

Chapter 10

- We want to complete our discussion of quantum mechanics this week by considering the *Schrödinger Equation*.
 - Mathematical equation which tells us how to solve for the energy eigenfunctions of a quantum system if we know the potential energy, V .
 - This is only appropriate for **nonrelativistic quantum mechanics**.
 - We will only consider the **time independent Schrödinger Equation**.
 - ❑ This implies that the potential energy function, V , must be time-independent.
 - ❑ It can be generalized to include time dependence...that will need to wait for a future class.
 - We will also only consider the *Schrödinger Equation* in one dimension.
 - ❑ The potential energy function, $V(x)$.
 - ❑ It can be generalized to three dimensions...but that will have to wait for a future class.
- We will develop/motivate the *Schrödinger Equation* by generalizing the de Broglie Relation.
$$\lambda = \frac{h}{p}$$
- Once we have the *Schrödinger Equation* we can then begin to look at its properties and predictions...that will be mostly a topic for Chapter 11.

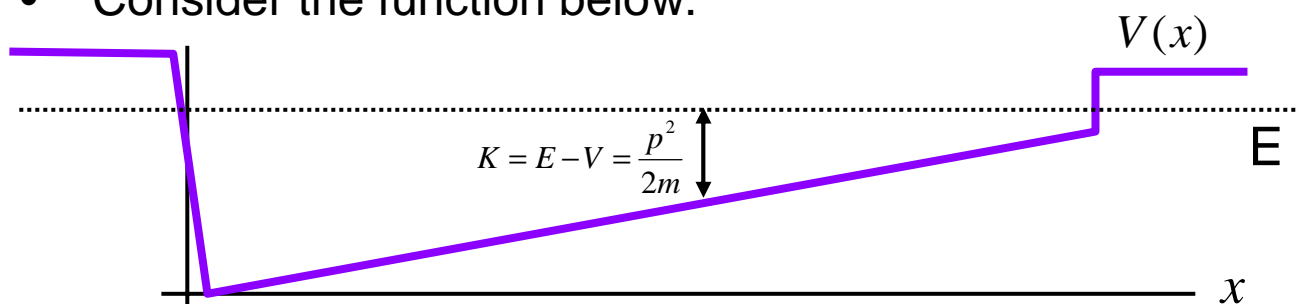
Generalized de Broglie Relation

- The de Broglie relation which started as a hypothesis seemed to stand up to experimental testing
 - e.g. Diffraction with monoenergetic electrons.
- However as it was first presented, the de Broglie relation:

$$\lambda = \frac{h}{p}$$

was only for a **free particle**. We saw that this wavelength could be matched to the wavelength of the wave function that encoded the probability of finding the particle in a particular location.

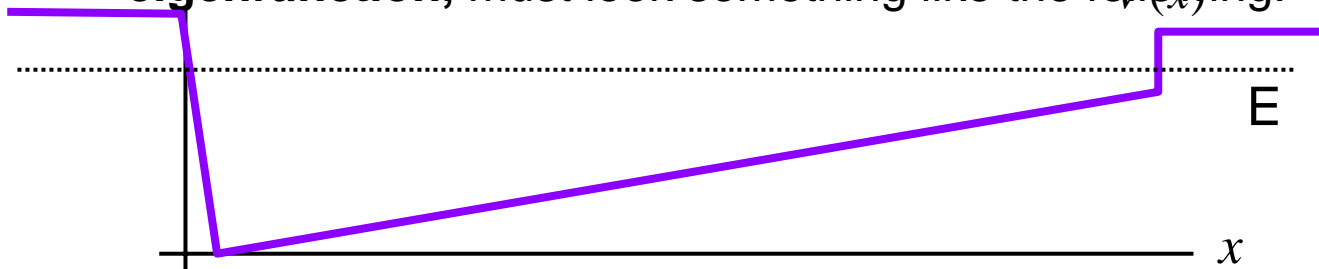
- We have seen that as a particle moves through a potential, $V(x)$, that is changing with position, as long as the particle is in a classically allowed region, the wave function still had the general shape of a oscillating wave...but the form was not a simple “sine” wave.
- Consider the function below.



- As the particle moves to the right, it slows down...so the wavelength should become longer (at least qualitatively).

Generalize de Broglie Relation

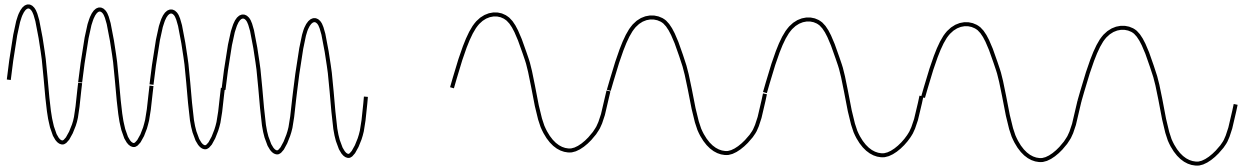
- For a particle at the fixed energy E , we have
- This implies as the particle moves to the right and $E - V$ gets smaller, the momentum gets smaller. If we somehow want to hold onto the *de Broglie* relation even for quanta that are not free. The “wavelength” must be getting larger as $E - V$ gets smaller (i.e. smaller p).
- The wave function, **which is an energy eigenfunction**, must look something like the following:



- However, at this point we are faced with a problem. The concept of a “wavelength” comes from measuring from crest to crest. It is not a “localize” quantity. Certainly, if we measure from crest to crest in the picture above, we get a number, but some how that is an *average* wavelength over that region. We need to define the “wavelength” at a point, x_0 .

Localize Wavelength

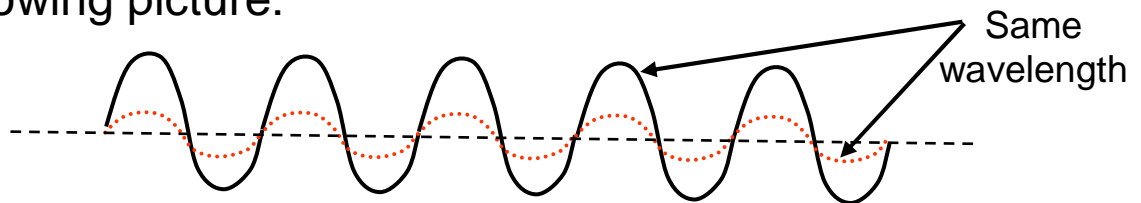
- To determine a way to define a local wavelength (defined at a point) lets consider two sine waves of different wavelengths:



- Observation:
- The curvature of a function is defined as the second derivative with respect to position:

$$\text{curvature} = \frac{d^2 f}{dx^2}$$

- However, it is a little more complicated. The curvature also seems to depend on the amplitude. Consider the following picture:



- In fact we can see this also if we take one of our classical wave functions and find the second derivative:

Local Wavelength

- From the previous equations, we can see:
 - Curvature depends on amplitude (the factor of A)
 - Curvature also has a dependence on the wavelength...this is what we were after!
 - In fact the dependence is as $\sim 1/\lambda^2$
- To remove the dependence on amplitude lets divide by the function itself.

- Now for our specific case we see:

- Solving for the (square) of the wavelength we find

- Although we have seen it for a specific case of a simple (single wavelength) wave, Moore shows that based on dimensional arguments that the general **localized** wavelength can be defined as:

Schrödinger Equation

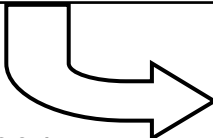
- Now that we have defined the localized wavelength as a function of position, we are ready to derive the *Schrödinger Equation*:
 - It is almost trivial!
- First recall what we derived for the momentum of our particle moving in a potential $V(x)$:
- I have shown the explicit dependencies on x and I have substituted the generalized de Broglie wavelength for the momentum. Take this equation and square both sides:

Now recall, that the function we are trying to solve for with the *Schrödinger Equation* is the **energy eigenfunction**:

$$\frac{h^2}{(\lambda(x))^2} = -\frac{h^2}{4\pi^2} \frac{d^2\psi_E/dx^2}{\psi_E} = 2m(E - V(x))$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_E}{dx^2} = (E - V(x))\psi_E$$

Schrödinger Equation



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

Solving the Equation

- Now that we have an equation we can in principle solve the equation to determine the energy eigenfunctions for any potential $V(x)$. There are a couple of problems:
 - (1) It is a **differential equation**. We can't just use algebra to solve for $\Psi(x)$ the way we would solve for a variable "y".
 - ❑ This equation describes how the function must behave at all x !
 - ❑ There are techniques for solving differential equations but they are not generalized...they depend on the form of the differential equation.
 - ❑ The best we can do here is "guess" the solution...if we guess right we will know because our function will satisfy the differential equation (*Schrödinger Equation*).
 - (2) We potentially have another unknown parameter, E , which is the *energy eigenvalue* for the *energy eigenfunction*.
 - ❑ In other words, we probably do not know the discrete energy levels *before* solving the problem.
- In order to try to solve the equation, it is usually easiest to express it in the following form:

$$\frac{\hbar^2}{2m} \frac{d^2\psi_E(x)}{dx^2} + [E - V(x)]\psi_E(x) = 0$$

Solving the Simple Harmonic Oscillator

- Let's try to solve the 1-d simple harmonic oscillator problem using the *Schrödinger Equation*.
 - Although there are mathematical techniques for solving differential equations, it often comes down to guessing a **form** for the solution, then trying it out.
 - In many cases you have constants that you must solve for in the mathematical form.
 - Let's give it a try.
- For the simple harmonic oscillator let's try the following solution for the energy eigenfunction:

$$\psi_E = A \sin(kx)$$

- This worked for the quantum in a box but does it work in this case. First thing is to calculate the second derivative.
- Now put that into the *Schrödinger Equation* and see if it satisfies the equality

A true Solution

- The choice of $A\sin(kx)$ was a failure, let's try another guess...this time we will get lucky.

$$\psi_E(x) = Ae^{-bx^2}$$

- Once again get the second derivative:

$$\frac{d\psi_E(x)}{dx} = A(-2xb)e^{-bx^2}$$

$$\frac{d^2\psi_E(x)}{dx^2} = -2Ab \frac{d}{dx}(xe^{-bx^2}) = -2Ab \left\{ e^{-bx^2} + x(-2bxe^{-bx^2}) \right\}$$

$$= -2Abe^{-bx^2}(1-2bx^2) = -2b(1-2bx^2)Ae^{-bx^2} = -2b(1-2bx^2)\psi_E(x)$$

- Now put this into the *Schrödinger Equation* and see what we get:

- The relation would be true if the following conditions were true:

- Notice how we now have some relations which allow us to determine the constants **and get the energy eigenvalue!**

$$\psi_E(x) = Ae^{-\frac{m\omega x^2}{2\hbar}} \quad \text{and} \quad E = \frac{\hbar\omega}{2}$$

We have the lowest energy state. Notice that the S.E. does not determine "A"...we get that from normalization requirement.

Let's try another one...

- How about we try the following solution:

$$\psi_E(x) = Axe^{-bx^2}$$

- We will just write down what the second derivative is:

$$\frac{d^2\psi_E(x)}{dx^2} = (4b^2x^2 - 6b)\psi_E(x)$$

- Now substitute into the *Schrödinger Equation* :

$$\frac{\hbar^2}{2m}(4b^2x^2 - 6b)\psi_E(x) + \left[E - \frac{1}{2}m\omega^2x^2\right]\psi_E(x) = 0$$

$$-\frac{6\hbar^2b}{2m} + \frac{4\hbar^2b^2x^2}{2m} + E - \frac{1}{2}m\omega^2x^2 = 0$$

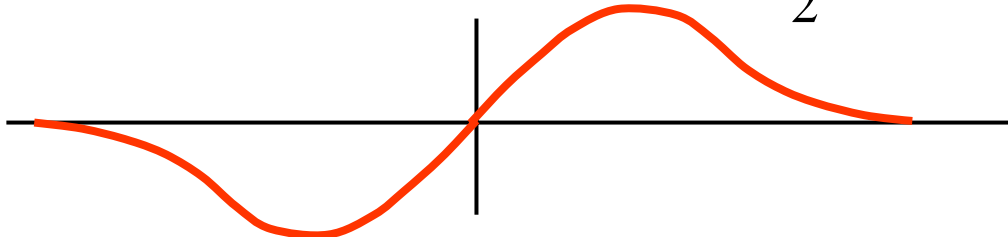
$$\left[E - \frac{3\hbar^2b}{m}\right] + \left[\frac{2\hbar^2b^2}{m} - \frac{m\omega^2}{2}\right]x^2 = 0$$

- Now we get the following conditions:

$$E = \frac{3\hbar^2b}{m} \quad \text{and} \quad \frac{2\hbar^2b^2}{m} = \frac{m\omega^2}{2} \Rightarrow b = \frac{m\omega}{2\hbar}$$

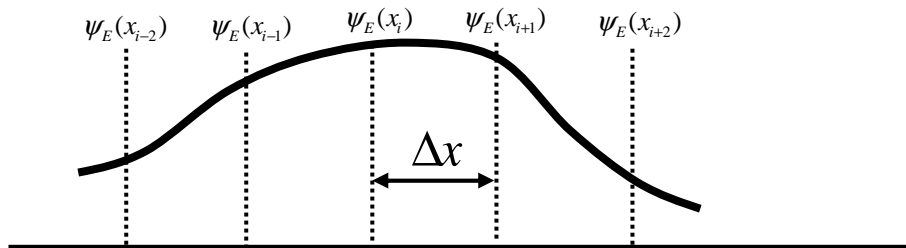
- We have the 2nd energy eigenfunction:

$$\psi_E(x) = Axe^{-\frac{m\omega x^2}{2\hbar}} \quad \text{and} \quad E = \frac{3\hbar\omega}{2}$$



Numerical Solutions

- Sometimes the potential is very complicated or it is not obvious what a good guess will be regarding the structure of the energy eigenfunctions. In these cases we can turn to a numerical solution for the *Schrödinger Equation*.
 - Rather than yielding a mathematical function, we end up with a list of numbers which represent the values of the energy eigenfunction at many different x_i .
- Think about logically dividing the x-axis into many intervals separated by Δx .



- We need to approximate a derivative in this sense.

$$\frac{\psi_E(x + \Delta x) - \psi_E(x)}{\Delta x} \approx \left. \frac{d\psi_E}{dx} \right|_{x + \frac{1}{2}\Delta x}$$

$$\frac{\psi_E(x) - \psi_E(x - \Delta x)}{\Delta x} \approx \left. \frac{d\psi_E}{dx} \right|_{x - \frac{1}{2}\Delta x}$$

- Now we approximate the second derivative in the same way using these equations above:

$$\frac{\frac{\psi_E(x + \Delta x) - \psi_E(x)}{\Delta x} - \frac{\psi_E(x) - \psi_E(x - \Delta x)}{\Delta x}}{\Delta x} = \frac{\psi_E(x + \Delta x) - 2\psi_E(x) + \psi_E(x - \Delta x)}{(\Delta x)^2} \approx \left. \frac{d^2\psi_E}{dx^2} \right|_x$$

Numerical Solution

- Now substitute this into the *Schrödinger Equation* :

$$\frac{\hbar^2}{2m} \left(\frac{\psi_E(x + \Delta x) - 2\psi_E(x) + \psi_E(x - \Delta x)}{(\Delta x)^2} \right) + [E - V(x)]\psi_E(x) = 0$$

$$\psi_E(x + \Delta x) - 2\psi_E(x) + \psi_E(x - \Delta x) + \frac{2m(\Delta x)^2}{\hbar^2} [E - V(x)]\psi_E(x) = 0$$

$$\psi_E(x + \Delta x) = 2\psi_E(x) - \psi_E(x - \Delta x) - \frac{2m(\Delta x)^2}{\hbar^2} [E - V(x)]\psi_E(x)$$

$$\psi_E(x_{i+1}) = 2\psi_E(x_i) - \psi_E(x_{i-1}) - \frac{2m(\Delta x)^2}{\hbar^2} [E - V(x_i)]\psi_E(x_i)$$

- This last equation gives us a relationship for calculating the next point (x_{i+1}) if we know the previous *two* points.
- So how do we find the first two points x_0 and x_1 ?
 - If we are dealing with a bound system, the value of the eigenfunction must go to zero as x goes to negative infinity. So, as an **approximation**:
 - ❑ $\Psi_E(x_0) = 0$
 - ❑ We must choose x_0 well into the classically forbidden region.
 - We might expect that we should choose the next point to be zero as well...but then we get zero for all x_i and this is not a very interesting solution. So choose it to be small
 - ❑ $\Psi_E(x_0) = \text{small value}$.
 - ❑ Because the *Schrödinger Equation* does not determine the normalization...the actual value does not matter...we can always rescale it to make it normalized.

SchroSolver

- The Six Ideas website has a program that you can download to actually carry out the calculation that we have just outlined.
- There are still one unresolved question
 - How do we determine the energy eigenvalue, E ?
 - When we guessed the functional form, we seem to get some equations which helped up determine E , but here **we must supply E for the calculation!**
- The answer is that we can put in any value of E which we choose.
 - That's easy.
 - However, the downside is that the numerical solution which we end up may not be a valid (physical) solution.
 - ❑ How can we tell.
 - ❑ Example from SchroSolver.
- Although as a starting point we forced Ψ_E to be 0 at x equal to negative infinity, we imposed no such constraint at x equal to positive infinity.
 - However, physically we know the eigenfunction must go to zero as x goes to positive infinity.
 - So if we pick $E = 4.5\dots$ and the numerical solution shows an eigenfunction that is **not** going to zero, then this is not a **valid** energy (i.e. it is not an energy eigenvalue)
 - We must try another energy (iteratively) in order to find a valid solution. (See Figure in Section 10.6).