Chapter 4: Trigonometry Plots

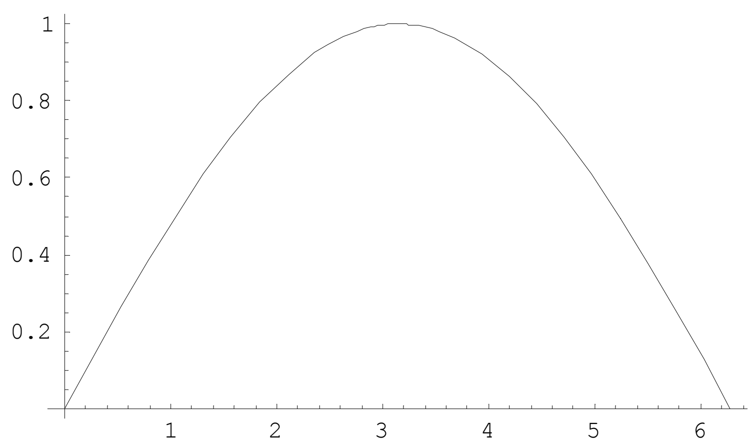
Basic Trig Commands

The trig commands are useful in plots and calculus. For this tutorial we will deal with the plots first, since sine plots are common for particle in a box problems.

The wave functions ψ_n that describe the motion of a particle inside a box resemble the normal modes of a standing wave. This means that the nth harmonic has n - 1 nodes. Let's plot the first three waves. Make the range equal to one sine period (2 π) and adjust the frequency of x to get the correct number of nodes. Keep in mind that *Mathematica* evaluates the trig commands in radians, not degrees. You can use the symbol π or *Pi*.

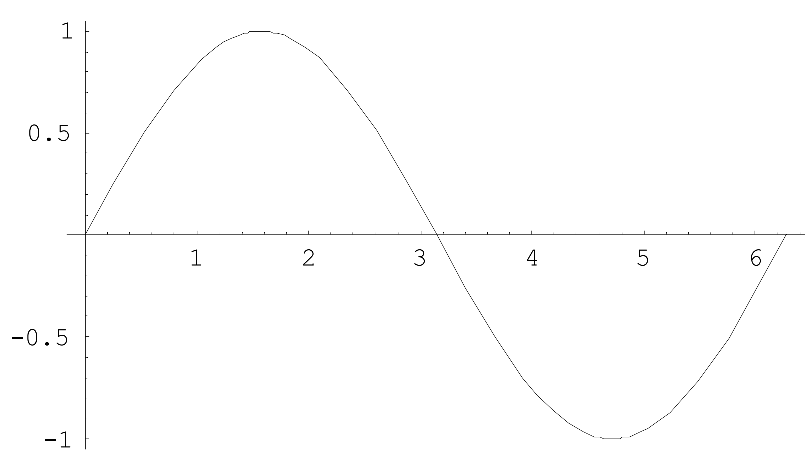
For n = 1, ψ_1 :

```
n1 = Plot[Sin[0.5 * x], {x, 0, 2 * π}];
```



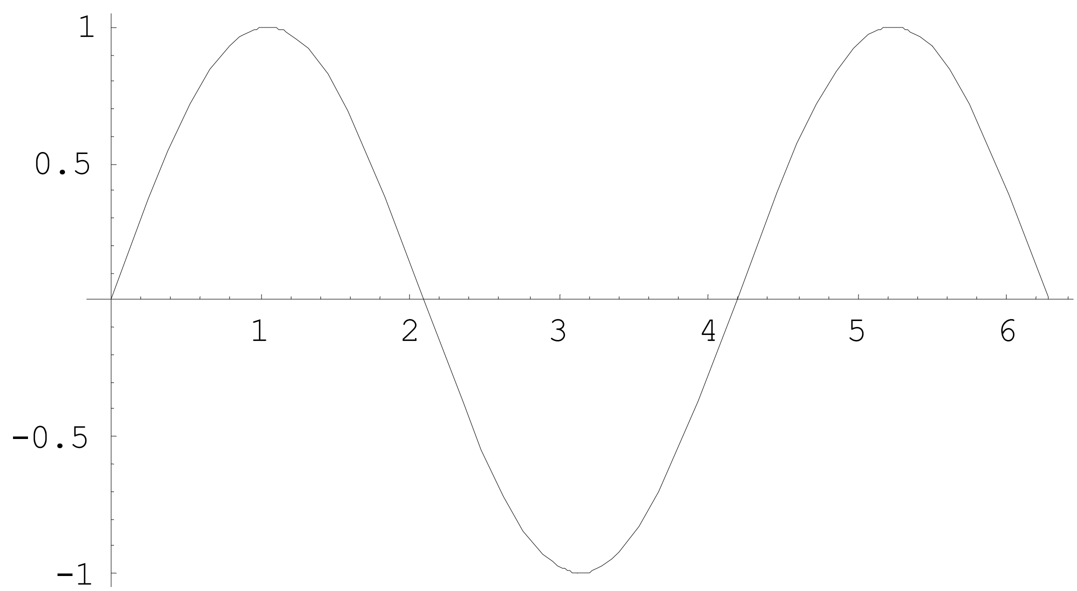
For n = 2, ψ_2 :

```
n2 = Plot[Sin[x], {x, 0, 2 * Pi}];
```



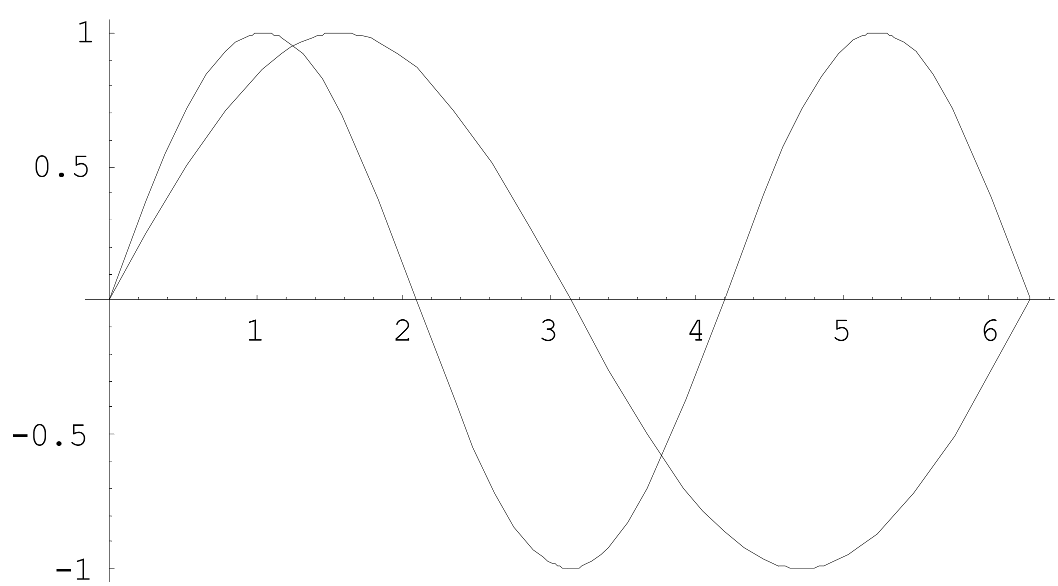
For n = 3, ψ_3 :

```
n3 = Plot[Sin[1.5 * x], {x, 0, 2 * Pi}];
```



Now display the ψ_2 and ψ_3 plots together using *Show*:

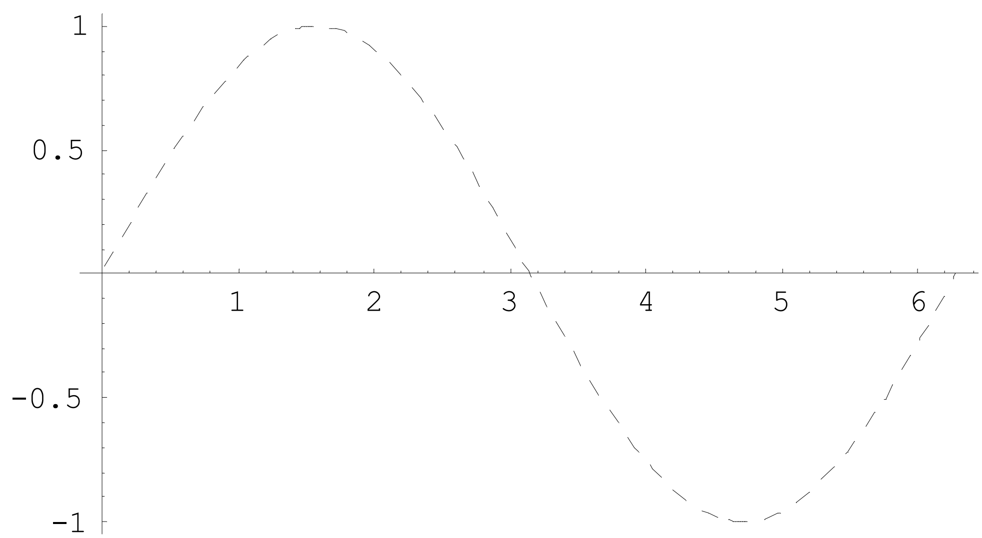
```
pic1 = Show[{n2, n3}];
```



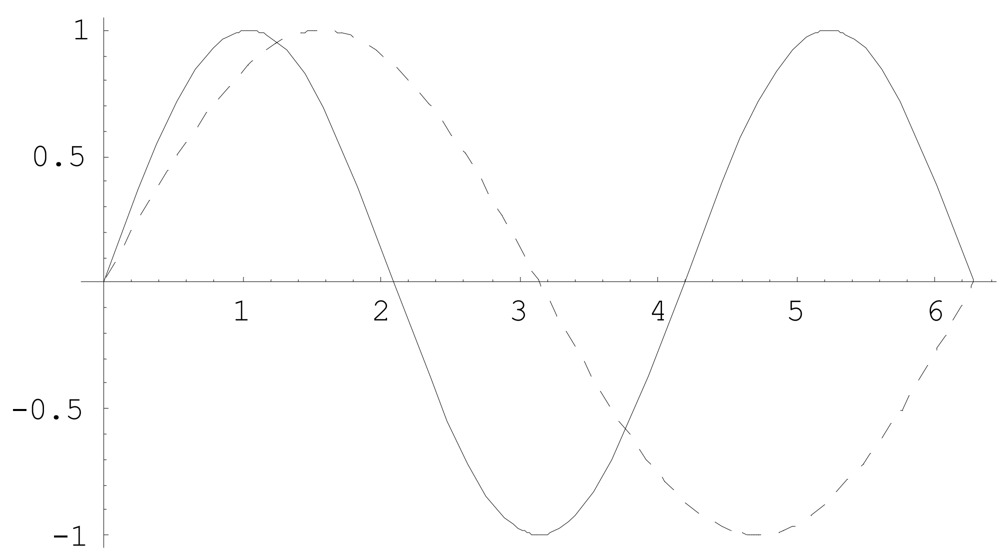
Dashed Lines

As you can see, it's difficult to tell one plot from another. Use: *PlotStyle→Dashing[{0.02}]* to redo one of the plots and then use *Show* to display them. Make sure to put list brackets inside the square brackets. Also, the length of the dashed line can be adjusted for longer or shorter dashes.

```
n2dash = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Dashing[{0.02}]];
```




```
pic2 = Show[{n2dash, n3}];
```



Now the plot is much easier to interpret.

Hue

PlotStyle→Hue[value] will assign a color based on the hue value you put in. Play with different values to get a sense of what numbers give what colors. Some values are listed below.

Green = $\frac{1}{3}$

```
n2hue1 = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Hue[1 / 3]];
```

Blue = $\frac{2}{3}$

```
n2hue2 = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Hue[2 / 3]];
```

Red = 1

```
n2hue3 = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Hue[1]];
```

Orange = $\frac{1}{10}$

```
n2hue4 = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Hue[1 / 10]];
```

Purple = $\frac{3}{4}$

```
n2hue5 = Plot[Sin[x], {x, 0, 2 * Pi}, PlotStyle → Hue[3 / 4]];
```

Unless you have a color printer, it's best to stick with black and use dashed lines to separate graphs.

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 14.9
In the "Free Electron Molecular Orbital" (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length *L*. Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict an equation for the minimum excitation energy of the molecule.

The tetraene CH_2=CHCH=CHCH=CHCH=CH_2 can be treated as a box of length 8*R* where *R* ≈140pm. Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO.

Energy of a particle in a box: $E_n = \frac{n^2 h^2}{8 m L^2}$

Change in energy: $E_{n+1} - E_n$

m = 9.10939 x 10^{-31} kg (mass of an electron)

h = 6.62608 x 10^{-34} J s

L = length of box (in meters)

1 pm = 1 x 10^{-12}m

$\Delta E = \frac{h c}{\lambda}$

c = 2.998 x 10^8 m/s

λ = wavelength (im meters)

Butadiene: CH_2=CH-CH=CH_2

Tetraene: CH_2=CHCH=CHCH=CHCH=CH_2

$$\psi_n = \left(\frac{2}{L}\right)^{\frac{1}{2}} \mathrm{Sin}\left(\frac{n \pi x}{L}\right)$$

Butadiene has 4 π electrons (2 from each double bond). Since the Pauli principle states that only 2 electrons can occupy each orbital, they must be in ψ_1 and ψ_2. The minimum excitation energy is the energy required to excite an electron from the HOMO to the LUMO. For butadiene it's $\psi_2 \rightarrow \psi_3$ (otherwise known as n = 2 → n = 3). Sketch the wave functions of the two occupied orbitals and write an equation for *ΔE.*

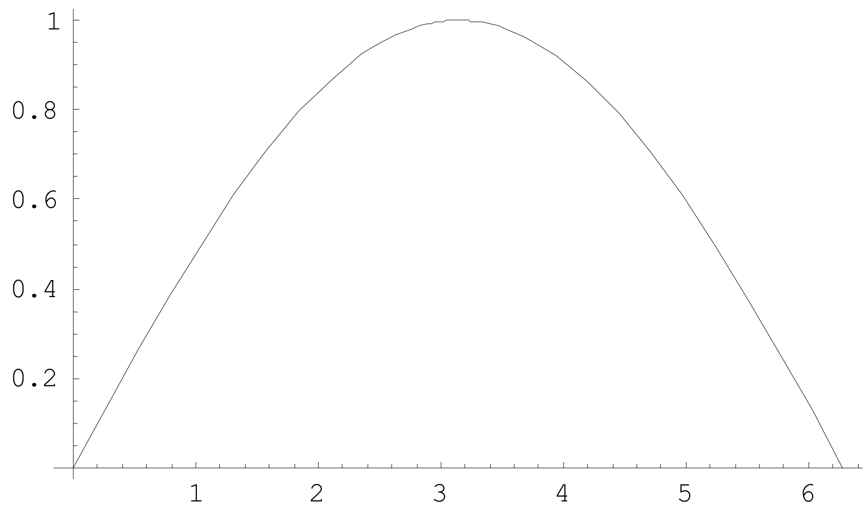
Tetraene has 8 π electrons. If 2 electrons lie in each orbital, what must be the HOMO and LUMO? Plot the HOMO and LUMO orbitals together on one graph. Use the minimum excitation energy to calculate the wavelength of the emitted photon as the electron falls from LUMO to HOMO.

Answer: Problem 14.9

For butadiene:

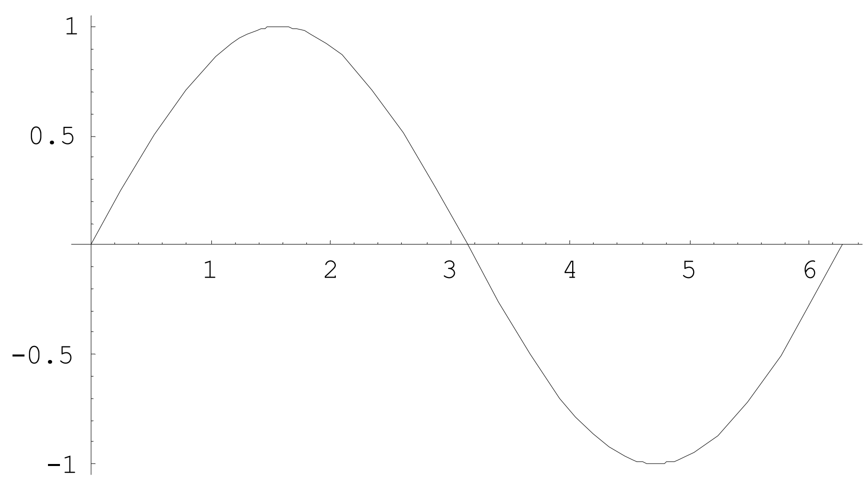
Plot of ψ_1:

```
plot1 = Plot[Sin[0.5 x], {x, 0, 2 π}];
```



Plot of ψ_2: HOMO

```
plot2 = Plot[Sin[x], {x, 0, 2 π}];
```



Define a function called *deltaE* to calculate the minimum excitation energy:

```
deltaE[nLUMO_, nHOMO_, L_] := (nLUMO^2 - nHOMO^2) * h^2 / (8 * m * L^2)
```

Since we're only writing an equation, we do not need to plug in the values of h, m or L.
We only need the values of nFinal and nInitial:

```
nLUMO = 3;
nHOMO = 2;
deltaE[nLUMO, nHOMO, L];
Print["Minimum excitation energy for butadiene = ", %]
```

Minimum excitation energy for butadiene = $\frac{5\,h^2}{8\,L^2\,m}$

For the tetraene:

Plot of ψ_4:

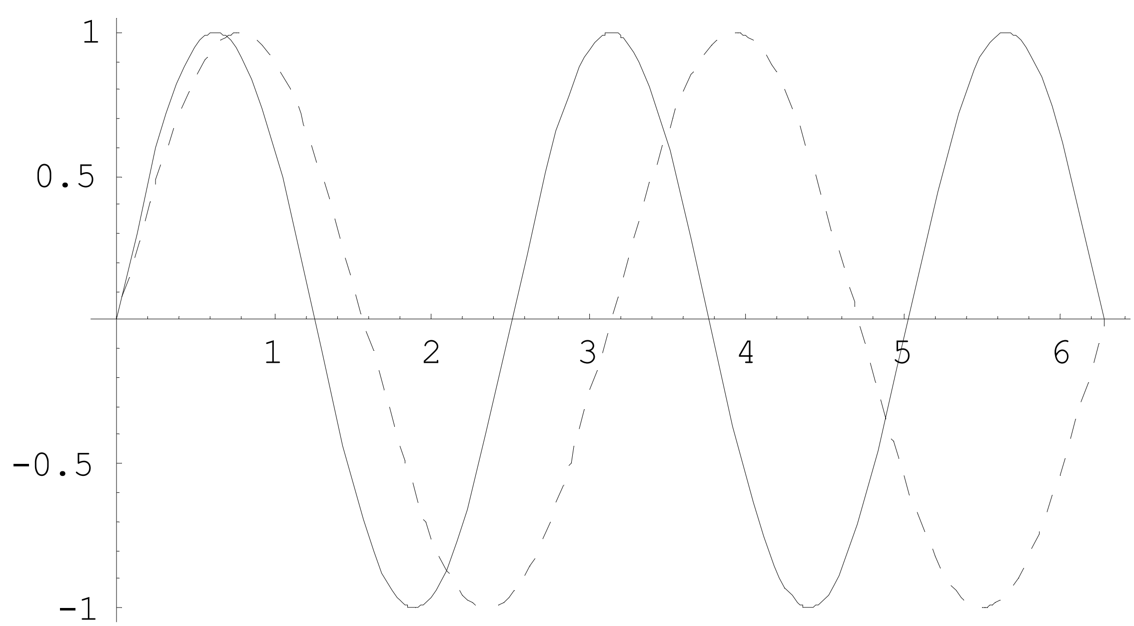
```
plot3 = Plot[Sin[2 x], {x, 0, 2 π}, PlotStyle → Dashing[{0.02}],
   DisplayFunction → Identity];
```

Plot of ψ_5: HOMO

```
plot4 = Plot[Sin[2.5 x], {x, 0, 2 π}, DisplayFunction → Identity];
```

Plot of ψ_4 (dashed line) and ψ_5 (solid line):

```
plot5 = Show[{plot3, plot4}, DisplayFunction → $DisplayFunction];
```



Use the *deltaE* function to calculate the minimum excitation energy in joules. Make sure to define all the constants with the proper units. You can substitute *kg* m^2 s^{-2} for *J* at the end using: */. kg* m^2 s^{-2} $\rightarrow$*J*

```
nLUMO = 5;
nHOMO = 4;
h = 6.62608 * 10^-34 kg m^2 s^-1;
mass = 9.10939 * 10^-31 kg;
r = 140 * 10^-12 m;
L = 8 * r;
energy = deltaE[nLUMO, nHOMO, L] /. kg m^2 s^-2 → J;
Print["The minimum excitation energy for the tetraene = ",
 energy]
```

The minimum excitation energy for the tetraene = 4.32256×10^{-19} J

Calculate the wavelength λ in nm:

```
c = 3.0 * 10^8 m s^-1;
λmeter = h * c / energy;
λnm = λmeter * 10^9 nm / m;
Print["The wavelength of the emitted photon is = ", λnm]
```

The wavelength of the emitted photon is = 459.872 nm

That wavelength corresponds to blue light so the compound will appear orange.