Solutions in wave mechanics

January 25, 2017

We have seen how free wave packets evolve in time. Now we consider bound and scattering solutions.

1 Infinite square well

This problem is simple, but note the sequence of steps we follow.

Let the potential be given by

$$V = \begin{cases} 0 & 0 < x < L \\ \infty & otherwise \end{cases}$$

The infinite potential completely excludes the particle, so the wave function must vanish there. From our discussion of boundary conditions, we see that the first integration across the boundaries at 0 and L is indeterminate – there may be a discontinuity in the derivative of the wave function, given by the limit

$$0 < \left| \lim_{\varepsilon \to 0, V \to \infty} (2V\psi\varepsilon) \right| < \infty$$

The finiteness of this limit shows, after a second integration across the boundary, that the wave function itself must be continuous.

Step 1: Solve the Schrödinger equation in each independent region We first solve the stationary state Schrödinger equation in each of the three regions:

$$\begin{array}{cc} I & x < 0 \\ II & 0 < x < L \\ III & L < x \end{array}$$

The solution is immediate since the wave function vanishes outside the well,

$$\begin{aligned} \psi_I(x) &= 0 \\ \psi_{II}(x) &= A \sin kx + B \cos kx \\ \psi_{III}(x) &= 0 \end{aligned}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$.

Step 2: Match boundary conditions The wave function must be continuous at 0 and L:

$$\begin{aligned} \psi_I(0) &= \psi_{II}(0) \\ \psi_{II}(L) &= \psi_{III}(L) \end{aligned}$$

The first of these implies $B = 0$, while the second gives

$$\psi_{II}(L) = A \sin kL = 0$$

It is characteristic of bound state problems that only certain energies will be allowed. In this case, the second boundary condition holds only if

$$kL = n\pi$$

This means that the wave vector k is restricted to a discrete set of values, $\frac{n\pi}{L}$, so the energy spectrum is discrete as well,

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

The situation here differs little from classical solutions – an organ pipe or a violin string will oscillate at a fundamental frequency determined by the boundary conditions, as well as harmonics of that frequency.

Step 3: Normalize the eigenstates The stationary eigenstates are now given by

$$\psi_n(x) = \begin{cases} 0 & x \le 0 \\ A \sin \frac{n\pi x}{L} & 0 < x < L \\ 0 & x \ge L \end{cases}$$

where the remaining constant is determined by the normalization condition,

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} A^2 \sin^2 \frac{n\pi x}{L} dx \\ &= A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{L}{2} A^2 \end{aligned}$$

so that $A = \sqrt{\frac{2}{L}}$ and the stationary states are

$$\psi_n(x) = \begin{cases} 0 & x \le 0 \\ \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} & 0 < x < L \\ 0 & x \ge L \end{cases}$$

Step 4: Expand the initial condition in the eigenstates In general, we will have some initial state and wish to see its time evolution. For example, suppose we are given a highly localized initial disturbance at the center of the square well,

$$\psi(x) = \delta\left(x - \frac{L}{2}\right)$$

and wish to find $\psi(x,t)$. We know the time evolution of a stationary state is given by

$$\psi_n(x,t) = \psi_n(x) e^{-\frac{i}{\hbar} E_n t}$$

The procedure is to write $\psi(x)$ as a superposition of stationary states,

$$\psi(x) = \sum_{n=1}^{\infty} a_n \psi_n(x)$$

Then we immediately have

$$\psi(x,t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{-\frac{i}{\hbar} E_n t}$$

For the delta-function example, we need to find constants a_n such that

$$\delta\left(x-\frac{L}{2}\right)=\sqrt{\frac{2}{L}}\sum_{n=1}^{\infty}a_n\sin\frac{n\pi x}{L}$$

Using the orthogonality of sines,

$$\begin{aligned}
\int_0^L\sqrt{\frac{2}{L}}\delta\left(x-\frac{L}{2}\right)\sin\frac{m\pi x}{L}dx &= \int_0^L\sum_{n=1}^{\infty}a_n\frac{2}{L}\sin\frac{n\pi x}{L}\sin\frac{m\pi x}{L}dx \\
\sqrt{\frac{2}{L}}\sin\frac{m\pi}{2} &= \sum_{n=1}^{\infty}a_n\delta_{mn} \\
\sqrt{\frac{2}{L}}\sin\frac{m\pi}{2} &= a_m
\end{aligned}$$

and therefore a_m vanishes for even m and alternates sign for odd m,

$$\begin{aligned}
a_{2k} &= 0 \\
a_{2k+1} &= (-1)^k
\end{aligned}$$

The series for the delta function is then

$$\delta\left(x-\frac{L}{2}\right)=\sqrt{\frac{2}{L}}\sum_{k=0}^{\infty}(-1)^k\sin\frac{(2k+1)\pi x}{L}$$

Step 5: Introduce the time dependence for each mode We immediately write the time evolution:

$$\begin{aligned}
\psi(x,t) &= \sqrt{\frac{2}{L}}\sum_{k=0}^{\infty}(-1)^k\sin\frac{(2k+1)\pi x}{L}\exp\left(-\frac{i}{\hbar}E_{2k+1}t\right) \\
&= \sqrt{\frac{2}{L}}\sum_{k=0}^{\infty}(-1)^k\sin\frac{(2k+1)\pi x}{L}\exp\left(-\frac{i\hbar\pi^2}{2mL^2}(2k+1)^2t\right)
\end{aligned}$$

To summarize:

1. Solve the Schrödinger equation in each independent region
2. Match boundary conditions
3. Normalize the eigenstates
4. Expand the initial condition in the eigenstates
5. Introduce the time dependence for each mode

Often, we are more interested in the eigenvalues of the energy, since differences in these energies characterize the measurable absorbtion and emission of radiation from the system. In this case is is sufficient to carry out the first two steps, then to explore the resulting quantization condition in detail. We take this approach with the next example.

2 Finite square well: bound states

Now let the square well be of finite depth, V_0, centered at the origin, with the potential given by

$$V = \begin{cases} -V_0 & -\frac{L}{2} < x < \frac{L}{2} \\ 0 & otherwise \end{cases}$$

where we now have regions

$$\begin{array}{cc} I & x < -\frac{L}{2} \\ II & -\frac{L}{2} < x < \frac{L}{2} \\ III & \frac{L}{2} < x \end{array}$$

Choosing the location in this way makes it easier to study symmetric and antisymmetric solutions.

2.1 Solve the stationary state Schrödinger equation in each region

We have the same three regions as last time, but the wave function no longer vanishes outside the well. From our classical experience, we expect bound states to be those with energies between $-V_0$ and zero, with higher energy states being free to propagate outside the well. Taking $E \equiv -\varepsilon$ in this range, $-V_0 < E < 0$, the Schrödinger equation in regions I and III takes the form

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= E\psi \\ \frac{d^2\psi}{dx^2} - \frac{2m\varepsilon}{\hbar^2}\psi &= 0 \end{aligned}$$

Remembering that $E < 0$, define

$$\kappa = +\sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

Then the general solution is

$$\begin{aligned} \psi_I &= Ae^{\kappa x} + Be^{-\kappa x} \\ \psi_{III} &= Ge^{\kappa x} + Fe^{-\kappa x} \end{aligned}$$

In region II the stationary state Schrödinger equation is

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi &= E\psi \\ \frac{d^2\psi}{dx^2} + \frac{2m\left(V_0 - \varepsilon\right)}{\hbar^2}\psi &= 0 \end{aligned}$$

Since $V_0 - \varepsilon$ is now positive, we define

$$k = +\sqrt{\frac{2m\left(V - \varepsilon E\right)}{\hbar^2}}$$

and find oscillating solutions,

$$\psi_{II} = Ce^{ikx} + De^{-ikx}$$

2.2 Impose the boundary conditions

The potential is finite everywhere, so we must match both the wave function and its first derivative at each boundary. In addition, to be normalizable, the wave function must vanish at infinity. This gives six conditions:

$$
\begin{aligned}
\psi_I(-\infty) &= 0 \\
\psi_I\left(-\frac{L}{2}\right) &= \psi_{II}\left(-\frac{L}{2}\right) \\
\frac{d\psi_I}{dx}\left(-\frac{L}{2}\right) &= \frac{d\psi_{II}}{dx}\left(-\frac{L}{2}\right) \\
\psi_{II}\left(\frac{L}{2}\right) &= \psi_{III}\left(\frac{L}{2}\right) \\
\frac{d\psi_{II}}{dx}\left(\frac{L}{2}\right) &= \frac{d\psi_{III}}{dx}\left(\frac{L}{2}\right) \\
\psi_{III}(+\infty) &= 0
\end{aligned}
$$

In addition to this, there will be one overall constant which we may use for normalization (this *must* be the case since the equations are linear). The system is therefore overdetermined and we will have a restriction on the energy.

The conditions at $\pm\infty$ are easiest since they eliminate the decreasing part of ψ_I, ($B = 0$) and the increasing part of ψ_{III}, ($G = 0$), leaving us with

$$
\begin{aligned}
\psi_I &= Ae^{\kappa x} \\
\psi_{III} &= Fe^{-\kappa x}
\end{aligned}
$$

The two conditions at $x = -\frac{L}{2}$ now give:

$$
\begin{aligned}
Ae^{-\frac{\kappa L}{2}} &= Ce^{-\frac{ikL}{2}} + De^{\frac{ikL}{2}} \\
A\kappa e^{-\frac{\kappa L}{2}} &= ikCe^{-\frac{ikL}{2}} - ikDe^{\frac{ikL}{2}}
\end{aligned}
$$

We can write this pair as a matrix equation,

$$
A\begin{pmatrix} e^{-\frac{\kappa L}{2}} \\ \kappa e^{-\frac{\kappa L}{2}} \end{pmatrix} = \begin{pmatrix} e^{-\frac{ikL}{2}} & e^{\frac{ikL}{2}} \\ ike^{-\frac{ikL}{2}} & -ike^{\frac{ikL}{2}} \end{pmatrix}\begin{pmatrix} C \\ D \end{pmatrix}
$$

The inverse of $\begin{pmatrix} e^{-\frac{ikL}{2}} & e^{\frac{ikL}{2}} \\ ike^{-\frac{ikL}{2}} & -ike^{\frac{ikL}{2}} \end{pmatrix}$ is

$$
\frac{1}{2}\begin{pmatrix} e^{\frac{ikL}{2}} & -\frac{i}{k}e^{\frac{ikL}{2}} \\ e^{-\frac{ikL}{2}} & \frac{i}{k}e^{-\frac{ikL}{2}} \end{pmatrix}
$$

so multiplying both sides by this, and dividing by A we have

$$
\begin{aligned}
\begin{pmatrix} \frac{C}{A} \\ \frac{D}{A} \end{pmatrix} &= \frac{1}{2}\begin{pmatrix} e^{\frac{ikL}{2}} & -\frac{i}{k}e^{\frac{ikL}{2}} \\ e^{-\frac{ikL}{2}} & \frac{i}{k}e^{-\frac{ikL}{2}} \end{pmatrix}\begin{pmatrix} e^{-\frac{\kappa L}{2}} \\ \kappa e^{-\frac{\kappa L}{2}} \end{pmatrix} \\
&= \begin{pmatrix} \frac{1}{2}\left(1 - \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{\frac{ikL}{2}} \\ \frac{1}{2}\left(1 + \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{-\frac{ikL}{2}} \end{pmatrix}
\end{aligned}
$$

The wave function ψ_{II} is therefore

$$
\begin{aligned}
\psi_{II} &= \frac{A}{2}e^{-\frac{\kappa L}{2}}\left(\left(1 - \frac{i\kappa}{k}\right)e^{ik\left(x+\frac{L}{2}\right)} + \left(1 + \frac{i\kappa}{k}\right)e^{-ik\left(x+\frac{L}{2}\right)}\right) \\
&= \frac{A}{2}e^{-\frac{\kappa L}{2}}\left(e^{ik\left(x+\frac{L}{2}\right)} + e^{-ik\left(x+\frac{L}{2}\right)} + \frac{i\kappa}{k}e^{-ik\left(x+\frac{L}{2}\right)} - \frac{i\kappa}{k}e^{ik\left(x+\frac{L}{2}\right)}\right) \\
&= Ae^{-\frac{\kappa L}{2}}\left(\cos k\left(x + \frac{L}{2}\right) + \frac{\kappa}{k}\sin k\left(x + \frac{L}{2}\right)\right)
\end{aligned}
$$

Finally, at $x = +\frac{L}{2}$,

$$\begin{aligned} Fe^{-\frac{\kappa L}{2}} &= Ce^{\frac{ikL}{2}} + De^{-\frac{ikL}{2}} \\ -F\kappa e^{-\frac{\kappa L}{2}} &= ikCe^{\frac{ikL}{2}} - ikDe^{-\frac{ikL}{2}} \end{aligned}$$

Dividing both sides by A and putting in the solutions for $\frac{C}{A}$ and $\frac{D}{A}$,

$$\begin{aligned} \frac{F}{A}e^{-\frac{\kappa L}{2}} &= \frac{1}{2}\left(1 - \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{ikL} + \frac{1}{2}\left(1 + \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{-ikL} \\ -\frac{F}{A}\kappa e^{-\frac{\kappa L}{2}} &= ik\frac{1}{2}\left(1 - \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{ikL} - ik\frac{1}{2}\left(1 + \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{-ikL} \end{aligned}$$

Cancelling the $e^{-\frac{\kappa L}{2}}$ factors and collecting terms, the first equation becomes

$$\begin{aligned} \frac{F}{A} &= \frac{1}{2}\left(e^{ikL} - \frac{i\kappa}{k}e^{ikL} + e^{-ikL} + \frac{i\kappa}{k}e^{-ikL}\right) \\ &= \cos kL + \frac{\kappa}{k}\sin kL \end{aligned}$$

This determines all of the available coefficients, up to the overall choice of A,

$$\begin{aligned} C &= \frac{A}{2}\left(1 - \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{\frac{ikL}{2}} \\ D &= \frac{A}{2}\left(1 + \frac{i\kappa}{k}\right)e^{-\frac{\kappa L}{2}}e^{-\frac{ikL}{2}} \\ F &= A\left(\cos kL + \frac{\kappa}{k}\sin kL\right) \end{aligned}$$

but we have one remaining condition. Substituting the solution for $\frac{F}{A}$, cancelling the decaying exponential, and collecting terms, this final equation constrains the energy,

$$\begin{aligned} -\left(\cos kL + \frac{\kappa}{k}\sin kL\right)\kappa &= \frac{1}{2}\left(ike^{ikL} + \kappa e^{ikL} - ike^{-ikL} + \kappa e^{-ikL}\right) \\ &= \left(-k\frac{e^{ikL} - e^{-ikL}}{2i} + \kappa\frac{e^{ikL} + e^{-ikL}}{2}\right) \\ &= -k\sin kL + \kappa\cos kL \end{aligned}$$

Rearranging,

$$\begin{aligned} \kappa\cos kL + \frac{\kappa^2}{k}\sin kL &= k\sin kL - \kappa\cos kL \\ \cos kL + \frac{\kappa}{k}\sin kL &= \frac{k}{\kappa}\sin kL - \cos kL \\ 2\cos kL &= \left(\frac{k}{\kappa} - \frac{\kappa}{k}\right)\sin kL \\ \frac{2k\kappa}{k^2 - \kappa^2} &= \tan kL \end{aligned}$$

The state is now described up to the overall normalization:

$$\begin{aligned} \psi_I &= Ae^{\kappa x} \\ \psi_{II} &= Ae^{-\frac{\kappa L}{2}}\left(\cos k\left(x + \frac{L}{2}\right) + \frac{\kappa}{k}\sin k\left(x + \frac{L}{2}\right)\right) \\ \psi_{III} &= Ae^{-\kappa x}\left(\cos kL + \frac{\kappa}{k}\sin kL\right) \end{aligned}$$

and it is straightforward to check that the boundary conditions are satisfied. The remaining constant A is chosen to normalize ψ, with the normalization integration being the sum of three integrals,

$$1 = \int_{-\infty}^{-L/2} \psi_I^* \psi_I dx + \int_{-L/2}^{L/2} \psi_{II}^* \psi_{II} dx + \int_{L/2}^{\infty} \psi_{II}^* \psi_{II} dx$$

2.3 Quantization of energy

Having fully determined the stationary state wave functions, we now examine the energy spectrum in detail.

The fraction on the left is

$$\begin{aligned} \frac{2k\kappa}{k^2 - \kappa^2} &= \frac{2\sqrt{\frac{2m(V-\varepsilon)}{\hbar^2} \frac{2m\varepsilon}{\hbar^2}}}{\frac{2m(V-\varepsilon)}{\hbar^2} + \frac{2m\varepsilon}{\hbar^2}} \\ &= \frac{2\sqrt{\varepsilon (V - \varepsilon)}}{V} \end{aligned}$$

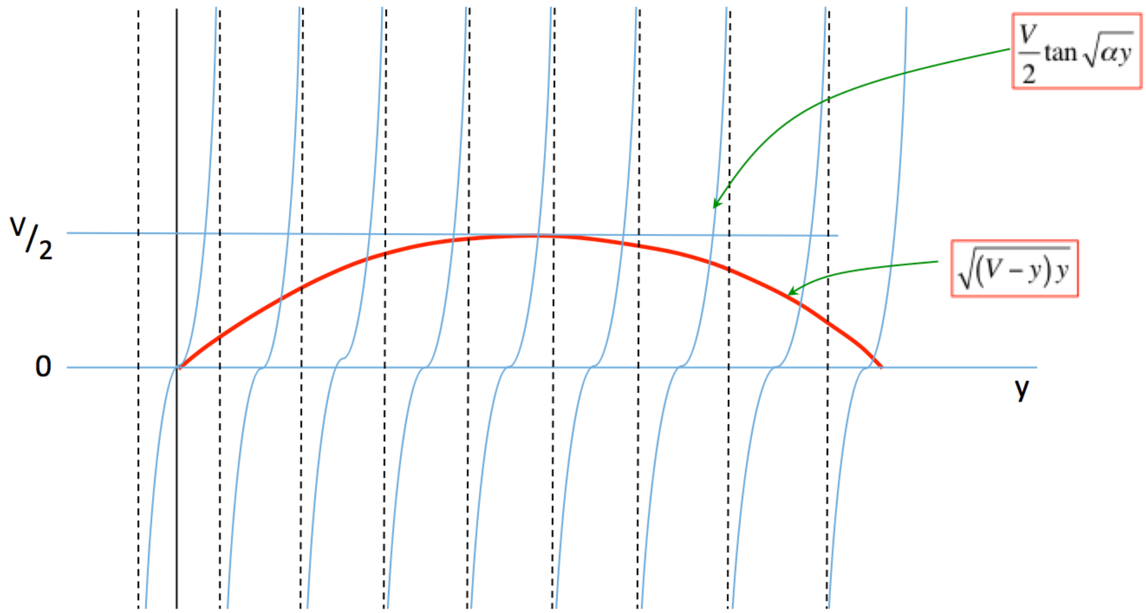
Then the quantization condition is

$$\begin{aligned} \frac{2\sqrt{\varepsilon (V - \varepsilon)}}{V} &= \tan \sqrt{\frac{2mL^2 (V - \varepsilon)}{\hbar^2}} \\ \sqrt{\varepsilon (V - \varepsilon)} &= \frac{V}{2} \tan \sqrt{\frac{2mL^2 (V - \varepsilon)}{\hbar^2}} \end{aligned}$$

This allows no closed form expression for the energies, but we may find many general properties nonetheless.

It is easiest to see the content of this condition by plotting each side of the equation as a function of $V + E = V - \varepsilon$. The arch described by $\sqrt{V\varepsilon - \varepsilon^2}$ has its maximum value at $\varepsilon = \frac{V}{2}$ and goes to zero at $\varepsilon = 0$ and $\varepsilon = V$. The right side of the equation runs repeatedly though all values. We have a solution every time $\frac{V}{2} \tan \sqrt{\frac{2mL^2(V-\varepsilon)}{\hbar^2}}$ intersects this arch. Both sides of the equation vanish at $\varepsilon = V$; this is not a solution since it gives $k = 0$.

Let $y = V - \varepsilon$. The, plotting both sides of the equation separately, we have



The positions of the dotted vertical lines are asymptotes of the tangent. These occur when the argument of the tangent is an odd multiple of $\frac{\pi}{2}$,

$$\begin{aligned} \frac{2mL^2(V-\varepsilon)}{\hbar^2} &= (2k+1)\frac{\pi}{2} \\ V-\varepsilon &= (2k+1)\frac{\pi\hbar^2}{4mL^2} \end{aligned}$$

The number of energy states depends on the size of the constant

$$\alpha = \frac{2mL^2V}{\hbar^2}$$

because this determines the number of cycles of the tangent that occur in the range $0 < \varepsilon < V$. If $\alpha \ll 1$ we may approximate the tangent to find the single bound state energy,

$$\begin{aligned} \varepsilon^2 - V\varepsilon &\approx -\frac{V^2}{4}\alpha\left(1-\frac{\varepsilon}{V}\right) \\ \varepsilon(V-\varepsilon) &= \frac{V}{4}\alpha(V-\varepsilon) \\ \varepsilon &= \frac{V}{4}\alpha \end{aligned}$$

As the value of α increases, but remains small, we require more and more terms in the expansion of the tangent. The resulting polyomial approximations have increasinly many roots.

At the other extreme, $\alpha \gg 1$, the tangent has many complete cycles, passing through zero whenever

$$\begin{aligned} \tan\sqrt{\frac{\alpha}{V}(V-\varepsilon)} &= 0 \\ \sqrt{\frac{\alpha}{V}y_n} &= n\pi \end{aligned}$$

While not giving the exact solution to the quantization condition, this does give the approximate *spacing* between adjacent energies since $\varepsilon(V-\varepsilon)$ is slowly changing compared to the tangent. The allowed energites are therefore spaced

$$y_n = \frac{V}{\alpha}n^2\pi^2$$

The spacing of levels is therefore close to

$$\begin{aligned}
\Delta\varepsilon = \varepsilon_{n+1} - \varepsilon_n &\approx y_{n+1} - y_n \\
&= \frac{V}{\alpha}(n+1)^2\pi^2 - \frac{V}{\alpha}n^2\pi^2 \\
&= \frac{V\pi^2}{\alpha}(2n+1) \\
&= \frac{\pi^2\hbar^2}{2mL^2}(2n+1)
\end{aligned}$$