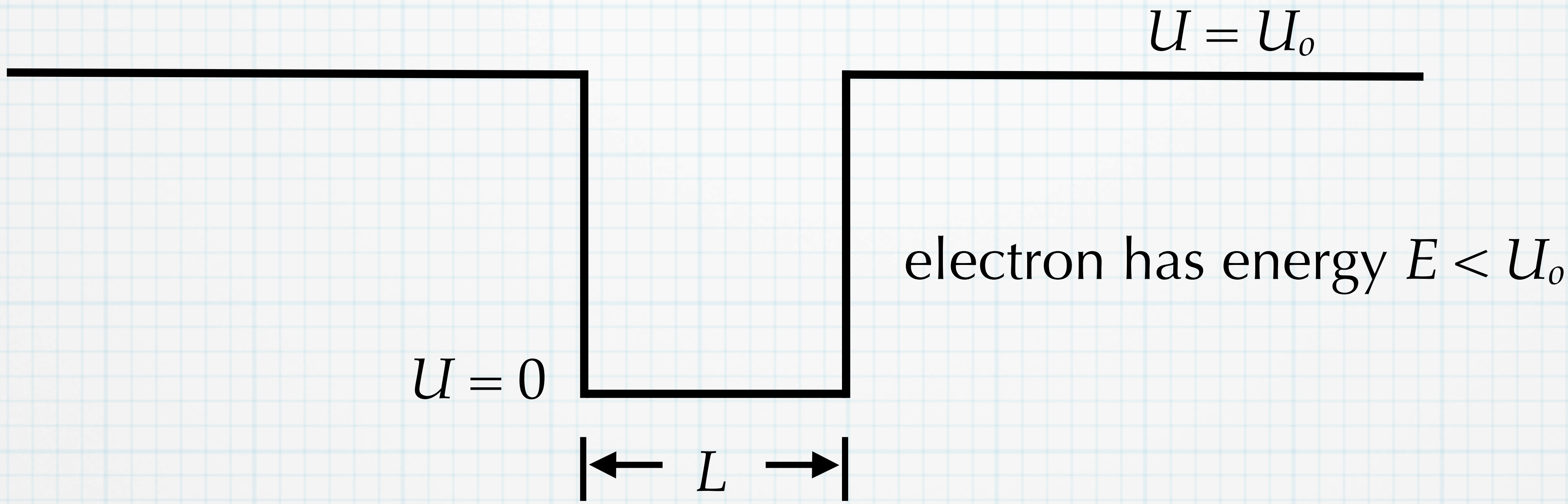
Square quantum wells

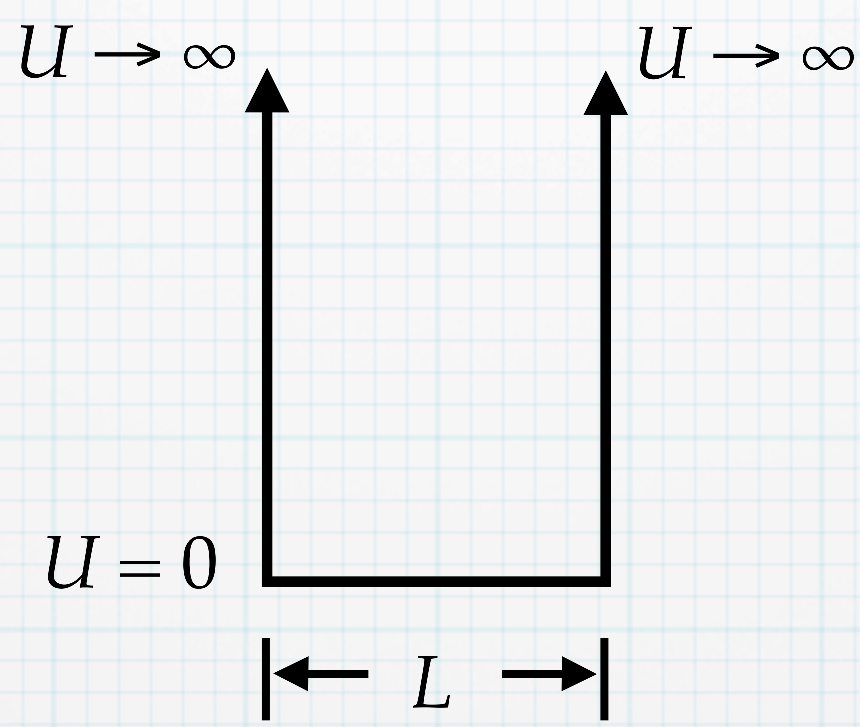
What happens when when a particle falls into an energetic well?



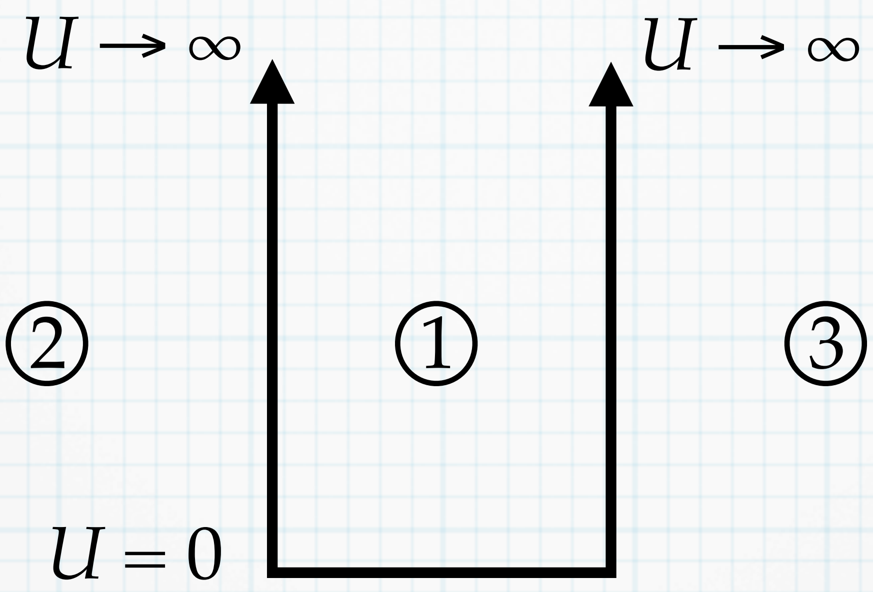
Again, we will handle this with plane waves. Because there are boundaries in this situation, we can normalize the wave functions and things aren't quite as strange at the unbounded plane wave.

Infinitely deep square well

Barriers are infinitely high. (No chance that the electron can tunnel into the barrier wall.



Determine the electron energy and wave functions.



TISE: $$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + U(x)\,\psi(x) = E\psi(x)$$

In regions 2 and 3: $\psi_2 = \psi_3 = 0$. (Otherwise, potential energy term goes to infinity.)

In region 1, $U = 0$: $\psi_1(x) = Ae^{ikx} + Be^{-ikx}$ $\qquad k = \sqrt{\frac{2mE}{\hbar^2}}$

Apply boundary conditions:

exception: Match only the wave functions, not derivatives.

Since $\psi_2 = \psi_3 = 0$ and derivatives are also zero, the wave function would have to be 0 as well.

The infinitely large barrier step makes it so that we don't have to force derivatives to match.

At $x = 0$: $\psi_1(0) = \psi_2(0)$.

$$A + B = 0$$

$$\psi_1(x) = A\left[e^{ikx} - e^{-ikx}\right]$$

$$= (i2A)\sin(kx)$$

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

At $x = L$: $\psi_1(L) = \psi_3(L)$.

$$A' \sin(kL) = 0$$

$kL = n\pi$ where n is an integer > 0.

(To avoid trivial solution.)

$$k = n\left(\frac{\pi}{L}\right)$$ k is quantized!

Momentum: $p = \hbar k$ Quantized!

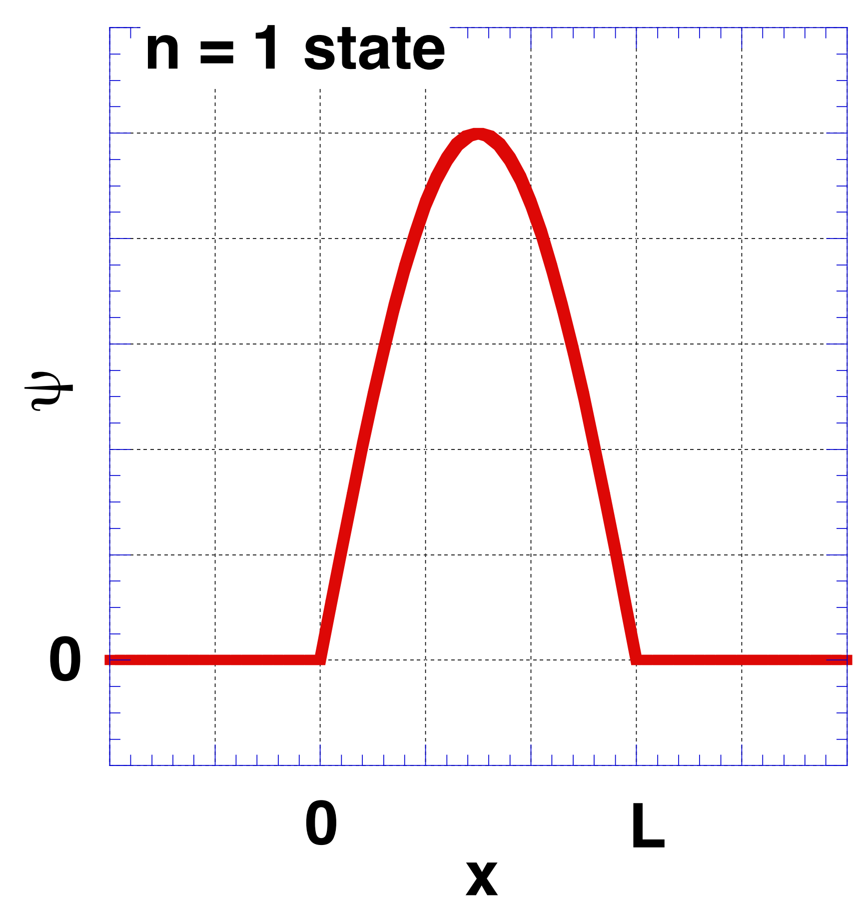
Energy: $E = \dfrac{\hbar^2 k^2}{2m}$ Quantized!

$$= n^2\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 0.377\text{eV}\left[n^2\left(\frac{m_o}{m}\right)\left(\frac{1\text{nm}}{L}\right)^2\right]$$

So only particular values of energy are allowed. For each allowed energy, there is a corresponding wave functions. An energy and its corresponding wave function define a "state" of the system.

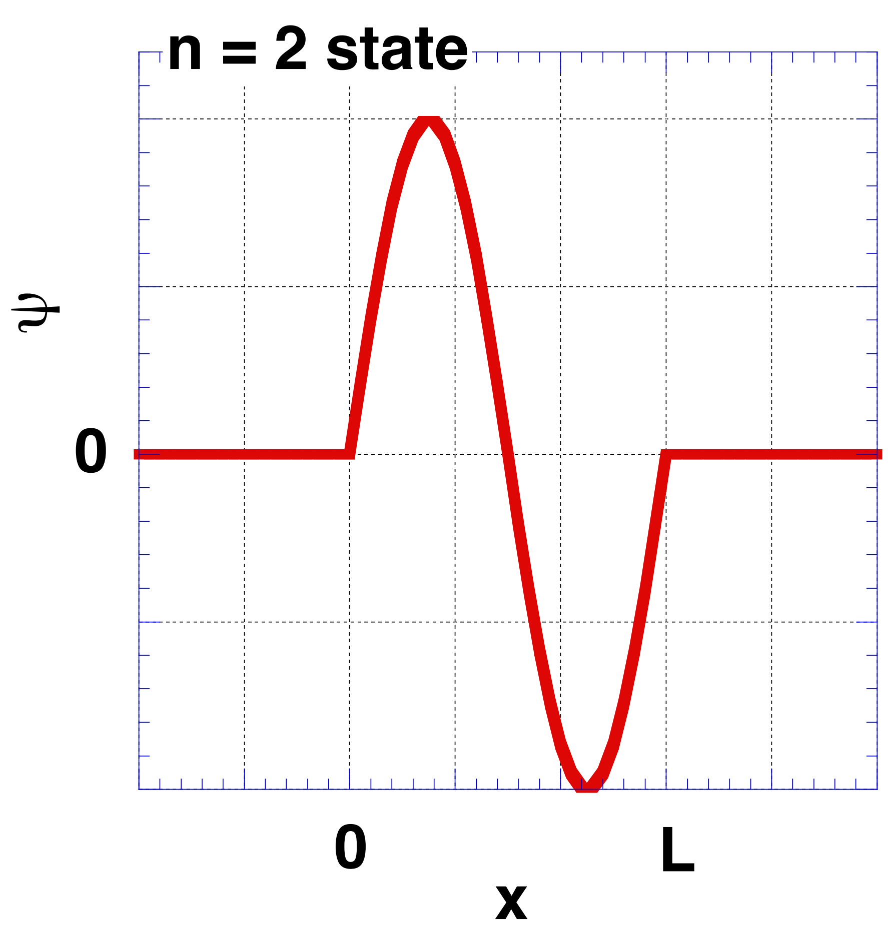
The lowest state is called the ground state.

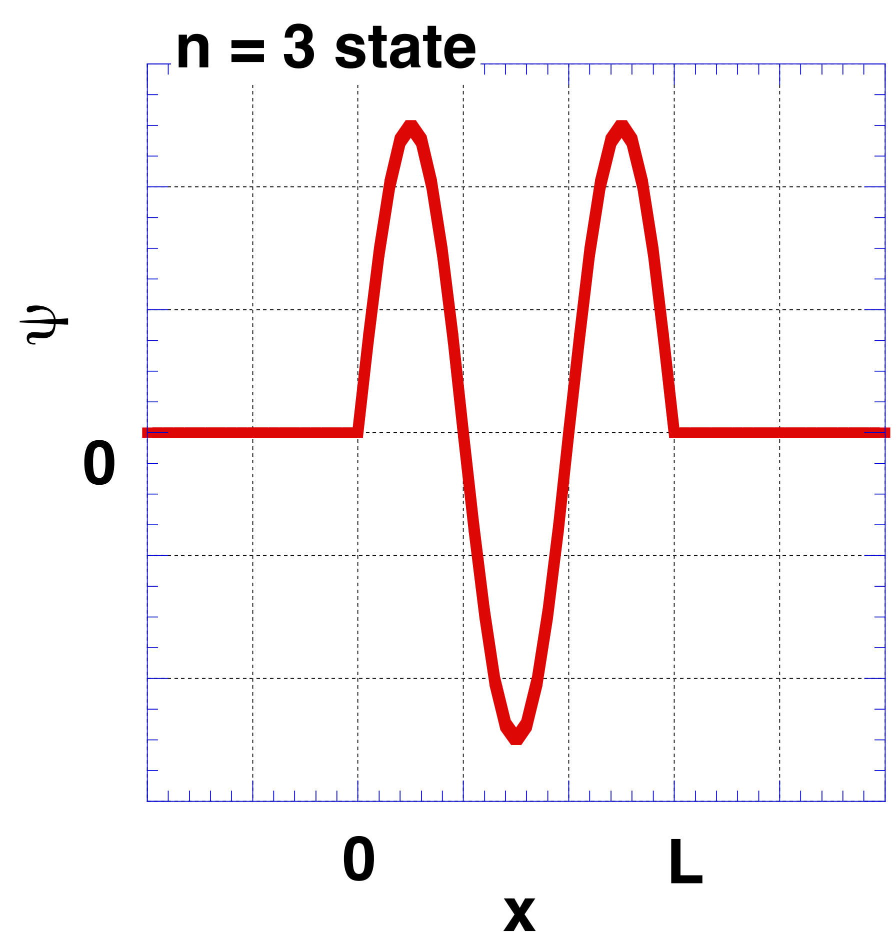
$$E_1 = \left(\frac{\pi^2 \hbar^2}{2mL^2}\right)$$



$$E_2 = \left(4\frac{\pi^2\hbar^2}{2mL^2}\right) = 4E_1$$

$$E_3 = \left(9\frac{\pi^2\hbar^2}{2mL^2}\right) = 9E_1$$





Normalization

Since this is a bound problem, it can be normalized easily.

$$\int_{-\infty}^{\infty} \psi^* \psi dx = \int_0^L A'^2 \sin^2(kx)\, dx = 1$$

Working through the integral leads the normalized coefficient

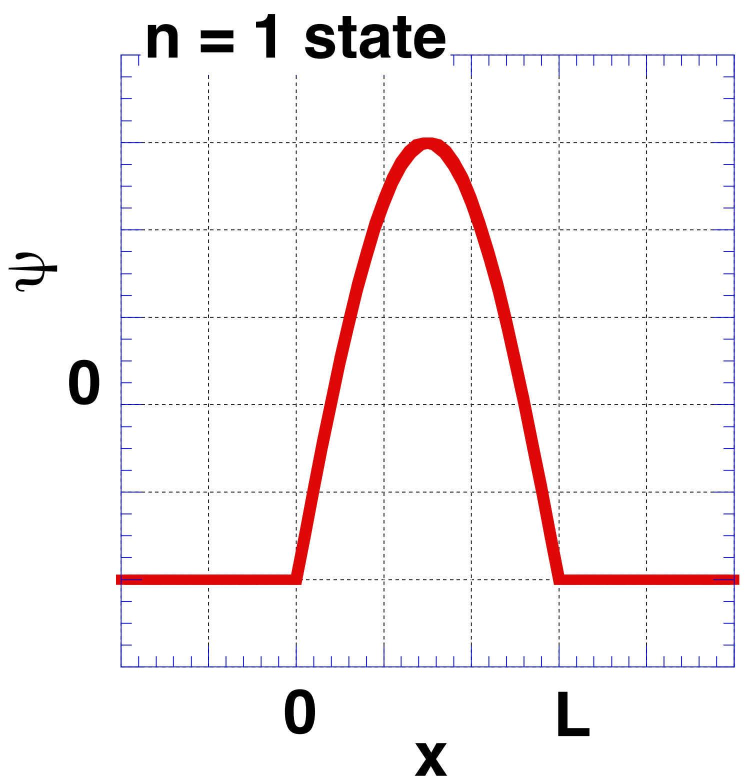
$$A' = \sqrt{\frac{2}{L}}$$

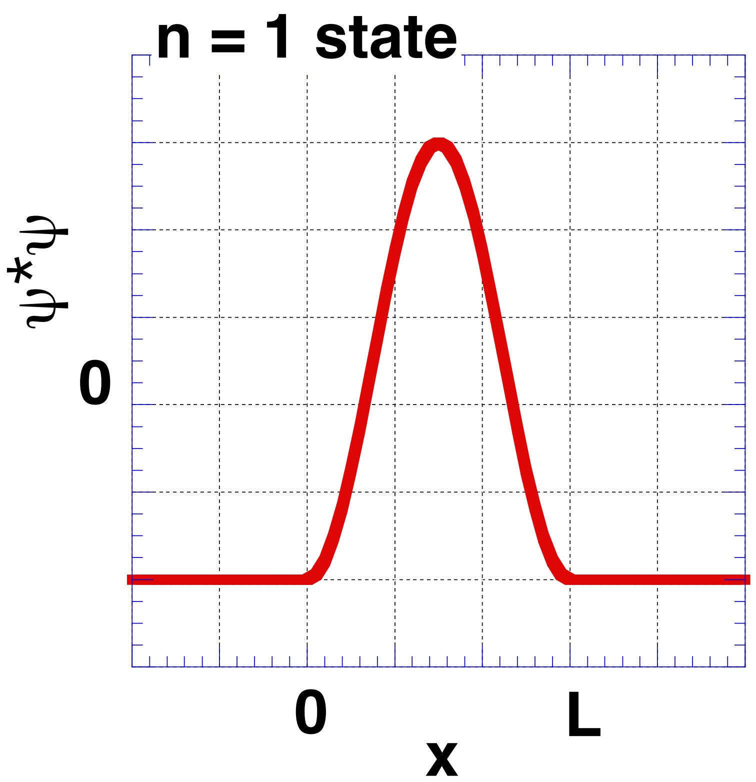
Same for all states.

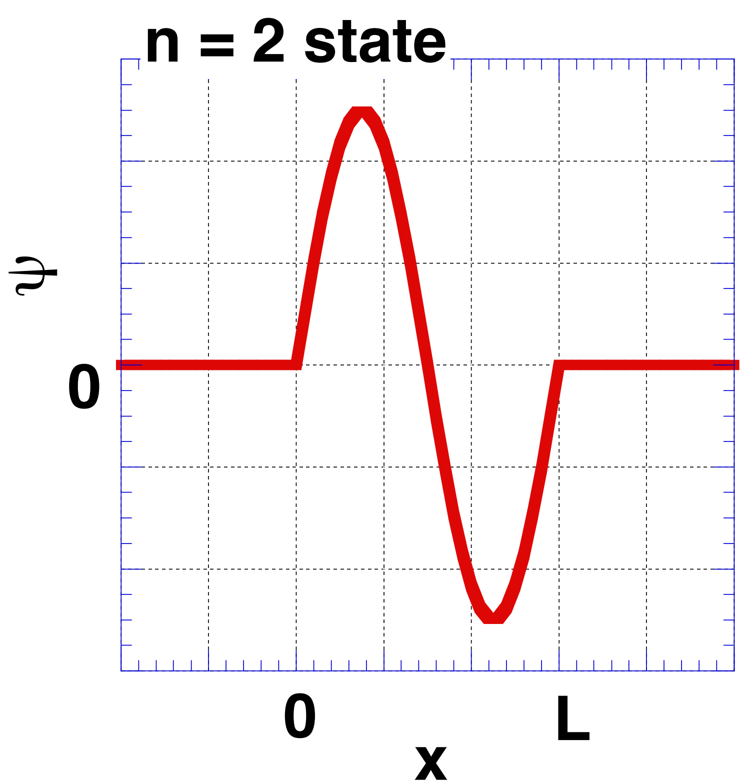
The probability function is then:

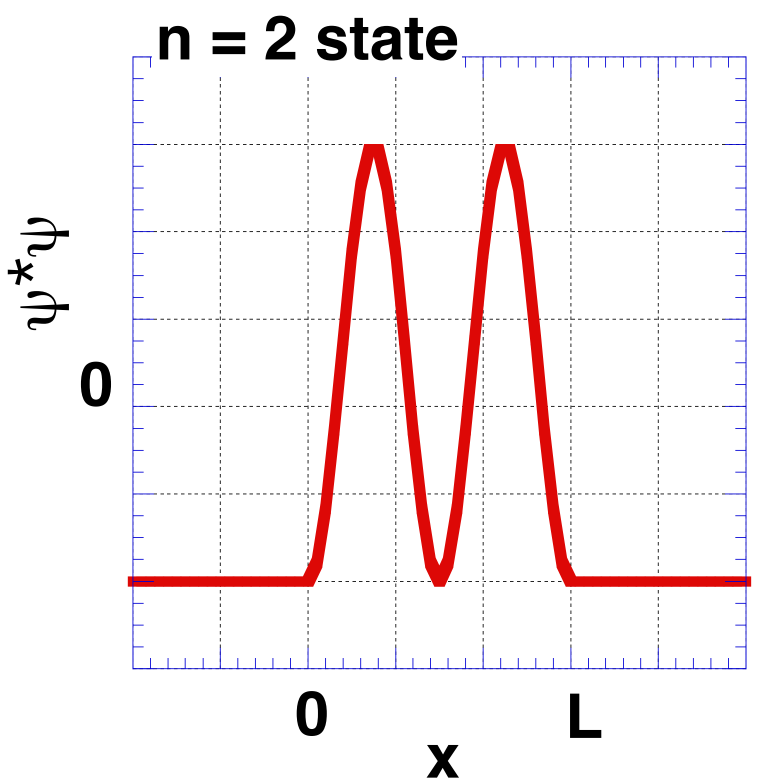
$$P_n(x) = \frac{2}{L} \sin^2(k_n x)$$

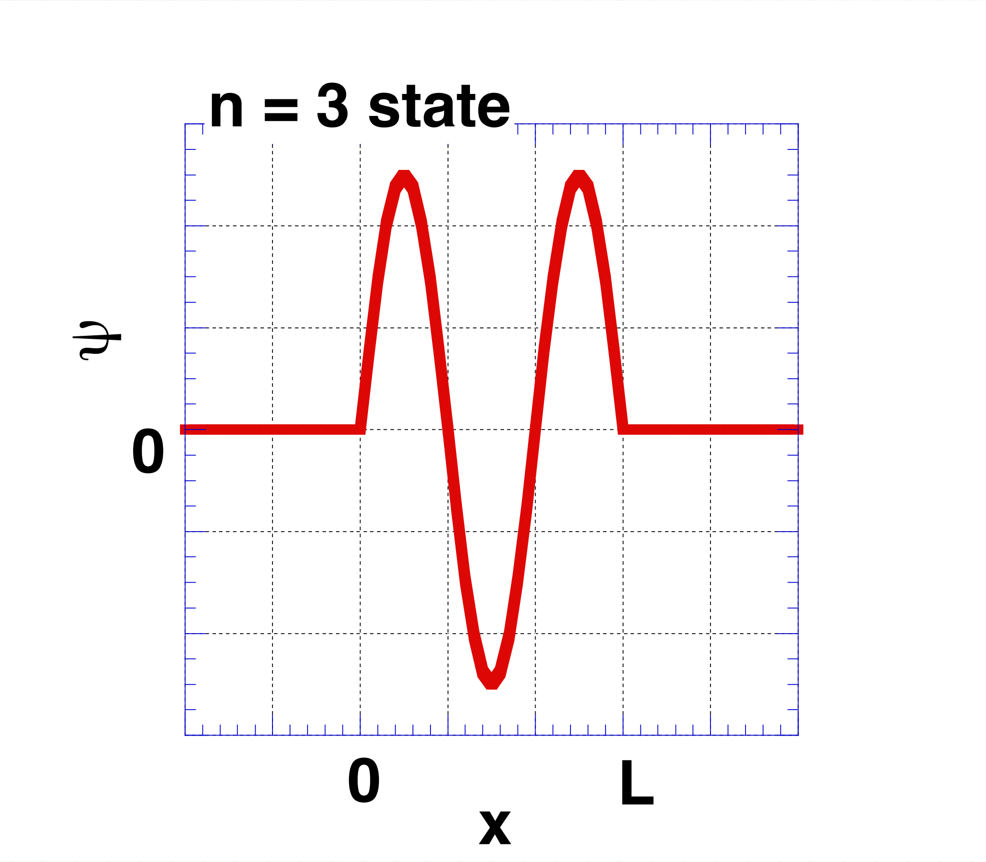
where we use the subscript to denote the *nth* state.

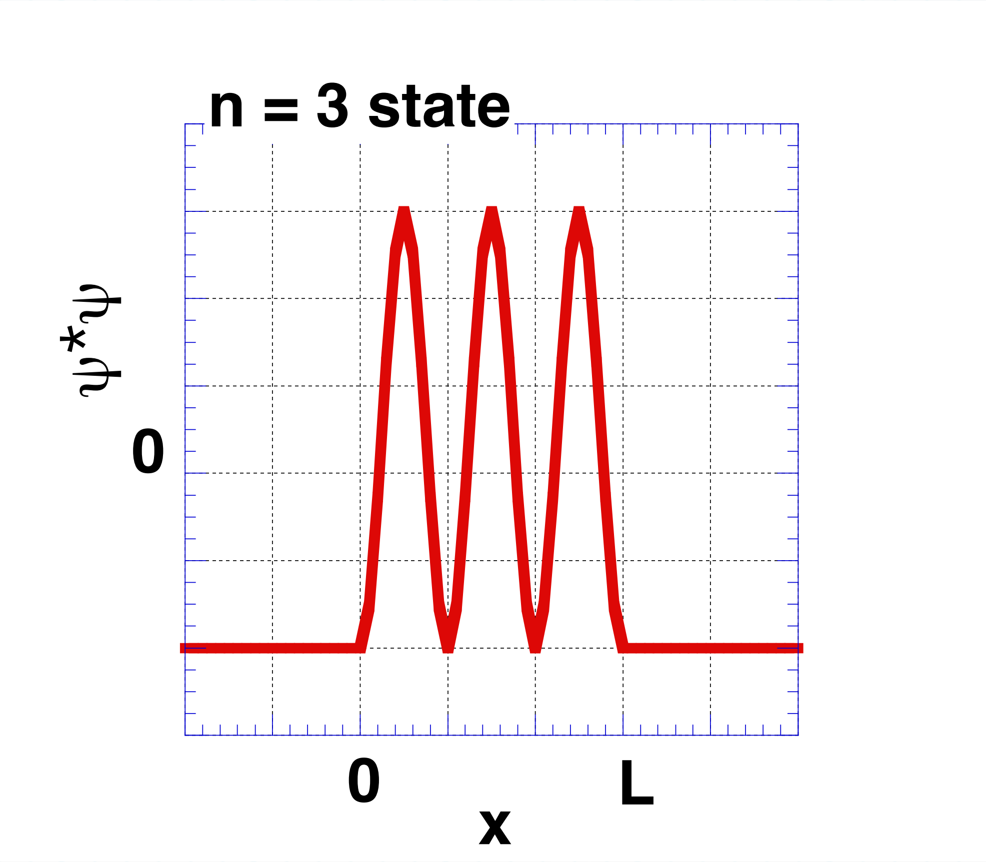

n = 1 state
ψ
0
0
L
x


n = 1 state
ψ*ψ
0
0
L
x


n = 2 state
ψ
0
0
L
x


n = 2 state
ψ*ψ
0
0
L
x





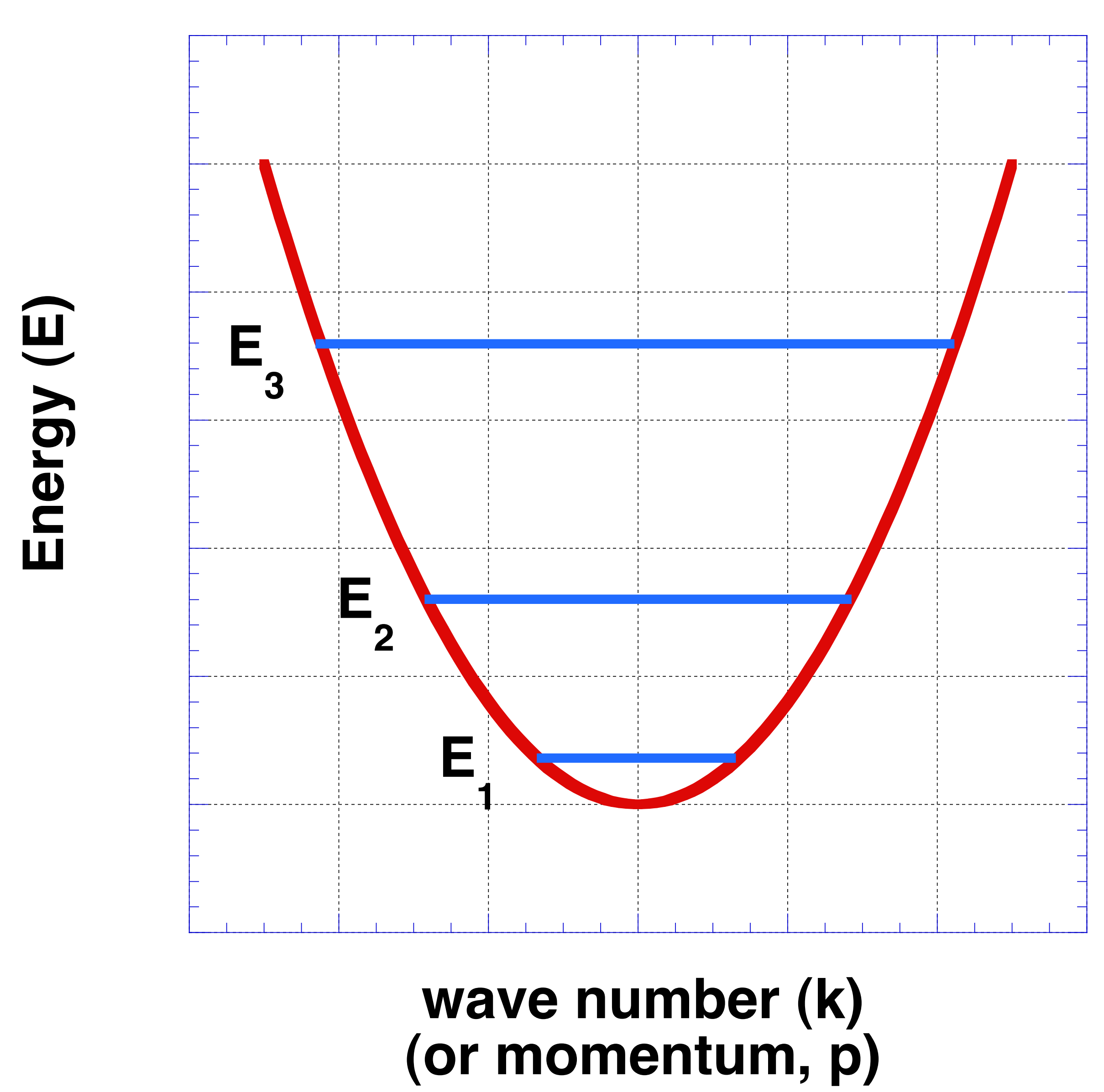
And this can go on and on…

Quantization is an interference effect

Why are only certain values of k (and hence E) allowed?

Consider the electron inside the well. It is a wave, bouncing back and forth between the barriers. As the wave rattles back and forth, it will interfere with itself.

If the interference is destructive, the wave cannot be sustained – it will cancel itself out. The only wave that can be sustained is one that adds constructively as it bounces back and forth. This leads directly to the requirement on k and the quantization of the energy.



$$2kL = n\,(2\pi)$$

$$k = n\left(\frac{\pi}{L}\right)$$

Anytime that we have a “confining” potential, we should expect “bound” states, and the energies will be quantized.

bound state: $\psi\left(x \rightarrow \pm\infty\right) = 0$

In the bound state problem, n is the “quantum number” which denotes the different different states.

Symmetry

Re-examine the probability density function plots (slides 9 & 10). Note that the functions are symmetric with respect to the center of the well.

$$P(\ L/2 + x\ ) = P(\ L/2 - x\ ) \qquad \text{(Mirror symmetry)}$$

The symmetry of the probability density follows from the symmetry of the potential energy function. In general, we expect to see the symmetry properties of the potential show up in the physical characteristics of the particle moving in the potential.

$$\psi^*\left(L/2 - x\right)\psi^*\left(L/2 - x\right) = \psi\left(L/2 + x\right)\psi\left(L/2 + x\right)$$

$$\psi\left(L/2 - x\right) = \pm\psi\left(L/2 + x\right)$$

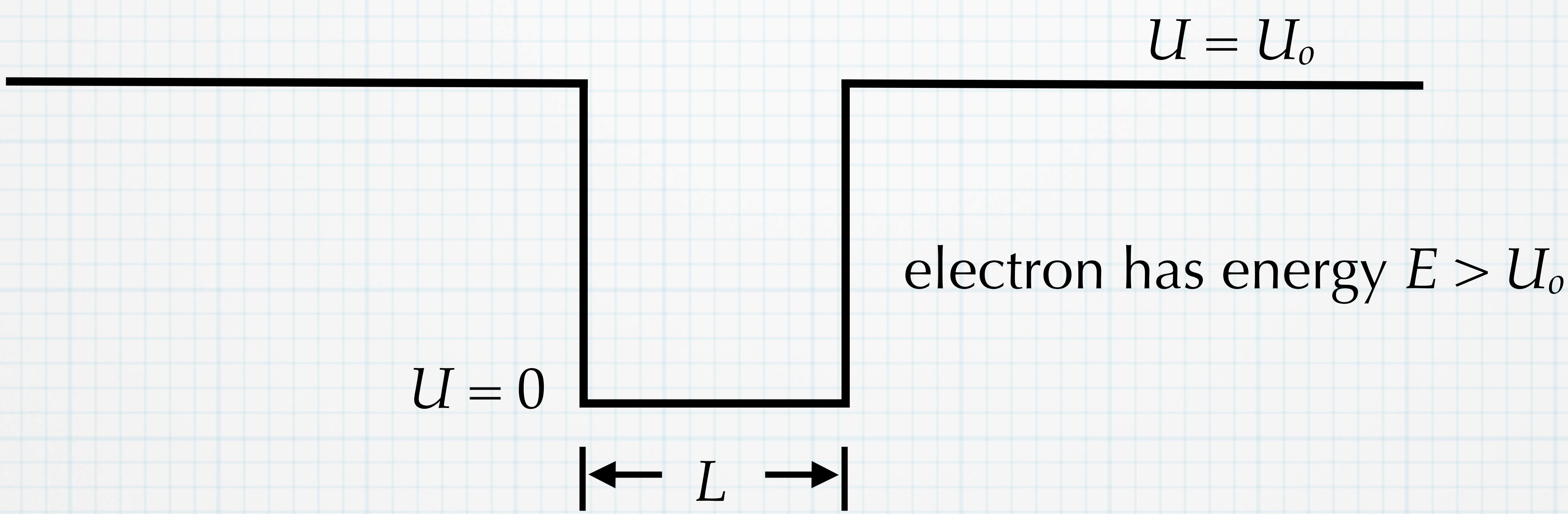
The wave function itself can be symmetric or anti-symmetric. Look back at the wave functions on slides 9&10 to see this.

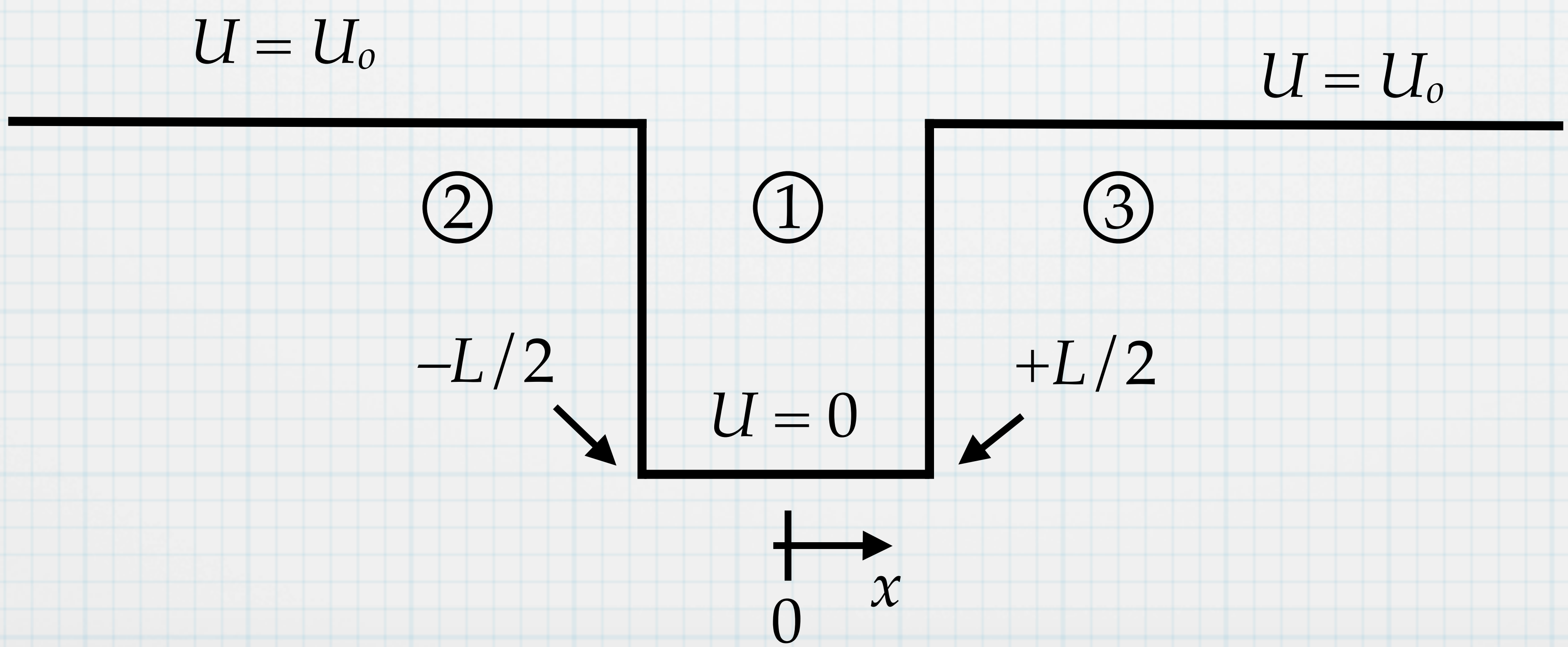
Use symmetry as a tool in helping to solve problems.

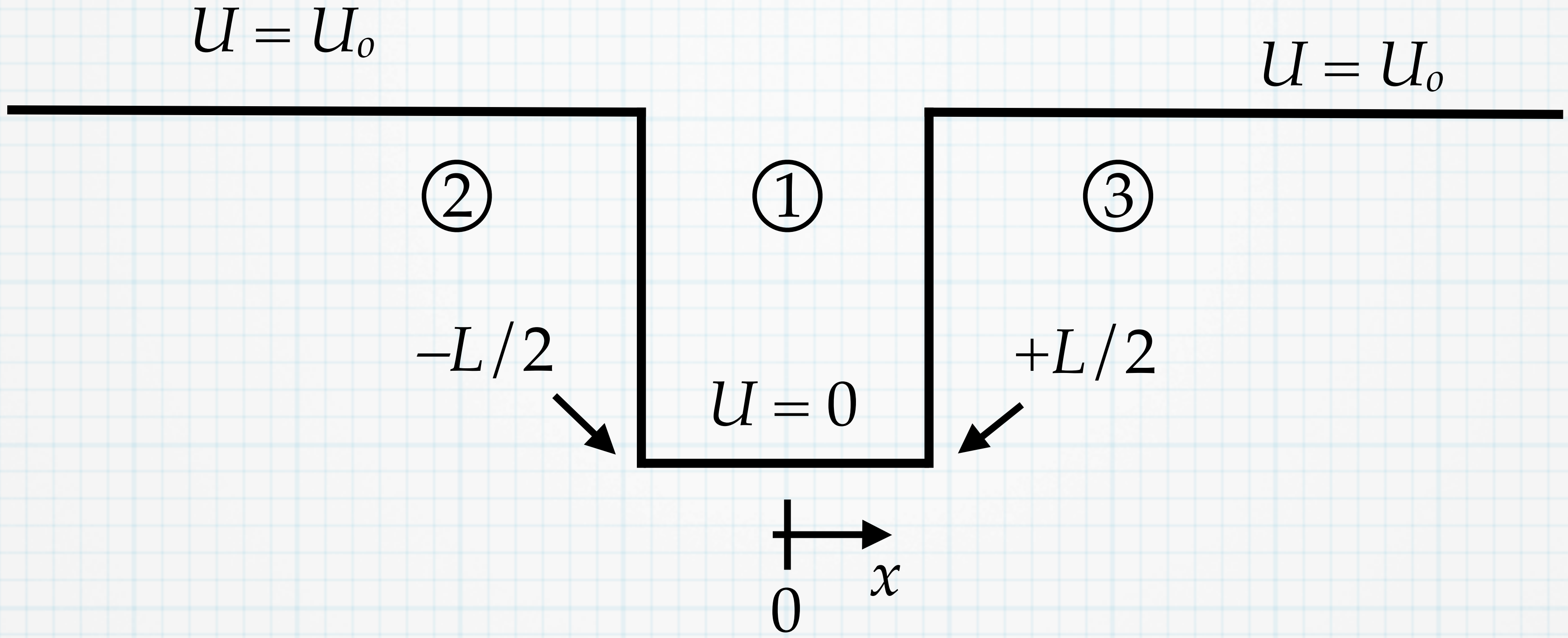
In this case, we might have considered putting $x = 0$ at the center of the well.

Finite height quantum well

Now let's consider the case of the finite well, where a potential region is confined by equal barriers an either side of height U_o.







① $\psi_1(x) = A'e^{ik_1x} + B'e^{-ik_1x}$ $\qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}} = k$

② $\psi_2(x) = C'e^{\alpha_2x} + D'e^{-\alpha_2x}$ $\qquad \alpha_2 = \alpha_3 = \sqrt{\frac{2m(U_o - E)}{\hbar^2}} = \alpha$

③ $\psi_3(x) = F'e^{\alpha_3x} + G'e^{-\alpha_3x}$

$D' = F' = 0$ Exponentials must remain finite for $x \to \pm\infty$

$C' = Ce^{\frac{\alpha L}{2}}$ $\qquad G' = Ge^{\frac{-\alpha L}{2}}$

① $\psi_1(x) = A' e^{ik_1 x} + B' e^{-ik_1 x}$

② $\psi_2(x) = C e^{\alpha\left(x + \frac{L}{2}\right)}$

③ $\psi_3(x) = G e^{-\alpha\left(x - \frac{L}{2}\right)}$

Now make use of symmetry. We expect the probability density to be symmetric, so the wave functions must be either symmetric or anti-symmetric.

symmetric: $\psi(-x) = \psi(x)$ — $G = C$ and $A' = B'$

$\psi_1(x) = A\cos(kx)$

anti-symmetric: $\psi(-x) = -\psi(x)$ — $G = -C$ and $A' = -B'$

$\psi_1(x) = A\sin(kx)$

symmetric (even):

① $\psi_1(x) = A\cos(kx)$

② $\psi_2(x) = Ce^{\alpha\left(x+\frac{L}{2}\right)}$

③ $\psi_3(x) = Ce^{-\alpha\left(x-\frac{L}{2}\right)}$

anti-symmetric (odd):

① $\psi_1(x) = A\sin(kx)$

② $\psi_2(x) = -Ce^{\alpha\left(x+\frac{L}{2}\right)}$

③ $\psi_3(x) = Ce^{-\alpha\left(x-\frac{L}{2}\right)}$

We will need to solve both cases.

The next step is to match boundary conditions. Then we can determine the allowed energies and the exact shape of the wave functions. Note that because of the symmetry, the information gained by matching boundary conditions at $x = +L/2$ will be exactly the same as what is learned from matching at $x = -L/2$. Meaning that we only need to match at one side.

Symmetric (even) case

$$\psi_1(L/2) = \psi_3(L/2) \longrightarrow A\cos\left(\frac{kL}{2}\right) = C$$

$$\left.\frac{\partial\psi_1(x)}{\partial x}\right|_{x=L/2} = \left.\frac{\partial\psi_3(x)}{\partial x}\right|_{x=L/2} \longrightarrow -Ak\sin\left(\frac{kL}{2}\right) = -\alpha C$$

The first step is to determine the allowed energies. We don't care that much about A and C yet. Take the coefficients out of the picture by dividing the second equation by the first.

$$k\tan\left(\frac{kL}{2}\right) = \alpha$$

This is the *characteristic equation* for the symmetric case. Since k and α both depend on E, we can solve this to find the allowed energy (energies).

$$k \tan\left(\frac{kL}{2}\right) = \alpha$$

Start by multiplying both sides by L/2.

$$\frac{kL}{2} \tan\left(\frac{kL}{2}\right) = \frac{\alpha L}{2}$$

Insert the expressions for k and α.

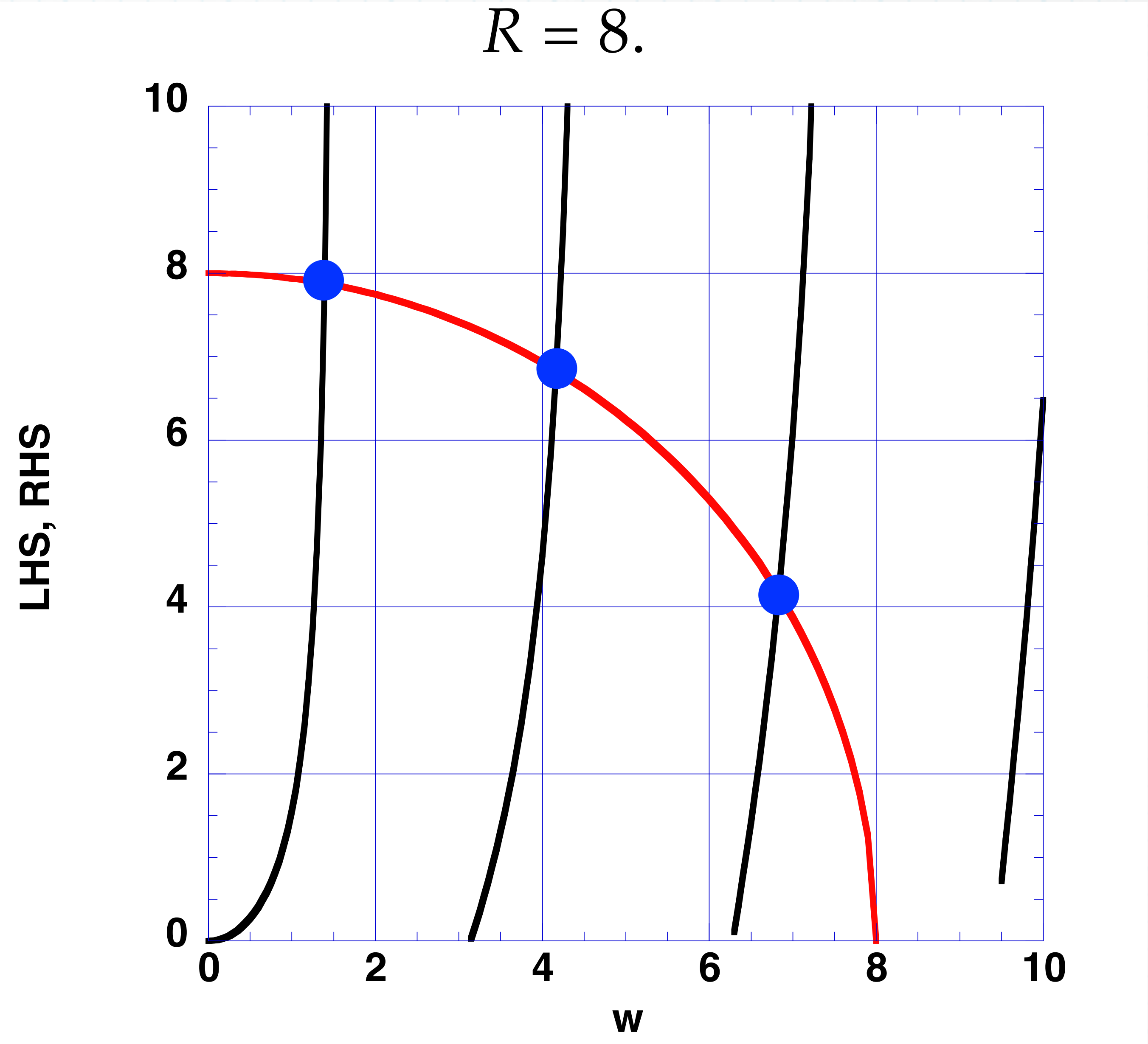
$$\sqrt{\frac{mU_o L^2}{2\hbar^2} - \frac{mEL^2}{2\hbar^2}} = \sqrt{\frac{mEL^2}{2\hbar^2}} \tan\left(\frac{mEL^2}{2\hbar^2}\right)$$

Messy. Use some *normalized* variables.

$$R^2 = \frac{mU_o L^2}{2\hbar^2} \qquad w^2 = \frac{mEL^2}{2\hbar^2} \qquad \sqrt{R^2 - w^2} = w \tan w$$

$$\sqrt{R^2 - w^2} = w \tan w$$

The LHS is the equation for a circle in the 1st quadrant. The RHS is a somewhat scaled version of the tangent function, with its multiple branches, etc. We can make a graph to help visualize what is going on and guide us toward a solution.



Plotting the LHS and RHS on the same set of axes shows the points of intersection, which correspond to the values of w that are solutions to the equation.

To finish up the even case, we need to find the actual values for the w's (and hence the E's) using a calculator or MATLAB (or similar). Although the graphical method is great for "seeing" the solutions, it is not an accurate method for getting the numbers. With R = 8, the three values of w are: 1.395, 4.165, and 6.831.

The values of w can be converted back to energies.

$$E = \frac{2\hbar^2 w^2}{mL^2}$$

If the well had L = 2 nm and U_o =2.44 eV (leading to R = 8), the energies of the even states are: E = 0.074 eV, 0.663 eV, and 1.782 eV.

At this point, we could go back and determine the exact value of A and C for each solutions. We can also normalize the wave functions, if needed.

Odd solutions

The approach for odd-symmetry states is nearly identical to the even-symmetry case, except that we look for states that have $\sin(kx)$ dependence inside the well.

① $$\psi_1(x) = A\sin(kx)$$

② $$\psi_2(x) = -Ce^{\alpha\left(x+\frac{L}{2}\right)}$$

③ $$\psi_3(x) = Ce^{-\alpha\left(x-\frac{L}{2}\right)}$$

Matching boundary conditions at $x = L/2$:

$$\psi_1(L/2) = \psi_3(L/2) \longrightarrow A\sin\left(\frac{kL}{2}\right) = C$$

$$\left.\frac{\partial\psi_1(x)}{\partial x}\right|_{x=L/2} = \left.\frac{\partial\psi_3(x)}{\partial x}\right|_{x=L/2} \longrightarrow Ak\cos\left(\frac{kL}{2}\right) = -\alpha C$$

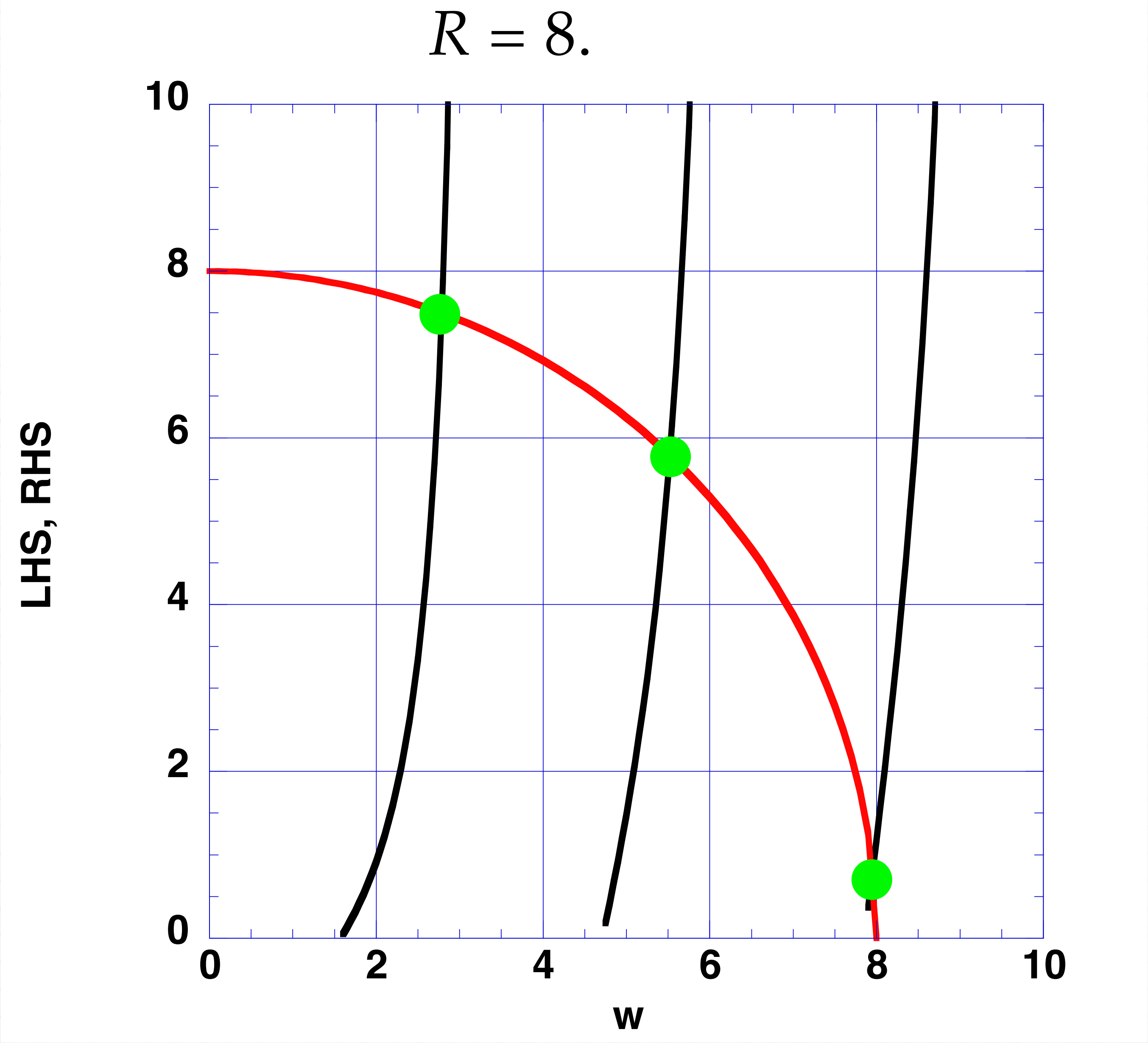
Dividing the first BC equation into the second gives the characteristic equation for the odd wave functions

$$k \cot\left(\frac{kL}{2}\right) = -\alpha$$

Taking the same mathematical steps as in the even case (multiply by $L/2$, insert expressions for k and α, use normalized variables) gives:

$$\sqrt{R^2 - w^2} = -w \cot w \qquad R^2 = \frac{mU_o L^2}{2\hbar^2} \qquad w^2 = \frac{mEL^2}{2\hbar^2}$$

$$\sqrt{R^2 - w^2} = -w \cot w$$



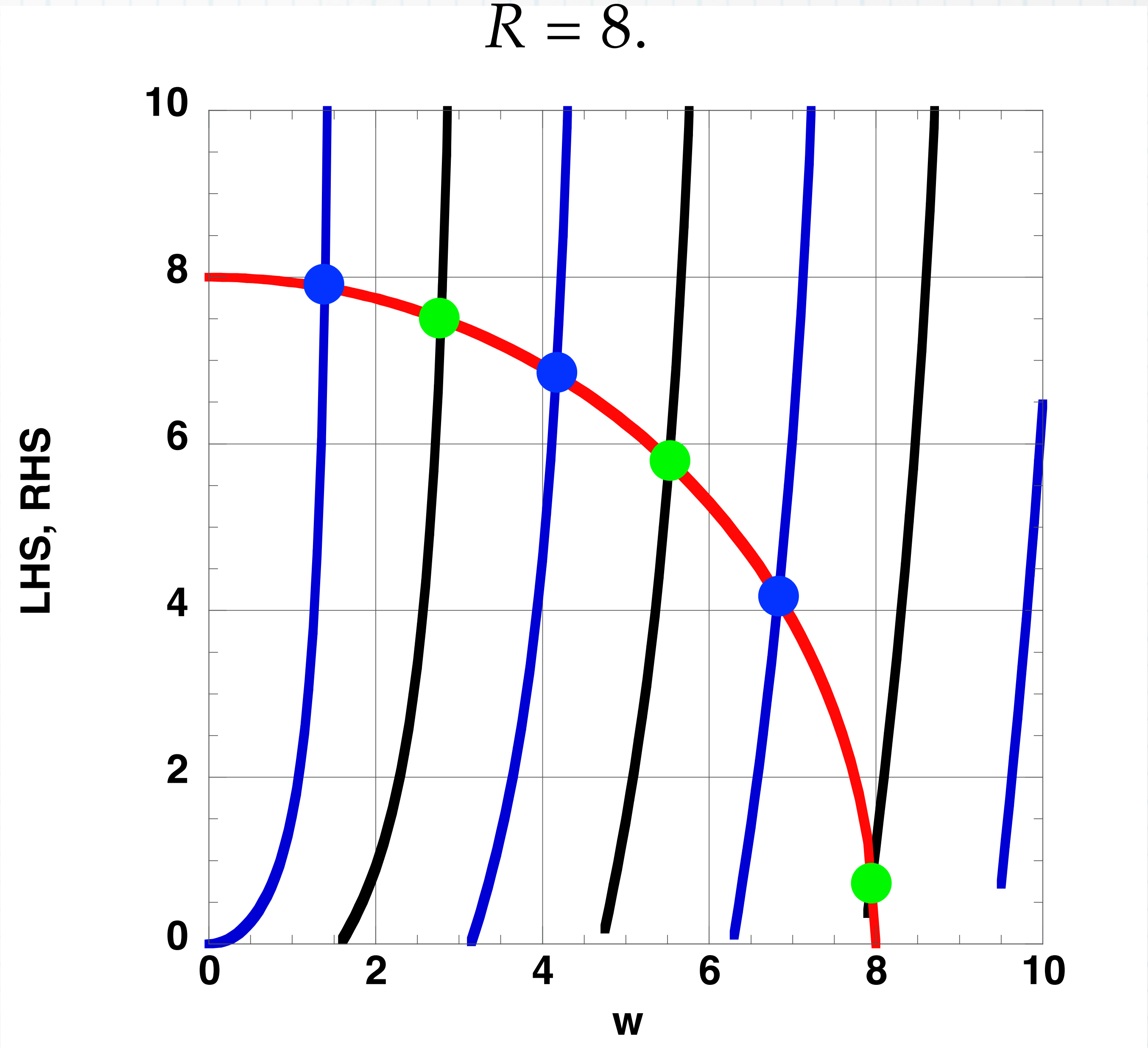
In the graph for the case of R = 8, we see that there are 3 odd-symmetry states.

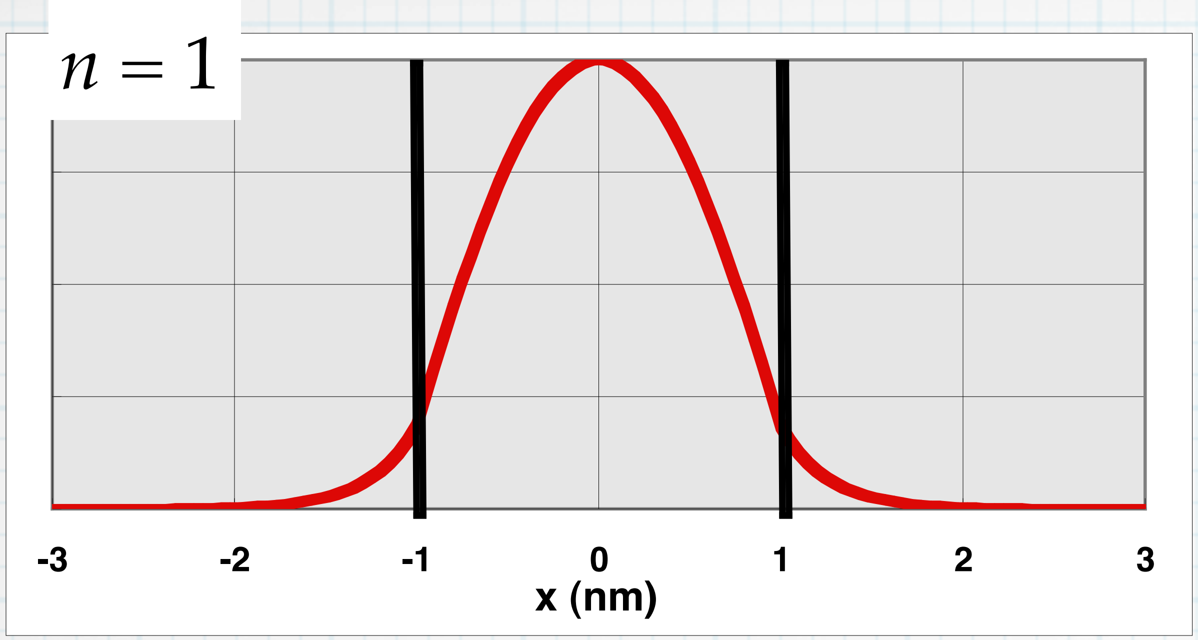
Working out the detailed numbers, we find that w = 2.786, 5.521, and 7.957. If L = 2 nm and U_o =2.44, the energies are 0.296 eV, 1.164 eV, and 2.417 eV. Note the highest level is nearly at the top of the barrier.

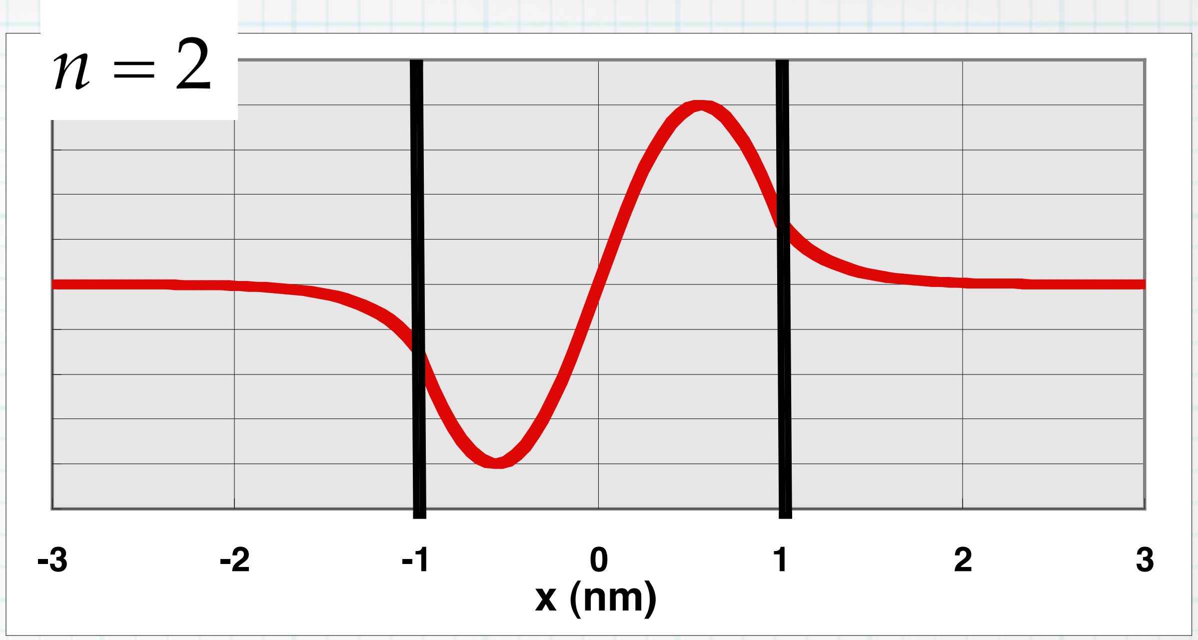
even	odd
0.074 eV	0.296 eV
0.663 eV	1.164 eV
1.782 eV	2.417 eV

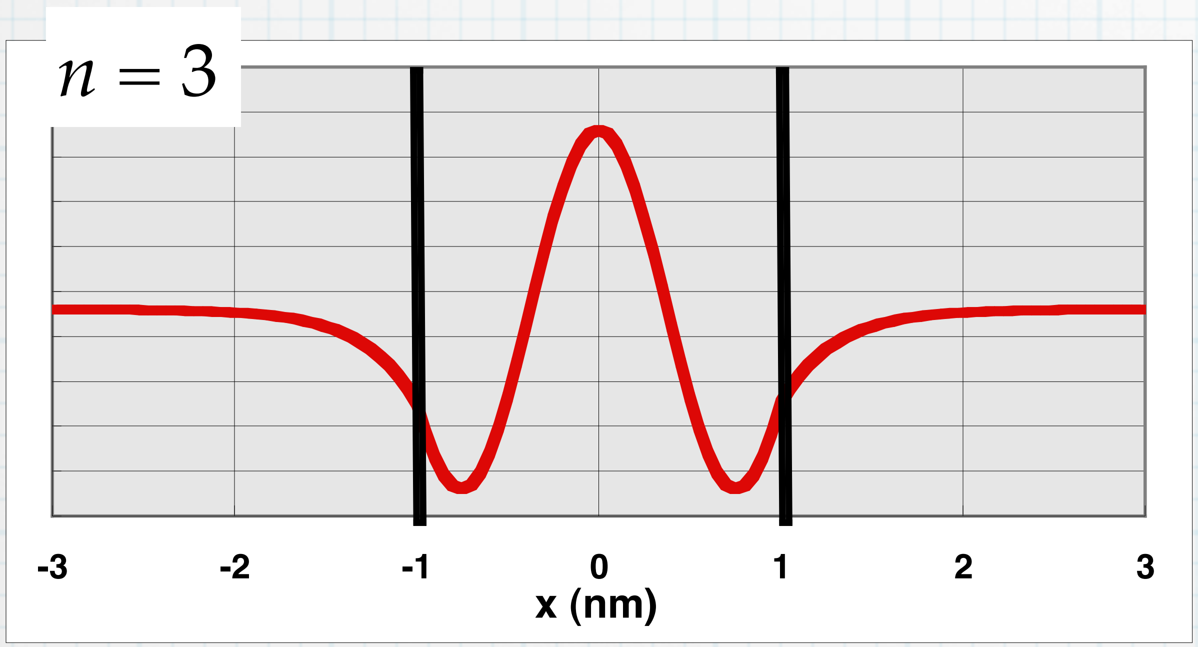
Note how the even and odd energies alternate. The lowest state is always even, and the states alternate between odd and even until the energy is over the top of the well.

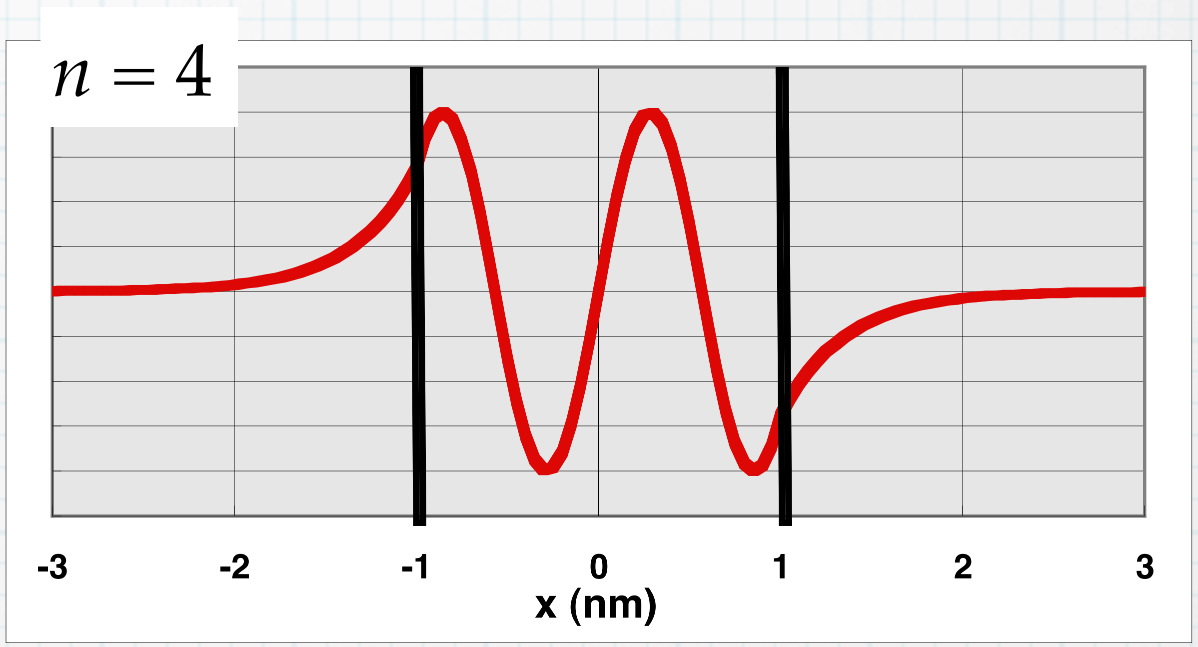
In fact, we can make a single plot for the two characteristic equations of the even and odd states. (In the plot, the blue branches correspond to even states and the black are odd.) The plot shows clearly the alternating nature of the even and odd states.

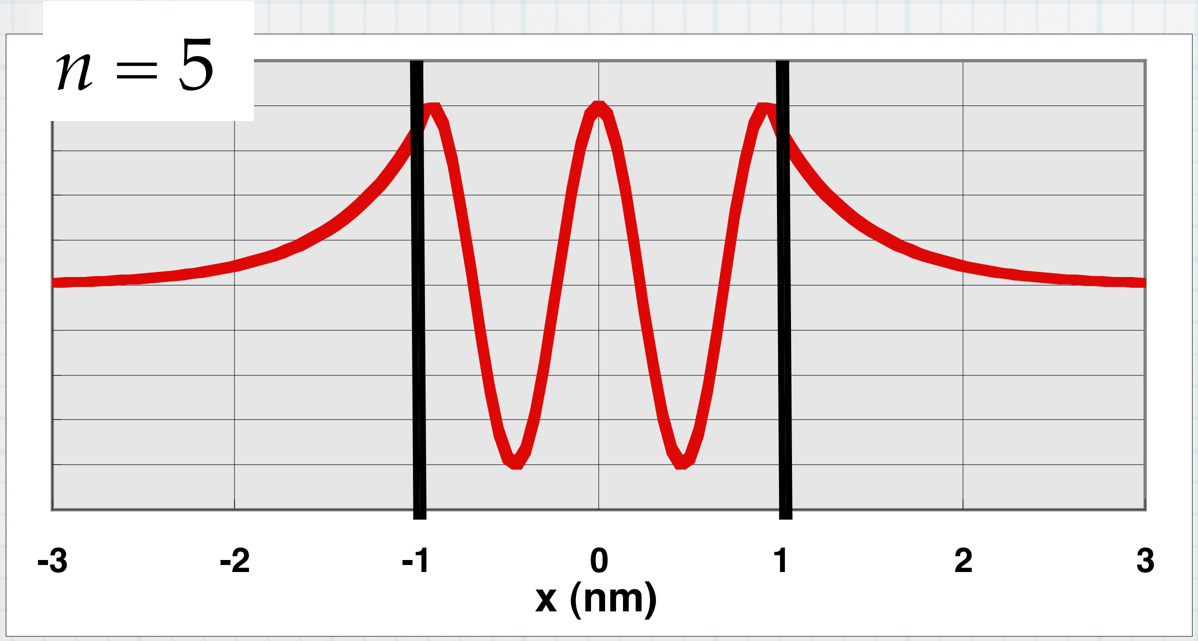


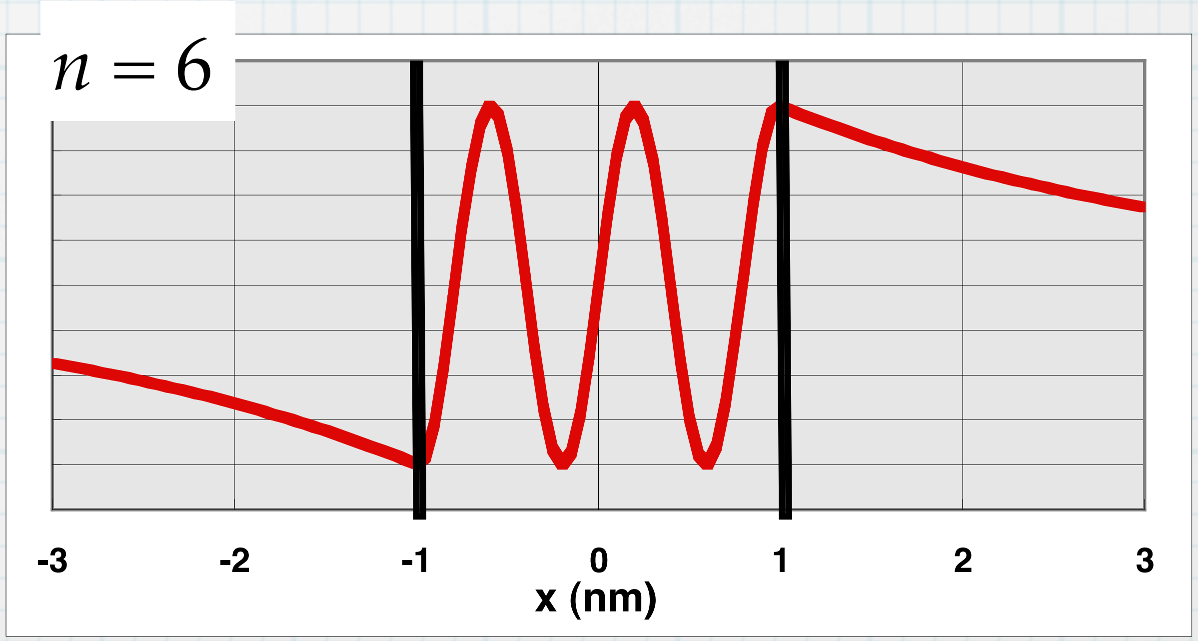

n = 1
-3
-2
-1
0
1
2
3
x (nm)


n = 2
-3
-2
-1
0
1
2
3
x (nm)


n = 3
-3
-2
-1
0
1
2
3
x (nm)


n = 4
-3
-2
-1
0
1
2
3
x (nm)


n = 5
-3
-2
-1
0
1
2
3
x (nm)


n = 6
-3
-2
-1
0
1
2
3
x (nm)