Chapter 5: Bound States

In the previous chapter, we saw how the plane wave was a solution to the free-particle Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

And we concluded that the Schrödinger equation, without considering external interactions, is an accounting of energy. It basically tells us that the energy of the particle is equal (only) to its kinetic energy

$$\frac{p^2}{2m} = E$$

$$\text{KE} = E$$

Now, we account for those external interactions by modifying the Schrödinger equation. But how? Just add potential energy $U(x)$!

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{5-2}$$

Note: the potential energy here implies an interaction via conservative forces only, such as the electrostatic force. Other (nonconservative) forces would change the total energy and we wouldn't be able to write an expression for potential energy.

5.2 stationary states

To solve (5-2), we use separation of variables to break up the differential equation. We assume that the wave function can be represented as a product of two wave functions: a **spatial part $\boldsymbol{\psi}(\boldsymbol{x})$** and a **temporal part $\boldsymbol{\phi}(\boldsymbol{t})$**

$$\Psi(x,t) = \psi(x)\phi(t) \tag{5-3}$$

Inserting this equation into (5-2), we have

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\,[\psi(x)\phi(t)] + U(x)[\psi(x)\phi(t)] &= i\hbar\frac{\partial}{\partial t}\,[\psi(x)\phi(t)] \\
-\frac{\hbar^2}{2m}\phi(t)\frac{\partial^2}{\partial x^2}\,[\psi(x)] + U(x)\psi(x)\phi(t) &= i\hbar\psi(x)\frac{\partial}{\partial t}[\phi(t)]
\end{aligned}$$

And diving both sides by $\psi(x)\phi(t)$,

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\cdot\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = i\hbar\frac{1}{\phi(t)}\cdot\frac{\partial\phi(t)}{\partial t}$$

which leads to the conclusion that both sides must be constant. Thus, we have two separate differential equations linked together by a single constant C

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\cdot\frac{\partial^2\psi(x)}{\partial x^2} + U(x) \quad = \quad i\hbar\frac{1}{\phi(t)}\cdot\frac{\partial\phi(t)}{\partial t} = C \tag{5-5}$$

Next, we must find the solutions $\psi(x)$ and $\phi(t)$.

The temporal part. When we solve for the temporal part, we end up with a complex exponential solution. After applying Euler's identity to that complex exponential, we find that the constant C is energy E, leaving us with

$$\phi(t) = e^{-i\frac{E}{\hbar}t}$$

If you plug this temporal part into (5-3), and calculate the probability density, the complex exponential goes away – thus, the time dependence disappears.

The spatial part. After replacing C with energy E in (5-5) and multiplying both sides by $\psi(x)$, we obtain the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) \quad = \quad E\psi(x) \tag{5-10}$$

Note that (5-10) has unique spatial solutions $\psi(x)$ for each case of $U(x)$, but the temporal part is always the same, so we ignore it for the rest of the chapter.

5.3 Physical Conditions: Well-behaved Functions

Mathematically, the Schrödinger equation (5-10) could have arbitrarily many solutions if energy E is treated as an arbitrary parameter. However, there are physical constraints that lead to E being only allowed certain discrete values: E_1, E_2, E_3, etc... And for each of those energies, there is a corresponding wave function: ψ_1, ψ_2, ψ_3, etc... In this section, we look at some of those conditions.

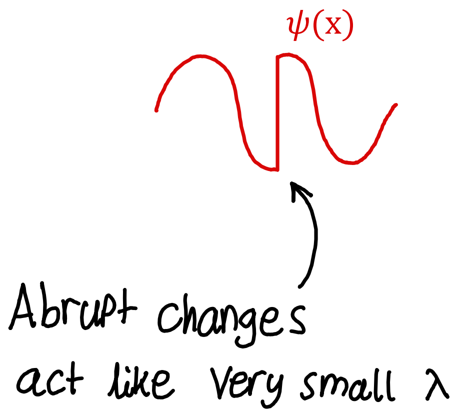
Normalization. The probability of finding a particle in all space must be 1 since the particle must be located *somewhere* in the universe. Thus, we should be able to integrate the probability density function to have

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \tag{5-11}$$

Smoothness. To be physically acceptable, a wave function must be "smooth," and there are two aspects to smoothness

1. Continuity of $\psi(x)$
2. Continuity of $\frac{d\psi(x)}{dx}$

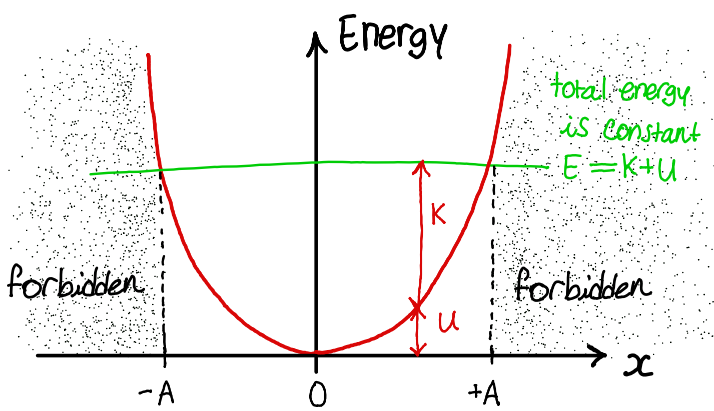
By continuity of $\psi(x)$, we mean there should be no abrupt changes in the wave function as those would imply instances of infinite kinetic energy



Continuity in $\frac{d\psi(x)}{dx}$ means that the second derivative—and thus the kinetic energy—will be finite, which must be the case if $U(x)$ and E are finite. There is one exception to this rule though; if we allow $U(x)$ to be infinite as in the case of the infinite well, then $\frac{d\psi(x)}{dx}$ is allowed to be discontinuous.

5.4 Bound States

A bound state results when a particle is caught between two turning points -A and +A, where the potential energy rises to meet the total energy E. The region outside these turning points is known as the "forbidden region" as getting there would require a change in energy – an impossibility if energy is conserved.

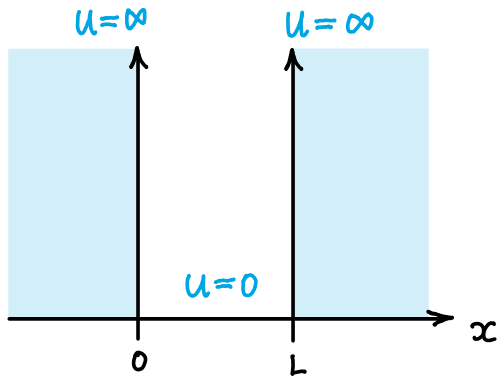


Classical bound states are found in systems such as the mass on a spring. In such cases, we are concerned with position of a particle in time. In **Quantum** bound states we are concerned with $\Psi(x, t)$. We consider three simple cases: the infinite well, the finite well, and the simple harmonic oscillator.

5.5 Case 1: The Infinite Well

The infinite well is a one-dimensional box of width L and "walls" made of infinitely high potential energy at either end, keeping a particle trapped within. Constraining a particle to such a box allows us to obtain the simplest possible solution to (5-10). The infinite well has the following definition

$$U(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x < 0, x > L \end{cases}$$



Potential energy is 0 inside the well, so the time-independent Schrödinger equation simplifies to

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \tag{5-12}$$

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

Equation (5-12) has only one acceptable solution due to one of the physical constraints of the wall discussed earlier. These constraints also lead to the conclusion that energy E, and thus the wave function, is quantized by an integer n

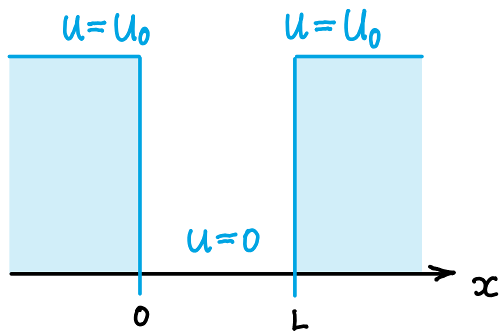
$$\Psi_n(x) = \begin{cases} \sqrt{2/\mathrm{L}} \cdot \sin\left(\frac{n\pi x}{L}\right) & 0 < x < L \\ 0 & x < 0, x > L \end{cases} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{5-16}$$

The reason for the quantization by n is related to the fact that sine will only be zero at the righthand wall if its argument is a multiple of π.

5.6 Case 2: The Finite Well

The finite well is similar to the infinite well, but the walls jump to a finite value U_0 rather than infinity. The finite well has the following definition

$$U(x) = \begin{cases} 0 & 0 < x < L \\ U_0 & x < 0, x > L \end{cases}$$



And for simplicity, we consider only the case where a particle has less energy than the height of the walls (i.e., when $E < U_0$). For the case when $E > U_0$, the particle would be able to escape the well.

The time-independent Schrödinger equation inside the finite well is

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(U(x) - E)}{\hbar^2}\psi(x) \tag{5-18}$$

Finding solutions to the Schrödinger equation is much more complicated than it was for the infinite well. Now, $\psi(x)$ and its second derivative are still proportional by a constant, but the sign of the constant changes depending on the value of $U(x)$. Consider the two cases

1. when $U = 0$ inside the walls

   $U - E$ is negative

2. when $U > E$ outside the walls

   $U - E$ is positive

Skipping all of the complicated derivations, we have **three wave functions** for the finite well

$$\psi(x) = \begin{cases} Ce^{+\alpha x} & x < 0 \\ A\sin(kx) + B\cos(kx) & 0 < x < L \\ Ge^{-\alpha x} & x > L \end{cases} \tag{5-21}$$

where $k \equiv \sqrt{\frac{2mE}{\hbar^2}}$ and $\alpha \equiv \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$

One of the key differences between the finite and infinite well is the wave function's penetration into the classically forbidden region. Recall that for the infinite well, we said that $\psi(x) = 0$ outside the walls, but for the *finite* well, $\psi(x)$ is nonzero because it is a decaying exponential.

The wave function penetration depth into the forbidden region is given by

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(U_0 - E)}} \tag{5-24}$$

5.7 The Simple Harmonic Oscillator

The harmonic oscillator is the most realistic of the three contrived bound states discussed in this chapter. The potential energy is now described by a smooth parabola

$$U(x) = \frac{1}{2}\kappa x^2$$

Inserting the potential energy definition into (5-10), we obtain the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}\kappa x^2\psi(x) = E\psi(x) \tag{5-25}$$

The solutions are too complicated to derive, but one possible solution is for the classical mass on a spring

$$\psi(x) = Ae^{-\frac{\sqrt{m\kappa}}{2\hbar}x^2}$$

The rigorous solution to (5-25) leads to the following allowed energies in the harmonic oscillator

$$E = \left(n + \frac{1}{2}\right)\hbar\omega_0 \quad n = 0,1,2,3,\ldots \tag{5-26}$$

$$\text{where } \omega_0 \equiv \sqrt{\frac{\kappa}{m}}$$

5.8 Expectation Values

Expectation values are like averages. If we do the same experiment many times to measure the value of x, the expectation value is the average of all those measurements. Note that the expectation value is **not** the most **probable** value of a measurement. In fact, the expectation value may have zero probability of occurring.

For position, the expectation value is

$$\bar{x} \equiv \int_{\text{all space}} x|\psi(x)|^2 dx$$

In general, we can use the symbol Q for any observable quantity, and the expectation value of that quantity will be

$$\bar{Q} = \int_{\text{all space}} \Psi^*(x,t)\hat{Q}\Psi(x,t)dx$$

where $\hat{Q}$ is the operator associated with quantity Q. There are unique operators for every observable. For position, $\hat{Q} = x$, but sometimes $\hat{Q}$ is a differential operator. Table 1 gives the basic operators.

Observable	**Momentum**	**Position**	**Energy**
Operator	$\hat{p} = -i\hbar\frac{\partial}{\partial x}$	$\hat{x} = x$	$\hat{E} = i\hbar\frac{\partial}{\partial t}$

Table 1. Basic operators

Using operators, we can rewrite the Schrödinger equation in a form that more clearly illustrates its foundation in energy

$$\widehat{\mathrm{KE}}\Psi(x,t) + \hat{U}(x)\Psi(x,t) = \hat{E}\Psi(x,t)$$