6.3: The Finite Square Well

Lowering the Walls

As instructive as the infinite square well is, it's not particularly physical that its depth is infinite. Well okay, it works well as an approximation when the depth is much greater than the ground-state energy (so that lots of energy levels are available), but now we are going to look at a case when the particle is only loosely-held by a square potential. The finite square well we are about to discuss is a bit tougher to compare to a classical system (like the ball bouncing between two walls for the infinite case). In the case of the infinite square well, we could sloppily (and incorrectly) state that the particle remains confined to the well thanks to the infinite force at the walls (where the potential function has infinite slope). But the fact that the force is infinite simply means that the interaction time with the wall is infinitesimal, since there is a finite change in momentum for the particle. If that case, if the particle is moving faster, then the infinite force must be greater to deliver a greater impulse. The infinite depth of the well simply assures that there is always a larger impulse available, if needed, to turn the particle around, no matter how fast it is moving.

For a square well with a finite depth, the walls will still deliver infinite forces over infinitesimal time intervals to provide an impulse to the particle, but if the particle's kinetic energy exceeds the height of the top of the well, then the impulse by the wall will only serve to slow down the particle, and it will continue in the same direction, not restricted to the confines of the well. In this case, we simply have an unbound particle that speeds up when it is in the x range defined by the well, and slows down when it exits.

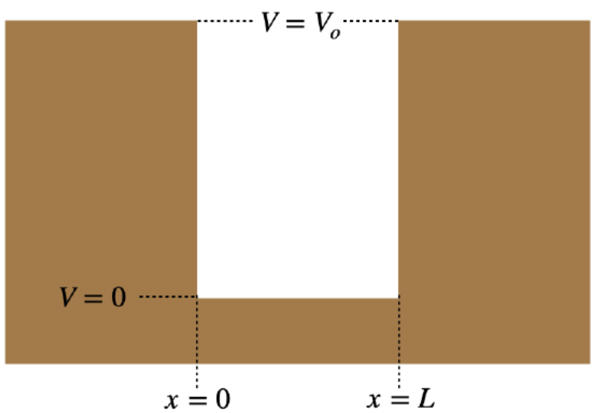
Having said all this, we are interested in the bound states (there is plenty of interesting quantum physics in the unbound case as well, but we will not cover that here). Keep in mind that the ground state is always above the bottom of the well, so if this well is particularly shallow, perhaps we will find that *no* bound states occur. For example, if we just look at the energy spectrum for the infinite square well, the ground state energy is $E_1=\frac{h^2}{8mL^2}$, so it might be that if the well is shallower than this number (defined by the mass of the particle and width of the well), then there is no bound state at all. We won't know the answer to this until we get into the details, because we can't expect the energy spectrum of the finite square well to be identical to that of its bigger sibling.

Start with Schrödinger's Equation

We begin, as usual, looking for the stationary-state solutions using the separated Schrödinger equation for our new potential. The mathematical description of the potential looks very much like it did for the infinite square well, with the exception that the height is no longer infinite:

$$V\left(x\right)=\left\{\begin{array}{ll} 0 & 0\le x\le L \\ V_o & x<0,\; x>L\end{array}\right. \tag{6.3.1}$$

Figure 6.3.1 – Finite Square Well



Plugging this potential into the time-independent Schrödinger equation, we create essentially two separate differential equations, as we did in the infinite square well case:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi\left(x\right)+\left\{\begin{array}{ll} 0 & \text{(inside well)} \\ V_o & \text{(outside well)}\end{array}\right\}\psi\left(x\right)=E\psi\left(x\right) \tag{6.3.2}$$

As we said above, we are interested in the bound states, so we insist that $E < V_o$. We see at the outset that there will be a difference here from the infinite well. We started the infinite well by noting that the wave function must necessarily vanish outside the confines of the box, but it is not obvious that that is the case here. We know that classically the object can't ever be outside the confines of the well (its total energy is less than the potential energy, which makes the kinetic energy impossibly negative), but the mathematics does not rule out a non-zero probability amplitude immediately, and we've learned not to trust our classical reasoning by now. So let's skip worrying about the wave function beyond the walls for now, and continue with the process we followed with the infinite potential well – by writing down a general wave function for the "free" particle inside the well. Following the lead from before, we'll go with two plane wave states that are separable solutions to the free particle:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \quad \Rightarrow \quad \psi_{\text{inside well}}(x) = Ae^{+ikx} + Be^{-ikx}\ , \quad E = \frac{\hbar^2 k^2}{2m} \tag{6.3.3}$$

As with the infinite well, these plane waves in the $V = 0$ region (for the solution to be steady-state) must be equally right- and left-moving, creating standing waves (these are the stationary-state solutions, after all!). We therefore take the "shortcut" of writing the internal wave function as a combination of sine and cosine functions:

$$\psi_{\text{inside well}}(x) = A\sin kx + B\cos kx\ , \quad E = \frac{\hbar^2 k^2}{2m} \tag{6.3.4}$$

Why does the cosine function make an appearance here, when it didn't show up for the infinite well, you ask? Well, the boundary conditions of the wave function vanishing at the boundaries is what led us to exclusive use sine in the previous case. Now with the boundary conditions allowing for a non-vanishing wave function, we need to account for both of these possibilities.

At this point in infinite square well case, we went immediately to the boundary conditions, but without the simplification of a vanishing wave function (nodes) at the endpoints, we need to exercise some restraint. That is, we cannot immediately relate the possible values of k to the length of the well L. So let's set this aside for now and have a closer look at the differential equation outside the walls:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = (E - V_o)\psi(x) \tag{6.3.5}$$

Well, this is basically the same differential equation as inside the well, with E replaced with $E - V_o$. So can't we just use the same solution as above? Yes and no. The solution is still a sum of exponentials, but above the value of E is positive, while the value of $E - V_o$ is negative (the particle's total energy has to be less than V_o for it to be bound). If the wave function is a sum of sinusoids (like $e^{ix} = \cos x + i\sin x$), then two derivatives changes the sine of the wave function, and the differential equation works. But with a negative value multiplying $\psi(x)$ on the right-hand side of the equation, the result is that our exponentials lose their i's. (The reader is encouraged to confirm for themself that this wave function satisfies the differential equation):

$$\psi_{\text{outside well}}(x) = Ce^{+\alpha x} + De^{-\alpha x}\ , \quad V_o - E = \frac{\hbar^2\alpha^2}{2m} \tag{6.3.6}$$

Let's separate the outside-the-well regions into "left" and "right". The equation above applies to both, but we can reduce the terms required by invoking the fact that the wave function must ultimately be normalized. Looking at the wave function in the left region, we see that with $x < 0$, the term with a negative exponent will grow without bound as $x \to -\infty$. This requires that the coefficient D is identically zero. Similarly, the wave function in the right region will grow without bound as $x \to +\infty$ unless the constant C is identically zero.

Summarizing what we have so far for the wave function:

$$\psi(x) = \begin{cases} Ce^{+\alpha x} & x < 0 \\ A\sin kx + B\cos kx & 0 \le x \le L \\ De^{-\alpha x} & x > L \end{cases} \tag{6.3.7}$$

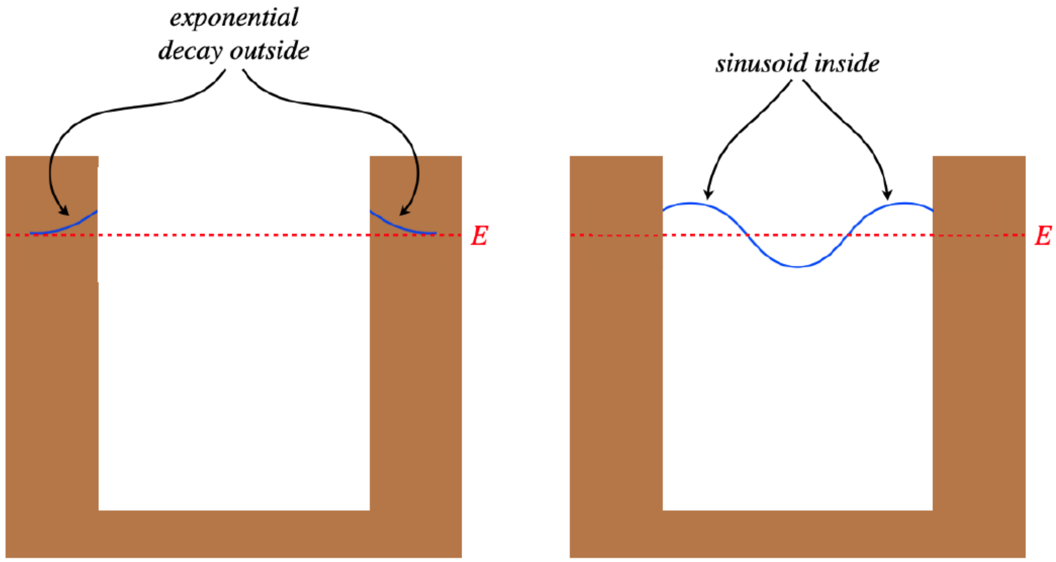
Energy Spectrum Quantization

With the presence of a non-zero wave function outside the walls, our task of matching boundary conditions is more daunting than it was for the infinite well. We have two conditions that must hold at the boundaries. The first is that the wave function must be continuous – it is unphysical for the particle to have a sudden jump in its probability density. That is, an infinitesimal change in position needs to be accompanied by an infinitesimal change in probability of finding the particle. And the second requirement is that the wave function's first derivative must also be continuous. If it is not, then the second derivative is not defined at the boundaries, throwing Schrödinger's equation into the garbage pail. This wasn't a problem when the infinite potential function covered-up this ugliness (the wave function was *identically* zero, which obviated any concern for its second derivative), but now we need to bow to the requirements of calculus.

So our task has now become setting the values and first derivatives of the wave functions equal on both sides of the borders $x=0$ and $x=L$, and using these to find the unknown constants. Ultimately we are looking for the energy spectrum: E. This means that we need either k or α, and we need to find the in terms of the known values m (mass of the particle), L (length of the well), and V_o (depth of the well). Before we delve into this math, it is interesting to see conceptually why the energy spectrum in this case must be quantized, as we have previously claimed without proof to be a general feature of bound states.

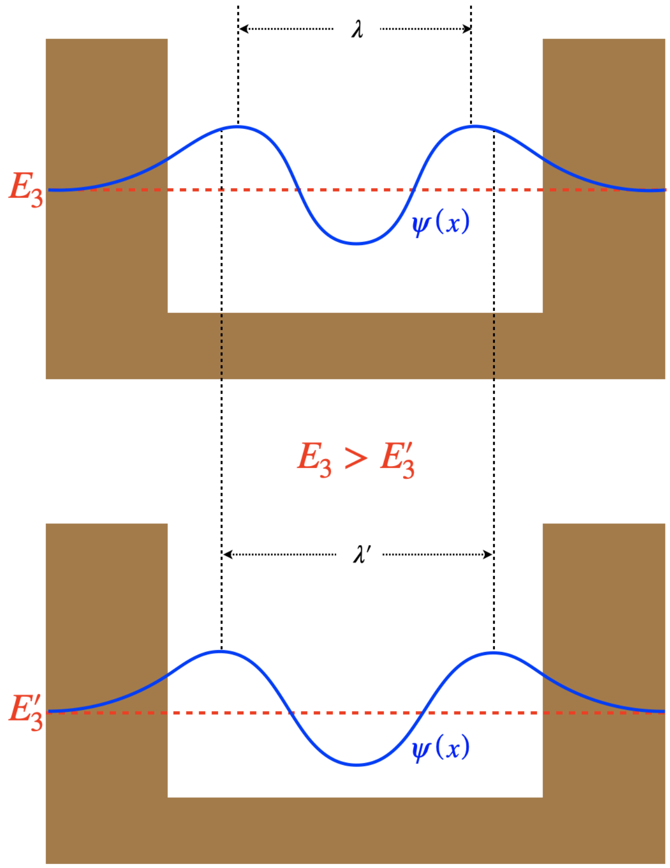
Consider an example of a wave function with three antinodes. What our math so far requires is:

Figure 6.3.2 – Requirements of Wave Function



This doesn't seem particularly restrictive. For example, we can conceive of two wave functions with different interior sinusoidal wavelengths (and therefore different wave numbers and energies) that satisfies these restrictions:

Figure 6.3.3 – Two Energies for n=3?



But there is a subtle flaw in these diagrams – looking closely reveals these waves don't remain "sinusoidal" all the way to the endpoints as they should (there should be no inflection point until the sinusoid reaches the axis). Let's see what it takes to satisfy this requirement. Let imagine constructing a ground-state wave function that satisfies the boundary conditions with an arbitrarily-chosen wavelength. We might proceed as follows:

1. Select an exponentially-decaying curve at the boundaries. Don't worry about the details yet, such as the value at the boundary or the decay constant.
2. Select a sinusoidal wave with our arbitrary wavelength. Well, it isn't totally arbitrary – to get a ground state, we need half this wavelength to be longer than the separation of the well walls, but this gives us a wavelength range of $L < \lambda < 2L$ to work with for the ground state.
3. Set the sinusoid into place, lowering it until the height of the sinusoid matches the height of the exponential at the boundary, satisfying the continuity of $\psi(x)$.
4. In general this will not allow the slopes of the exponential and sinusoid to match, so we can fix that by changing the amplitude of the sinusoid until the slopes do match.
5. Voilà! The wave function's boundary conditions match, and we selected the wavelength we wanted.

Figure 6.3.4 – A Scheme for Matching Boundary Conditions for a Given Wavelength

The last step, which seems like a trivial one, is to check to see if the wave function is fully normalized over the range $(-\infty, +\infty)$. Suppose the normalization integral comes out to be too small. Then we "just" have to raise the whole wave function (sinusoid and exponentials) together, making sure that we raise the points at the boundaries the same amount. But the problem is that these are two very different functions – changing parameters to increase the value at a specific point will not result in changing the slopes the same amount as well. If, for the moment, we call the center of the well the origin, then the sinusoid for the ground state is clearly just a cosine, and calling position of the right wall x_o, continuity of the wave function requires:

$$\psi\left(x_o\right) = A\cos kx_o = Be^{-\alpha x_o} \tag{6.3.8}$$

We can adjust A and B however we like to adjust the normalization, as long as this relation holds. Let's suppose that the changes we had to make to A and B to assure normalization were ΔA and ΔB, respectively:

$$\psi_{new}\left(x_o\right) = \left(A+\Delta A\right)\cos kx_o = \left(B+\Delta B\right)e^{-\alpha x_o} \quad \Rightarrow \quad \Delta A\cos kx_o = \Delta Be^{-\alpha x_o} \tag{6.3.9}$$

The original wave function was constructed to match the derivatives at the boundaries:

$$\psi'\left(x_o\right) = -Ak\sin kx_o = -B\alpha e^{-\alpha x_o} \tag{6.3.10}$$

For the derivatives to also match at the boundaries after the change of the values of A and B requires:

$$\psi'\left(x_o\right) = -\left(A+\Delta A\right)k\sin kx_o = -\left(B+\Delta B\right)\alpha e^{-\alpha x_o} \quad \Rightarrow \quad -k\Delta A\sin kx_o = -\alpha\Delta Be^{-\alpha x_o} \tag{6.3.11}$$

Dividing the two equations we obtained reveals that both boundary conditions remain matched after the shifts of ΔA and ΔB only under specific conditions related to k and α:

$$\frac{-\Delta Ak\sin kx_o}{\Delta A\cos kx_o} = \frac{-\alpha\Delta B\alpha e^{-\alpha x_o}}{\Delta Be^{-\alpha x_o}} \quad \Rightarrow \quad k\tan kx_o = \alpha \tag{6.3.12}$$

In short, while we could make the boundary conditions match with this scheme, we can't also assure the most essential feature of the wave function – that it be normalized – unless the wave has a very specific wavelength. This means that like the infinite square well, the energy spectrum of the finite square well is quantized.

The Math

All that remains to this problem is to apply all the boundary conditions to obtain the energy spectrum and energy eigenfunctions. Well, in principle this is the idea, but unlike the infinite square well, where the energy eigenvalues are a simple function of the eigenstate number n, the math does not behave so nicely here, as we will see...

There are four boundary conditions here – two boundaries, and two conditions each:

$\boldsymbol{\psi\left(x\right)}$ continuous at $\boldsymbol{x=0}$

$\psi\left(0\right) = Ce^0 = A\sin 0 + B\cos 0 \quad \Rightarrow \quad C = B$

$\boldsymbol{\psi\left(x\right)}$ continuous at $\boldsymbol{x=L}$

$\psi\left(L\right) = De^{-\alpha L} = A\sin kL + B\cos kL$

$\frac{d}{dx}\psi(x)$ **continuous at $x=0$**

$\psi'(0) = \alpha Ce^0 = kA\cos 0 - kB\sin 0 \quad \Rightarrow \quad \alpha C = kA$

$\frac{d}{dx}\psi(x)$ **continuous at $x=L$**

$\psi'(L) = -\alpha De^{-\alpha L} = kA\cos kL - kB\sin kL$

We have four equations and four constants to eliminate. Leaving the tedious algebra as an exercise for the reader, we end up with:

$$\tan kL = \frac{2\alpha k}{k^2-\alpha^2}\ , \quad k = \frac{\sqrt{2mE}}{\hbar}\ , \quad \alpha = \frac{\sqrt{2m\left(V_o - E\right)}}{\hbar} \tag{6.3.13}$$

One would of course like to solve these for the energy E in terms of m, L, and V_o, but we cannot do this in closed-form for this transcendental equation. The periodic nature of the tangent function ensures that the spectrum is quantized, but numerical/graphical methods show that there is a limited number of these solutions, depending upon the energy of the particle and the depth of the well.

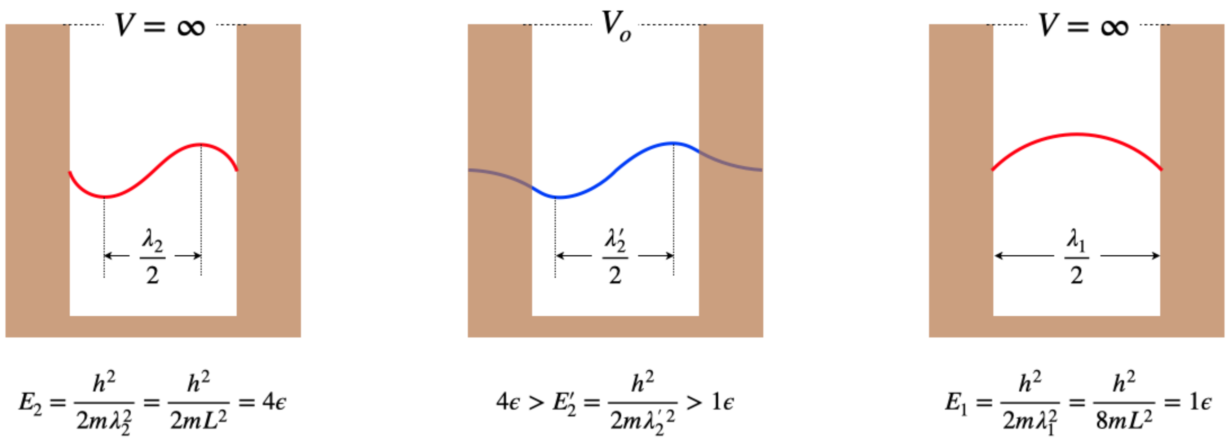
Effects of Varying the Well Depth

It is instructive to summarize what happens to the stationary state solutions and energy eigenvalues for a given particle in a well of a fixed length, as the depth of the well grows. The first thing that we note the states are characterized by the number of antinodes between the walls. In the case of the infinitely-high walls, there were nodes at the endpoints, but even though that restriction is lifted for the finite well, we can use this same criterion to determine if an eigenstate exists for the well, as follows:

Suppose there are 2 antinodes between the walls. This puts limits on the wavelength that the sinusoid can have. The wavelength must be no shorter than L, and no longer than $2L$. As we are holding the particle mass and well length fixed, one quantity that comes up frequently in these calculations is the ground state energy of the same particle in an infinite well of the same length, so we will scale all the energies of the finite well using this constant:

$$\epsilon \equiv \frac{h^2}{8mL^2} \tag{6.3.14}$$

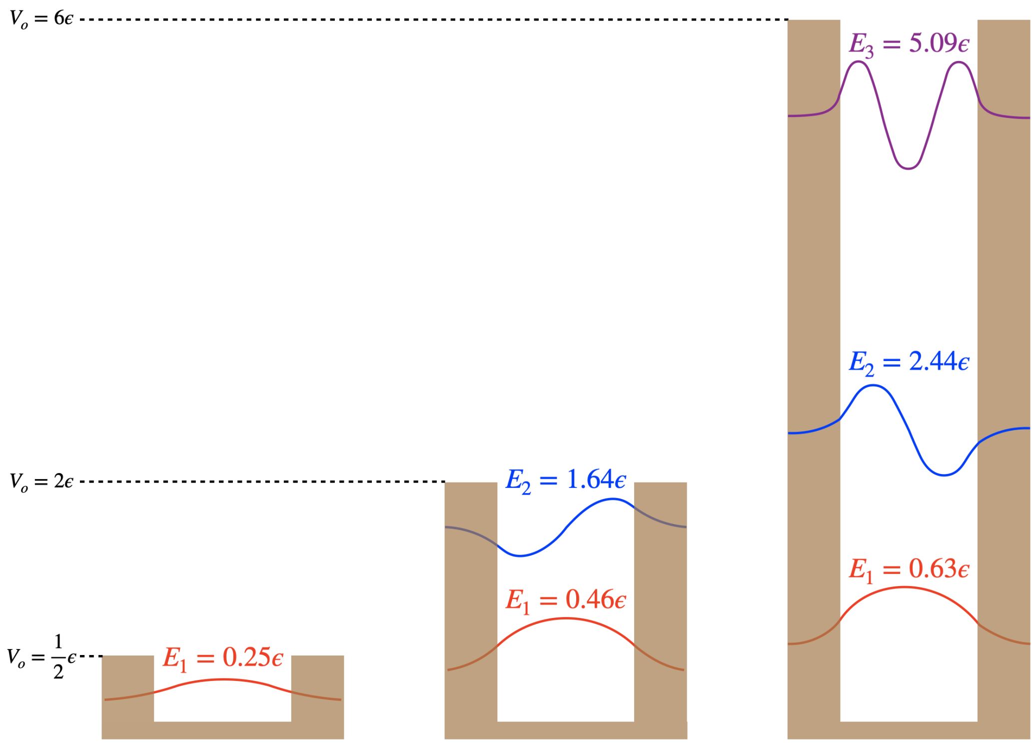
Figure 6.3.5 – Limits of Wavelength for 2 Antinode Wave Function



This clearly limits the number of eigenstates for a given value of V_o. In particular, there can exist no bound eigenstate with an energy greater than V_o, and the eigenstate energy is determined by the wavelength. So the highest possible energy eigenstate for the finite well is the one with the lowest n for which $V_o < n^2\epsilon$.

The figure below shows solutions generated through numerical means, and depicts how the energy spectrum of a finite square well changes when only its depth is changed (while the particle mass and length of the well remains fixed).

Figure 6.3.6 – A Few Well Depths



Some things to note:

- The energy of the n^{th} eigenstate rises as V_o increases, and in the limit of $V_o \to \infty$ converges to $E_n = n^2\epsilon$.
- As V_o increases, a greater fraction of the wave function for a given eigenstate exists within the well (i.e. the probability of finding the particle in the classically-forbidden region drops). In the limit of $V_o \to \infty$, this probability drops to zero.
- As noted above, the energy of the n^{th} eigenstate always falls between $(n-1)^2\epsilon$ and $n^2\epsilon$. As the well is made deeper, it "picks up" new eigenstates when V_o crosses those special $n^2\epsilon$ values.

The Classically-Forbidden Region

A few more words need to be said about the non-zero probability of finding the particle in the region that is forbidden by classical physics. The constant in the exponential decaying probability is, from Equation 6.3.6:

$$\alpha = \frac{\sqrt{2m\left(V_o - E\right)}}{\hbar} \tag{6.3.15}$$

We can see immediately that when the walls of the potential well are infinitely-high, this value goes to ∞, and this has the effect of decaying the wave function to zero immediately, leaving no wave function outside the well, as we expect:

$$\lim_{V_o \to \infty} Ae^{-\alpha|x|} = 0 \tag{6.3.16}$$

But for finite values of V_o, the particle will not be so constrained, and it should be clear that α makes for a good proxy for how far the wave function "penetrates" into the classically forbidden region. The smaller α is (i.e. the closer E is to V_o) is, the more probable it is that the particle will be found outside the well. It is conventional to express this property as a characteristic distance, called the *penetration depth*, equal to the inverse of the value of α (which has units of length^{-1}):

$$\delta \equiv \alpha^{-1} = \frac{\hbar}{\sqrt{2m\left(V_o - E\right)}} \tag{6.3.17}$$

We can relate the penetration depth to an expectation value – something that we can measure experimentally. Suppose we make many measurements of the position of a particle that is restarted in the same state, and then only keep the results where the particle was found outside the well. We can then average the distances from the wall, to get an expectation value of the position of the particle *given it has penetrated into this region*. We can see how this expectation relates to the penetration depth δ with a simple calculation. For simplicity, we will define the right wall's position as $x=0$ (the length of the well is still L and the particle's mass is still m). Then the unnormalized wave function for positive values of x is:

$$\psi\left(x\right)=Ae^{-\alpha x}\;,\quad x\geq 0 \tag{6.3.18}$$

Normalizing (so that probabilities and then expectation values work out properly) gives:

$$1=\int\limits_0^\infty\left|\psi\left(x\right)\right|^2dx=\int\limits_0^\infty\left|A\right|^2e^{-2\alpha x}dx\quad\Rightarrow\quad A=\sqrt{2\alpha} \tag{6.3.19}$$

And now the expectation value of x in this $x\geq 0$ region is:

$$\left<x\right>=\int\limits_0^\infty x\left[\sqrt{2\alpha}e^{-\alpha x}\right]^2dx=2\alpha\int\limits_0^\infty xe^{-2\alpha x}dx=\frac{1}{2\alpha}=\frac{1}{2}\delta \tag{6.3.20}$$

So on average, when we look only at locations of the particle in the classically-forbidden range, we find it at a position equal to half of what we have defined as the penetration depth. We can of course also calculate the uncertainty of this measurement. The details of the integration are not diffficult, and are left to the reader, but the result is:

$$\Delta x=\sqrt{\left<x^2\right>-\left<x\right>^2}=\frac{1}{2}\delta \tag{6.3.21}$$

So treating the uncertainty as a range over which we have some sense of confidence in our experiment, we find that given we measure the particle in the classically forbidden region, we are confident that it ended up somewhere in the region from the wall to the penetration depth.

Okay, so let's close by addressing the confusing question of how a particle could be found in this region at all, given it would have to have negative kinetic energy to be in that region. If we measure the momentum of the particle in one of the eigenstates inside the well, then of course all we ever see is the plane-wave momentum, which means it has a well-defined kinetic energy as well. But outside the well, the momentum is not well-defined, as the wave function is not sinusoidal, and is generally a (Fourier) mix of plane waves associated with many possible momenta. There is a finite uncertainty in the position of the particle in this region (we just computed it), so the uncertainty principle tells us that there is a minimum uncertainty in the momentum in that region as well:

$$\Delta p\geq\frac{\hbar}{2\Delta x}=\frac{\hbar}{\delta} \tag{6.3.22}$$

The kinetic energy of the particle that has this uncertain momentum is also uncertain. Without working out the math, we can say estimate the uncertainty in this kinetic energy. Let's just define the "range" of momentum as being between $\left<p\right>-\Delta p$ and $\left<p\right>+\Delta p$. We can compute the minimum and maximum values of the kinetic energy in this range. While this minimum and maximum do not define the precise uncertainty for the kinetic, it is a good number to use as a lower limit of this uncertainty. This means that the uncertainty of the kinetic energy is:

$$\Delta KE>\frac{\Delta p^2}{2m}=\frac{\hbar^2}{2m\delta^2}=V_o-E \tag{6.3.23}$$

So the uncertainty in the kinetic energy measurement is greater than what we calculate to be the entire negative kinetic energy (using the kinetic energy of the particle inside the well), meaning that our measurement does not confirm to within uncertainty that the kinetic energy had to become negative.