# 9. Multiple Wells

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Very often, in molecules and solids, a quantum particle finds itself in a potential that has two or more local minima, separated by one or more barriers. For example, each electron in a hydrogen (H_2) molecule is attracted to both nuclei, so its potential is a "double well" with a barrier in between. Another example is the ammonia molecule, NH_3, in which the three hydrogens form a triangle that defines a plane, and the nitrogen has two stable locations relative to them, one on either side of that plane (public domain image from Wikimedia Commons):
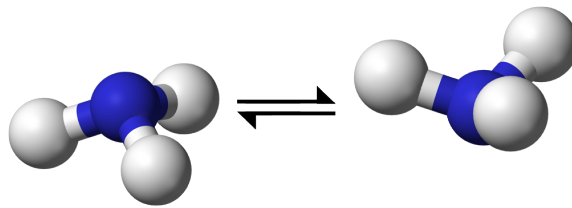
Laboratory-fabricated double-well potentials are also being investigated for use as "gates" in quantum computing. Finally, a double-well potential gives us a starting point for understanding periodic potentials with more than two wells, such as the potential felt by a conduction electron in a crystalline metal.

A two-well model

The most important properties of double wells don't depend on the exact shape of the potential, so I'll use a simple "rectangular" function:
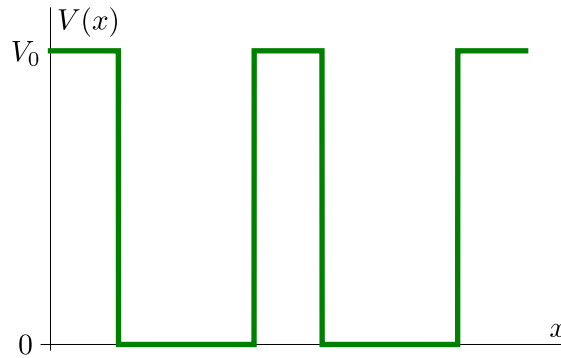

Assuming that this potential has several bound states, can you guess the shapes of the wavefunctions and reach some qualitative conclusions about their energies? Take some time now to try to make some sketches and educated guesses.

To solve this problem quantitatively, it's convenient to use the matrix diagonalization method. Here is some Mathematica code to define a rectangular potential with any number of wells:

```
nWells = 2;
bHeight = 50;
bWidth = 0.5;
xMax = nWells + (nWells+1)*bWidth;
v[x_] := If[Mod[x-bWidth, 1+bWidth] < 1, 0, bHeight];
```

The first three lines define constants for the number of wells, the height of the barriers between them (V_0 in the plot above), and the width of each barrier. The width a of each well is taken to be one unit of distance, and energies are measured in multiples of $\hbar^2/ma^2$. The fourth line calculates the maximum value of x, which will be the width of the infinite well used to define the sine-wave basis functions; note that this width includes a "barrier" on either side, as well as the one(s) between the wells. The fifth line defines the potential energy function itself, using Mathematica's `Mod` function to make the pattern repeat over a distance of the well width (1) plus the barrier width.

The next steps are to define the infinite square well basis functions, calculate all the matrix elements, and diagonalize the Hamiltonian. The code to carry out these steps is essentially identical to that in Lesson 7, so I won't repeat it here. (I used the first 50 basis functions to build a 50×50 Hamiltonian matrix, but you can get pretty good results with only 25.) The result is that there are seven eigenvalues less than 50, corresponding to bound states, but I'll neglect the highest of these (47.9) because it's so weakly bound that the infinite square well embedding potential affects it significantly. The other six bound-state eigenvalues are approximately 3.406, 3.424, 13.43, 13.53, 29.24, and 29.71. Notice that they come in closely spaced *pairs*, and that the values are quite close to those for a *single* square well with the same width and depth (see Lesson 7). The reason for this behavior becomes clearer if we look at the corresponding wavefunctions, which I've numbered here in order by energy:
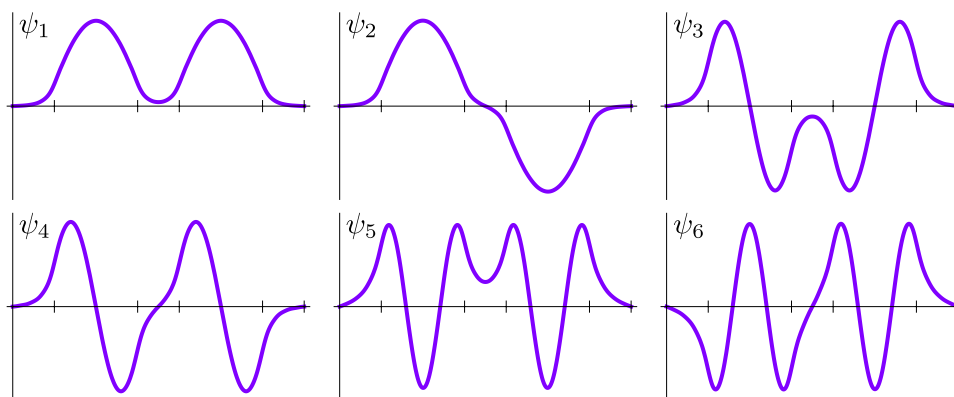
Each of these functions consists essentially of two single-well eigenfunctions, modified slightly so they can be joined smoothly in the middle. Because the modifications are so small, the energies are almost the same as for the single well. Notice, though, that the total number of nodes for each eigenfunction is what you would expect for the system as a whole (no nodes for the ground state, one for the first excited state, and so on).

You could, of course, obtain these same eigenfunctions, along with more accurate eigenvalues, using the shooting method.

Once you have the eigenvalues and eigenfunctions, you can use them in the usual ways to examine probabilities and time evolution. As you can see, for each of these eigenfunctions the particle is equally likely to be found in either of the two wells. But by superimposing an equal mixture of the two eigenfunctions in any of the pairs (e.g., ψ_1 and ψ_2), you can construct a wavefunction for which the particle is almost entirely within one well or the other. Over time, this wavefunction will oscillate at a frequency determined by the *difference* between the two energies—and that difference is quite small compared to the energies themselves. During the course of the oscillation the probability density will gradually shift from one well to the other and back again. This is an example of quantum mechanical *tunneling* through a barrier.

More than two wells

I've cleverly written the code above so you can add more potential wells simply by increasing the value of `nWells`. Can you guess what happens to the pattern in the energy eigenvalues when there are three, four, or more wells? Can you guess what the wavefunctions look like? (The detail that's probably hardest to guess is what happens when the number of wells is odd and the wavefunction needs to be an odd function, with a node in the middle. But this is just a detail.)

Rather than showing you more results here, let me just invite you to think about what should happen with more than two wells, and then to use Mathematica to check your guesses and derive some numbers and plots. You might also enjoy exploring the results from two "canned" simulations: Quantum Bound States from the PhET project at Colorado, and the 1-d Quantum States Applet by Paul Falstad. Falstad's applet can even animate the time dependence of superposition states and tunneling through barriers.

When there are *many* potential wells in a periodic structure, the allowed energies come not in pairs or small groups but in quasi-continuous *bands*, each consisting of a very large number of closely spaced energies. The bands are separated by wide *gaps* in which no energies are allowed. This behavior underlies the dramatic differences between insulators, conductors, and semiconductors, as you can explore further in a course on solid state physics.