(111,projection='3d') #generates a different plot
for each graph, includes the size of the graph, makes dimension of
the graph '3d'
if Type_plot == 'surface' or Type_plot == 'Surface' :
   # ax.plot_surface(X, Y, P_Density,cmap = 'magma') #includes the
variables required to plot graph (x,y,z) , plots 'X'
   ax.plot_surface(X, Y, P_Density,cmap = plt.cm.winter_r)
   # vs 'Y' vs 'A*Psi'
elif Type_plot == 'contour' or Type_plot == 'Contour' :
   ax.contourf(X, Y, P_Density)
elif Type_plot == 'wireframe' or Type_plot == 'Wireframe' :
   ax.plot_wireframe(X, Y, P_Density,color = 'xkcd:coral')

#includes info of the curve
#labels our x,y,z axis
plt.xlabel('X')
plt.ylabel('Y')
ax.set_zlabel('Psi^2')
plt.title('Probability Density of Particle in a 2D Box for nx =
'+str(n_x)+' ,ny = '+str(n_y),color='red') #gives the graph a title
```

```
plt.savefig('2D box Probability Density.png')    #saves the plot as well for us
plt.show()
```

***Note that if the box were rectangular rather than square, then instead of having a length of L on both sides, there would be two different lengths L_x and L_y. The formulas for the energies and wavefunctions become only slightly more complicated:**

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \tag{25}$$

instead of **Equation 19**

$$\psi_{n_x,n_y}(x,y) = \frac{2}{\sqrt{L_x L_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{26}$$

Degeneracy in two dimensional system:

Two distinct wavefunctions are said to be degenerate if they correspond to the same energy.Degeneracies in quantum physics are most often associated with symmetries in this way.

Particle in a Rectangular Box:

The permitted energy values for particle in a rectangular box is given by equation 25 i.e.

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

all the states would be non-degenerate as $L_x \neq L_y$ since the box is rectangular . However, a degeneracy will be "accidentally" observed for states that fulfill this requirement:

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}. \tag{27}$$

Particle in a Square Box:

The most degenerate case is the square, $L_x=L_y$, for which clearly $E_{m,n}=E_{n,m}$ Degeneracies in quantum physics are most often associated with symmetries in this way.

The energy of the particle in a 2-D square box (i.e., $L_x=L_y=L$) in the ground state is given by Equation 25 with $n_x=1$ and $n_y=1$. This energy (E_{11}) is hence

$$E_{1,1} = \frac{2\hbar^2\pi^2}{2mL^2} \tag{28}$$

For the ground state of the particle in a 2D box, there is one wavefunction (and no other) with this specific energy; the ground state and the energy level are said to be **non-degenerate.**

However, in the 2-D box potential, the energy of a state depends upon the sum of the squares of the two quantum numbers.

Degenerate states are also obtained when the sum of squares of quantum numbers corresponding to different energy levels are the same.

For example, the three states (n_x = 7, n_y = 1), (n_x = 1, n_y = 7) and (n_x = n_y = 5) all have

$$E = 50\frac{\pi^2\hbar^2}{2mL^2} \quad (29)$$

and constitute a degenerate set.

Corresponding to these combinations three different wavefunctions and two different states are possible. Hence, the first excited state is said to be doubly degenerate. The number of independent wavefunctions for the stationary states with a shared energy is called as the degree of degeneracy of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers.

$$n^2 = n_x^2 + n_y^2 \quad (30)$$

Degrees of degeneracy of different energy levels for a particle in a square box:

$n_x^2 + n_y^2$	Combinations of Degeneracy (n_x, n_y)		Total Energy (E_{n_x,n_y})	Degree of Degeneracy
2	(1, 1)		$\frac{2\hbar^2\pi^2}{2mL^2}$	1
5	(2, 1)	(1, 2)	$\frac{5\hbar^2\pi^2}{2mL^2}$	2
8	(2, 2)		$\frac{8\hbar^2\pi^2}{2mL^2}$	1
10	(3, 1)	(1, 3)	$\frac{10\hbar^2\pi^2}{2mL^2}$	2
13	(3, 2)	(2, 3)	$\frac{13\hbar^2\pi^2}{2mL^2}$	2
18	(3,3)		$\frac{18\hbar^2\pi^2}{2mL^2}$	1

Table 1 : Degeneracy properties of the particle in a 2-D box with L_x=L and L_y=L .

Conclusion :

We have interpreted the results of a particle in a 2D Box, via relevant plots of Wave Function and Probability Density via Python Coding Language.

*Note : We tried to animate the same plots during our coding period, still due to complexity of the matter, we were not able to replicate the same.

References :

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