Chapter 6: Integral Calculus

Indefinite Integrals

Mathematica can evaluate integrals without limits using the command *Integrate*.

From Calculus Early Transcendentals, 4th Edition by James Stewart:

Chapter 5.4, Example 1: Find the general indefinite integral

$\int (10x^4 - 2\sec^2 x)\,dx$

Clear all variables and define a function called *f*:

```
Clear[f, x]
f = 10*x^4 - 2*(Sec[x])^2
10 x^4 - 2 Sec[x]^2
```

The *Integrate* command require two arguments. The first is the function and the second is the variable of integration:

```
ans = Integrate[f, x]
2 x^5 - 2 Tan[x]
```

Mathematica will not give a +*C* in the output although the actual answer is $2x^5 - 2\,\mathrm{Tan}[x] + C$.

From Calculus Early Transcendentals, 4th Edition by James Stewart:

Chapter 5.4: Find the general indefinite integral

1. $\int x^{-3/4}dx$

2. $\int \frac{Sin2x}{Sinx}dx$

3. $\int (x^3 + 6x + 1)dx$

Answers: Chapter 5.4

Problem 1:

Clear all variables and define a function called *f1*:

```
Clear[f1, f2, f3, x]
f1 = x^(-3/4)
```

$\frac{1}{x^{3/4}}$

```
ans1 = Integrate[f1, x]
```

$4 x^{1/4}$

Problem 2:

```
f2 = Sin[2*x] / Sin[x]
Csc[x] Sin[2 x]

ans2 = Integrate[f2, x]
2 Sin[x]
```

Problem 3:

```
f3 = x^3 + 6*x + 1
```

$1 + 6 x + x^3$

```
ans3 = Integrate[f3, x]
```

$x + 3 x^2 + \frac{x^4}{4}$

Definite Integrals

Mathematica can also evaluate integrals with limits. The first argument is still the function, but the second argument is a list containing the variable of integration, the minimum limit and the maximum limit.

From Calculus Early Transcendentals, 4th Edition by James Stewart:

Chapter 5.2, Example 6:

Evaluate $\int_0^1 (4 + 3x^2)\, dx$

Clear all variables and define a function called *f*:

```
Clear[f, x, ans]
f = 4 + 3 * x^2
4 + 3 x^2

ans = Integrate[f, {x, 0, 1}]
5
```

From Calculus Early Transcendentals, 4th Edition by James Stewart:

Chapter 5.2: Evaluate the integral

1. $\int_{-1}^{5}(1+3x)dx$

2. $\int_{0}^{2}(2-x^2)dx$

Answers: Chapter 5.2

Problem 1:

```
Clear[f1, f2, x]
f1 = 1 + 3 * x
1 + 3 x

ans1 = Integrate[f1, {x, -1, 5}]
42
```

Problem 2:

```
f2 = 2 - x^2
2 - x^2

ans2 = Integrate[f2, {x, 0, 2}]
4
-
3
```

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 $\psi(x) = \text{Sin}\left(\frac{n \pi x}{L}\right)$. 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 $\psi(x) = A\ \text{Sin}\left(\frac{n \pi x}{L}\right)$ 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, psi];
psi[n_, L_] := Sin[n * Pi * x / L];
ans = Integrate[psi[1, L] ^ 2, {x, 0, L}];
Print[" ∫_0^L ψ² (x) dx = ", ans]
```

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

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[ans];
Print["A = ", A]
Print["The normalized wavefunction is ψ(x) = ", A,
  "Sin(n π x / L)"]
```

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

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

Now that you've found the normalized wavefunction for a particle in a box, define a new function for ψ(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

Mean Displacement

The mean displacement of a particle in a box is symbolized by <x> where $\langle x \rangle = A^2 \int_0^L x\, \psi^2(x)\, dx$. The mean square displacement is symbolized by $\langle x^2 \rangle$ where $\langle x^2 \rangle = A^2 \int_0^L x^2\, \psi^2(x)\, dx$. The spread about <x> is otherwise known as the variance σ_x^2, where $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$

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, L]^2, {x, 0.49 L, 0.51 L}];
Print["Probability = ", %, " at n = 1"]
```

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

For n = 2:

```
Integrate[psiNorm[2, L]^2, {x, 0.49 L, 0.51 L}];
Print["Probability = ", %, " at n = 2"]
```

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

Answer: Problem 3-20

Start by defining the normalized wavefunction ψ (x):

$$\texttt{psiNorm[n\_, a\_] :=} \sqrt{\frac{2}{a}}\ \texttt{Sin[n * Pi * x / a];}$$

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

```
meanX[ψ_] := Integrate[ψ^2 * x, {x, 0, a}];
meanSquareX[ψ_] := Integrate[ψ^2 * x^2, {x, 0, a}];
```

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

```
ψ = psiNorm[2, a];
x1 = meanX[ψ];
Print["<x> = ", x1]
```

$$\langle x \rangle = \frac{a}{2}$$

```
x2 = meanSquareX[ψ];
Print["<x^2> = ", x2]
```

$$\langle x^2 \rangle = \frac{2\left(\frac{a^3}{6} - \frac{a^3}{16\,\pi^2}\right)}{a}$$

$< x^2 >$ can be simplified using *Expand*:

```
x2 = meanSquareX[ψ] // Expand;
Print["<x²> = ", x2]
```

$$\langle x^2 \rangle = \frac{a^2}{3} - \frac{a^2}{8\pi^2}$$

Now solve for σ_x:

```
sigmaSq = x2 - x1²;
sigma = Sqrt[sigmaSq];
Print["σx= ", sigma]
```

$$\sigma_x = \sqrt{\frac{a^2}{12} - \frac{a^2}{8\pi^2}}$$

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