Notes for Quantum Mechanics

Richard Seto

Updated for 2005

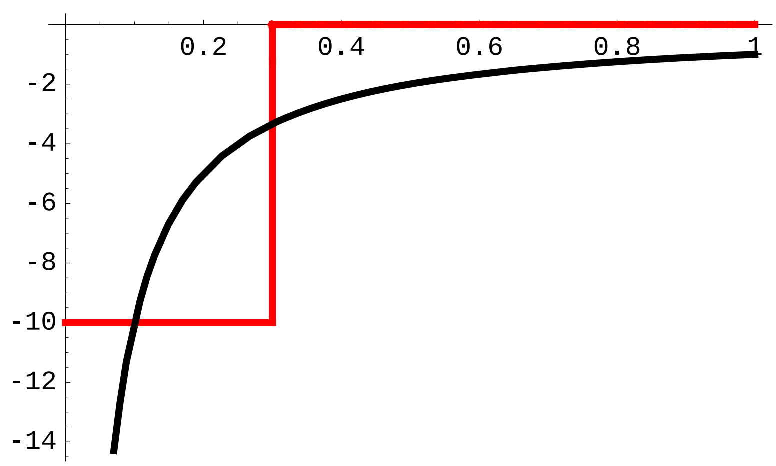
Date[]

```
{2005, 10, 3, 13, 5, 25.2008992}
```

Lecture 3
A particle in a box

The particle in a box

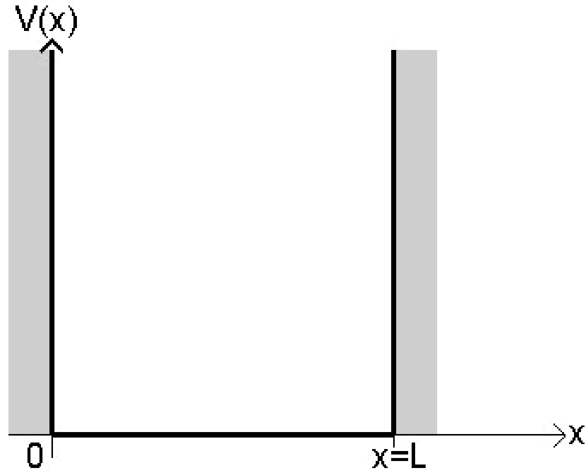
Before going on to learning about bra's and kets, we will take a look at a very simple problem using the notation we have learned. This notation is the notation of wave mechanics. The standard kind of thing we want to do is to look at a particle, say an electron as it moves held by some potential - perhaps the electromagnetic potential $\frac{e^2}{r}$ around a proton. As I said, this a hard problem to solve. So lets make it simpler. First of all, lets forget about 3-D. Lets just solve the 1-D problem. Also a $\frac{1}{r}$ potential is a pain. Lets just make the potential a box. That is, V=0 inside the potential, and V=∞ outside the potential. This would of course work to limit the movement of the particle and its easy to work with. So instead of looking like the black curve below, we will approximate it with the red curve. It will give us some idea of what this wave function might look like, although, as you might guess its not such a great approximation.



So now our task is to solve the Schrodinger's eqn in 1D for the red box potential above. It turns out this is still too hard. Lets assume that the height of the sides is infinitely steep, and that the bottom is reset to 0. [this is not very realistic since this is like an infinitely hard box but anyway we will go with it for now] We will also assume that the side on the left is at

0 (instead of being around x=0 like the 1/r potential is symmetric around r=0) and the right side at L. [later we can make it a bit more realistic by using the above red line symmetric around 0 and go into 3-D}

The potential now looks like this



So let us write a form down for V(x)

$$V(x)= \begin{array}{ll} 0 & 0 < x < L \\ \infty & x < 0 \text{ or } x > L \end{array} \tag{1}$$

Now when I write down the Schrodinger eqn. I will ignore the time dependence for now and write down the time INDEPENDENT eqn, and write ψ(x,t) as φ(x). This is the same notation as in the book.

$$\left(\frac{\hat{p}^2}{2m} + V(x)\right)\varphi(x) = E\varphi(x) \tag{2}$$

OK. Now lets first think about the Sch eqn for x>L. It looks like this

$$\left(\frac{\hat{p}^2}{2m} + \infty\right)\varphi(x) = E\varphi(x)$$

The only way this can be true is for E to be ∞, which is not realistic. Or the wave function can be zero, which is realistic. It means that the electron is never beyond x=L. (remember that $|\varphi(x)|^2$ is the probability of finding something at x. That makes sense. The electron is always stuck inside the box.

Now an important fact is that the wave function is continuous. Why is this so? Well if it is discontinuous at any point, it means that the derivative $\frac{\partial\varphi}{\partial x}$ is infinite at that point. Remember that the operator $\hat{p}$ is proportional to the derivative. The average momentum there will also be infinite. That again makes no physical sense. It turns out that the 1st derivative also has to be continuous otherwise the energy is infinite at that point, since the derivative of the first derivative (the 2nd derivative) is infinite. In our case we have set the potential V(x) to be infinite at x=0 and x=L which is really not a physical problem (imagine something with an infinite potential - what a fortress you could make with that!.) So in our case we will only match the wave function φ(x) across the boundary. Usually you will have to make sure $\varphi_{\text{inside}}(L)=\varphi_{\text{outside}}(L)$ and $\varphi'_{\text{inside}}(L)=\varphi'_{\text{outside}}(L)$ (same for zero)

Well then this means that φ(x=L)=0. This is from matching the wave function at the boundary. Since the left hand wall is at x=0 this means that φ(0)=0 as well. So now we have already solved for the wave function outside x=L. [this is why we made the potential infinite out there - you see how it simplifies the problem] So we now have to solve the Schrodinger eqn with the boundary condition (BC) φ(x=0 or x=L)=0.

Now lets rewrite the Sch eqn, with $\hat{p}$ as a derivative.

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

Note that I have already set V(x)=0, since we are now only worried about the solutions for 0<x<L

Now we will rewrite this as

$$\frac{\partial^2}{\partial x^2}\varphi(x) + \frac{2\,mE}{\hbar^2}\varphi(x) = 0$$

Now how do you solve a diff equation?The basic answer is to guess. There is a handout (written by Jose Wudka) which explains how to solve these things more generally. Often its a pain. As most of you know this eqn has solutions like $\varphi(x) = e^{\pm i\mathrm{kx}}$, so lets try plugging in $\varphi(x) = e^{\pm i\mathrm{kx}}$.

We get $-k^2 e^{\pm i\mathrm{kx}} + \frac{2\,\mathrm{mE}}{\hbar^2}\mathrm{A}e^{\pm i\mathrm{kx}}=0$ which immediately tells you that k=$\frac{\sqrt{2\,\mathrm{mE}}}{\hbar}$ or $E = \frac{k^2\hbar^2}{2m}$

Now we have two solutions, the + solution and the - solution. We know that a linear combination of these things will work so we will then use φ(x)=A$e^{+i\mathrm{kx}}$+ B$e^{-i\mathrm{kx}}$ as our most general solution.

Now we should try to match the boundary conditions. So using the BC at x=0 we get

A$e^{+i\mathrm{k}0}$+ B$e^{-i\mathrm{k}0}$=0

if we solve these for A and B, we get the solution that $A = -B$, so this gives us something proportional to Asin(kL) (changing the definition for A) since sinθ=$\frac{e^{\mathrm{i}\theta}-e^{-\mathrm{i}\theta}}{2i}$

Looking at the BC at x=L: A sin(kL)=0 we get that kL=nπ, or that $k = \frac{\mathrm{n}\pi}{L}$ where n=0, 1,2,3,....

Now we should normalize this (so we get probabilities that make sense when we square it) as follows. We will sum up the value of the probability $|\varphi(x)|^2$ over its whole range -∞<x<∞. Now since φ is 0 for x<0 and x>L we only have to sum it up from 0 to L as follows

$\int_0^L |\varphi(x)|^2\,\mathrm{dx} = A^2\int_0^L \sin^2\left(\frac{\mathrm{n}\pi\mathrm{x}}{L}\right)\mathrm{dx} = A^2\,\frac{L}{2} = 1$ which means that $A = \sqrt{\frac{2}{L}}$ and remembering $k = \frac{\mathrm{n}\pi}{L}$ we finally have a family of solutions

$$\begin{gathered}\varphi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{\mathrm{n}\pi\mathrm{x}}{L}\right) \text{ with } E_n = \frac{n^2\hbar^2\pi^2}{2\,\mathrm{mL}^2}\,,\ n = 0,\ 1,\ 2,\ 3,\ \ldots \text{for } 0 < x < L \\ \varphi_n(x) = 0 \text{ for } x < 0 \text{ or } x > L \\ \text{now the } n = 0 \text{ solution doesn' } t \text{ make sense because then } \varphi(x) = 0 \text{ everywhere.}\end{gathered} \tag{3}$$

Notice that we have only discreet energy levels that are allowed, just like we expected.

What else can we do with this?. First lets let L=1.

I will also start to use mathematica, which should be available to you. It makes some of the calculations easier once you get used to it. It also draws nice pictures. You don't need it for this class, but it makes life easy. In the following - the things that mathematica types out are in pink. The graphs are all made by mathematica.

Now how about if we take some solution (say the n=1 solution for simplicity) and ask what the probability that the electron is between $\left[\frac{3}{10}, \frac{4}{10}\right]$. It is for these type of questions that the normalization is important.

Remember that $|\varphi_n(x)|^2$ is a probability of the electron being at x, so the probability we are looking for is

$\frac{2}{L}\int_{\frac{3}{10}L}^{\frac{4}{10}L}\sin^2\left(\frac{\pi x}{L}\right)dx = 2\int_{\frac{3}{10}}^{\frac{4}{10}}\sin^2(\pi x)\,dx$

Integrate[2 Sin[Pi * x] * Sin[Pi * x],{x,0.3,0.4}]

```
0.157816
```

So there is about a 16% probability to find the electron between 0.3 and 0.4

Just to check lets make sure that between x=0 and 1 the probability is 100%

Integrate[2 Sin[Pi * x] * Sin[Pi * x],{x,0.,1.}]

```
1.
```

Good - it is.

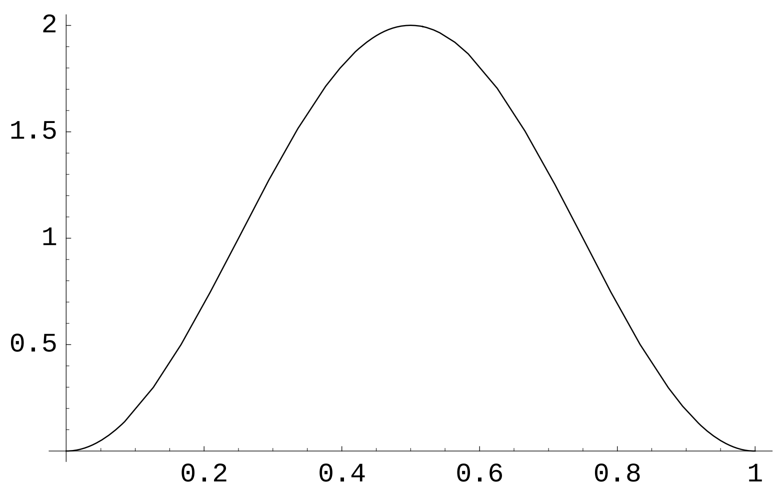
Let try .45 and .55, that is right in the middle of the box

Integrate[2 Sin[Pi * x] * Sin[Pi * x],{x,.45,.55}]

```
0.198363
```

OK now lets Plot the probability

Plot[2 Sin[Pi * x] * Sin[Pi * x],{x,0.,1.}]




```
- Graphics -
```

OK now lets try setting n=3. First we ask how much is between .3 and .4

Integrate[2 Sin[3. * Pi * x] * Sin[3. * Pi * x],{x,0.3,0.4}]


```
0.0183619
```

Wow. Now the answer is much different than for the n=1 case. Less than 2% is between .3 and .4

Again lets check lets make sure that between x=0 and 1 the probability is 100%

Integrate[2 Sin[3. * Pi * *x*] * Sin[3. * Pi * *x*],{x,0.,1.}]

```
1.
```

Good - it is.

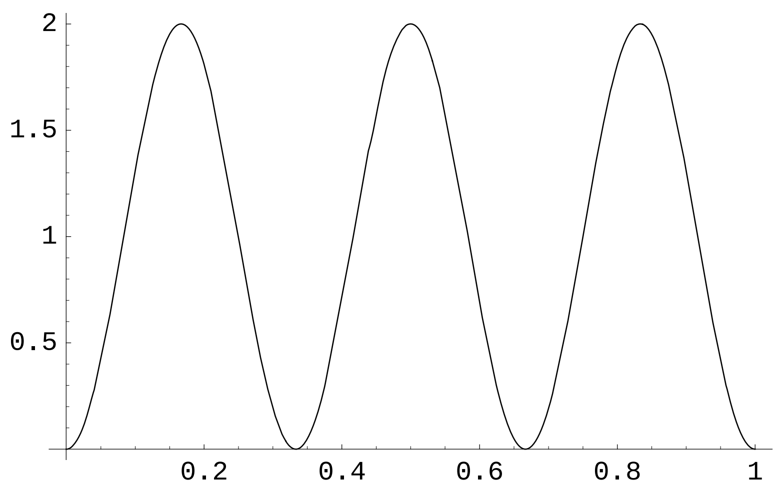
Let try .45 and .55, that is right in the middle of the box

Integrate[2 Sin[3. * Pi * *x*] * Sin[3. * Pi * *x*],{x,.45,.55}]

```
0.185839
```

OK now lets Plot the probability

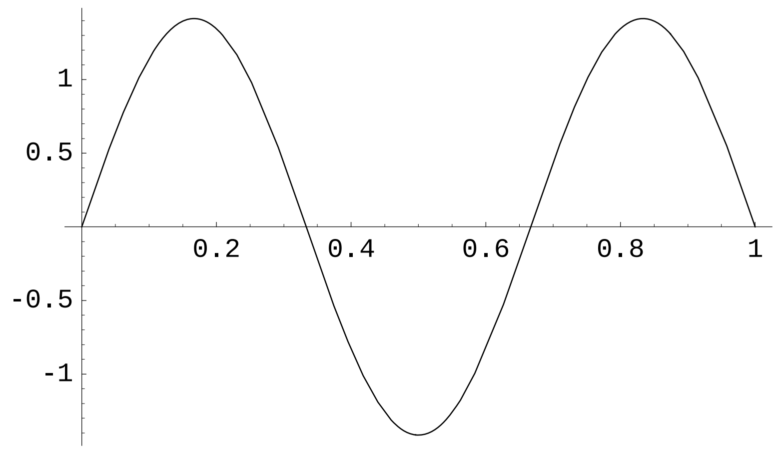
Plot[2 Sin[3. * Pi * *x*] * Sin[3. * Pi * *x*],{x,0.,1.}]




```
- Graphics -
```

So we can understand why the answers are so different. For the n=3 case, our first look of between .3 and .4 is at a minimum of the probability. We are plotting probabilities here - the thing that is easy to think about. Lets also plot the wave function

Plot[Sqrt[2.] * Sin[3. * Pi * *x*],{x,0.,1.}]




```
- Graphics -
```

Notice that the wave function actually is negative is the middle. The probability is ALWAYS positive however.

Expectation Values

Now lets do something different. We are going to define something called the expectation value of an operator Later when I talk about bra's and kets it will become clearer (and simpler) Sometimes you just want the average of something like the momentum That is what the expectation value gives you. The definition of the expectation value of an operator $\hat{A}$ for a state ψ (denoted as $\langle\hat{A}\rangle$) is

$$\langle\hat{A}\rangle=\int_0^L \psi^*(x)\,\hat{A}\,\psi(x)\,\mathrm{dx} \quad , \text{ where the operator } \hat{A} \text{ only operates on the } \psi(\mathrm{x}) \text{ to the right of } \hat{A}. \qquad (4)$$
$\psi^*(x)$ is the complex conjugate of $\psi(x)$

So this thing is asking the question - what is the average value of the operator for some wave function ψ

An important comment should be made here. In general the integrals are all taken over the full interval, in our case its [-∞,∞]. Since we should that the wave function is always 0 outside the interval [0,L] we are now just integrating between 0 and L. Its the same thing as integrating from [-∞,∞] with a zero wave function outside [0,L]. Now in the case of finding probabilities, I used the fact that Probabaility$(x) = |\psi(x)|^2$, so I could then ask the questions about a certain smaller interval.

Here, however, I am finding expectation values - I must integrate over the full interval [0,L]. When I start using bras and kets, this will become clear. The real definition of $\langle\hat{A}\rangle=\langle\psi|\hat{A}|\psi\rangle$. But we will get to it later.

So lets find the average value of the momentum operator (2.5) $\hat{p} \to \frac{\hbar}{i}\frac{\partial}{\partial x}$ for the n=3 state of the electron in a box (above)

$\langle\hat{p}\rangle= 2\int_0^L \psi^*(x)\,\frac{\hbar}{i}\,\frac{\partial}{\partial x}\,\psi(x)\,\mathrm{dx}$ and letting $L = 1$ again

$\langle\hat{p}\rangle= 2\int_0^1 \sin(3\,\pi\mathrm{x})\,\frac{\hbar}{i}\,\frac{\partial}{\partial x}\,\sin\left(\frac{3\,\pi\mathrm{x}}{L}\right)\mathrm{dx}$

This gives $\langle\hat{p}\rangle = 2\,\frac{\hbar}{i}\,3\pi\int_0^1 \sin(3\pi x)\cos(3\pi x)\,dx$ which gives zero. This makes sense since the electron just bounces back and forth and it has to average out to zero. How about the energy? To figure out the average energy, we use the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} = \frac{-\hbar}{2m}\,\frac{\partial^2}{\partial x^2}$ inside the box

So $\langle\hat{H}\rangle = 2\,\frac{\hbar^2}{2m}\int_0^1 \sin(3\pi x)\,\frac{\partial^2}{\partial x^2}\sin(3\pi x)\,dx = \frac{\hbar^2}{m}\,9\pi^2\int_0^1 \sin^2(3\pi x)dx$. Now the average value of $\sin^2$ over *a* full cycle is $\frac{1}{2}$. It this is *a* good inegral to remember. So the final answer is

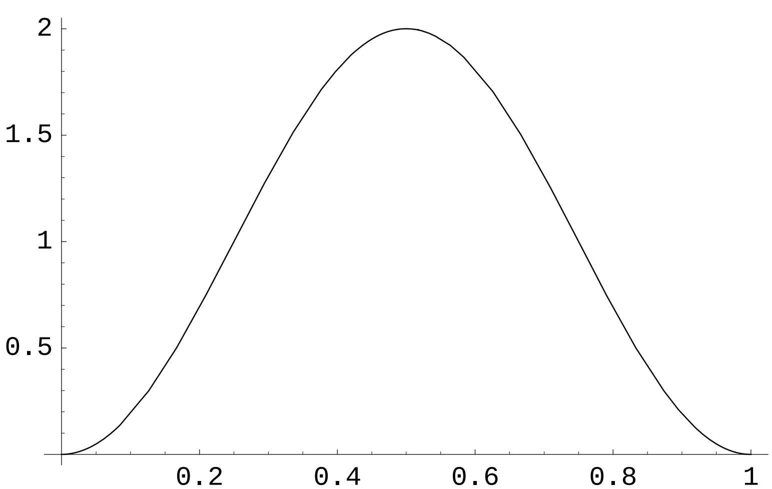
$$\langle\hat{H}\rangle = \frac{\hbar^2}{2m}\,9\pi^2$$

Lets compare this with the actual energy of that wave function $E_n = \frac{n^2\hbar^2\pi^2}{2\,mL^2}$. Set L = 1, n = 3 and you get the same answer. This makes sense since the average value of the energy must be equal to the energy. Good!.

Bohr's correspondence principle

You may wonder when things look like you would think they should in the world of people. After all, if you look at the probability distribution of the n=1 state, it says its mostly in the middle of the box.

Plot[2 Sin[1.*Pi*x]*Sin[1.*Pi*x],{x,0.,1.}]

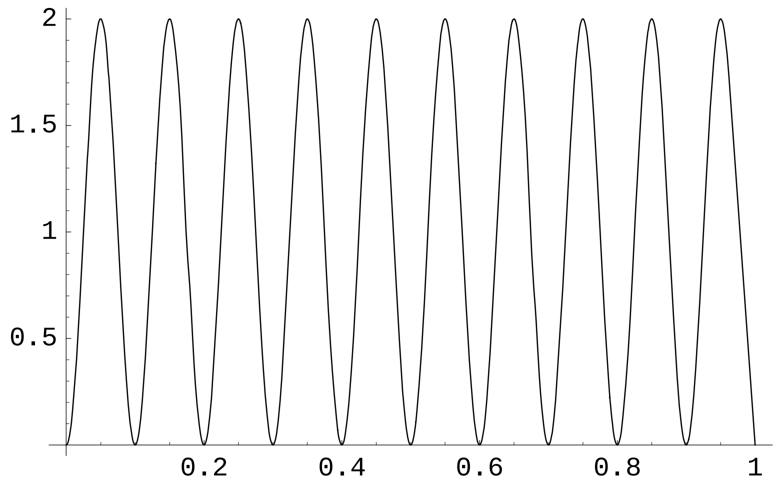


You might expect that the probability would be pretty much the same for finding it anywhere, i..e. the distribution should be flat. This is what we would expect, classically. Notice that the integer n (which we will now start calling quantum number, is always followed around by an $\hbar$. Now $\hbar$ is a pretty small number, about $1.05457148 \times 10^{-34}\ m^2$ kg /s. So you would think that n would have to be pretty big for it to start looking classical. This is Bohr's Correspondence principle. For instance look at the energy $E_n = \frac{n^2\hbar^2\pi^2}{2\,mL^2}$. Classically we would think that the energy spectrum would be continuous. This is NOT true at all for small n since n=2 has an energy 4 times that of n=1. But by the time n is large, lets say 1000, the difference between energy levels is small relative to the energy - in this case, less than 0.2% - so the spectrum look pretty continuous.

So now lets take a look at the probability distribution for n=10 and see if its flatter..

- Graphics -

Plot[2 Sin[10. * Pi * x] * Sin[10. * Pi * x],{x,0.,1.}]

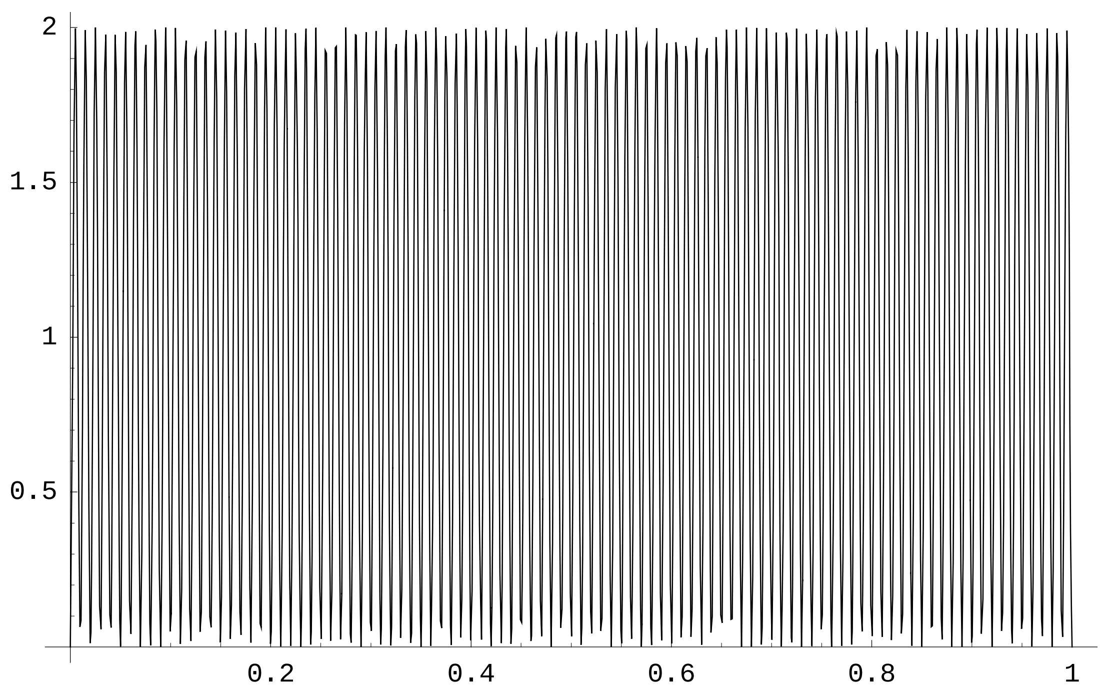


- Graphics -

Its getting flatter

Now once we get to n=100, its pretty flat.

Plot[2 Sin[100. * Pi * x] * Sin[100. * Pi * x],{x,0.,1.}]



```
- Graphics -
```

So the classical limit is when n is large which is where most of us think and breathe.