CHM 305 - Lecture 7 - Tunneling

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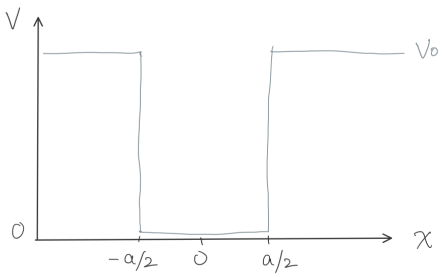
A few lectures ago we discussed the particle-in-a-box, where a quantum particle is confined in a "box" with infinite potential walls. This lecture we will consider particles in potentials with finite walls. A particle can tunnel underneath a barrier of finite height, even if doing so is classically forbidden!

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:

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



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

What will the eigenfunctions of this system look like for particles with energies $E < V_0$? Our strategy here will be to solve the time-independent Schrödinger equation in different regions of space.

1.1 Inside the box

If our particle is inside the 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 traditional particle in a box with infinitely high walls:

$$\hat{H}\psi_i(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_i(x) = E\psi_i(x) \tag{2}$$

$$\rightarrow \quad \frac{d^2\psi_i(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi_i(x) \tag{3}$$

We therefore expect to have the usual sinusoidal (or complex exponential) solutions inside the box:

$$\psi_i(x) = Ae^{ikx} + Be^{-ikx} \quad \text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \tag{4}$$

Note that because the walls are finite, we won't have the same boundary conditions that we did for the PIB. In other words, the wavefunction need not go to zero at the walls of the box when $x = \pm a/2$.

1.2 Outside the box, within the walls

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

$$\hat{H}\psi_o(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_o(x) + V_0\psi_o(x) = E\psi_o(x) \tag{5}$$

$$\rightarrow \quad \frac{d^2\psi_o(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi_o(x) \tag{6}$$

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.

The solutions outside the box will take the form:

$$\psi_o(x) = \begin{cases} Ce^{\kappa x} & \text{for} \quad -\infty \leq x \leq -\frac{a}{2} \\ De^{-\kappa x} & \text{for} \quad \frac{a}{2} \leq x \leq \infty \end{cases} \tag{7}$$

where

$$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \tag{8}$$

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 the particle must travel into the wall for the wavefunction to decay by a factor of $1/e$.

1.3 Stitching the solutions together

In order to determine the coefficients A, B, C, and D that describe the amplitudes of the various pieces of the wavefunction inside and outside the box, we would stitch together the wavefunction at $x = \pm a/2$ such that both $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous at the places where the potential takes a sudden step:

$$\psi_i(a/2) = \psi_o(a/2) \quad \rightarrow \quad Ae^{ika/2} + Be^{-ika/2} = De^{-\kappa a/2} \tag{9}$$

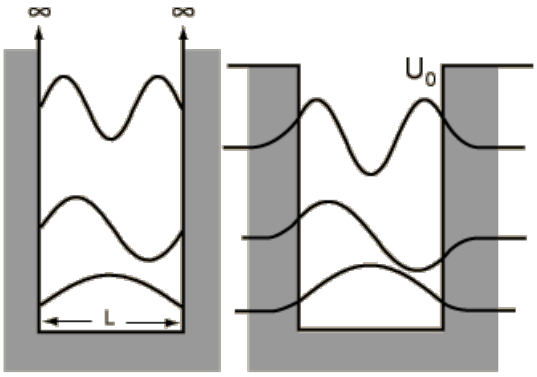
$$\psi_i(-a/2) = \psi_o(-a/2) \quad \rightarrow \quad Ae^{-ika/2} + Be^{ika/2} = Ce^{-\kappa a/2} \tag{10}$$

$$\left[\frac{d\psi_i(x)}{dx}\right]_{x=a/2} = \left[\frac{d\psi_o(x)}{dx}\right]_{x=a/2} \quad \rightarrow \quad ikAe^{ika/2} - ikBe^{-ika/2} = -\kappa De^{-\kappa a/2} \tag{11}$$

$$\left[\frac{d\psi_i(x)}{dx}\right]_{x=-a/2} = \left[\frac{d\psi_o(x)}{dx}\right]_{x=-a/2} \quad \rightarrow \quad ikAe^{-ika/2} - ikBe^{ika/2} = \kappa Ce^{-\kappa a/2} \tag{12}$$

When solved, this system of equations (along with normalization requirements) will determine all the coefficients. These boundary conditions will also constrain the allowed value of the particle's energy E, which gives rise to discrete states within the box (for $E < V_0$). The number of discrete 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^{th} state still has $n-1$ nodes.
- The exponential tails of the finite PIB wavefunctoins decay more slowly as they get closer to the top of the well. The reason for this becomes clear by inspecting our expression for the decay constant $\kappa = \sqrt{2m(V_0 - E)}/\hbar$, 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. The solutions for $E > V_0$ are sinusoidal everywhere along x and have continuously allowed energies. They are akin to free particle wavefunctions, but with the particle experiencing slightly different momenta as it travels over the well – like hitting a pothole.

Note that we call the states with $E < V_0$ *bound* states, as they are confined to the region of space around the well, and $\psi(x) \rightarrow 0$ 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.

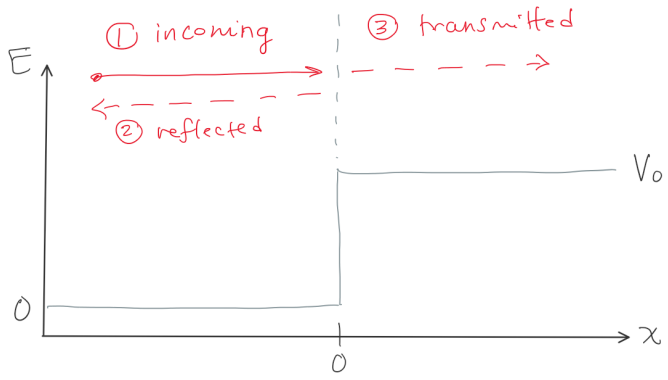
The potential surface here will be described by:

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \tag{13}$$

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." A good analogy is to picture an ocean wave hitting a submerged sandbar: the wave will be perturbed and break, even though the sandbar is well below the surface.

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:

$$\psi_1(x) = c_1 e^{+ik_1 x}, \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}} \tag{14}$$

2. **Reflected wave**, $x < 0$: part of the incoming wave is reflected back towards the negative x axis:

$$\psi_2(x) = c_2 e^{-ik_1 x} \tag{15}$$

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:

$$\psi_3(x) = c_3 e^{+ik_2 x}, \qquad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \tag{16}$$

As we did for the finite PIB, 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 at the potential step at $x = 0$:

$$\Big[\psi_1(x) + \psi_2(x)\Big]_{x=0} = \Big[\psi_3(x)\Big]_{x=0} \tag{17}$$

$$\frac{d}{dx}\Big[\psi_1(x) + \psi_2(x)\Big]_{x=0} = \frac{d}{dx}\Big[\psi_3(x)\Big]_{x=0} \tag{18}$$

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

Practice problem: Qualitatively, what do you expect to happen for an incoming particle with insufficient energy to surmount hte barrier? $E < V_0$? Use what we learned about the finite PIB to write down general expressions for the three pieces of the total wavefunction (incoming, reflected, and transmitted waves). What are the relevant boundary conditions you would use to constrain these general expressions?

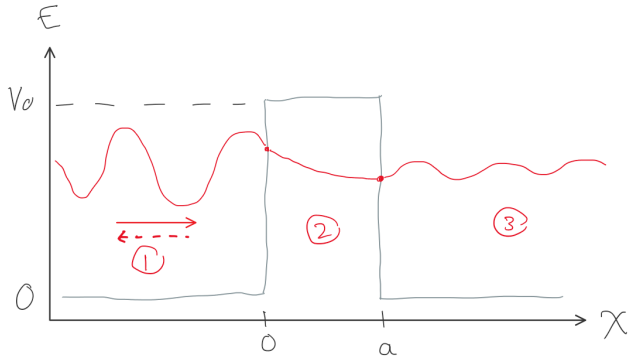
2.2 A Finite Barrier

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

$$V(x) = \begin{cases} V_0 & 0 \leq x \leq a \\ 0 & \text{elsewhere} \end{cases} \tag{19}$$

Again, we'll think about a particle moving in from negative x. If the particle's energy was below the barrier, $E < V_0$, 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 its way through.

By this point, we can just 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:

$$\psi_1(x) = Ae^{ik_1 x} + Be^{-ik_1 x}, \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}} \tag{20}$$

Note that we can think of the relative weighting of the reflected wave compared to the forward-going incident wave $|B|^2/|A|^2$ as the *reflection probability.*

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

$$\psi_2(x) = Ce^{-\kappa x}, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \tag{21}$$

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:

$$\psi_3(x) = De^{ikx} \tag{22}$$

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

Note that we can think of the relative weighting of the transmitted wave compared to the forward-going incident wave $|D|^2/|A|^2$ as the *transmission probability.*

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 $x = a$.

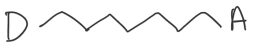
We can just note a few things qualitatively here:

- We expect tunneling to be exponentially less likely as the barrier gets thicker or taller (e.g. the amplitude of $\psi_3(x)$ will decrease)
- We expect tunneling to be more likely the higher the particles' energy, as it comes in closer to the top of the barrier. This is because the decay length $1/\kappa$ increases as E approaches V_0.

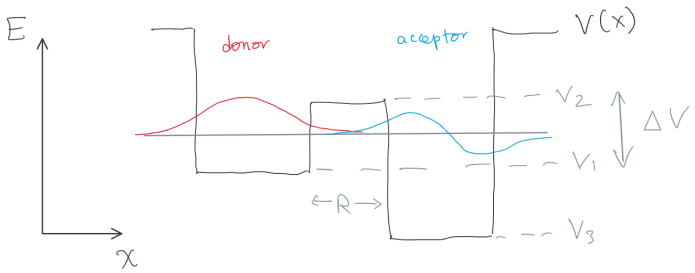
3 Finite Barriers and Chemical Reactions

3.1 Electron Transfer

Let's try to tie this idea of a particle tunneling through a finite barrier to chemistry. We first think about electron tunneling. Imagine a long chain-like molecule with an electron donor moiety (D) on one end and an acceptor moiety (A) on the other. Imagine that the molecular chain connecting D and A is insulating, and therefore energetically unfavorable for the electron to be located in the chain.



We might sketch a potential energy surface for this system that looks something like the image below. 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 initialize the particle's wavefunction as a finite PIB state in the donor well. We might want to find the probability that we tunnel



through the barrier, which will depend on how much the tail of our initial wavefunction reaches into the acceptor well.

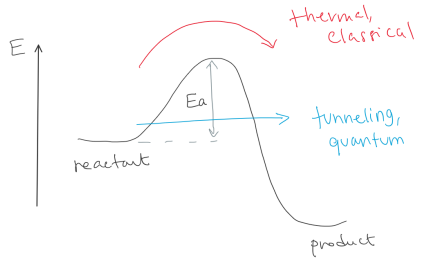
Again, the tunneling rate will be highly dependent on the barrier height ΔV and width R. We expect this rate to look something like:

$$rate_{QM} \sim \exp(-\kappa R) \tag{23}$$

where $\kappa = \sqrt{\frac{2m(\Delta V - E)}{\hbar^2}}$ should be becoming a familiar quantity! The tunneling rate therefore decreases as we increase either ΔV (the barrier height) or R (the barrier width).

3.2 Quantum Tunneling of Atoms

We can also consider a simple chemical reaction whose reaction coordinate involves, for instance, the motion of a proton. We 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 can often be modeled with the Arrhenius equation:

$$k_{rxn} \sim e^{-E_a/k_B T} \tag{24}$$

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. 23.

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. 23 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, H atoms are most commonly observed tunneling; D atoms are much less likely to tunnel. This can be an important component of the kinetic isotope effect!