Finite Square Well

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1 Solving Schroedinger's Equation for the Finite Square Well

Consider the following piecewise continuous, finite potential energy:

$$U = U_0 \qquad x < 0, \tag{1}$$
$$U = 0 \qquad 0 \leqslant x \leqslant L \tag{2}$$
$$U = U_0 \qquad L < x. \tag{3}$$

We want to solve Schroedinger's Equation for this potential to get the wavefunctions and allowed energies for $E < U_0$. I will refer to the three regions as regions 0, 1, and 2 with associated wavefunctions ψ_0, ψ_1, ψ_2.

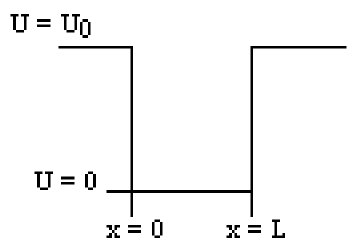

Figure 1: Finite Square Well Potential Energy

The time-invarient, non-relativistic Schroedinger's equation is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = E\psi \tag{4}$$

that can be rearranged to give

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(U - E)\psi \tag{5}$$

It is convenient to define two new variables (both positive), one for regions 0 and 2, and one for region 1—they are wavenumbers:

$$\kappa_0^2 = \frac{2m}{\hbar^2}(U_0 - E) \tag{6}$$

$$k_1^2 = \frac{2m}{\hbar^2}E \tag{7}$$

and Schroedinger's equation becomes

$$\frac{d^2\psi_{0,2}}{dx^2} = \kappa_0^2\psi_{0,2} \qquad x < 0 \; or \; L < x \tag{8}$$

and

$$\frac{d^2\psi_1}{dx^2} = -k_1^2\psi_1 \qquad 0 < x < L \tag{9}$$

In regions 0 and 2 the general solution is a linear combination of exponentials with the same form, but with different constants, namely

$$\psi_0 = A\exp(-\kappa_0 x) + B\exp(+\kappa_0 x) \qquad x < 0 \tag{10}$$

$$\psi_2 = F\exp(-\kappa_0 x) + G\exp(+\kappa_0 x) \qquad L < x \tag{11}$$

In region 1 we have the same general solution that we had for the infinite square well,

$$\psi_1 = C\sin(k_1 x) + D\cos(k_1 x) \qquad 0 < x < L \tag{12}$$

Equations (10) to (12) have 7 unknowns—A, B, C, D, F, G and the energy E that is implicitly contained in the variables κ_0, k_1. Therefore we need to get 7 equations to be able to solve for the unknowns.

We will first use the requirement that the wavefunction remain finite everywhere. Consider ψ_2 as $x \to \infty$. For this to remain finite we must require $G = 0$. Similarly, as $x \to -\infty$, we require $A = 0$. Our solutions become

$$\psi_0 = B\exp(+\kappa_0 x) \qquad x < 0 \tag{13}$$

$$\psi_2 = F\exp(-\kappa_0 x) \qquad L < x \tag{14}$$

The next step is to require that the wavefunction and its first derivative be continuous everywhere, and in our case we look at the boundaries, $x = 0$ and $x = L$.

$$\psi_0(0) = \psi_1(0)$$

$$B = D \tag{15}$$

hence $\psi_0 = D\exp(+\kappa_0 x)$.

Take derivatives of the wavefunctions,

$$\frac{d\psi_0}{dx} = \kappa_0 D\exp(\kappa_0 x) \tag{16}$$
$$\frac{d\psi_1}{dx} = k_1 C\cos(k_1 x) - k_1 D\sin(k_1 x) \tag{17}$$
$$\frac{d\psi_2}{dx} = -\kappa_0 F\exp(-\kappa_0 x) \tag{18}$$

and at $x = 0$ we get

$$\begin{aligned}\frac{\psi_0}{dx}(0) &= \frac{d\psi_1}{dx}(0)\\ \kappa_0 D &= k_1 C\end{aligned} \tag{19}$$

So

$$\psi_1 = \frac{\kappa_0}{k_1}D\sin(k_1 x) + D\cos(k_1 x) \tag{20}$$
$$\frac{d\psi_1}{dx} = \kappa_0 D\cos(k_1 x) - k_1 D\sin(k_1 x) \tag{21}$$

There remain 3 unknowns, D, F, and E. Finding them is a bit messier! Consider the boundary conditions at $x = L$,

$$\begin{aligned}\psi_1(L) &= \psi_2(L)\\ \frac{\kappa_0}{k_1}D\sin(k_1 L) + D\cos(k_1 L) &= F\exp(-\kappa_0 L)\end{aligned} \tag{22}$$

$$\begin{aligned}\frac{d\psi_1}{dx}(L) &= \frac{d\psi_2}{dx}(L)\\ \kappa_0 D\cos(k_1 L) - k_1 D\sin(k_1 L) &= -\kappa_0 F\exp(-\kappa_0 L)\end{aligned} \tag{23}$$

We are not going much farther, but if we divided Equation (22) by Equation (23), we can see that the constants D and F cancel leaving us with one rather ugly equation to solve for energy E (remember this is implicitly included in the values of k_1 and κ_0.) The solution must be done numerically, and is left for other courses. At the end of this document the next steps are shown.

How can we get the remaining constants? There is one remaining condition, normalization, that for this problem is

$$\int_{-\infty}^{0}\psi_0^2\,dx + \int_0^L \psi_1^2\,dx + \int_L^\infty \psi_2^2\,dx = 1 \tag{24}$$

Even without solving the entire problem we can make some conclusions about the wavefunction and the allowed energy levels. Recall that for an infinite square well potential of width L the allowed energies are quantized and

$$E_n^\infty = n^2 \frac{\hbar^2 \pi^2}{2mL^2} \tag{25}$$

with n being any positive integer. Outside the well the wavefunction is 0. We are certain that the particle is somewhere inside the box, so $\Delta x^\infty = L$.

With the finite well, the wavefunction is not zero outside the well, so $\Delta x^{finite} > L$, hence from the uncertainty principle, $\Delta p_x^{finite} < \Delta p_x^\infty$. This suggests that the average value of momentum is less for the finite well, and therefore that the kinetic energy inside the well is less for the finite well than for the infinite well. Indeed this is borne out with detailed analysis. In addition, the number of allowed energy levels is finite, and there is a possibility that a well may be sufficiently narrow or sufficiently shallow that no energy levels are allowed.

Also note that the non-zero wavefunctions in regions 0 and 2 mean that there is a non-zero probability of finding the particle in a region that is classically forbidden, a region where the the total energy is less than the potential energy so that the kinetic energy is negative. We will have more to say about this later when we discuss quantum mechanical tunneling.

2 More of the solution

Just in case you want to see more, I'll do some. Here is $\frac{Equation(22)}{Equation(23)}$

$$\begin{aligned}
\frac{\frac{\kappa_0}{k_1} D \sin(k_1 L) + D \cos(k_1 L)}{\kappa_0 D \cos(k_1 L) - k_1 D \sin(k_1 L)} &= \frac{F \exp(-\kappa_0 L)}{-\kappa_0 F \exp(-\kappa_0 L)} \\
\frac{\kappa_0 \sin(k_1 L) + k_1 \cos(k_1 L)}{\kappa_0 k_1 \cos(k_1 L) - k_1^2 \sin(k_1 L)} &= \frac{1}{-\kappa_0} \\
\kappa_0^2 \sin(k_1 L) + \kappa_0 k_1 \cos(k_1 L) &= -\kappa_0 k_1 \cos(k_1 L) + k_1^2 \sin(k_1 L) \\
\kappa_0^2 \tan(k_1 L) + \kappa_0 k_1 &= -\kappa_0 k_1 + k_1^2 \tan(k_1 L) \\
2\kappa_0 k_1 &= (k_1^2 - \kappa_0^2) \tan(k_1 L) \qquad (26)
\end{aligned}$$

Now put in the values of κ_0 and k_1 from Equations (6) and (7) and do some algebra to get

$$2\sqrt{(U_0 - E)E} = (2E - U_0) \tan\left(\sqrt{\frac{2mEL^2}{\hbar^2}}\right) \tag{27}$$

This equation is a single equation in a single unknown, $E < U_0$. Once we have the details of our particle (its mass) and the potential energy (depth U_0 and width L), we can solve it. There is no analytic solution, only a numerical one.

Consider an electron in a finite well 0.5 nm wide and 25 eV deep. Energy levels for the finite well are compared to an equal-width infinite well in the table below. Notice that the energies for the finite well are less than the corresponding energies for the infinite well, and that the difference becomes greater as the energy nears the well depth. The finite well has only 5 "bound states."

I had Excel so here is what I did. I made one column of energy in steps of 0.1 eV from 0.1 to 25 eV. Then I made a column for

$$LHS = \frac{2\sqrt{(U_0 - E)E}}{(2E - U_0)} \tag{28}$$

and a column for

$$RHS = \tan\left(\sqrt{\frac{2mEL^2}{\hbar^2}}\right) \tag{29}$$

I then made a graph of LHS and RHS on the vertical versus energy on the horizontal and looked for intersections of the graphs. I adjused the energy at the intersection to get something close to a perfect fit, i.e. LHS = RHS.

Energy level	Infinite well (eV)	Finite well (eV)
1	1.504	1.123
2	6.015	4.461
3	13.533	9.905
4	24.059	17.162
5	37.593	24.782
6	54.133	None