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 x=0 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:

$$x < 0\ (left): \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_I(x) = E \cdot \psi_I(x)$$

$$x > 0\ (right): frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_{II}(x) + V_0 \cdot \psi_{II}(x) = E \cdot \psi_{II}(x)$$

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”:

$$\psi_I = A \cdot e^{ik_1 x} + B \cdot e^{-ik_1 x}$$

The wavevector k_1 can be found by rearranging the Schrödinger equation: $\frac{\partial^2}{\partial x^2}\psi_I(x) = \frac{2mE}{\hbar^2} \cdot \psi_I(x)$, which makes $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$.

Now as for the 2^{nd} region, we first rearrange the Hamiltonian as:

$$x > 0\ (right): frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_{II}(x) = (E - V_0) \cdot \psi_{II}(x)$$

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 k_2:

$$\psi_{II} = C \cdot e^{ik_2 x} + D \cdot e^{-ik_2 x}$$

The wavevector k_2 can be found by simply replacing ” E ” in k_1 with $(E - V_0)$: $k_2 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$. 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:

$$\psi_I(x) = A \cdot e^{ik_1 x}$$

When the particle strikes the barrier at 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:

$$\psi_I(x) = A \cdot e^{ik_1 x} + B \cdot e^{-ik_1 x}$$

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

$$\psi_{II}(x) = C \cdot e^{ik_2 x}$$

If you wonder why there is no leftward moving $e^{-ik_2 x}$ "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 $A \cdot e^{ik_1 x}$ as the incoming "A-wave", $B \cdot e^{-ik_1 x}$ as the reflected "B-wave" and $C \cdot e^{ik_2 x}$ as the transmitted "C-wave". This is because the probability amplitude of the incoming wave is:

$$\left|A \cdot e^{ik_1 x}\right|^2 = |A|^2 \cdot e^{-ik_1 x} \cdot e^{ik_1 x} = |A|^2 \cdot e^0 = |A|^2$$

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

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 x=0, which is the boundary of the step potential. This gives us two equations to solve for our two unknowns:

$\psi_{I,(x=0)} = \psi_{II,(x=0)}$ (continuous) and: $\frac{\partial \psi_{I,(x=0)}}{\partial x} = \frac{\partial \psi_{II,(x=0)}}{\partial x}$ (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 }_I}^'={{\psi }_{II}}^' by the continuous one: $\psi_I = \psi_{II}$ at the boundary:

\[\frac

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(For those readers who are mathematically inclined, this is the log derivative \partial \ln \left(\psi \right)=\frac{{\psi }^'}{\psi })

When we insert the equations and make x=0 we are left with:

$$\frac{A \cdot ik_1 e^0 - B \cdot ik_1 e^0}{A \cdot e^0 + B \cdot e^0} = \frac{C \cdot ik_2 e^0}{C \cdot e^0}$$

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

$$k_1 A - k_1 B = k_2 A + k_2 B$$

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 (m=9.109$\times 10^{-31}$ kg) striking against a $V_0 = 1$ electron volt step (an electron volt is the energy an electron experiences travelling through a 1 Volt potential, $1\ eV = 1.602 \times 10^{-19}\ J$). 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-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 $= \frac{(k_1 - k_2) \cdot (k_1 - k_2)^*}{(k_1 + k_2) \cdot (k_1 + k_2)^*} = \frac{E + E - V_0}{E + E - V_0} = 1$. 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 $E < V_0$ has implications for the wavefunction in region II. If we substitute k_2=i\cdot k^'_2, where k^'_2 is a real positive number into the wavefunction we find:

{\psi }_{II}\left(x\right)=C\cdot e^{i^2\cdot k^'_2x}=C\cdot e^{-k^'_2x} \nonumber

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, $\psi_{III}(x) = E \cdot e^{ik_1 x}$, 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 $T = \frac{|E|^2}{|A|^2}$, 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 positions x=0 and x=L. Unfortunately, this is a very time-consuming 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 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-a-box", which has a potential energy surface defined in three regions by:

$$x < 0 V(x) = \infty$$

$$0 \leq x \leq L \; V(x) = 0$$

$$x > L V(x) = \infty$$

This surface is shown in Figure 13.5. We seek a solution to the Schrödinger 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:

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

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 (x=0) and right sides (x=L) of the box. The fact that the wavefunction must disappear at 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 $sin\left(k \cdot x\right) = A \cdot e^{ik \cdot x} - A \cdot e^{-ik \cdot x}$ if $A = \frac{1}{2i}$. Thus, the boundary condition reveals that:

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

Now we have to apply the second boundary condition at x=L:

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

This can only be true if $k_1 L = n\pi$, allowing us to solve for the wave vector:

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

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

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

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:

$$N^2 \int_0^L sin^2\left(\frac{n\pi}{L}x\right) \partial x = 1$$

which allows N to be defined as:

$$N = \frac{1}{\sqrt{\int_0^L sin^2\left(\frac{n\pi}{L}x\right) \partial x}}$$

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 $N = \sqrt{\frac{2}{L}}$ and the full particle in a box wavefunction is: $\psi_{II}\left(x\right) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi}{L}x\right)$. These wavefunctions are also orthogonal to each other: \int{}{\psi }^*_{{\upsilon }^'}{\psi }_{\upsilon }\partial x={\delta }_{{\upsilon }^',\upsilon }, where {\delta }_{{\upsilon }^',\upsilon } is the Kronecker delta function that is {\delta }_{{\upsilon }^',\upsilon }=1 if {\upsilon }^'=\upsilon, which is the normalization condition, and {\delta }_{{\upsilon }^',\upsilon }=0 if {\upsilon }^'\neq \upsilon. 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 $\hat{H}\psi = E\psi$:

\[\frac{-\hslash^2}{2m}\frac

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sin\left(\frac{n\pi }{L}x\right)=\frac{\hslash^2n^2{\pi }^2}{2mL^2}\sqrt{\frac{2}{L}}sin\left(\frac{n\pi }{L}x\right)=E\cdot {\psi }_{II}\left(x\right) \nonumber \]

and thus:

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

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 (n=1) and the 1^{st} excited state (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^{st} excited state levels. For a particle in a box that quantity is: $\Delta E = \frac{(n=2)^2h^2}{8mL^2} - \frac{(n=1)^2h^2}{8mL^2} = \frac{3h^2}{8mL^2}$, 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 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 $E<V_0$, meaning that the energy is quantized into discrete values. For energies greater than the potential trap ($E>V_0$) 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 $E<V_0$.

Let's first attempt to solve the ground state wavefunction. The potential has even symmetry about x=0, and as such we assume that the trap region also has even symmetry like a cosine function. As a result, $\psi_{II}(x) = B \cdot cos\,(k_2 x)$, where the wavevector $k_2 = \sqrt{\frac{2mE}{\hbar^2}}$. If the particle penetrates into the barrier region I on the left it will continue in that direction, implying $\psi_I = A \cdot e^{k_1 \cdot x}$ where $k_1 = \sqrt{\frac{2m(V-E)}{\hbar^2}}$. Using the same logic $\psi_{III} = C \cdot e^{-k_1 \cdot x}$. As per the boundary conditions, the wavefunctions must be continuous and smooth at the region I/II boundary:

\(A\cdot e^\

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=B\cdot cos\left(-k_2\frac{L}{2}\right)\) and \(k_1\cdot A\cdot e^\

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={-k}_2\cdot B\cdot sin\left({-k}_2\frac{L}{2}\right)\)

and likewise for region II/III:

$B \cdot cos\left(k_2 \frac{L}{2}\right) = C \cdot e^{-k_1 \cdot \frac{L}{2}}$ and $-k_2 \cdot B \cdot sin\left(k_2 \frac{L}{2}\right) = -k_1 \cdot C \cdot e^{-k_1 \cdot \frac{L}{2}}$

Solving using log boundary conditions yields what is called a "transcendental" equation for k_1 and k_2:

$$tan\left(k_2 \frac{L}{2}\right) = \frac{k_1}{k_2}$$

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^{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!
