## Chapter 13. Potential Surfaces and the Heisenberg Uncertainly Principle.

Inarguably the most recognized statement in quantum mechanics is, "You can't know where something is and how fast it is going", which is the Heisenberg uncertainty principle. However, the real meaning is more far-reaching and unfortunately complex than this statement reveals. The uncertainty principle exists due to the statistical nature of quantum mechanics, and the fact that different physical properties are connected to each other by the quantum mechanical operators that describe them. Furthermore, the Heisenberg uncertainty principle is dynamic. For example, let's say that you know a quantum particle is trapped in a very small spot. As a result, you can't know the velocity at all, which makes the speed (and kinetic energy) very high. Last, there are actually several different uncertainty principles beyond the famous one between position and speed.

Before we go further, we must first introduce more complex systems to study, which is dependent on the nature of the potential energy surface. In the process, we will understand why some dyes are red or green, discuss new materials such as "quantum dots", and reveal new phenomenon such as tunneling.

### 13.1 Potential Energy Surfaces.

13.1.1 The step. In the previous chapter we discussed the simplest potential surface possible, a one-dimensional flat surface that never ends. This was called the "freewave" example. Unfortunately, the Universe is usually quite a bit more complicated because potential energy exists and may look like a bumpy barrier or curvy parabola. Introduced here is literally the first step towards understanding more complex problems: the step potential shown in Figure 13.1. To the left is a flat potential energy surface; however, at $\mathrm{x}=0 \mathrm{a}$ "bump" in the form of a finite barrier appears that continues to the right forever. The potential surface requires that the Schrödinger equation be solved in two parts, one for the particle left of the barrier or to the right:


Figure 13.1. The step potential problem demonstrates how a quantum object reflects off a barrier.

$$
\begin{array}{rr}
\mathrm{x}<0 \text { (left): } & \frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \psi_{\mathrm{I}}(\mathrm{x})=\mathrm{E} \cdot \psi_{\mathrm{I}}(\mathrm{x}) \\
\mathrm{x}>0 \text { (right) }: & \frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \psi_{\mathrm{II}}(\mathrm{x})+\mathrm{V}_{0} \cdot \psi_{\mathrm{II}}(\mathrm{x})=\mathrm{E} \cdot \psi_{\mathrm{II}}(\mathrm{x})
\end{array}
$$

As a result we have to solve the Schrödinger equation twice. However, it is important to note that there is just one wavefunction that has a single energy. Furthermore, the wavefunction must be smooth and continuous.

The potential energy surface is flat to the left of the barrier, and we already know that the proper wavefunction for a flat potential is the "freewave":

$$
\psi_{I}=A \cdot e^{i k_{1} x}+B \cdot e^{-i k_{1} x}
$$

The wavevector $\mathrm{k}_{1}$ can be found by rearranging the Schrödinger equation: $\frac{\partial^{2}}{\partial \mathrm{x}^{2}} \psi_{\mathrm{I}}(\mathrm{x})=\frac{2 \mathrm{mE}}{\hbar^{2}}$. $\psi_{\mathrm{I}}(\mathrm{x})$, which makes $\mathrm{k}_{1}=\sqrt{\frac{2 \mathrm{mE}}{\hbar^{2}}}$. Now as for the $2^{\text {nd }}$ region, we first rearrange the Hamiltonian as:

$$
\mathrm{x}>0(\text { right }): \quad \frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \psi_{\mathrm{II}}(\mathrm{x})=\left(\mathrm{E}-\mathrm{V}_{0}\right) \cdot \psi_{\mathrm{II}}(\mathrm{x})
$$

Here we see that the Schrödinger equation to the right of the barrier is no different that to the left, albeit with a reduced energy due to the potential. Furthermore, the potential surface to the right is flat, so the same "freewave" solution applies albeit with a different momentum wavevector $\mathrm{k}_{2}$ :

$$
\psi_{\mathrm{II}}=\mathrm{C} \cdot \mathrm{e}^{\mathrm{i} \mathrm{k}_{2} \mathrm{x}}+\mathrm{D} \cdot \mathrm{e}^{-\mathrm{i} \mathrm{k}_{2} \mathrm{x}}
$$

The wavevector $k_{2}$ can be found by simply replacing "E" in $k_{1}$ with $\left(E-V_{0}\right): k_{2}=\sqrt{\frac{2 m\left(E-V_{0}\right)}{\hbar^{2}}}$. It is apparent that $k_{2}<k_{1}$, and as a result if the particle has enough energy to cross the barrier the transmitted wavefunction's de Broglie wavelength must increase. This makes sense since the k's are related to the kinetic energy, which is the difference in the total energy minus the potential energy. Hence, when the particle crosses the barrier into region II it must be moving slower, which is evident from the longer wavelength.
13.1.1.1 Reflection and transmission. The next step is to question what can be learned from the finite step problem? The utility of this example is that it shows what happens when a quantum mechanical particle encounters a barrier. Up until now, you have been told that if a moving mass has enough kinetic energy it will traverses over a potential hill. Here, we will show you that light quantum mechanical particle such as an electron isn't as cooperative.

First, we create a model whereby a 1-dimensional universe is created with a particle to the right of the barrier. The particle is thrown at the barrier, giving it a positive amount of momentum and energy. A wavefunction that describes a right-moving particle is:

$$
\psi_{\mathrm{I}}(\mathrm{x})=\mathrm{A} \cdot \mathrm{e}^{\mathrm{ik} \mathrm{k}_{1} \mathrm{x}}
$$

When the particle strikes the barrier at $\mathrm{x}=0$ it may reflect off of it, resulting in leftwards movement with the same kinetic energy and momentum due to conservation laws. Thus, the wavefunction in region I is:

$$
\psi_{\mathrm{I}}(\mathrm{x})=\mathrm{A} \cdot \mathrm{e}^{\mathrm{i} \mathrm{k}_{1} \mathrm{x}}+\mathrm{B} \cdot \mathrm{e}^{-\mathrm{i} \mathrm{k}_{1} \mathrm{x}}
$$

If the particle transmits over the barrier it can only continue on to the right:

$$
\psi_{I I}(x)=C \cdot e^{i k_{2} x}
$$

If you wonder why there is no leftward moving $\mathrm{e}^{-\mathrm{ik} \mathrm{k}_{2} \mathrm{x}}$ "D-wave" in region 2 , it 's because there are no other barriers in that region to reflect off of. As a result, if the particle crosses into region II it will forever more move to the right. We refer to the expression $A \cdot e^{i k_{1} \mathrm{x}}$ as the incoming " A wave", B•e $\mathrm{e}^{-\mathrm{i} k_{1} \mathrm{x}}$ as the reflected "B-wave" and C• $\mathrm{e}^{\mathrm{ik} \mathrm{k}_{2} \mathrm{x}}$ as the transmitted "C-wave". This is because the probability amplitude of the incoming wave is:

$$
\left|A \cdot e^{i k_{1} x}\right|^{2}=|A|^{2} \cdot e^{-i k_{1} x} \cdot e^{i k_{1} x}=|A|^{2} \cdot e^{0}=|A|^{2}
$$

The probability of reflecting is related to $|\mathrm{B}|^{2}$ and likewise the probability of transmission is related to $|\mathrm{C}|^{2}$.

The finite step potential can be used to calculate whether a quantum object transmits through or reflects off of a barrier. The reflection is the probability that a wave turns left divided by the probability it was moving right to begin with. Due to the fact that the absolute value of a wavefunction is related to probability we can define the reflection $(R)$ as: $R=\frac{|B|^{2}}{|A|^{2}}$ and thus we must find expressions for the coefficient A and B as a function of energy. First, we invoke a stipulation that wavefunctions must be smooth and continuous at $\mathrm{x}=0$, which is the boundary of the step potential. This gives us two equations to solve for our two unknowns:

$$
\Psi_{\mathrm{I},(\mathrm{x}=0)}=\psi_{\mathrm{II},(\mathrm{x}=0)}(\text { continuous }) \text { and: } \frac{\partial \Psi_{\mathrm{I},(\mathrm{x}=0)}}{\partial x}=\frac{\partial \Psi_{\mathrm{II}, \mathrm{x}=0)}}{\partial x} \text { (smooth) }
$$

While these relationships are enough for us to solve the problem, there is a shortcut that is very helpful. What you do is to divide the smooth equation: $\psi_{\mathrm{I}}{ }^{\prime}=\psi_{\mathrm{II}}{ }^{\prime}$ by the continuous one: $\psi_{\mathrm{I}}=$ $\psi_{\text {II }}$ at the boundary:

$$
\frac{\psi_{I_{(x=0)}}^{\prime}}{\psi_{\mathrm{I}_{(\mathrm{x}=0)}}}=\frac{\psi_{\mathrm{II}_{(\mathrm{x}=0)}^{\prime}}^{\prime}}{\Psi_{\mathrm{II}(\mathrm{x}=0)}}
$$

(For those readers who are mathematically inclined, this is the $\log$ derivative $\partial \ln (\psi)=\frac{\psi^{\prime}}{\psi}$ ) When we insert the equations and make $x=0$ we are left with:

$$
\frac{A \cdot i k_{1} \mathrm{e}^{0}-B \cdot \mathrm{ik}_{1} \mathrm{e}^{0}}{A \cdot \mathrm{e}^{0}+B \cdot \mathrm{e}^{0}}=\frac{C \cdot \mathrm{ik}_{2} \mathrm{e}^{0}}{C \cdot \mathrm{e}^{0}}
$$

Since $\mathrm{e}^{0}=1$ and the C 's on the right cancel:

$$
\mathrm{k}_{1} \mathrm{~A}-\mathrm{k}_{1} \mathrm{~B}=\mathrm{k}_{2} \mathrm{~A}+\mathrm{k}_{2} \mathrm{~B}
$$

which can be rearranged to reveal:

$$
\frac{B}{A}=\frac{k_{1}-k_{2}}{k_{1}+k_{2}}=\frac{\sqrt{E}-\sqrt{E-V_{0}}}{\sqrt{E}+\sqrt{E-V_{0}}}
$$

To study this result we must create a model with realistic parameters. As such, we describe an electron ( $\mathrm{m}=9.109 \times 10^{-31} \mathrm{~kg}$ ) striking against a $\mathrm{V}_{0}=1$ electron volt step (an electron volt is the energy an electron experiences travelling through a 1 Volt potential, $1 \mathrm{eV}=1.602 \times 10^{-19} \mathrm{~J}$ ). Plotted in Figure 13.2 is the reflection and transmission as a function of the energy of the particle, where the transmission is simply $1-\mathrm{R}$. If the particle's energy is less than the 1 eV barrier then it will always reflect. This makes sense, and mathematically results from the fact that $\sqrt{E-V_{0}}$ is an imaginary number which makes $R=\frac{\left(k_{1}-k_{2}\right) \cdot\left(k_{1}-k_{2}\right)^{*}}{\left(k_{1}+k_{2}\right) \cdot\left(k_{1}+k_{2}\right)^{*}}=\frac{E+E-V_{0}}{E+E-V_{0}}=1$. However, if the particle has enough energy to get over a barrier, it may or may not! The only thing that the particle can do to improve the odds of transmission is to strike the barrier with as much energy as possible.
13.1.1.2 Wavefunctions. The fact that $k_{2} \sim \sqrt{E-V_{0}}$ is an imaginary number if $\mathrm{E}<\mathrm{V}_{0}$ has implications for the wavefunction in region II. If we substitute $\mathrm{k}_{2}=\mathrm{i} \cdot \mathrm{k}_{2}^{\prime}$, where $\mathrm{k}_{2}^{\prime}$ is a real positive number into the wavefunction we find:


Figure 13.2. Reflection and transmission as a function of the particle's energy.

$$
\psi_{\mathrm{II}}(\mathrm{x})=\mathrm{C} \cdot \mathrm{e}^{i^{2} \cdot \mathrm{k}_{2}^{\prime} \mathrm{x}}=\mathrm{C} \cdot \mathrm{e}^{-\mathrm{k}_{2}^{\prime} \mathrm{x}}
$$

Here we see that the wavefunction is exponentially decaying into the barrier. This is why the reflection has to be $100 \%$, because the particle can't keep moving to the right into region II. It is interesting to note that the particle has some probability to travel though the barrier even though it doesn't have the energy to move into region II at all. We next ask, what if the barrier was thin such that the particle's wavefunction didn't completely decay before exiting the other side?
13.1.2 The finite barrier and tunneling. The next step up in complexity is the step potential that steps back down after a length of L. As shown in Figure 13.3, we might find that a particle wavefunction with an energy less than the potential might not decay to 0 before it reaches the end of the barrier. This means that the particle has some probability to travel through, despite not having enough energy to do so, and continues on to the right forevermore. This is called tunneling, and you may have heard that this phenomenon means you can walk through a door. This is in fact true; however, the probability that you can do so is exceptionally low.

As in the previous example there are three regions; to the left are the on-coming A-wave and the reflected B-wave. In region III we find the transmitted E-wave, $\psi_{\text {III }}(x)=E \cdot e^{i k_{1} x}$, which represents the particle that has tunneled through the barrier. In between are the " C " and "D" waves, where the C-wave represents the particle penetrating the front of the barrier while the D-wave is a reflection off the back end. You might wonder why there is a D-wave, after all, the particle isn't encountering a higher potential barrier. The reason that the D -wave exists is because all interfaces cause reflection, even when one traverses from a higher potential to a lower one. For example, you can see your reflection in a car with new black paint, right? This is the same phenomenon.

The transmission
probability is $T=\frac{|E|^{2}}{|\mathrm{~A}|^{2}}$, and to calculate it we must determine all the wavefunctions' coefficients as a function of energy. This can be done using the boundary conditions for smooth and continuous wavefunctions at


Figure 13.3. The finite barrier problem demonstrates the process of tunneling through a barrier.
positions $\mathrm{x}=0$ and $\mathrm{x}=\mathrm{L}$.
Unfortunately, this is a very timeconsuming calculation due to the overuse of algebraic manipulation, and we won't go through that here. Rather, we simply present the end result in Figure 13.4. Unlike the step potential, there is a small chance for transmission to occur for energies less than the barrier due to tunneling as discussed previously; this is highlighted in green in Figure 13.4. At the same


Figure 13.4. The transmission of a quantum particle reveals tunneling and resonant behavior. Inset shows that a wavefunction's $\lambda$ is the same as the length of the trap when on resonance. time, transmission is not assured if there is enough energy to go over the barrier is in the step potential. Most interesting of all is the wavy structure in the transmission as a function of increasing energy see in Figure 13.4.
Occasionally the transmission reaches $100 \%$; these are called "resonances" and they occur when the particle's de-Broglie wavelength is the same as the length of the barrier. Such behavior is frequently observed in sophisticated spectroscopy experiments, especially in X-ray studies of gas atoms and molecules.
13.1.3 The particle in a box. The next model problem on our list is the "particle-in-abox", which has a potential energy surface defined in three regions by:

$$
\begin{array}{cc}
x<0 & V(x)=\infty \\
0 \leq x \leq L & V(x)=0 \\
x>L & V(x)=\infty
\end{array}
$$

This surface is shown in Figure 13.5. We seek a solution to the Schrodinger equation in the form of a wavefunction, which must be 0 everywhere outside the box because the particle couldn't be found there unless it has an infinite amount of kinetic energy. Thus, we don't need to concern solving the wavefunctions anywhere except region II, the interior of the box. Since region II has a flat potential surface, the wavefunction must be the same as the freewave solution:

$$
\psi_{\mathrm{II}}(\mathrm{x})=\mathrm{A} \cdot \mathrm{e}^{\mathrm{i} \cdot} \cdot \mathrm{x}+\mathrm{B} \cdot \mathrm{e}^{-\mathrm{i} k \cdot \mathrm{x}}
$$

The coefficients A and B must be determined, as well as the wave vector $k$. Defining a wavefunction in such a manner is generally resolved by satisfying boundary conditions; additionally the wavefunction must be normalized. For example, the fact that a wavefunction must be continuous requires that $\psi=0$ at the left $(\mathrm{x}=0)$ and right sides $(\mathrm{x}=\mathrm{L})$ of the box. The fact that the wavefunction must disappear at $\mathrm{x}=0$ requires:

$$
A \cdot e^{0}+B \cdot e^{0}=0
$$

and as a result $B=-A$. This implies that the wavefunction is a sine wave as $\sin (k \cdot x)=A$. $e^{i k \cdot x}-A \cdot e^{-i k \cdot x}$ if $A=\frac{1}{2 i}$. Thus, the boundary condition reveals that:

$$
\psi_{\mathrm{II}}(\mathrm{x})=\sin (\mathrm{k} \cdot \mathrm{x})
$$

Now we have to apply the second boundary condition at $\mathrm{x}=\mathrm{L}$ :

$$
\sin (k \cdot L)=0
$$

This can only be true if $\mathrm{k}_{1} \mathrm{~L}=\mathrm{n} \pi$, allowing us to solve for the wave vector:

$$
\mathrm{k}=\frac{\mathrm{n} \pi}{L}
$$

where n is an integer that goes from $1,2,3 \ldots$ As a result, the wavefunction is:

$$
\psi_{\mathrm{II}}(\mathrm{x})=\mathrm{N} \cdot \sin \left(\frac{\mathrm{n} \pi}{\mathrm{~L}} \mathrm{x}\right)
$$

and 0 everywhere else due to the infinite potential.
13.1.3.1. Orthonormalization. The last piece of the puzzle is to solve for N, the normalization constant. To go about this, we write the condition for normalization $\int|\psi|^{2}=1$ and insert the result thus far:

$$
\mathrm{N}^{2} \int_{0}^{\mathrm{L}} \sin ^{2}\left(\frac{\mathrm{n} \pi}{\mathrm{~L}} \mathrm{x}\right) \partial \mathrm{x}=1
$$

which allows N to be defined as:

$$
\mathrm{N}=\frac{1}{\sqrt{\int_{0}^{\mathrm{L}} \sin ^{2}\left(\frac{\mathrm{n} \pi}{\mathrm{~L}} \mathrm{x}\right) \partial \mathrm{x}}}
$$

We solved the integral by looking it up on the internet: $\int_{0}^{L} \sin ^{2}\left(\frac{n \pi}{L} x\right) \partial x=\frac{L^{2}}{4}$, which means $N=$ $\sqrt{\frac{2}{\mathrm{~L}}}$ and the full particle in a box wavefunction is: $\Psi_{\text {II }}(\mathrm{x})=\sqrt{\frac{2}{\mathrm{~L}}} \sin \left(\frac{\mathrm{n} \pi}{\mathrm{L}} \mathrm{x}\right)$. These wavefunctions are also orthogonal to each other: $\int \psi_{v^{\prime}}^{*} \psi_{v} \partial \mathrm{x}=\delta_{v^{\prime}, \mathrm{u}}$, where $\delta_{v^{\prime}, \mathrm{v}}$ is the Kronecker delta


Figure 13.5 A. The particle in a box potential and first two states. B. The potential is a good model for cyanine dyes. As the number of conjugated bonds increases, the absorption energy drops to longer and longer wavelengths.
function that is $\delta_{v^{\prime}, v}=1$ if $v^{\prime}=v$, which is the normalization condition, and $\delta_{v^{\prime}, v}=0$ if $v^{\prime} \neq v$. This is a result of the fact that the Hamiltonian is a Hermitian operator (see Ch. 12, section 12.4.5).
13.1.3.2 Energy levels. In our previous examples, we were able to solve the wavefunction for any value of energy. As a result, these models are called "unbounded". The particle in a box energy is different, we can see after it is calculated from the Hamiltonian acting on the wavefunction via $\widehat{\mathrm{H}} \psi=\mathrm{E} \psi$ :

$$
\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \sqrt{\frac{2}{\mathrm{~L}}} \sin \left(\frac{\mathrm{n} \pi}{\mathrm{~L}} \mathrm{x}\right)=\frac{\hbar^{2} \mathrm{n}^{2} \pi^{2}}{2 \mathrm{~mL}^{2}} \sqrt{\frac{2}{\mathrm{~L}}} \sin \left(\frac{\mathrm{n} \pi}{\mathrm{~L}} \mathrm{x}\right)=\mathrm{E} \cdot \Psi_{\mathrm{II}}(\mathrm{x})
$$

and thus:

$$
\mathrm{E}=\frac{\mathrm{n}^{2} \hbar^{2} \pi^{2}}{2 \mathrm{~mL}^{2}}=\frac{\mathrm{n}^{2} \mathrm{~h}^{2}}{8 \mathrm{~mL}^{2}}
$$

where we used the fact that $\hbar^{2}=\frac{h^{2}}{4 \pi^{2}}$. Given that n is an integer, we see that the particle in a box cannot have just any energy. There are gaps between the ground state $(\mathrm{n}=1)$ and the $1^{\text {st }}$ excited state ( $\mathrm{n}=2$ ), which is why we refer to the system as "bounded". The energy comes in discrete steps, or quanta, which is where quantum mechanics gets its name! Anther facet of quantum mechanics is the need for an integer quantum number, here n , which can delineate the ground
state from all the excited states. Quantum numbers will appear in all the systems we will study from now on and are usually part of the equation for energy. It is interesting to note that the ground state has some finite kinetic energy, called the "zero point energy". As we will discuss later in this chapter zero point energy is due to the Heisenberg uncertainty principle.

The particle in a box describes several phenomena, many of which can be seen with your own eyes! Shown in Figure 13.5B are the spectra of several cyanine dyes, which reveal lower energy absorptions as the dye becomes longer. An analogy can be made that the number of alternating double bonds in the center of the cyanine molecule is the same as the length L of the particle in a box. It should be noted that the absorptions are not related to the energy of a single quantum level, rather, the differences between the ground and $1^{\text {st }}$ excited state levels. For a particle in a box that quantity is: $\Delta \mathrm{E}=\frac{(n=2)^{2} \mathrm{~h}^{2}}{8 \mathrm{~mL}^{2}}-\frac{(n=1)^{2} \mathrm{~h}^{2}}{8 \mathrm{~mL}^{2}}=\frac{3 \mathrm{~h}^{2}}{8 \mathrm{~mL}^{2}}$, which reveals an expected $1 / L^{2}$ dependence to the absorption between states as the box size changes.

Shown in Figure 13.6 is a more dramatic example using nanotechnology, specifically semiconductor CdSe quantum dots. The emission of the particles can be tuned to lower (redder) energies by increasing the diameter of the particle on the order of just a few nanometers. And as solid-state materials, quantum dots are significantly more robust against degradation from the environment, which is why they are being incorporated into displays including television sets!
13.1.3.3 The particle in the finite box. Imagine the particle in a box potential surface where the barriers to the outside are not infinite as shown in Figure 13.7A. Note that we have centered the box at $\mathrm{x}=0$ for mathematical convenience as you will see. There are two issues to consider, namely that there are three regions each of which has a different wavefunction. As in the previous example, we will use boundary conditions to solve for the wavefunctions and allowed energy levels. Furthermore, it should be noted that there are bound solutions for $\mathrm{E}<\mathrm{V}_{0}$,


Figure 13.7A. The finite box problem is centered at $x=0$, and has alternating even- and oddsymmetric solutions. B. The ground and 1st excited state of a particle between two finite boxes look like bonding and antibonding orbitals.
meaning that the energy is quantized into discrete values. For energies greater than the potential trap $\left(\mathrm{E}>\mathrm{V}_{0}\right)$ the solutions are unbound, meaning that the wavefunctions are just waves and any energy is allowed. We won't consider that situation and will instead only study the case where $\mathrm{E}<\mathrm{V}_{0}$.


Figure 13.6. Semiconductor quantum dots change their emission color based on the size of the nanoparticle. Typical sizes are $2 \rightarrow 10 \mathrm{~nm}$. region also has even symmetry like a cosine function. As a result, $\psi_{\text {II }}(x)=B \cdot \cos \left(k_{2} x\right)$, where the wavevector $\mathrm{k}_{2}=\sqrt{\frac{2 \mathrm{mE}}{\hbar^{2}}}$. If the particle penetrates into the barrier region I on the left it will continue in that direction, implying $\psi_{\mathrm{I}}=\mathrm{A} \cdot \mathrm{e}^{\mathrm{k}_{1} \cdot \mathrm{x}}$ where $\mathrm{k}_{1}=\sqrt{\frac{2 \mathrm{~m}(\mathrm{~V}-\mathrm{E})}{\hbar^{2}}}$. Using the same logic $\psi_{\text {III }}=\mathrm{C} \cdot \mathrm{e}^{-\mathrm{k}_{1} \cdot \mathrm{x}}$. As per the boundary conditions, the wavefunctions must be continuous and smooth at the region I/II boundary:

$$
\mathrm{A} \cdot \mathrm{e}^{-\mathrm{k}_{1} \cdot \mathrm{~L} / 2}=\mathrm{B} \cdot \cos \left(-\mathrm{k}_{2} \frac{\mathrm{~L}}{2}\right) \quad \text { and } \quad \mathrm{k}_{1} \cdot \mathrm{~A} \cdot \mathrm{e}^{-\mathrm{k}_{1} \cdot \mathrm{~L} / 2}=-\mathrm{k}_{2} \cdot \mathrm{~B} \cdot \sin \left(-\mathrm{k}_{2} \frac{\mathrm{~L}}{2}\right)
$$

and likewise for region II/III:

$$
B \cdot \cos \left(k_{2} \frac{L}{2}\right)=C \cdot e^{-k_{1} \cdot L / 2} \quad \text { and } \quad-k_{2} \cdot B \cdot \sin \left(k_{2} \frac{L}{2}\right)=-k_{1} \cdot C \cdot e^{-k_{1} \cdot L / 2}
$$

Solving using log boundary conditions yields what is called a "transcendental" equation for $\mathrm{k}_{1}$ and $\mathrm{k}_{2}$ :

$$
\tan \left(\mathrm{k}_{2} \frac{\mathrm{~L}}{2}\right)=\frac{\mathrm{k}_{1}}{\mathrm{k}_{2}}
$$

The relationship above requires you to define the model system (length of the box, potential height, and mass of the particle) and then search for energies that equate the two sides using a computer. Once you know the allowed energies you can determine the A, B etc. coefficients and then plot the wavefunctions as shown in Figure 13.7A.

This model system can be applied to understand many real phenomena and can also be used to describe electrons in atoms. For the latter case, this works because an electron sees a hydrogen's proton like a trap- Coulomb's law keeps it close by since there is a huge energy penalty to be far away. The finite box can give us an idea about how chemical bonds work if we
allow two boxes to get close to each other. Shown in Figure 13.7B are the ground and $1^{\text {st }}$ excited states for a particle between two finite boxes. It can be seen that the wavefunction "bunches" between the two traps in the ground state while a node prevents the same in the excited state. This represents ground state bonding and excited state antibonding orbitals!
13.2. Complex Potential Energy Surfaces: Vibration. We now take our first step into non-flat potential surfaces by studying the quantum mechanics of springs; this is called the harmonic oscillator problem. Incidentally, chemical bonds work just like springs. Two atoms form a bond along the " $x$ " direction, with an equilibrium bond distance of $x_{0}$. Any displacement from equilibrium results in a linear restoring force: $F=-\frac{\partial V}{\partial x}=-\mathrm{k}_{\mathrm{f}}\left(\mathrm{x}-\mathrm{x}_{0}\right)$, the strength of which is dictated by the spring constant $\mathrm{k}_{\mathrm{f}}$. Since we want to know the potential energy V as a function of the position we note that $\frac{\partial \mathrm{V}}{\partial x}--F(x)$ and integrate as follows:

$$
\int \partial \mathrm{V}=\mathrm{V}(\mathrm{x})=-\int-\mathrm{k}_{\mathrm{f}}\left(\mathrm{x}-\mathrm{x}_{0}\right) \partial x=\frac{1}{2} \mathrm{k}_{\mathrm{f}}\left(\mathrm{x}-\mathrm{x}_{0}\right)^{2}
$$

To place this in a quantum mechanical context we simply insert the position operator $\hat{\mathrm{x}}$ as so: $\widehat{V}=\frac{1}{2} k_{f}\left(\hat{x}-x_{0}\right)^{2}$, which likewise makes the potential energy an operator. And while we are ready to put this into the Schrödinger equation, however, before we do so there is a very small change that significantly simplifies everything. This is to simply drop the equilibrium distance $x_{0}$ from the potential energy operator as shown here:

$$
\widehat{\mathrm{V}}=\frac{1}{2} \mathrm{k}_{\mathrm{f}}\left(\hat{\mathrm{x}}-\mathrm{x}_{0}\right)^{2} \rightarrow \frac{1}{2} \mathrm{k}_{\mathrm{f}} \hat{\mathrm{X}}^{2}
$$

The implication is that the position operator $\hat{\mathrm{x}}$ is now interpreted as the bond's displacement away from equilibrium. Thus, a positive $\langle\hat{\mathrm{x}}\rangle$ means that the bond is stretched and a negative $\langle\hat{\mathrm{x}}\rangle$ means compressed. There is one more issue to examine, which is the fact that the kinetic energy operator $\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}}$ has the familiar factor of mass. However, when describing vibrational motion between two bonded atoms then it is no longer clear which atom's mass should be used. The solution is to use the reduced mass: $\mu=\frac{m_{1} \cdot m_{2}}{m_{1}+m_{2}}$, where $m_{1}$ and $m_{2}$ are the masses of atoms 1 and 2 , respectively.
13.2.1.1 Wavefunctions. With knowledge of the Schrodinger equation:

| $v$ | $\mathrm{H}_{v}$ | There is an interesting mathematical relationship that <br> can be demonstrated with Hermite polynomials: |
| :---: | :---: | :--- |
| 0 | 1 | $\mathrm{H}_{\mathrm{v}+1}=\frac{2 \mathrm{x}}{\alpha} \cdot \mathrm{H}_{\mathrm{v}}-2 \mathrm{v} \cdot \mathrm{H}_{\mathrm{v}-1}$ |
| 1 | $\frac{2 \mathrm{x}}{\alpha}$ | This is called a recursion and allows all the Hermite <br> polynomials to be determined with just the first one: |
| 2 | $\frac{4 \mathrm{x}^{2}}{\alpha^{2}}-2$ | $\mathrm{H}_{\mathrm{v}=0}=1$. |
| 3 | $\frac{8 \mathrm{x}^{3}}{\alpha^{3}}-\frac{12 \mathrm{x}}{\alpha}$ |  |

Table 13.1 Hermite polynomials.

$$
\frac{-\hbar^{2}}{2 \mu} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \psi(\mathrm{x})+\frac{1}{2} \mathrm{k}_{\mathrm{f}} \hat{\mathrm{X}}^{2} \cdot \psi(\mathrm{x})=\mathrm{E} \cdot \psi(\mathrm{x})
$$

we are ready to solve for the wavefunction $\psi$. This effort is somewhat complex; as such, we will simply assure you that the mathematics are tractable and that the wavefunctions are as shown in Figure 13.8. These solutions can be succinctly described using the following formula:

$$
\psi_{v}(x)=N_{v} H_{v} e^{-x^{2} / 2 \alpha^{2}}
$$

where $\alpha=\left(\frac{\hbar^{2}}{\mu \mathrm{k}_{\mathrm{f}}}\right)^{\frac{1}{4}}, v \rightarrow 0,1,2 \ldots$ is the principal quantum number, $\mathrm{N}_{v}=\left(\frac{1}{v!2^{v} \alpha \sqrt{\pi}}\right)^{\frac{1}{2}}$ is the normalization constant, and $\mathrm{H}_{v}$ are the Hermite polynomials listed in Table 13.1.

Let's turn our attention to the ground state wavefunction which has a bell-shape as shown in Figure 13.8. Subsequent excited states have additional nodes due to the Hermite polynomials; these increase the curvature and thus the kinetic energy of each state. Note how, in calculus, the double derivative found in the kinetic energy operator is called the "curvature" of a function! The Hermite polynomials


Figure 13.8. The parabolic potential surface (blue line), ground and several excited state wavefunctions for the harmonic oscillator.
also assures that the wavefunctions are orthogonal to each other.
There are many other quantum mechanical properties to examine, including the fact that $\langle\hat{x}\rangle=\int \psi_{v}^{*} \cdot x \cdot \psi_{v} \partial \mathrm{x}=0$ regardless of the state. From this we learn that the bond is on average at the equilibrium bond length, even in highly excited states. Calculation of the energy E as a function of principle quantum number $v$ reveals the relationship: $E(v)=\left(v+\frac{1}{2}\right) \hbar \omega$, where $\omega$ is the angular frequency: $\omega=\left(\frac{\mathrm{k}_{\mathrm{f}}}{\text { mass }}\right)^{\frac{1}{2}}$. An important implication is the fact that the ground state has energy is finite: $\mathrm{E}_{\mathrm{v}=0}=\frac{1}{2} \hbar \omega$. Like the particle in a box this is the zero-point energy, and it means that the atoms are always vibrating. There are other interesting analogies to the particle in a box problem; the wavefunctions look surprisingly similar including the way they pick up additional nodes in each excited state. One significant difference is that the harmonic oscillator energies are linear with the principal quantum number, $\mathrm{E} \propto \mathrm{v}$, whereas the particle in a box is quadratic in proportion to its principal quantum number, $\mathrm{E} \propto \mathrm{n}^{2}$.
13.2.1.2 Kinetic Isotope Effect and Turning Points. An interesting implication of the zero-point energy is that it is inversely proportional to the reduced mass. This has an effect on the rate of a chemical reaction as dictated by the $\Delta \mathrm{G}^{*}$ barrier. Take for example the breaking of a carbon-hydrogen $\left(\mathrm{R}_{3} \mathrm{C}-\mathrm{H}\right)$ bond. Given that the reduced mass is less for a $\mathrm{C}-\mathrm{H}$ bond vs. the deuterated analog C-D, there is a smaller barrier for the C-H bond to break as shown in Figure 13.9 A. As a reaction rate is proportional to the barrier $\mathrm{k} \sim \mathrm{e}^{-\Delta \mathrm{G}^{*}}$ (like the Arrhenius equation), the relative rates of reaction involving a proton are generally faster to the same with deuterium according to the formula:

$$
\frac{\mathrm{k}_{\mathrm{CH}}}{\mathrm{k}_{\mathrm{CD}}} \sim \frac{\mathrm{e}^{-\Delta \mathrm{G}_{\mathrm{CH}}^{*}}}{\mathrm{e}^{-\Delta \mathrm{G}_{\mathrm{CD}}^{*}}}
$$

While this ratio can be as high as $8 \times$, in reality there are many other factors in play and as such the kinetic enhancement can be less. Regardless, the


Figure 13.9. A. The kinetic isotope effect is due to the zero-point energy difference between $\mathrm{C}-\mathrm{H}$ vs. C-D bonds. $\mathbf{B}$. A turning point is where the spring has no more kinetic energy.
kinetic isotope effect is quite useful because it gives organic chemists a method to investigate which bonds break in a reaction. Thus, it is often used for mechanistic analysis.

The wavefunction shown in Figure 13.8 are for a carbon monoxide molecule, which has a high spring constant $\mathrm{k}_{\mathrm{f}}=1860 \mathrm{~N} / \mathrm{m}$. As such, the bond doesn't stretch far as evident from the fact that the wavefunctions do not have significant amplitude past $\sim 1 / 2$ Bohr, where a Bohr is a unit of length and is equal to $0.53 \AA$. In contrast, $\mathrm{I}_{2}$ has a very weak bond as evident from a $\mathrm{k}_{\mathrm{f}}=170$ $\mathrm{N} / \mathrm{m}$, and as such it can stretch almost twice as much as CO. Regardless of how strong a bond is, the atoms have a way of stretching further than they should as revealed by the vibrational potential energy surface and ground state wavefunction shown in Figure 13.9 B. The point where the total energy is equal to the potential, where there must be no more kinetic energy:

$$
\frac{1}{2} \hbar \omega=\frac{1}{2} \mathrm{k}_{\mathrm{f}} \cdot \mathrm{x}_{\mathrm{tp}}^{2} \rightarrow \mathrm{x}_{\mathrm{tp}}= \pm \sqrt{\frac{\hbar \omega}{\mathrm{k}_{\mathrm{f}}}}
$$

This is marked in the figure as the turning point $\left(\mathrm{X}_{\mathrm{tp}}\right)$, which is where a normal spring would stretch to the point where it stops and starts to compress back. However, this isn't true for the quantum mechanical spring, as the wavefunction has some finite value for any x . As a result:

$$
\int_{x_{\operatorname{tp}}}^{\infty}\left|\Psi_{v=0}\right|^{2} \partial x=0.078
$$

Consequently, there is $\sim 8 \%$ chance that a bond will stretch past the point of having no kinetic energy, which is analogous to tunneling discussed previously. Does this mean that the kinetic energy is in fact negative? What does negative kinetic energy motion look like? This is one of the wonders of quantum mechanics as there is no analogy to our everyday experiences that would help describe this.

### 13.3 Uncertainty and Superposition: Wavefunctions as Waves. The uncertainty

 principle, "you can't know where something is and how fast it is going," is one of the most important aspects of quantum mechanics. In our explanation of this phenomenon, we will study bell-shaped wavefunctions that are centered inside a box that goes from $0 \leq \mathrm{x} \leq \mathrm{L}$ :$$
\psi(x)=\frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} e^{\frac{-(x-L / 2)^{2}}{4 \sigma^{2}}}
$$



Figure 13.10. A. Localized (red) and delocalized (blue) Gaussian-type wavefunctions have different kinetic energies due to the uncertainty principle. B. Freewave states can be summed into a superposition that equates to any other function, such as the localized and delocalized states shown in A .

We will analyze two different wavefunctions, a narrow one that we call "localized" and a wide one that we call "delocalized". Hopefully it is intuitively clear that there is more certainty in the position of the localized wavefunction compared to the delocalized state.

In the previous chapter we introduced the idea that an eigenfunction $\psi$ of one operator can be expressed as a linear combination of the eigenfunctions $\Phi_{\mathrm{n}}$ of a different operator. This is called a superposition:

$$
\psi=\sum_{n} \mathrm{c}_{\mathrm{n}} \cdot \Phi_{\mathrm{n}}
$$

and for our purposes we will make all the $\Phi_{\mathrm{n}}$ 's freewave states:

$$
\Phi_{\mathrm{n}}=\mathrm{e}^{\mathrm{i} \mathrm{k}_{\mathrm{n}} \mathrm{x}}
$$

were the wavevector k is defined so that the freewaves fit in the box: $\mathrm{k}_{\mathrm{n}}=\frac{\mathrm{n} \pi}{\mathrm{L}}$ and $\mathrm{n}= \pm 1, \pm 2, \pm 3$, etc. The bell-shaped wavefunctions and the freewaves are all graphed in Figure 13.10.

An example of a superposition is shown in Figure 13.11, where we see that the wider delocalized bell-shaped state can be equated to a sum of wave states weighted by an appropriate constant. Here only three waves are needed to create a superposition that appears identical to the delocalized function as shown in Figure 13.11. A very different result is observed with the localized state shown in Figure 13.12. Here, it is necessary to sum at least 5 wave states to


Figure 13.11. A delocalized (blue) Gaussian-type wavefunctions can be constructued by summing several freewave states times appropriate weighing functions. The freewave states must be of even symmetry to contribute. A sum of just three freewaves provide a near-pefect representation of the delocalized state.
provide a reasonable representation of the localized function. Even then the overlap isn't as good as observed with the delocalized state in Figure 13.11 despite the fact that more functions were used!

Now you are probably asking- what any of this has to do with the uncertainty principle? To answer, let's now measure the momentum of the localized and delocalized states. The measurements require us to do an experiment, and we will be repeat the experiment several times to statistically quantify the average value and standard deviation which is the uncertainty. This is necessary because it is reasonable to expect some variation in the measurements from experiment to experiment. In fact, we contend that each measurement will return the momentum of one of the wave states, which is $\hbar \mathrm{k}_{\mathrm{n}}=\hbar \cdot \frac{\mathrm{n} \pi}{\mathrm{L}}$, with a probability $\left|\mathrm{c}_{\mathrm{n}}\right|^{2}$. Thus, measuring the momentum from the delocalized state will return one of the three composing wave state's momenta with corresponding probabilities of $\left|c_{1}\right|^{2},\left|c_{2}\right|^{2}$, or $\left|c_{3}\right|^{2}$. We can also calculate the expectation value of the momentum via:


Figure 13.12. A localized (red) Gaussian-type wavefunctions requires the summation of at least 5 free waves to provide a reasonable representation of the original state.

$$
\langle\mathrm{p}\rangle=\left|\mathrm{c}_{1}\right|^{2} \cdot \hbar \mathrm{k}_{1}+\left|\mathrm{c}_{2}\right|^{2} \cdot \hbar \mathrm{k}_{3}+\left|\mathrm{c}_{3}\right|^{2} \cdot \hbar \mathrm{k}_{5}
$$

In contrast, when the same experiment is repeated on the localized state, each measurement returns one of five values of wave momenta with corresponding probabilities of $\left|c_{1}\right|^{2},\left|c_{2}\right|^{2},\left|c_{3}\right|^{2}$, $\left|c_{4}\right|^{2}$, or $\left|c_{5}\right|^{2}$.

Do you have more or less confidence in the measurement of the momentum of the delocalized vs. localized state? Of course, there is greater certainty for the delocalized state since each measurement returns one of just three values, and probably we won't have to make too many measurements before we are comfortable with the average. However, measuring the localized state is problematic since the result varies more from experiment to experiment! This is due to the fact that the experiment samples from five different wave states, and thus we will have to make more measurements to have the confidence in the result. We conclude that the certainty in position is anticorrelated to the certainty in momentum. This is in fact the Heisenberg uncertainty principle, "you can't know where something is and how fast it's going at the same time." Mathematically, this is expressed by the variance in the function, the square root of which is the standard deviation $(\sigma)$ you may recall from your introduction into statistics; more on this later.

The above demonstration involved some approximations and was meant to give you a graphical description of uncertainty in quantum mechanics. Now, we must slog through more rigorous mathematics. First, let's define uncertainty via the variance, and we will start with the variance in position:

$$
\langle\operatorname{Var}(\hat{\mathrm{x}})\rangle=\left\langle\frac{1}{\mathrm{~N}-1} \sum_{\mathrm{i}=1}^{\mathrm{N}}(\mathrm{x}-\overline{\mathrm{x}})^{2}\right\rangle=\left\langle\hat{\mathrm{x}}^{2}\right\rangle-\langle\hat{\mathrm{x}}\rangle^{2}
$$

You may be familiar with this formula from your first introduction to statistics, and also note that the expressions $\langle\hat{\mathrm{x}}\rangle$ and $\left\langle\hat{\mathrm{x}}^{2}\right\rangle$ are expectation (average) values. Let's calculate the variance in the position for our bell-shaped wavefunction: $\psi(x)=\frac{1}{\sqrt{2 \pi} \sigma} \mathrm{e}^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{2 \sigma^{2}}}$ using the $\hat{\mathrm{x}}$ and $\hat{\mathrm{x}}^{2}$ operators.

$$
\langle\hat{x}\rangle=\int_{-\infty}^{\infty} \psi^{*} \cdot \hat{x} \cdot \psi \cdot \partial x=\int_{-\infty}^{\infty}\left(\frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}}\right)^{*} \cdot x \cdot \frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \partial x
$$

$$
=\frac{1}{\sqrt{2 \pi \sigma^{2}}} \int_{-\infty}^{\infty} x \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{2 \sigma^{2}}} \cdot \partial x=\frac{L}{2}
$$

Next:

$$
\left\langle\hat{\mathrm{x}}^{2}\right\rangle=\frac{1}{\sqrt{2 \pi \sigma^{2}}} \int_{-\infty}^{\infty} \mathrm{x}^{2} \cdot \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{2 \sigma^{2}}} \cdot \partial \mathrm{x}=\sigma^{2}+\left(\frac{\mathrm{L}}{2}\right)^{2}
$$

As a result: $\left\langle\hat{\mathrm{x}}^{2}\right\rangle-\langle\hat{\mathrm{x}}\rangle^{2}=\sigma^{2}+\left(\frac{\mathrm{L}}{2}\right)^{2}-\left(\frac{\mathrm{L}}{2}\right)^{2}=\sigma^{2}$. This is a perfectly sensible result, and in fact it is a standard statistical definition that the variance of a bell-shaped curve is $\sigma^{2}$ !

Let's determine the variance in momentum, $\operatorname{var}(\hat{\mathrm{p}})=\left\langle\mathrm{p}^{2}\right\rangle-\langle\mathrm{p}\rangle^{2}$ :

$$
\begin{gathered}
\langle\hat{\mathrm{p}}\rangle=\int_{-\infty}^{\infty} \psi^{*} \cdot \hat{\mathrm{p}} \cdot \psi \cdot \partial \mathrm{x}=\int_{-\infty}^{\infty}\left(\frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{4 \sigma^{2}}}\right)^{*} \cdot \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}} \frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \partial \mathrm{x}= \\
\frac{\hbar}{\mathrm{i} \sqrt{2 \pi \sigma^{2}}} \int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \frac{\partial}{\partial \mathrm{x}} \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \partial \mathrm{x}=\frac{\hbar}{\mathrm{i} \sqrt{8 \pi} \sigma^{3}} \int_{-\infty}^{\infty}\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right) \cdot \mathrm{e}^{\frac{-\left(\mathrm{x}-\frac{\mathrm{L}}{2}\right)^{2}}{2 \sigma^{2}}} \cdot \partial \mathrm{x}=0
\end{gathered}
$$

No average momentum, which shouldn't be interpreted as the particle not moving. Rather, the particle can move left or right equally averages out to 0 . Next, calculating the average of the momentum squared takes a bit more effort:

$$
\begin{aligned}
& \left\langle\hat{p}^{2}\right\rangle=\int_{-\infty}^{\infty} \psi^{*} \cdot \hat{p}^{2} \cdot \psi \cdot \partial x=-\hbar^{2} \int_{-\infty}^{\infty}\left(\frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}}\right)^{*} \cdot \frac{\partial^{2}}{\partial x^{2}} \frac{1}{\left(2 \pi \sigma^{2}\right)^{1 / 4}} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \partial x= \\
& \frac{-\hbar^{2}}{\sqrt{2 \pi \sigma^{2}}} \int_{-\infty}^{\infty} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \frac{\partial^{2}}{\partial x^{2}} e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{4 \sigma^{2}}} \cdot \partial x=\frac{-\hbar^{2}}{\sqrt{32 \pi} \sigma^{5}} \int_{-\infty}^{\infty}\left(\frac{L^{2}}{4}-2 \sigma^{2}-L x+x^{2}\right) \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^{2}}{2 \sigma^{2}}} \cdot \partial x=\frac{\hbar^{2}}{4 \sigma^{2}}
\end{aligned}
$$

As a result, the variance in momentum is: $\left\langle\hat{\mathrm{p}}^{2}\right\rangle-\langle\hat{\mathrm{p}}\rangle^{2}=\frac{\hbar^{2}}{4 \sigma^{2}}-0^{2}=\frac{\hbar^{2}}{4 \sigma^{2}}$
The results reveal that the uncertainty in position and momentum are anticorrelated; the position uncertainty scales as $\sigma^{2}$, however, the momentum uncertainty is inversely proportional to $\sigma^{2}$. Thus, if the particle is localized in position then there is an increasing uncertainty in momentum. This becomes clearer when we multiply the two variances:

$$
\operatorname{Var}(\hat{\mathrm{x}}) \cdot \operatorname{Var}(\hat{\mathrm{p}})=\sigma^{2} \frac{\hbar^{2}}{4 \sigma^{2}}=\frac{\hbar^{2}}{4}
$$

which results in a constant. This is, in fact, the mathematical version of the Heisenberg uncertainty principle.
13.3.1 The Heisenberg Uncertainty Principle. There is a math theorem that can assist us with understanding the previous example called the Cauchy-Schwartz inequality. It is analogous to the fact that a dot product between two vectors: $\vec{a} \cdot \vec{b}=|a||b| \cos (\theta)$, is equal to or less that $|\mathrm{a}||\mathrm{b}|$ due to the fact that the maximum $\cos (\theta)$ can be is 1 . This concept allows us to express the Heisenberg uncertainty principle as an equation:

$$
\operatorname{Var}(\hat{\mathrm{x}}) \cdot \operatorname{Var}(\hat{\mathrm{p}}) \geq \frac{1}{4}|\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle|^{2}
$$

where a new mathematical entity called the commutator appears on the right:

$$
[\hat{x}, \hat{p}]=\hat{x} \cdot \hat{p}-\hat{p} \cdot \hat{x}
$$

The expectation value of the commutator is simply $\langle[\hat{x}, \hat{p}]\rangle=\langle\hat{x} \cdot \hat{p}-\hat{p} \cdot \hat{x}\rangle=\langle\hat{x} \cdot \hat{p}\rangle-\langle\hat{p} \cdot \hat{x}\rangle$. Normally, expectation values have to be evaluated using specific wavefunctions. However, there is a simple and general way to evaluate $\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle$. This works by applying a "dummy" $\psi$ on the right of the operators, allowing them to act on it and then dividing $\psi$ out on the left:

$$
\langle[\hat{x}, \hat{p}]\rangle=\frac{1}{\psi}[\hat{x}, \hat{p}] \psi
$$

Inserting $[\hat{x}, \hat{p}]=\hat{x} \cdot \hat{p}-\hat{p} \cdot \hat{x}$ and the definition of the momentum operator $\hat{p}=\frac{\hbar}{i} \frac{\partial}{\partial x}$ and $\hat{x}=x$ into the above yields:

$$
\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle=\frac{1}{\psi}(\hat{\mathrm{x}} \cdot \hat{\mathrm{p}}-\hat{\mathrm{p}} \cdot \hat{\mathrm{x}}) \psi=\frac{\hbar}{\mathrm{i}} \frac{1}{\psi}\left(\mathrm{x} \cdot \frac{\partial}{\partial \mathrm{x}}-\frac{\partial}{\partial \mathrm{x}} \cdot \mathrm{x}\right) \psi=\frac{\hbar}{\mathrm{i}} \frac{1}{\psi}\left(\mathrm{x} \cdot \frac{\partial}{\partial \mathrm{x}} \psi-\frac{\partial}{\partial \mathrm{x}} \cdot \mathrm{x} \cdot \psi\right)
$$

Noting the need for the product rule on the right-hand side results in:

$$
\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle=\frac{\hbar}{\mathrm{i}} \frac{1}{\psi}\left(\mathrm{x} \cdot \psi^{\prime}-\mathrm{x} \cdot \psi^{\prime}+\psi\right)=\frac{\hbar}{\mathrm{i}} \frac{\psi}{\psi}=\frac{\hbar}{\mathrm{i}}
$$

This can be re-inserted into the expression from our previous formula: $\frac{1}{4}|\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle|^{2}=\frac{1}{4}\left|\frac{\hbar}{i}\right|^{2}=\frac{\hbar^{2}}{4}$ to yield:

$$
\operatorname{Var}(\hat{\mathrm{x}}) \cdot \operatorname{Var}(\hat{\mathrm{p}}) \geq \frac{\hbar^{2}}{4}
$$

13.3.1.1 Interpretation. The Heisenberg uncertainty principle states that once cannot know position and momentum, or speed, of a quantum mechanical object simultaneously. Better knowledge of position increases the uncertainty in momentum, and the only way the uncertainty
in momentum can rise is for the average momentum to increase. To understand why, take for example a car going 10 miles per hour on average. Do you have more, or less uncertainty in its speed compared to a car going 100 mph on average? Of course, there must be greater uncertainty in the velocity of the faster moving car because it has considerably more leeway for its momentum to vary more. As a result, a greater uncertainty in momentum must be associated with greater momentum in general, which also means that the object must have greater kinetic energy. Thus, if a delocalized quantum mechanical particle, such as an electron in an aromatic ring, becomes localized on a single atom, then it's kinetic energy must increase. This is why quantum particles like to become delocalized if possible, and also describes why the energy of a particle in a box increases if the box is smaller: $\mathrm{E} \propto \frac{1}{\mathrm{~L}^{2}}$. The Heisenberg uncertainty principle is often used to explain nanoscale phenomena including the size dependence of the emission of quantum dots shown in Figure 13.6.

The commutator $[\hat{x}, \hat{p}]=\hat{x} \cdot \hat{p}-\hat{p} \cdot \hat{x}$ can be interpreted in a way that makes sense out of the uncertainty principle. Since $[\hat{\mathrm{x}}, \hat{\mathrm{p}}] \neq 0$, then $\langle\hat{\mathrm{x}} \cdot \hat{\mathrm{p}}\rangle \neq\langle\hat{\mathrm{p}} \cdot \hat{\mathrm{x}}\rangle$, and as a result measuring the position of a particle, and then its momentum, would yield a different result than if you first measured momentum and then position! However, there is no "right" way to do this, so the result is arbitrary depending on what order the experimentalist happened to use when making measurements on small, quantum mechanical particles. Thus, there is uncertainty.
13.3.1.1 Generalization. The Heisenberg uncertainly principle simply states that, at best, the product of the position and momentum variances is no more than $\frac{\hbar^{2}}{4}$. If one has a specific system with a known wavefunction then one has to evaluate the product of $\operatorname{var}(\hat{\mathrm{x}})$ and $\operatorname{var}(\hat{\mathrm{p}})$ directly. In fact we did so in the previous section using the bell-shaped wavefunction and found that the equality held for the uncertainty principle: $\operatorname{var}(\hat{\mathrm{x}}) \cdot \operatorname{var}(\hat{\mathrm{p}})=\frac{\hbar^{2}}{4}$. These Gaussian functions are considered special as a result and are often referred to as "minimum uncertainty" wavefunctions. In some of the problem set questions at the end of this chapter you will find that the products of the variances in position and momentum for various particle in a box wavefunctions are indeed greater than $\frac{\hbar^{2}}{4}$.

It is important to realize that, while the position / momentum uncertainty principle is "famous", there are in fact a very large number of other examples. For any two operators $\widehat{\Omega}_{1}$ and $\widehat{\Omega}_{2}$ the uncertainty principle states:

$$
\operatorname{Var}\left(\widehat{\Omega}_{1}\right) \cdot \operatorname{Var}\left(\widehat{\Omega}_{2}\right) \geq \frac{1}{4}\left|\left\langle\left[\widehat{\Omega}_{1}, \widehat{\Omega}_{2}\right]\right\rangle\right|^{2}
$$

and as a result there is uncertainty if $\left[\widehat{\Omega}_{1}, \widehat{\Omega}_{2}\right] \neq 0$. We will find examples using quantum rotational motion and when describing the spin angular momentum of electrons. Here is one you can try on your own; determine the uncertainty between the position $\hat{x}=x$ and kinetic energy operators $\widehat{\mathrm{KE}}=\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}}$. If you evaluate the uncertainty principle by simplifying the commutator using: $\left[\mathrm{x}, \frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}}\right] \Psi$ one finds that:

$$
\operatorname{Var}(\hat{\mathrm{x}}) \cdot \operatorname{Var}(\widehat{\mathrm{KE}}) \geq \frac{\hbar^{2}}{4 \mathrm{~m}}|\langle\hat{\mathrm{p}}\rangle|^{2}
$$

This at first may appear hard to interpret as the commutator is an operator rather than a constant. What is meant here is that the uncertainty between position and kinetic energy is dependent on the expectation of momentum. Thus, if the particle has no momentum then there is a potential for there to be no uncertainty between position and kinetic energy. However, the uncertainty increases as the particle is moving faster and faster.

There is one last implication of the uncertainty principle, which is that the eigenfunctions of one operator $\widehat{\Omega}_{1}$ cannot be the same as the other operator $\widehat{\Omega}_{2}$ if $\left[\widehat{\Omega}_{1}, \widehat{\Omega}_{2}\right] \neq 0$. This is generally a topic that one encounters when studying more advanced quantum mechanical phenomena such as rotation, spin angular momentum and the spin-orbit effect discussed in latter chapters.
Conclusions. In this chapter we showed how increasing the complexity of model systems through their potential energy surfaces reveals new quantum phenomena. Specifically, how a particle may bounce off a wall even if it is higher than it. Also, quantum particles can tunnel through barriers like they have a negative kinetic energy. Furthermore, the kinetic energy of a particle increases if we trap it, which is why we can change the color of a quantum dot by changing its size. While this chapter discusses most of the basic principles of quantum mechanics, in the next few chapters we are going to move away from one dimensional example problems and discuss real systems leading up to the hydrogen atom. To do so we have to understand how quantum mechanics works in 3D and how to deal with rotational motion.

## Problems: Numerical

1. In class, I mentioned that the uncertainty principal "does things". Here is what I mean; we decomposed the particle in a box wavefunctions shown below ( $\mathrm{A} \& \mathrm{~B}$ ) into momentum wave eigenstates (i.e. $\mathrm{e}^{\mathrm{ik} \cdot \mathrm{x}}$ ) as shown below:


Recall that, as the " A " state has more uncertainty in position, it can be decomposed into just a few momentum waves. However, the "B" state requires more momentum waves, perhaps $\sim 100$ of them. Also look at the handout for a definitive example that was done with computer analysis.
a. How does the energy of the momentum waves change? Simply state which momentum wave below has more energy and why:

b. Given your answer in pt. a, which of the two wavefunctions (the delocalized state "A" or more localized state " $B$ ") have more kinetic energy and why?

Hint: I have made up a table of components $1 \rightarrow 5$ that have respective energies of $1 \mathrm{~J} \rightarrow 5 \mathrm{~J}$, and the percent that each contributes to states A and B. Use these data to find the average values of energies for states A and B, which should give you some insight into how to answer this problem.

| Energy (eV) | \%A | \%B |
| :---: | :---: | :---: |
| 1 | $75 \%$ | $30 \%$ |
| 2 | $15 \%$ | $30 \%$ |
| 3 | $10 \%$ | $20 \%$ |
| 4 | $0 \%$ | $10 \%$ |
| 5 | $0 \%$ | $10 \%$ |

This should help you understand how increasing the percent of higher energy states will affect the total energy.
2. In class, I mentioned that the uncertainty principal "does things". Here is what I mean:

We decomposed the particle in a box wavefunctions shown below ( $\mathrm{A} \& \mathrm{~B}$ ) into momentum wave eigenstates (i.e. $\mathrm{e}^{\mathrm{ik} \cdot \mathrm{x}}$ ) as shown below:


Recall that, as the " A " state has more uncertainty in position, it can be decomposed into just a few momentum waves. However, the " $B$ " state requires more momentum waves, perhaps $\sim 100$ of them. Also look at the handout for a definitive example that was done with computer analysis.
a. How does the energy of the momentum waves change? Better yet, just tell me which momentum wave below has more energy and why:
(2 pts)

VS.

b. Given your answer in pt. a, which of the two wavefunctions (the delocalized state "A" or more localized state " $B$ ") have more kinetic energy and why?

Hint: I have made up a table of components $1 \rightarrow 5$ that have respective energies of $1 \mathrm{~J} \rightarrow 5 \mathrm{~J}$, and the percent that each contributes to states A and B. Use these data to find the average values of energies for states A and B, which should give you some insight into how to answer this problem.

| Energy (eV) | \%A | \%B |
| :---: | :---: | :---: |
| 1 | $50 \%$ | $30 \%$ |
| 2 | $30 \%$ | $20 \%$ |
| 3 | $20 \%$ | $20 \%$ |
| 4 | $0 \%$ | $15 \%$ |
| 5 | $0 \%$ | $15 \%$ |

This should help you understand how increasing the percent of higher energy states will affect the total energy. 3. HCl gas has an absorption at $2990 \mathrm{~cm}^{-1}$; this is one of the highest frequencies that is known in the infrared spectrum (the IR range is $200 \rightarrow 13,000 \mathrm{~cm}^{-1}$ ). Using this information can you estimate the force constant $\mathrm{k}_{\mathrm{f}}$ of the spring (bond) that connects the H and Cl ? Recall that the energy of a harmonic oscillator is $\mathrm{E}=\left(v+\frac{1}{2}\right) \hbar \omega=$ $\left(v+\frac{1}{2}\right) \hbar \sqrt{\frac{\mathrm{k}_{\mathrm{f}}}{\mu}}$, where $\mu$ is the reduced mass: $\mu=\frac{\mathrm{m}_{1} \mathrm{~m}_{2}}{\mathrm{~m}_{1}+\mathrm{m}_{2}}$. Hint: The ground state has $v=0$, and $1 \mathrm{~cm}^{-1}=1.986 \times 10^{-23}$
J. The mass of H is 1 amu and Cl is 35.5 amu .

Hint-hint: Did you get $\sim 2050 \mathrm{~N} / \mathrm{m}$ ? Then you forgot that absorption wavelength is due to the difference in energy between the $1^{\text {st }}$ excited and ground state (final energy - initial energy).
4. Deuterium chloride ( DCl ) gas has an absorption at $2144 \mathrm{~cm}^{-1}$ in the infrared (the IR range is $200 \rightarrow 13,000 \mathrm{~cm}^{-1}$ ). Using this information can you estimate the force constant $\mathrm{k}_{\mathrm{f}}$ of the spring (bond) that connects the D and Cl ? Recall that the energy of a harmonic oscillator is $E=\left(v+\frac{1}{2}\right) \hbar \omega=\left(v+\frac{1}{2}\right) \hbar \sqrt{\frac{k_{f}}{\mu}}$, where $\mu$ is the reduced mass: $\mu=$ $\frac{\mathrm{m}_{1} \mathrm{~m}_{2}}{\mathrm{~m}_{1}+\mathrm{m}_{2}}$. Hint: The ground state has $\mathrm{v}=0$, and $1 \mathrm{~cm}^{-1}=1.986 \times 10^{-23} \mathrm{~J}$. The mass of D is 2 amu and Cl is 35.5 amu . Hint-hint: Did you get $\sim 2050 \mathrm{~N} / \mathrm{m}$ ? Then you forgot that absorption wavelength is due to the difference in energy between the $1^{\text {st }}$ excited and ground state (final energy - initial energy).

## Problems: Theoretical or Explain in Words

1. If I have a potential energy surface as shown on the right, then the solution to the Schrödinger equation to the left of $x=L$ is:

$$
\Psi_{\mathrm{I}}(\mathrm{x})=\mathrm{A} \cdot \sin \left(\pi \cdot \frac{\mathrm{x}}{2 \mathrm{~L}}\right)
$$

To the right of $\mathrm{x}=\mathrm{L}$ is:

$$
\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{B} \cdot \mathrm{e}^{-(\mathrm{x}-\mathrm{L})^{2}}
$$

a. Why is the wavefunction in region I a sine function? Why not a cosine function?
(3 pts)

b. What is the relationship between constants A and B? (3 pts)

Hint: This is a derivation question, and the wavefunctions must be continuous. Thus, the "right" wavefunction must equal the "left" one at $x=L$.
c. Show that the wavefunctions are smooth at $x=L$.

Hint: Now that you know how $A$ is related to $B$, you can show that the derivatives of the wavefunctions are equal at $\mathrm{x}=\mathrm{L}$.
2. If I have a potential energy surface as shown on the right, then the solution to the Schrödinger equation to the left of $x=0$ is:

$$
\Psi_{\mathrm{I}}(\mathrm{x})=\mathrm{A} \cdot \cos \left(\pi \cdot \frac{\mathrm{x}}{2 \mathrm{~L}}\right)
$$

To the right of $x=0$ is:

$$
\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{B} \cdot \mathrm{e}^{-\mathrm{x}^{2}}
$$

a. Why is the wavefunction in region $I$ a cosine function? Why not a sine function?
(3 pts)
b. What is the relationship between constants A and B?
(3 pts)
Hint: This is a derivation question, and the wavefunctions must be continuous. Thus, the "right" wavefunction must equal the "left" one at $x=0$.
c. Show that the wavefunctions are smooth at $\mathrm{x}=0$.
(3 pts)
Hint: Now that you know how $A$ is related to $B$, you can show that the derivatives of the wavefunctions are equal at $\mathrm{x}=0$.
3. I have calculated a wavefunction, in blue, for one of the potential surfaces (red) below. Only one of them is correctcan you identify which potential function is correct and please state why?
( 7 pts )

4. For a free wave hitting a barrier:

$$
\frac{\mathrm{B}}{\mathrm{~A}}=\frac{\mathrm{k}_{1}-\mathrm{k}_{2}}{\mathrm{k}_{1}+\mathrm{k}_{2}}
$$

were $k_{1}$ is real since $k_{1}=\frac{\sqrt{2 m \mathrm{E}}}{\hbar}$ and E is a positive number. However, if $\mathrm{E}<\mathrm{V}$, then: $\mathrm{k}_{2}=\frac{\sqrt{2 \mathrm{~m}(\mathrm{E}-\mathrm{V})}}{\hbar}$ and is imaginary and can be expressed as $\mathrm{k}_{2}=\mathrm{i} \cdot \mathrm{k}_{2}^{\prime}=\mathrm{i} \cdot \frac{\sqrt{2 \mathrm{~m}(\mathrm{~V}-\mathrm{E})}}{\hbar}$ (note how V and E have switched place when " i " is added). The equation for reflection is then: $\frac{B}{A}=\frac{k_{1}-i \cdot k_{2}^{\prime}}{k_{1}+i \cdot k_{2}^{\prime}}$. Since the percent reflection is actually $\frac{|B|^{2}}{|A|^{2}}=\frac{B^{*} B}{A^{*} A}$, please show that reflection is always $100 \%$ if $\mathrm{E}<\mathrm{V}$.
( 5 pts)
5. Consider the following potential energy surface that has an infinite potential at $\mathrm{x}=0$ :
a. Which of the wavefunctions below is the correct for region I and why?
( 5 pts)

1. $\cos (k \cdot x)$
2. $\operatorname{Sin}(k \cdot x)$
3. $E^{i k x}$
4. $\mathrm{E}^{-\mathrm{ikx}}$
b. Is there any boundary condition that dictates what $k$ is? In other words, can k take on any value so long at the correct form (question
 a) is determined?
(3 pts)
c. If there is no boundary condition that limits the value of $k$, are there limits on the energy? Please explain, and hint: this is basically a freewave problem.
5. The "quantum" in quantum mechanics describes when only certain energy levels are allowed. Thus, there are finite energy differences between the ground state and other excited states. Not all systems have quantized energy levels. Look at the figure below and try to answer the following questions:
a. For the free wave: is energy quantized? b. What about the particle in a box? c. What about the particle in a finite box, if the energy is $>\mathrm{V}_{0}$ (like the blue wave)?

6. The "half-baked well" potential has infinite potential energy at $x=-L$, and a step at $x=0$ :
a. Which wavefunction below is the correct for region I and why? Hint: what stipulation does the infinite potential place on the wavefunction?
7. $\cos \left(\mathrm{k}_{1}\{\mathrm{x}+\mathrm{L}\}-\frac{\pi}{2}\right)$
8. $\sin \left(\mathrm{k}_{1} \cdot \mathrm{x}\right)$
9. $\mathrm{e}^{\mathrm{ik} \mathrm{k}_{1} \mathrm{x}}$
10. $\mathrm{e}^{-\mathrm{i} k_{1} \mathrm{x}}$
(5 pts)
b. In the $1^{\text {st }}$ region, since $\mathrm{V}=0$ the Schrödinger equation is:

$$
\frac{\hbar^{2} \mathrm{k}_{1}^{2}}{2 \mathrm{~m}} \cdot \Psi_{\mathrm{I}}(\mathrm{x})=\mathrm{E} \cdot \Psi_{\mathrm{I}}(\mathrm{x})
$$

Solve for $\mathrm{k}_{1}$. Hint: this is just an algebra problem.
c. In the $2^{\text {nd }}$ region where the potential step $\mathrm{V}=\mathrm{V}_{0}$ exists:

$$
\frac{\hbar^{2} \mathrm{k}_{2}^{2}}{2 \mathrm{~m}} \cdot \Psi_{\mathrm{II}}(\mathrm{x})=\left(\mathrm{E}-\mathrm{V}_{0}\right) \cdot \Psi_{\mathrm{II}}(\mathrm{x})
$$

Solve for $\mathrm{k}_{2}$ in this case.
d. The wavefunction $\Psi_{\text {II }}(x)$ is in a region of constant potential, therefore possible wavefunctions are:

1. $\cos \left(\mathrm{k}_{2}\{\mathrm{x}+\mathrm{L}\}-\frac{\pi}{2}\right)$
2. $\sin \left(k_{2} \cdot x\right)$
3. $\mathrm{e}^{\mathrm{ik} k_{2} \mathrm{x}}$
4. $\mathrm{e}^{-\mathrm{i} \mathrm{k}_{2} \mathrm{x}}$

Figuring out which one is correct is a bit harder. Here is how you reason through it: if a particle passes through the wall from region 1 into region 2, it will continue moving to the right and do so forever since there are no more walls to bounce off of. Therefore, which of the functions above (1-4) correctly describe a particle always moving right?
( 5 pts )
e. Now unfortunately we run into two possible solutions for region 2. Let's say that in region $2: \mathrm{k}_{2}=\frac{\sqrt{2 \mathrm{~m}\left(\mathrm{E}-\mathrm{V}_{0}\right)}}{\hbar}$, and thus the two possibilities are that the particle has more energy that the potential barrier $\left(E>V_{0}\right)$ or it has less $\left(E<V_{0}\right)$. In the former case $\left(E>V_{0}\right), \Psi_{I I}(x)=e^{i \frac{\sqrt{2 m\left(E-V_{0}\right)}}{h}}$ which is a wave that travels to the right forever. If the energy is less than the potential energy, can you justify substituting $\mathrm{k}_{2}=\mathrm{i} \frac{\sqrt{2 \mathrm{~m}\left(\mathrm{~V}_{0}-\mathrm{E}\right)}}{\hbar}$ for $\frac{\sqrt{2 \mathrm{~m}\left(\mathrm{E}-\mathrm{V}_{0}\right)}}{\hbar}$ ? Please explain.
f. If you plug $\mathrm{k}_{2}=\mathrm{i} \cdot \frac{\sqrt{2 \mathrm{~m}\left(\mathrm{~V}_{0}-\mathrm{E}\right)}}{\hbar}$ into $\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{e}^{\mathrm{i} \mathrm{k}_{2} \mathrm{x}}$, does the wavefunction continue to oscillate like a sine or cosine or does it behave differently? Please explain your answer.
8. I have drawn here two wavefunctions that are solutions to the half-baked well if the energy of the particle is less than $V_{0}$. Obviously, the wavefunctions are continuous and smooth, which is due to using the "right" energies. To show that this is the case, let's do the following:
a. Set:

$$
\Psi_{\mathrm{I}}(\mathrm{x})=\cos \left(\frac{\sqrt{2 \mathrm{mE}}}{\hbar}\{\mathrm{x}+\mathrm{L}\}-\frac{\pi}{2}\right)
$$

and:

$$
\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{e}^{\frac{-\sqrt{2 \mathrm{~m}\left(\mathrm{~V}_{0}-\mathrm{E}\right)}}{\hbar}} \mathrm{x}
$$

equal at $x=0$.
b. Calculate the derivative of $\Psi_{\mathrm{I}}(\mathrm{x})$ and $\Psi_{\mathrm{II}}(\mathrm{x})$, and set the two derivatives equal at $\mathrm{x}=0$.
c. Divide the equation in $\mathbf{b}$ by the equation in a to derive the relationship:

$$
\tan \left(\frac{\sqrt{2 \mathrm{mE}}}{\hbar} \mathrm{~L}-\frac{\pi}{2}\right)=\frac{\sqrt{\left(\mathrm{V}_{0}-\mathrm{E}\right)}}{\sqrt{\mathrm{E}}}
$$

This equation does not allow one to solve for E analytically. Basically, you have to plug in numbers for $\mathrm{L}, \mathrm{m}$, and $\mathrm{V}_{0}$ and then determine what energy E makes the left side equals the right side.
( 6 pts )
d. If the mass of the particle is that of an electron, L is 1 nm , and the barrier is 3 eV , can you show that energies E of $4.8492 \times 10^{-20} \mathrm{~J}$ and $1.9146 \times 10^{-19} \mathrm{~J}$ (the same shown in the figure) satisfy the relationship in pt. c?(4 pts)
e. Drawn above are the two wavefunctions for the states with $\mathrm{E}=4.8492 \times 10^{-20} \mathrm{~J}$ and the other with $\mathrm{E}=1.9146 \times 10^{-}$
19 J. How would you describe these two states to a student in freshman chemistry?
(4 pts)


9. I have drawn here two wavefunctions that are solutions to the half-baked well if the energy of the particle is less than $V_{0}$. Obviously, the wavefunctions are continuous and smooth, which is due to using the "right" energies. To show that this is the case, let's do the following:
a. Set:

$$
\Psi_{\mathrm{I}}(\mathrm{x})=\cos \left(\frac{\sqrt{2 \mathrm{mE}}}{\hbar}\{\mathrm{x}+\mathrm{L}\}-\frac{\pi}{2}\right)
$$

and:

$$
\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{e}^{\frac{-\sqrt{2 \mathrm{~m}\left(\mathrm{~V}_{0}-\mathrm{E}\right)}}{\hbar}} \mathrm{x}
$$

equal at $x=0$.
( 2 pts )
b. Calculate the derivative of $\Psi_{\mathrm{I}}(\mathrm{x})$ and $\Psi_{\mathrm{II}}(\mathrm{x})$, and set the two derivatives equal at $x=0$.
( 6 pts )
c. Divide the equation in $\mathbf{b}$ by the equation in a to derive the relationship:


$$
\tan \left(\frac{\sqrt{2 \mathrm{mE}}}{\hbar} \mathrm{~L}-\frac{\pi}{2}\right)=\frac{\sqrt{\left(\mathrm{V}_{0}-\mathrm{E}\right)}}{\sqrt{\mathrm{E}}}
$$

This equation does not allow one to solve for E analytically. Basically, you have to plug in numbers for $L, m$, and $V_{0}$ and then determine what energy $E$ makes the left side equals the right side.
( 6 pts)
d. If the mass of the particle is that of a proton, L is 0.1 nm , and the barrier is 0.1 eV , can you show that
 energies E of $2.4895 \times 10^{-21} \mathrm{~J}$ and $9.6710 \times 10^{-21} \mathrm{~J}$ (the same shown in the figure) satisfy the relationship in pt. c ?
(4 pts)
e. Drawn above are the two wavefunctions for the states with $\mathrm{E}=2.4895 \times 10^{-21} \mathrm{~J}$ and the other with $\mathrm{E}=9.6710 \times 10^{-21}$
J. How would you describe these two states to a student in freshman chemistry?
(4 pts)
10. In the particle-in-a-half-bakedwell problem, you see that the wavefunction decayed exponentially into the barrier when $\mathrm{E}<\mathrm{V}$ as shown on the left. Now the question is- what do you think happens if the right barrier was

 "thin", such that the wavefunction doesn't decay to 0 before the end of the barrier as shown here? Please draw and explain your result.
11. Units! a. In a previous problem, an electron (mass $=9.109 \times 10^{-31} \mathrm{~kg}$ ) was trapped in a $1 \mathrm{~nm}\left(\mathrm{~L}=1 \times 10^{-9} \mathrm{~m}\right), 3 \mathrm{eV}$ $\left(V_{0}=4.807 \times 10^{-19} \mathrm{~J}\right)$ potential well. I gave you the ground and excited state energies $\left(4.85 \times 10^{-20} \mathrm{~J}\right.$ and $\left.1.91 \times 10^{-19} \mathrm{~J}\right)$, which I found with: $\tan \left(\frac{\sqrt{2 \text { mass } \cdot \mathrm{E}}}{\hbar} \cdot \mathrm{L}-\frac{\pi}{2}\right)=\frac{\sqrt{\left(\mathrm{V}_{0}-\mathrm{E}\right)}}{\sqrt{\mathrm{E}}}$ using the Wolfram zeros calculator.

Now you do the same- please use the equation, with SI units inputted to find the energies that solve the expression above. $\left(\hbar=1.0546 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}\right)$ Hint: to answer just send us a screen clip of the website, and most important the website won't work so don't try too hard!
b. The website won't return any values because the input parameters are too small. To resolve the problem you are going to use atomic units, in which $\hbar=1, \frac{1}{4 \pi \epsilon_{0}}=1, \mathrm{e}^{2}=1$ (the charge of an electron), length is in Bohrs (=0.0529
$n m$ ), and the mass of an electron is: $m_{e}=1$. In this system of units energy is in Hartrees, where 1 Hartree $=27.2114$ $\mathrm{eV}=4.36 \times 10^{-18} \mathrm{~J}$. So, if you do the conversions, and re-insert into the $\tan \left(\frac{\sqrt{2 \mathrm{mass} \cdot \mathrm{E}}}{\hbar} \cdot \mathrm{L}-\frac{\pi}{2}\right)=\frac{\sqrt{\left(\mathrm{V}_{0}-\mathrm{E}\right)}}{\sqrt{\mathrm{E}}}$ equation, the website should return the correct answers; please send us a screen shot and verify that the energies are the same as the ones I gave. Hint: the website can crash if you put in more than three significant figures.
(7 pts)
12. Concerning the finite barrier problem, let's think about what happens when a particle hits a barrier (region II) with the same amount of energy as the potential energy barrier, i.e. $\mathrm{E}=\mathrm{V}$. Free wavefunctions in the presence of a flat potential are the solution to:


$$
\widehat{\mathrm{H}} \Psi=\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \Psi(\mathrm{x})+\mathrm{V} \cdot \Psi(\mathrm{x})=\mathrm{E} \cdot \Psi(\mathrm{x})
$$

which is simplified into:

$$
\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \Psi(\mathrm{x})=(\mathrm{E}-\mathrm{V}) \cdot \Psi(\mathrm{x})
$$

For region II, the wavefunction has a general solution of the form: $\Psi(x)=C \cdot e^{i \cdot k_{2} \cdot x}+D \cdot e^{-i \cdot k_{2} \cdot x}$, where $C$ and $D$ are constants and $\mathrm{k}_{2}$ is defined as: $\mathrm{k}_{2}=\frac{\sqrt{2 \mathrm{~m}(\mathrm{E}-\mathrm{V})}}{\hbar}$.

It turns out that, if $\mathrm{E}=\mathrm{V}$, then $\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{C}+\mathrm{D} \cdot \mathrm{x}$. Can you show that this wavefunction is a solution to $\frac{-\hbar^{2}}{2 \mathrm{~m}} \frac{\partial^{2}}{\partial \mathrm{x}^{2}} \Psi(\mathrm{x})=$ $(\mathrm{E}-\mathrm{V}) \cdot \Psi(\mathrm{x}) ?$
13. In the previous problem of the finite barrier when $\mathrm{E}=\mathrm{V}$, we need to solve what is the probability of reflection and transmission. To do so, we must solve a system of four equations- the continuity and smoothness of the wavefunctions $\Psi_{\mathrm{I}} \& \Psi_{\text {II }}$ at $\mathrm{X}=0$ and the same for $\Psi_{\text {II }}$ and $\Psi_{\text {III }}$ at $\mathrm{x}=\mathrm{L}$.
a. If $\Psi_{I}(x)=A \cdot e^{i \cdot k_{1} \cdot x}+B \cdot e^{-\mathrm{i} \cdot \mathrm{k}_{1} \cdot \mathrm{x}}$ and $\Psi_{\mathrm{II}}(\mathrm{x})=\mathrm{C}+\mathrm{D} \cdot \mathrm{x}$, what are the two equations that stipulate that the wavefunction is continuous and smooth at $\mathrm{x}=0$ ?
b. Now if $\Psi_{I I}(\mathrm{x})=\mathrm{C}+\mathrm{D} \cdot \mathrm{x}$ and $\Psi_{\mathrm{III}}(\mathrm{x})=\mathrm{E} \cdot \mathrm{e}^{\mathrm{i} \cdot \mathrm{k}_{1} \cdot \mathrm{x}}$, what are the two equations that stipulate that the wavefunction is continuous and smooth at $\mathrm{x}=\mathrm{L}$ ?
14. Now let's solve the equations we derived in the previous question by insert values. We have already assumed that $\mathrm{E}=\mathrm{V}$, and let's use a finite value for $\mathrm{k}_{1}=\frac{4 \pi}{\mathrm{~L}}$. This gives us four equations to work with:

$$
\begin{gathered}
\mathrm{A}+\mathrm{B}=\mathrm{C} \\
\mathrm{i} \cdot \frac{4 \pi}{\mathrm{~L}} \cdot \mathrm{~A}-\mathrm{i} \cdot \frac{4 \pi}{\mathrm{~L}} \cdot \mathrm{~B}=\mathrm{D} \\
\mathrm{C}+\mathrm{D} \cdot \mathrm{~L}=\mathrm{E} \cdot \mathrm{e}^{\mathrm{i} \cdot 4 \pi} \\
\mathrm{D}=\mathrm{i} \cdot \frac{\pi}{\mathrm{~L}} \cdot \mathrm{E} \cdot \mathrm{e}^{\mathrm{i} \cdot 4 \pi}
\end{gathered}
$$

While we can use and note that $\mathrm{e}^{\mathrm{i} \cdot 4 \pi}=1$ to simplify the above, unfortunately, this system of four equations has 5 unknowns (A, B, C, D, and E). However, if we want the (reflection) ${ }^{1 / 2}$, that is equal to the ratio of $\mathrm{B} / \mathrm{A}$. Likewise, (transmission) ${ }^{1 / 2}$ is the ratio of E/A. Using this information, we can rewrite the system of equations as:

$$
\begin{gathered}
1+r=C \\
i \cdot \frac{4 \pi}{L}-i \cdot \frac{4 \pi}{L} \cdot r=D \\
C+D \cdot L=t \\
D=i \cdot \frac{4 \pi}{L} \cdot t
\end{gathered}
$$

where $\mathrm{r}=\mathrm{B} / \mathrm{A}$ (the square root of the reflectance) and $\mathrm{t}=\mathrm{E} / \mathrm{A}$ (the square root of the transmission). Now you can plug these into the Mathematica Online system of equations solver found here:
http://www.wolframalpha.com/widgets/view.jsp?id=ae438682ce61743f90d4693c497621b7
and determine what r and t are.
When you do, note that you need to take the absolute value of the results for $r$ and $t$ to get the real values like you did in question 3. For example, if you find that $r=\frac{2 \pi}{2 \pi+i}$, then:
$|\mathrm{r}|^{2}=\left(\frac{2 \pi}{2 \pi+\mathrm{i}}\right)^{*}\left(\frac{2 \pi}{2 \pi+\mathrm{i}}\right)=\left(\frac{2 \pi}{2 \pi-\mathrm{i}}\right)\left(\frac{2 \pi}{2 \pi-\mathrm{i}}\right)=\frac{4 \pi^{2}}{4 \pi^{2}+1}=0.975$, which is $\sim 97.5 \%$. Note that $1-|\mathrm{r}|^{2}=|\mathrm{t}|^{2}$.
Hint: Show me what the web site returns of r and t , and then determine the absolute values. Also I found that the Wolfram web site can hang, if so, hit the equal sign as indicated here.
15. Now let's solve the equations we derived in the previous question by insert values. We have already assumed that $\mathrm{E}=\mathrm{V}$, and let's use a finite value for $\mathrm{k}_{1}=\frac{2 \pi}{\mathrm{~L}}$. This gives us four equations to work with:

$$
\begin{gathered}
A+B=C \\
i \cdot \frac{2 \pi}{L} \cdot \mathrm{~A}-\mathrm{i} \cdot \frac{2 \pi}{\mathrm{~L}} \cdot \mathrm{~B}=\mathrm{D} \\
\mathrm{C}+\mathrm{D} \cdot \mathrm{~L}=\mathrm{E} \cdot \mathrm{e}^{\mathrm{i} \cdot 2 \pi} \\
\mathrm{D}=\mathrm{i} \cdot \frac{\pi}{\mathrm{~L}} \cdot \mathrm{E} \cdot \mathrm{e}^{\mathrm{i} \cdot 2 \pi}
\end{gathered}
$$

While we can use and note that $\mathrm{e}^{\mathrm{i} \cdot 2 \pi}=1$ to simplify the above, unfortunately, this system of four equations has 5 unknowns (A, B, C, D, and E). However, if we want the (reflection) ${ }^{1 / 2}$, that is equal to the ratio of $\mathrm{B} / \mathrm{A}$. Likewise, (transmission) ${ }^{1 / 2}$ is the ratio of $\mathrm{E} / \mathrm{A}$. Using this information, we can rewrite the system of equations as:

$$
\begin{gathered}
1+r=C \\
\mathrm{i} \cdot \frac{2 \pi}{\mathrm{~L}}-\mathrm{i} \cdot \frac{2 \pi}{\mathrm{~L}} \cdot \mathrm{r}=\mathrm{D} \\
\mathrm{C}+\mathrm{D} \cdot \mathrm{~L}=\mathrm{t} \\
\mathrm{D}=\mathrm{i} \cdot \frac{2 \pi}{\mathrm{~L}} \cdot \mathrm{t}
\end{gathered}
$$

where $\mathrm{r}=\mathrm{B} / \mathrm{A}$ (the square root of the reflectance) and $\mathrm{t}=\mathrm{E} / \mathrm{A}$ (the square root of the transmission). Now you can plug these into the Mathematica Online system of equations solver found here:
http://www.wolframalpha.com/widgets/view.jsp?id=ae438682ce61743f90d4693c497621b7
and determine what $r$ and $t$ are. When you do, note that you need to take the absolute value of the results for $r$ and $t$ to get the real values like you did in question 3 . For example, if you find that $r=\frac{\pi}{\pi+i}$, then:
$|r|^{2}=\left(\frac{\pi}{\pi+\mathrm{i}}\right)^{*}\left(\frac{\pi}{\pi+\mathrm{i}}\right)=\left(\frac{\pi}{\pi-\mathrm{i}}\right)\left(\frac{\pi}{\pi-\mathrm{i}}\right)=\frac{\pi^{2}}{\pi^{2}+1}=0.908$, which is $\sim 91 \%$. Note that $1-|r|^{2}=|\mathrm{t}|^{2}$.

Hint: Show me what the web site returns of r and t , and then determine the absolute values. Also I found that the Wolfram web site can hang, if so, hit the equal sign as indicated here.
16. For this problem we will evaluate the variance in position $\sigma_{\mathrm{x}}^{2}=$ $\left\langle\mathrm{x}^{2}\right\rangle-\langle\mathrm{x}\rangle^{2}$ for a wavefunction of the form: $\Psi(\mathrm{x})=\frac{2}{\mathrm{~L}} \cdot \sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{L}} \mathrm{x}\right)$ using the following steps:
a. First calculate $\langle\mathrm{x}\rangle$
(6 pts)
b. Next calculate $\left\langle\mathrm{x}^{2}\right\rangle$
(6 pts)
c. And now determine $\left\langle\mathrm{x}^{2}\right\rangle-\langle\mathrm{x}\rangle^{2}$


Hint: $\frac{1}{2}-\frac{3}{2 \pi^{2}}-\left(\frac{2}{3}-\frac{1}{\pi^{2}}\right)^{2} \approx 0.0284$
17. For this problem we will evaluate the variance in momentum $\sigma_{p}^{2}=\left\langle p^{2}\right\rangle-\langle p\rangle^{2}$ using the wavefunction: $\Psi(x)=$ $\frac{2}{L} \cdot \sqrt{x} \cdot \sin \left(\frac{\pi}{\mathrm{~L}} \mathrm{x}\right)$ in the following steps:
a. First determine: $\left(\frac{\hbar}{\mathrm{i}}\right) \frac{\partial}{\partial \mathrm{x}}\left(\frac{2}{\mathrm{~L}} \sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{L}} \mathrm{x}\right)\right)$
( 6 pts )
b. Set up the $\langle p\rangle$ as:
(4 pts)

$$
\langle\mathrm{p}\rangle=\frac{4}{\mathrm{~L}^{2}} \int_{0}^{L}\left(\sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{~L}} \mathrm{x}\right)\right)^{*}\left(\frac{\hbar}{\mathrm{i}}\right) \frac{\partial}{\partial \mathrm{x}}\left(\sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{~L}} \mathrm{x}\right)\right) \cdot \partial \mathrm{x}
$$

And using your answer from pt. a you should be able to find the answer in the list of identities.
c. Now as for:

$$
\left\langle\mathrm{p}^{2}\right\rangle=\frac{4}{\mathrm{~L}^{2}} \int_{0}^{\mathrm{L}}\left(\sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{~L}} \mathrm{x}\right)\right)^{*}\left(\frac{\hbar^{2}}{\mathrm{i}^{2}}\right) \frac{\partial^{2}}{\partial \mathrm{x}^{2}}\left(\sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{~L}} \mathrm{x}\right)\right) \cdot \partial \mathrm{x}
$$

Unfortunately, this one requires sophisticated mathematical software to solve, from which one finds $\left\langle\mathrm{p}^{2}\right\rangle \approx \frac{11 \hbar^{2}}{\mathrm{~L}^{2}}$. From this you can now calculate $\sigma_{\mathrm{p}}{ }^{2}=\left\langle\mathrm{p}^{2}\right\rangle-\langle\mathrm{p}\rangle^{2}$ ?
18. If the uncertainty principal for position and momentum is: $\sigma_{\mathrm{x}}{ }^{2} \cdot{\sigma_{\mathrm{p}}}^{2} \geq \frac{1}{4}|\langle[\hat{\mathrm{x}}, \hat{\mathrm{p}}]\rangle|^{2} \sim \frac{\hbar^{2}}{4}$, can you show that this principle is consistent with the $\sigma_{\mathrm{x}}^{2}$ and $\sigma_{\mathrm{p}}^{2}$ determined in the preceding two problems for $\Psi(\mathrm{x})=\frac{2}{\mathrm{~L}} \cdot \sqrt{\mathrm{x}} \cdot \sin \left(\frac{\pi}{\mathrm{L}} \mathrm{x}\right)$ ?

