Chapter 6: Integral Calculus

Probability and Particle in a Box

The real advantage of using *Mathematica* is its ability to integrate multiple functions. The wavefunction describing a particle in a 1D box of length L is $\psi(x) = \mathrm{Sin}\left(\frac{n\pi x}{L}\right)$. This gives an equation for probability P = $\int_{L_1}^{L_2} \psi^2(x)\, dx$. Since the probability of finding the particle inside the entire length of the box is 1, $\int_0^L \psi^2(x)\, dx = 1$.

The integral of $\psi^2(x)$ from 0 to L will not naturally equal one, meaning that to use this equation, the wavefunction must first be *normalized*. A normalized wavefunction can be written as ψ (x) = A Sin $\left(\frac{n\pi x}{L}\right)$ where A can be determined from the probability over the entire length of the box: $A^2\int_0^L \psi^2(x)\, dx = 1$. Let's determine what A must be.

Define a function called psi and integrate the square of psi from 0 to L at the first quantum number, n = 1. The Integrate command requires four arguments: the function, the variable, the lower limit and the upper limit, with the last three arguments in a list. Make sure to clear all variables before integrating.

```
Clear@n, x, L, psiD;
psi@n_, L_D := Sin@n * Pi * x • LD;
ans = Integrate@psi@1, LD^2, 8x, 0, L<D;
PrintA"à_0^L y^2HxLâx = ", ansE
```

$$\int_0^L \psi^2(x)\, dx = \frac{L}{2}$$

We know that $A^2\int_0^L \psi^2(x)\, dx = 1$ so $A^2 = \frac{1}{\int_0^L \psi^2(x)\, dx}$. Take the square root using Sqrt to find A:

```
A = 1 • Sqrt@ansD;
Print@"A = ", AD
PrintA"The normalized wavefunction is yHxL = ", A,
 "SinH n p x / L L"E
```

$$A = \frac{\sqrt{2}}{\sqrt{L}}$$

The normalized wavefunction is $\psi(x) = \frac{\sqrt{2}}{\sqrt{L}}\,\mathrm{Sin}\left(\frac{n\pi x}{L}\right)$

Now that you've found the normalized wavefunction for a particle in a box, define a new function for $\psi(x)$ and to solve the problem below:

```
psiNorm[n_, L_] := Sqrt[2/L] Sin[n * Pi * x / L]
```

From Physical Chemistry, 6th Edition by Peter Atkins:

Exercise 12.2
Calculate the probability that a particle will be found between 0.49L and 0.51L in a box of length L when it has:

a) n = 1

b) n = 2

Harmonic Oscillator

The harmonic oscillator model is a fundamental part of quantum chemistry. The mean displacement of a particle in a box is symbolized by <x> where <x> = $A^2\int_0^L x\,\psi^2(x)\,dx$. The mean square displacement is symbolized by < x^2> where < x^2> = $A^2\int_0^L x^2\,\psi^2(x)\,dx$. The spread about <x> is otherwise known as the variance, σ_x^2:

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2$$

Using the normalized wavefunction defined previously, solve the following problem:

From Physical Chemistry A Molecular Approach, by Donald McQuarrie and John Simon:

Problem 3-20
Calculate <x> and < x^2> for the n = 2 state of a particle in a one-dimensional box of length *a*.

Show that $\sigma_x = \frac{a}{4\pi}\sqrt{\frac{4\pi^2}{3} - 2}$

Answers: Exercise 12.2

For n = 1:

```
Integrate@psiNorm@1, LD^2, 8x, 0.49 L, 0.51 L<D;
Print@"Probability = ", %, " at n = 1"D
```

```
Probability = 0.0399868 at n = 1
```

For n = 2:

```
Integrate@psiNorm@2, LD^2, 8x, 0.49 L, 0.51 L<D;
Print@"Probability = ", %, " at n = 2"D
```

```
Probability = 0.0000525963 at n = 2
```

Answer: Problem 3-20
Start by defining the normalized wavefunction y (x):

```
psiNorm@n_, a_D := $ 2/a Sin@n * Pi * x • aD;
```

Write a function for <x> and < x^2>:

```
meanX@y_D := Integrate@y^2 * x, 8x, 0, a<D;
meanSquareX@y_D := Integrate@y^2 * x^2, 8x, 0, a<D;
```

Use y (x) for n = 2 and length *a* to calculate <x> and < x^2>:

```
y = psiNorm@2, aD;
x1 = meanX@yD;
Print@"<x> = ", x1D
```

$$<x> = \frac{a}{2}$$

```
x2 = meanSquareX@yD;
Print@"<x^2> = ", x2D
```

$$<x^2> = \frac{2 \left(\frac{a^3}{6} - \frac{a^3}{16 p^2} \right)}{a}$$

< x^2> can be simplified using Expand:

```
x2 = meanSquareX@yD •• Expand;
Print@"<x^2> = ", x2D
```

$$<x^2> = \frac{a^2}{3} - \frac{a^2}{8 p^2}$$

Now solve for s_x:

```
sigmaSq = x2 - x1^2;
sigma = Sqrt@sigmaSqD;
Print@"s_x= ", sigmaD
```

$$s_x = \sqrt{\frac{a^2}{12} - \frac{a^2}{8 p^2}}$$

Do a series of algebra steps and you'll see that $s_x = \sqrt{\frac{a^2}{12} - \frac{a^2}{8 p^2}} = \frac{a}{4 p} \sqrt{\frac{4 p^2}{3} - 2}$