

11 One-dimensional Step Function

1. Consider a step potential:

$$\begin{aligned} V(x) &= 0 & x < 0 \\ V(x) &= V_0 & x \geq 0 \end{aligned} \quad (11.37)$$

So this is an unbound system.

2. The time-independent Schrödinger Equation in the two regions:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) &= E\psi(x), & x < 0 \\ \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 \right] \psi(x) &= E\psi(x), & x \geq 0 \end{aligned} \quad (11.38)$$

or

$$\begin{aligned} \frac{\partial^2}{\partial x^2} \psi(x) + k_0^2 \psi(x) &= 0, & k_0 &= \frac{\sqrt{2mE}}{\hbar} & x < 0 \\ \frac{\partial^2}{\partial x^2} \psi(x) + k^2 \psi(x) &= 0, & k &= \frac{\sqrt{2m(E - V_0)}}{\hbar} & x \geq 0 \end{aligned} \quad (11.39)$$

3. Recognize that these equations look very similar to the PIB case and hence $\psi(x) = \exp\{sx\}$ leads to

$$\begin{aligned} s^2 + k_0^2 &= 0, & k_0 &= \frac{\sqrt{2mE}}{\hbar} & x < 0 \\ s^2 + k^2 &= 0, & k &= \frac{\sqrt{2m(E - V_0)}}{\hbar} & x \geq 0 \end{aligned} \quad (11.40)$$

and

$$s = \pm ik_0 \quad x < 0 \quad (11.41)$$

$$s = \pm ik \quad x \geq 0 \quad (11.42)$$

and the solutions in the two regions are:

$$\psi_I(x) = A \exp\{ik_0x\} + B \exp\{-ik_0x\} \quad (11.43)$$

$$\psi_{II}(x) = C \exp\{ikx\} + D \exp\{-ikx\} \quad (11.44)$$

4. Now the *boundary conditions*.

(a) Continuity of the wavefunction at $x=0$:

$$A + B = C + D \quad (11.45)$$

(b) We require that the derivative of the wavefunction be continuous at $x=0$. *Note: We never used this in the particle-in-a-box.* Does it make sense to use this? The kinetic energy operator is the second derivative operator, *i.e.* it is the first deviation of $\frac{\partial\psi}{\partial x}$. Hence if $\frac{\partial\psi}{\partial x}$ is not continuous, it cannot be differentiated and hence the $\frac{\partial^2\psi}{\partial x^2}$ will not be defined. Invoking this we have:

$$k_0(A - B) = k(C - D) \quad (11.46)$$

(c) Equations (11.45) and (11.46) can be used to eliminate B :

$$C = \frac{2k_0}{k_0 + k}A - \frac{k_0 - k}{k_0 + k}D \quad (11.47)$$

which is obtained by multiplying Eq. (11.45) by k_0 and adding with Eq. (11.46). We can also use Equations (11.45) and (11.46) to eliminate C :

$$B = \frac{k_0 - k}{k_0 + k}A + \frac{2k}{k_0 + k}D \quad (11.48)$$

which is obtained by multiplying Eq. (11.45) by k and subtracting from Eq. (11.46).

(d) Substituting B and C into Eqs. (11.43) and (11.44), we can write:

$$\psi_I(x) = \psi_{II}(x) = A\psi_1(x) + D\psi_2(x) \quad (11.49)$$

where

$$\psi_1(x) = \exp\{ik_0x\} + \frac{k_0 - k}{k_0 + k} \exp\{-ik_0x\}, \quad x < 0 \quad (11.50)$$

$$\psi_1(x) = \frac{2k_0}{k_0 + k} \exp\{ikx\}, \quad x \geq 0 \quad (11.51)$$

and

$$\psi_2(x) = \frac{2k}{k_0 + k} \exp\{-ik_0x\}, \quad x < 0 \quad (11.52)$$

$$\psi_2(x) = \exp\{-ikx\} - \frac{k_0 - k}{k_0 + k} \exp\{ikx\}, \quad x \geq 0 \quad (11.53)$$

Homework: Prove these equations.

(e) Note: ψ_1 and ψ_2 are themselves solutions to the Schrödinger Equation. Furthermore, they are continuous at $x = 0$ and they have the same derivatives at $x = 0$. (**Homework: Show this.**) Hence these are acceptable solutions for us. !!!

5. Lets now analyze these equations:

- $\exp\{ikx\}$ is a plane wave.
- What is k ? You may recall from the homework assignment in Eq. (H.9) that the plane wave is an eigenstate of the momentum operator and $\hbar k$ is the corresponding eigenvalue. Since \hbar is a constant this implies that k is proportional to the value of the momentum.
- Hence, we may say $\exp\{ikx\}$ is a plane wave with positive momentum and $\exp\{-ikx\}$ is a plane wave with negative momentum. (Remember: k is the wave vector.)
- In that case we can analyze Eqs. (11.50), (11.51), (11.52) and (11.53) in the following fashion.
- Lets take Eq. (11.50). A wave with momentum k_0 (represented by the first term in Eq. (11.50)) moves towards the step-function potential. The wave gets scattered off the potential and a portion of it gets reflected back. The wave reflected back is represented in the second term in Eq. (11.50).
- Note that this second term has a negative value for the wave-vector, as should be the case since this wave is moving backwards, that is away from the step function potential. The intensity of the reflected wave is given by the pre-factor $\frac{k_0 - k}{k_0 + k}$. (Shall we call this a reflection coefficient. We most certainly can.)

- (g) In a similar fashion the term in Eq. (11.51) represents what happens on the other side of the step-function potential. That is a portion of the incident wave actually makes it through the potential (gets transmitted through) and continues to go along the positive direction. So the pre-factor in front of this term should be the transmission coefficient.
- (h) OK. So the function $\psi_1(x)$ represents a scattering process. The scattering of a wave that is coming in from the left hand side with momentum k_0 , gets scattered off the step-function potential, part of the wave gets reflected from the potential and the other part gets transmitted through.
- (i) OK. So what does $\psi_2(x)$ represents. Turns out we can follow the exact same logic as we did for $\psi_1(x)$, while we analyze $\psi_2(x)$.
- (j) Consider Eq. (11.53). A wave is coming from the right(!) with a momentum k . Goes towards the potential. The potential this wave sees is exactly the opposite as the incoming wave in $\psi_1(x)$ felt. (Remember the incoming wave in $\psi_1(x)$ felt a step function which was an increase in the potential energy as it approached $x = 0$. The incoming wave in $\psi_2(x)$ feels now the opposite potential, *i.e.*, a step potential that goes down a step.)
- (k) The incoming wave from the right gets scattered off this potential and gets *reflected* off this potential (the second term in Eq. (11.53)). And then some get *transmitted* through the potential (the term in Eq. (11.52)).
- (l) Both $\psi_1(x)$ and $\psi_2(x)$ represent functions corresponding to scattering processes. One from the right and the other from the left. **Both allow for waves to get reflected and scattered through the potential that they see!!**
- (m) Any general solution (such as $\psi_I(x)$ and $\psi_{II}(x)$) is a linear combination of these two scattering states as seen in Eq. (11.49).
6. But we have now found a rather “different” way of solving such problems. We can use the scattering phenomenon to solve these problems.

7. Consider the reflection coefficient for the wave $\psi_1(x)$. Lets call this R_1 . The probability of reflection is then defined as the square of this function:

$$|R_1|^2 = \left| \frac{k_0 - k}{k_0 + k} \right|^2 = \left| \frac{1 - \mu}{1 + \mu} \right|^2 \quad (11.54)$$

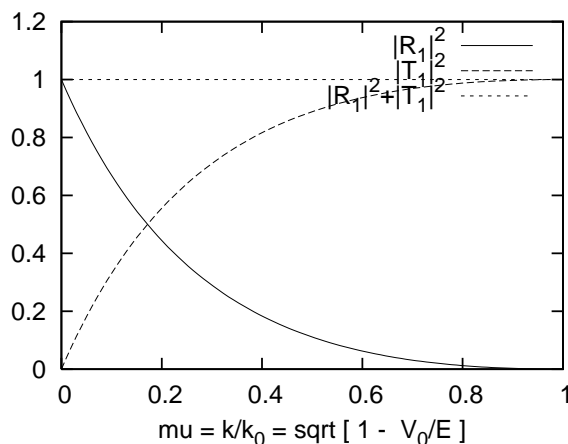
where

$$\mu = \sqrt{1 - \frac{V_0}{E}} = \frac{k}{k_0} = \frac{\frac{\sqrt{2m(E-V_0)}}{\hbar}}{\frac{\sqrt{2mE}}{\hbar}} \quad (11.55)$$

and the transmission coefficient T_1 :

$$|T_1|^2 = \left| \frac{2k}{k_0 + k} \right|^2 = \left| \frac{2\mu}{1 + \mu} \right|^2 \quad (11.56)$$

8. There are two possibilities for the energy $E < V_0$, $E > V_0$.
9. Lets first consider $E > V_0$. Below, $|R_1|^2$ and $|T_1|^2$ are shown as a function of μ . Here $\mu = 0$ when $E = V_0$, that is the top of the barrier and $\mu = 1$ when $E \rightarrow \infty$, that is infinitely higher than the barrier.



10. This plot shows that for finite values of $E > V_0$ the wave can still get reflected (since $|R_1|^2$ is non-zero and becomes zero only as $E \rightarrow \infty$). This is really weird and completely non-classical. **Over-barrier reflection!!**
11. Furthermore, the transmission is never equal to 1 unless the energy E is infinitely large (which is consistent with the previous result for R_1).
12. For $E > V_0$ $|R_1|^2 + |T_1|^2 = 1$.

13. Let us now consider $E < V_0$. μ is pure imaginary. Note from Eq. (11.55) that μ is real for $E > V_0$. But for $E < V_0$, μ is *purely imaginary*, because k is purely imaginary (Why?)!
14. But $|R_1|^2 = 1$. **Homework: Prove this for $E < V_0$.**
15. *But: the wavefunction on the right side is not zero.*

$$\psi_1(x) = \frac{2k_0}{k_0 + k} \exp\{ikx\}, \quad x \geq 0 \quad (11.57)$$

and note that k is imaginary. Hence this function goes down exponentially as we move further to the right from the step.

16. But the particle can *tunnel* through into the classically forbidden region.
17. We have now treated the simplest collision problem that we can think of. This problem will also introduce the concept of flux conservation in quantum mechanics which replaces momentum conservation. We will see this when flux is introduced.
18. We have treated the collision of a particle off a barrier, and we find that the particle can transmit through the barrier, irrespective of whether its energy is lower or higher than the barrier height.
19. In many ways this is the simplest chemically reactive system that we can think of. (We will see more about this in the next subsection.)
20. If we consider the states to the left as the reactants and the states to the right as the products we may consider this process starting from the reactants and producing the products (for ψ_1) or vice versa (for ψ_2).
21. The transition probabilities (from reactants to products or vice versa) at any given energy are given by the respective reflection and transmission coefficients.
22. Quantum reaction dynamics (or quantum scattering theory as it is more appropriately called) is essentially a generalization of the procedure we just saw, for arbitrary potentials. (Arbitrary potentials as in two general reactants may exert a potential on each other that is different from the step function that we have seen here. We have approximated this to be the case here so as to illustrate the concepts.)
23. Note: We have done all this in the time-independent perspective. But one could choose to treat it in the time-dependent perspective and the math would be different!! (*You may get different solutions depending on whether separation of space and time is valid or not !!*)
24. If you wonder what the thermal rate constant is: it is the canonical average (at constant temperature) of the transition probabilities that we just calculated. (We calculated the simplest form.)

11.1 Isomerization of ammonia using a square potential barrier in one-dimension

1. Consider a symmetric double-well potential using straight edges as shown on the board. This is a simple model for isomerization of ammonia. It could also be considered a simple model for a homo-nuclear diatomic molecule. For a hetero-nuclear diatomic, one nucleus may be more electronegative as compared to the other, and hence may be deeper!
2. **Homework:** Purely based on inspection can you draw typical forms for the wavefunctions, above, below and exactly on top of the barrier for the ammonia problem? No math.
3. Now the mathematical treatment: We will split the region into 3 portions and we will proceed as we did in the previous section.
4. As we saw in the last section, we may construct this problem by looking at it in a “scattering” sense.
5. We have one wave coming from the left and hits the target.
6. Part of the wave gets reflected off the target and a portion gets transmitted through the first edge.
7. The wave transmitted through the first edge again gets scattered off the second edge, part of it getting reflected backwards and a part of it getting transmitted through.
8. Hence we may write the contributions to the wavefunction in the three regions as

$$\psi_1(x) = \exp\{ik_0x\} + R \exp\{-ik_0x\}, \quad (x < -a) \quad (11.58)$$

$$\psi_1(x) = A_1 \exp\{ikx\} + B_1 \exp\{-ikx\}, \quad x \in [-a, +a] \quad (11.59)$$

$$\psi_1(x) = T \exp\{ik_0x\}, \quad (x > a) \quad (11.60)$$

$$(11.61)$$

where $k_0^2 = \frac{2mE}{\hbar^2}$ and $k^2 = \frac{2m(E-V_0)}{\hbar^2}$ as earlier.

9. A similar set of equations may be obtained when we consider a wave going towards the target from the right. (Note this would be similar to what we wrote down as ψ_2 in the previous section.)
10. But here we can invoke symmetry. And we can say *it does not matter from which side you hit the target*. Since the potential is completely symmetric. (*The left and the right side (or the target) are the same here . :-).*)
11. **We are lucky symmetry holds here. But in nature, we are generally lucky!! Some kind of a symmetry or other always holds in chemical problems we study.**

12. So we need to solve for the four constants R , A_1 , B_1 and T . Using continuity of function and derivative at $-a$ we get

$$\exp\{-ik_0a\} + R \exp\{ik_0a\} = A_1 \exp\{-ika\} + B_1 \exp\{ika\} \quad (11.62)$$

$$ik_0 [\exp\{-ik_0a\} - R \exp\{ik_0a\}] = ik [A_1 \exp\{-ika\} - B_1 \exp\{ika\}] \quad (11.63)$$

Using continuity of function and derivative at $x = +a$ we get

$$T \exp\{ik_0a\} = A_1 \exp\{ika\} + B_1 \exp\{-ika\} \quad (11.64)$$

$$Tik_0 \exp\{ik_0a\} = ik [A_1 \exp\{ika\} - B_1 \exp\{-ika\}] \quad (11.65)$$

Four equations in four variables that we can solve this to get R , A_1 , B_1 and T .

13. **Homework:** Consider the corresponding simplified model for the hetero-nuclear diatomic (or an endothermic reaction). Can you draw the wavefunctions based on your physical understanding, for the full range of energies?
- Write down the time-independent Schrödinger Equation in all three regions.
 - Write the general solution in the three regions using the scattering approach we considered. (Note: This situation is unlike what we studied in class, in that it is not symmetric. Hence you will need to write down both solutions, *i.e.* scattering due to waves coming from the left and those coming from the right.)
 - Write down the boundary conditions that you will use to solve for the coefficients.
 - Use these boundary conditions to write the equations that will be used to obtain the coefficients.
 - Explain in words how you will solve for R and T .
 - Extra Credit:** Go ahead and solve the equations to get R and T .

The reflection and transmission coefficients are, as you know, related to the transition probabilities in this “chemical reaction” and the chemical reaction rate can be obtained from these. When a more realistic potential is used, you can get results in very good agreement with experiment. *Hence quantum mechanics is predictive!!*