Finite Square Well Bound States

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Preliminaries

1. First, note that for the infinite square well (which we just completed), we placed the well in the region $0 < x < L$, but the physics of the situation would be the same regardless of where we put it. Pictures of the wavefunctions would look identical, the energies would be the same, the standard deviations, Δx and Δp would be the same (of course, $< x >$ and $< x^2 >$ would be different).
   It is often convenient to put $x = 0$ at the symmetry point of a potential energy function. Then, in our case, the well extends $-L/2 < x < L/2$. We then can "phase shift" the sinusoidal wavefunctions to write
   $$\psi_n(x) = \sqrt{\frac{2}{L}} \begin{cases} \cos k_n x, \ n \text{ odd} \\ \sin k_n x, n \text{ even} \end{cases}$$
   with $k_n = \frac{\pi}{a}n$, as before. These functions do exactly what the simple, $\sin k_n x$ functions did previously (students should verify that the same shapes are obtained and the boundary conditions are satisfied). One advantage here is that these functions clearly show a symmetry property: Since $V(x) = V(-x)$, we expect that $P(x) = P(-x)$ and this requires (for real wavefunctions) that
   $$\boxed{\psi_n(x) = \pm\psi_n(-x).}$$
   The cosine functions are symmetric while the sines are antisymmetric about $x = 0$. This *parity* property of the wavefunctions can be impose whenever the potential energy is symmetric about the origin. This observation can save considerable algebra in future work!
2. For the infinite square well, we solved the time independent equation in the region where $V(x)$ was analytic (inside the well, not including the infinite walls) and then applied a physically intuitive boundary condition: the probability of finding the particle at a point with infinite potential energy should be zero. This boundary condition gave rise to the discrete spectrum of energies and associated wavefunctions for the trapped particle's stationary states.
3. For a finite square well (pictured below), the situation is not so clear.
4. We will again solve the time independent equation in regions where $V(x)$ is analytic (in this case, again constant) and will again have to impose boundary conditions that mathematically match up the solutions so that they have the correct behavior at the steps. This will again give rise to a discrete set of energy eigenvalues for bound particles.
5. We will find that "following the math" in this way leads to some very non-intuitive behavior! But this strange, non-classical behavior is verified in real systems and gives rise to, for example, the scanning tunneling microscope and alpha decay of some radioactive nuclei.
6. To get started, let's think about the solutions to the Schrodinger equation in the presence of a constant potential energy, V_0, and consider two possible situations: $E >$

V_0 (which makes sense classically) and $E < V_0$ (which does not make sense classically since we normally think that $K = E - V_0$ and this condition would correspond to a negative kinetic energy...but we proceed).

7. Solving the Schrodinger equation for the wavefunction curvature, $\psi''(x) = d^2\psi/dx^2$, we have

$$\psi'' = -\frac{2m}{\hbar^2}\,(E - V_0)\;\psi(x).$$

In the classically allowed case, $E > V_0$ (positive kinetic energy), we see that the sign of the curvature is opposite to that of the wavefunction – this leads to oscillatory behavior (sketch a few cases for yourself). On the other hand, where $E < V_0$ (negative kinetic energy?), which is a case never encountered in a classical system, the wavefunction and the curvature have the same sign which implies that the function curves away from the x-axis and will tend to diverge in general if the relevant region where this happens extends to infinity in x. This is what happens in the finite square well for bound states; we have $E < V_0$ for bound states, where V_0 is the barrier height, so in the regions $|x| > a/2$, the potential energy is higher than the total energy. Note that in the region $|x| < a/2$, the potential energy is zero and we expect oscillatory behavior just like in the infinite well case. We will have to impose a boundary condition on our solutions that requires the wavefunction to remain finite; the only way to do this is to have $\lim_{|x|\to\infty} \psi(x) = 0$. This requirement should be clear since we cannot find that the probability for finding the particle in a classically disallowed region is large.

8. The situation at $x = \pm a/2$: Given the curvature arguments above, it is clear that the curvature undergoes a discontinuity at $x = \pm a/2$. In order for this to happen, the curvature must be defined and this requires that the function and first derivative must be continuous. We therefore require that, for example at $x = +a/2$,

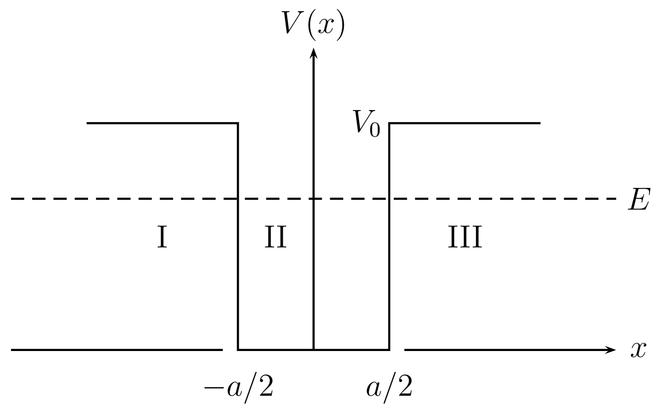
$$\boxed{\psi_{II}(a/2) = \psi_{III}(a/2)}$$

and that

$$\boxed{\left.\frac{d\psi_{II}}{dx}\right|_{x=a/2} = \left.\frac{d\psi_{III}}{dx}\right|_{x=a/2}}$$

With a similar statement at $x = -a/2$ (but if we apply the parity property to the wavefunction, one procedure is sufficient to impose the condition in both cases).

The solution. Consider a particle of mass m in a finite depth potential well as shown below; we wish to consider bound states for which $E < V_0$.



By using the symmetry of the potential energy, we can write the wavefunction as

$$\psi_I(x) = \pm A e^{\alpha x}, \; x < -a/2 \tag{1}$$
$$\psi_{II}(x) = B\cos kx \text{ or } C\sin kx, \; -a/2 < x < a/2 \tag{2}$$
$$\psi_{III}(x) = A e^{-\alpha x}, \; x > a/2 \tag{3}$$

where in the first equation, we use the + to go with the cosine and the − with the sine and

$$\alpha^2 = \frac{2m}{\hbar^2}(V_0 - E) \tag{4}$$
$$k^2 = \frac{2m}{\hbar^2}E. \tag{5}$$

We've already imposed the boundary condition that the wavefunction must remain finite at all x: only the appropriate exponential terms are included in the outside regions.

Even functions: We apply the boundary conditions at $x = +a/2$ and $x = -a/2$ to obtain four equations:

$$Ae^{-\alpha a/2} = B\cos ka/2 \tag{6}$$
$$\alpha Ae^{-\alpha a/2} = +Bk\sin ka/2 \tag{7}$$
$$Ae^{-\alpha a/2} = B\cos ka/2 \tag{8}$$
$$\alpha Ae^{-\alpha a/2} = +Bk\sin ka/2. \tag{9}$$

Because of our use of symmetry, the conditions at $x = \pm a/2$ are the same – we don't really need both. In addition, we only have two unknown coefficients, so four independent equations wouldn't make sense anyway.

The two boundary conditions, say, (6) and (7), can be regarded as two homogeneous equations in A and B. In order to have a solution other than $A = B = 0$, we require the determinant of the coefficients to be zero. This puts a constraint on α and k – i.e., on the energy, E. Only special values of E will allow solutions.

One can either compute the determinant or solve each equation for A/B. Doing the latter leads to

$$\frac{A}{B} = e^{\alpha a/2}\ \cos ka/2 = \frac{k}{\alpha} e^{\alpha a/2}\ \sin ka/2. \tag{10}$$

or, using the second equality,

$$k \tan ka/2 = \alpha \tag{11}$$

which we write as

$$\xi \tan \xi = \eta, \tag{12}$$

with $\xi = ka/2$ and $\eta = \alpha a/2$. For a given potential energy with given V_0 and a, (11) or (12) express the condition on E required for a solution of the Schrodinger equation satisfying the "smoothness" boundary conditions.

Odd functions. The boundary conditions here are

$$Ae^{-\alpha a/2} = -C \sin ka/2 \tag{13}$$

$$\alpha A e^{-\alpha a/2} = Ck \cos ka/2, \tag{14}$$

which can be solved as before for A/C to yield

$$-k \cot ka/2 = \alpha \tag{15}$$

$$-\xi \cot \xi = \eta. \tag{16}$$

Graphical solutions. Equations 12 and 16 must be solved numerically. Here is a graphical approach. The first thing to do before getting into numerics is to simplify the equations by putting them into dimensionless variable forms. Doing this algebra up front will be rewarded by having simple forms in the plots that are more transparent to interpret.

First, we scale the energy to units of V_0 by defining $\epsilon = E/V_0$. For bound states, $0 \le \epsilon \le 1$. Note that $\xi = ka/2 = \sqrt{\frac{2m}{\hbar^2}E}\ a/2 = \sqrt{\frac{ma^2}{2\hbar^2}E}$; we let $\epsilon_0 = \frac{ma^2}{2\hbar^2}V_0$, so that we get $\xi = (\epsilon_0\epsilon)^{1/2}$ by multiplying and dividing by V_0. Similarly, we can write $\eta = [\epsilon_0(1-\epsilon)]^{1/2}$. For even functions, we need to solve

$$(\epsilon_0\epsilon)^{1/2} \tan[(\epsilon_0\epsilon)^{1/2}] = [\epsilon_0(1-\epsilon)]^{1/2} \tag{17}$$

and for odd functions,

$$-(\epsilon_0\epsilon)^{1/2} \cot[(\epsilon_0\epsilon)^{1/2}] = [\epsilon_0(1-\epsilon)]^{1/2}. \tag{18}$$

The factor of $\epsilon_0^{1/2}$ can be canceled and we have for even functions,

$$\epsilon^{1/2} \tan[(\epsilon_0\epsilon)^{1/2}] = (1-\epsilon)^{1/2} \tag{19}$$

and for odd functions,

$$-\epsilon^{1/2} \cot[(\epsilon_0\epsilon)^{1/2}] = (1-\epsilon)^{1/2}. \tag{20}$$

ϵ_0 depends on the shape of the well: the depth, V_0, and the width, a, through the product, V_0a^2. This parameter sets the "strength" of the well and the number of bound states. As

ϵ_0 increases, the trig functions go through more and more cycles as ϵ goes from 0 to 1; this leads to more and more solutions to the above equations and hence more and more bound states.

The plots on the following page show, for selected values of ϵ_0, the graphical solution of equations (19) and (20). The horizontal axis is $\epsilon = E/V_0$, the scaled energy which extends from 0 (the bottom of the well) to 1 (the top of the well). The vertical axes show the left and right sides of the equations with the right side (which is the same for even and odd cases) in blue and the left side of (19) in green and the left side of (20) in red. Wherever the left and right sides are equal (i.e., the curves cross), the boundary conditions on the wavefunction are satisfied and we have a solution to the time independent Schrodinger equation.

As ϵ_0 increases, the tangent and cotangent functions vary more rapidly with ϵ and solutions move to lower energy while at the same time, new solutions pop into existence near the top of the energy scale. Again, note that at least one solution exists for any ϵ_0 – this only occurs in the one dimensional case.

Questions: You should be able to sketch the first few wavefunctions: if we label the solutions with $n = 1, 2, 3, ...$, how many zero crossings exist for each? What happens to the exponential decay length outside of $\pm a/2$ as we go up in n? What would a wavefunction with E slightly larger than V_0 look like?

If instead of a graphical solution you want to solve the problem on numerically, how would you search for solutions? How would you know when you have obtained all solutions for a particular value of ϵ_0?

$$\epsilon_0 = \frac{ma^2}{2\hbar^2} V_0$$