A few classes ago we discussed the particle-in-a-box, where a quantum particle is confined in a “box” with infinite potential walls. This lecture we will consider particles in potentials with finite walls. A particle can tunnel underneath a barrier of finite height, even if doing so is classically forbidden!

1 Particle in a finite box

Let’s first think about a variant of the particle in a box we discussed before: the particle in a finite box. This particle sits in a potential defined by:

\[ V(x) = \begin{cases} 0 & -\frac{a}{2} \leq x \leq \frac{a}{2} \\ V_0 & \text{elsewhere} \end{cases} \] (1)

Note that we have defined our \( x \) axis so that \( x = 0 \) is in the center of the box, for mathematical convenience.

What do we think the eigenfunctions of this system might look like for particles with energies \( E < V_0 \)? Our strategy here will be to solve the Schrödinger equation in the different regions of space.

1. **Inside the box:** if our particle is inside the finite box, with \(-\frac{a}{2} \leq x \leq \frac{a}{2}\), we have \( V(x) = 0 \)
and the Schrödinger equation is identical to that of the particle in a box:

\[ \hat{H} \psi(x) = -\hbar^2 \frac{d^2}{2m \, dx^2} \psi(x) = E \psi(x) \]  

(2)

\[ \rightarrow \quad \frac{d^2 \psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x) \]  

(3)

We therefore expect to have the usual sinusoidal solutions inside the box:

\[ \psi(x) = A e^{ikx} + B e^{-ikx} \quad \text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \]  

(4)

Note that because the walls are finite, we won’t have the same boundary conditions that we did for the PIB. In other words, \( \psi(-a/2) \) and \( \psi(a/2) \) need not = 0.

2. **Outside of the box:** within the walls of the box, with \( x > |\frac{a}{2}| \), we have \( E < V(x) \), and we might naively expect with our classical intuition that the particle would never be found in this region. But what if we try to solve the Schrödinger equation anyway?

\[ \hat{H} \psi(x) = -\hbar^2 \frac{d^2}{2m \, dx^2} \psi(x) + V_0 \psi(x) = E \psi(x) \]  

(5)

\[ \rightarrow \quad \frac{d^2 \psi(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2} \psi(x) \]  

(6)

While Eqn. 6 looks very similar to Eqn. 3, it’s fundamentally different because \( V_0 - E > 0 \). Our solutions are therefore no longer sinusoids or complex exponentials. Instead, we need functions that when differentiated twice give themselves multiplied by a positive coefficient. **Can anyone guess what these solutions might look like?**

The solutions outside the box will take the form:

\[ \psi(x) = \begin{cases} 
C e^{\kappa x} & \text{for} \quad -\infty \leq x \leq -\frac{a}{2} \\
D e^{-\kappa x} & \text{for} \quad \frac{a}{2} \leq x \leq \infty 
\end{cases} \]  

(7)

where

\[ \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \]  

(8)

These “outside-the-box” solutions decay exponentially into the “forbidden regions” in the walls of the box. This is what we call **tunneling:** when a particle has some probability of being found inside a classically forbidden region of the potential. We can think of \( 1/\kappa \) as the “decay length,” e.g. the distance it takes the wavefunction to decay by a factor of \( 1/e \).

In order to determine the coefficients \( A, B, C, \) and \( D \), we would need to stitch together the two pieces of wavefunction such that both \( \psi(x) \) and \( \frac{d\psi}{dx} \) are continuous. This would constrain both the coefficients as well as the particle’s energy \( E \), giving rise to discrete states within the box. The number of allowed states and their energies depend on the depth and width of the box.

This is as far as we will go here mathematically, but it is still useful to plot some solutions and compare them to the original particle in a box.
Two useful observations upon comparing the PIB (left) and finite PIB (right):

- The nodal structure of the PIB is preserved in the discrete states of the finite PIB. The \( n^{\text{th}} \) state still has \( n-1 \) nodes.

- The exponential tails decay more slowly closer to the top of the well. The reason for this should be clear by inspecting our expression for the decay constant \( \kappa \), which gets smaller as \( E \) approaches \( V_0 \). The decay length \( 1/\kappa \) therefore increases as you approach the top of the barrier.

What might one expect the wavefunctions to look like for \( E > V_0 \)? They will be unbound, meaning not spatially confined. They will therefore be sinusoidal everywhere along \( x \) and have continuously allowed energies, like the free particle. On the other hand, we call the states with \( E < V_0 \) bound states, as they are confined to the region of space around the well, and we have \( \psi(x) \rightarrow 0 \) as \( x \rightarrow \pm \infty \).

## 2 Traveling Waves and Barriers

### 2.1 A Finite Step

Let’s now consider a traveling quantum wave hitting a finite step in the potential. This will give us a framework to start thinking about tunneling in the context of chemical reactivity.

The potential surface here will be described by:

\[
V(x) = \begin{cases} 
0 & x < 0 \\
V_0 & x \geq 0
\end{cases}
\tag{9}
\]

Imagine a quantum particle coming in from the left with \( E = E_{KE} \). Classically, if \( E > V_0 \), the particle will continue on its way unimpeded with 100% probability, and if \( E < V_0 \), it will be reflected back the way it came with 100% probability.

The quantum mechanical result is different: the step potential will function as a partially reflective “mirror.” For \( E > V_0 \), we can break the problem down into three pieces, as labeled in the figure below:

1. **Incoming wave, \( x < 0 \):** this is simply a free particle moving in from the negative \( x \) axis:

\[
\psi_1(x) = c_1 e^{ik_1x}, \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}}
\tag{10}
\]
2. **Reflected wave**, $x < 0$: part of the incoming wave is reflected back towards the negative $x$ axis:

$$\psi_2(x) = c_2 e^{-i k_1 x}$$

(11)

3. **Transmitted wave**, $x \geq 0$: part of the incoming wave is transmitted over the potential step, and behaves as a free particle with a different momentum, because the potential underneath it has changed:

$$\psi_3(x) = c_3 e^{i k_2 x}, \quad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

(12)

We will not go through the math here, but one can solve for the coefficients $c_1$, $c_2$, and $c_3$ by requiring that the total wavefunction and its first derivative be continuous, e.g.

$$\left[ \psi_1(x) + \psi_2(x) \right]_{x=0} = \left[ \psi_3(x) \right]_{x=0}$$

(13)

$$\frac{d}{dx} \left[ \psi_1(x) + \psi_2(x) \right]_{x=0} = \frac{d}{dx} \left[ \psi_3(x) \right]_{x=0}$$

(14)

You will work through some of these results in this week’s problem set.

**Qualitatively, what do you expect to happen for an incoming particle with $E < V_0$?**

Use what we learned about the particle in a finite box to consider how these three components of the total wavefunction (incoming, reflected, transmitted) behave.

### 2.2 A Finite Barrier

We are now approaching a model potential that is more relevant to chemical reactions. Consider the “inversion” of the particle in a finite box: the finite barrier. This potential is described by

$$V(x) = \begin{cases} 
V_0 & 0 \leq x \leq a \\
0 & \text{elsewhere}
\end{cases}$$

(15)

Again, we’ll think about a particle moving in from negative $x$. If the particle’s energy $E < V_0$, classically we’d just expect such a particle to hit the barrier and bounce back the way it came. You can’t throw a baseball through a wall – only over it! But a quantum mechanical particle behaves...
differently. If the barrier is thin enough, or not too high, there is some probability that the particle can tunnel through.

This time, we can sketch out what the wavefunction looks like in three regions of space:

1. **Region 1**, $x < 0$: Here we have the free particle coming in from the left, and its partial reflection back the way it came, so we expect the wavefunction in this region to be:

   $$
   \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}, \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}}
   $$

2. **Region 2**, $0 \leq x \leq a$: Here we are inside the barrier, much like being inside the walls of the particle in a finite box. We therefore expect an exponentially decaying wavefunction in this region

   $$
   \psi_2(x) = Ce^{-\kappa x}, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}
   $$

3. **Region 3**, $x > a$: Finally, we have tunneled through to the other side of the barrier, like the quantum Shawshank Redemption. If a particle reached this region it would behave like a free particle, the same as Region 1. In our system, the only particle present would have to tunnel through the barrier to reach Region 3 from the left, so we expect the wavefunction to look like:

   $$
   \psi_3(x) = De^{ikx}
   $$

   where the amplitude $D$ may be quite small, depending on what wavefunction amplitude has managed to make it through the barrier.

Just like the finite step problem, we could solve for the complete solution to this system by mandating that $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous at both $x = 0$ and $x = a$. We can note a few things qualitatively however:

- We expect tunneling to be exponentially less likely (e.g. the amplitude of $\psi_3(x)$ will decrease) as the barrier gets thicker or taller

- We expect tunneling to be more likely if the particle has higher energy, and thereby comes in closer to the top of the barrier. This is because the decay length $1/\kappa$ increases as $E$ approaches $V_0$. 

\[5\]
3 Finite Barriers and Chemical Reactions

3.1 Electron Transfer

How can we tie this idea of a particle tunneling through a finite barrier to chemistry? Let’s first think about electron tunneling. Say we have a long chain-like molecule with an electron donor moiety (D) on one end and an acceptor moiety (A) on the other. We’ll also state that the molecular chain is insulating, or energetically unfavorable for accommodating an electron.

Can you sketch or describe what $V(x)$ might look like for one of these electron acceptor-donor systems?

We might sketch a potential energy surface for this system that looks something like this:

Where the insulating molecular chain region acts as a barrier that the electron must tunnel through. One way to think about this system is that you can sketch particle in a finite box wavefunctions in both the donor and acceptor well, and consider that the probability to tunnel from one state to the other will depend on the overlap of the tails of these two wavefunctions.

Again, the tunneling rate is highly dependent on the barrier height $\Delta V$ and width $R$. Does the tunneling rate increase or decrease with $\Delta V$? What about $R$?

We expect this rate to look something like:

$$rate_{QM} \sim \exp(-\kappa R)$$

where $\kappa = \sqrt{\frac{2m(\Delta V - E)}{\hbar^2}}$ should be becoming a familiar quantity!

3.2 Quantum Tunneling of Atoms

We can also think about a simple chemical reaction whose reaction coordinate involves, for instance, the motion of a proton. We now have two different avenues for reaction: (a) the classical, thermally activated Arrhenius reaction, and (b) quantum tunneling through the reaction barrier.
Recall from general chemistry that thermally activated reaction rates are temperature dependent and are given by the Arrhenius equation:

\[ k_{rxn} \sim e^{-E_a/k_B T} \]  

where \( E_a \) is the barrier height, or activation energy.

The tunneling rate, on the other hand, is temperature-independent and depends only on the shape of the potential surface, as given in Eqn. 19.

**Which pathway might you expect to be most important at high temperatures, and which at low temperatures?** At high temperatures, the classical pathway is likely to dominate, but at very low temperatures, quantum tunneling may be the only significant channel for chemistry to proceed.

Further inspection of Eqn. 19 also shows that the mass of the tunneling atom is very important. A lighter atom is much more likely to tunnel through a given barrier than a heavier atom. For this reason, hydrogen is the most common atom observed tunneling - though its deuterium counterpart is much worse at tunneling. This can be an important component of the kinetic isotope effect!

4 Wrapping Up

In the next lecture, we will discuss Heisenberg’s uncertainty principle, and explore our ability to make simultaneous quantum measurements with operators that do and do not commute.