Notes on Solution of the Time Independent Schrödinger Equation (TISE) for the Finite Square Well

October 12, 1995

Massachusetts Institute of Technology

Department of Physics

Physics 8.04 October 12, 1995

In the course, we have established so far all that is needed in principle to predict quantum phenomena. We have a theory of operators and averages which tells us how to predict the statistical outcome of experiments given the wavefunction describing a system at the time the experiments are performed. To tell us the dynamics of quantum states we have the the time dependent Schrödinger equation (TDSE) to tell us how the wavefunction of a system evolves in time. We have even shown to prove Newton's equation of motion, $\vec{F} = m\vec{a}$ as a consequence of our quantum dynamics.

The next phase of the scientific program is to predict *new* phenomena using the quantum theory. In order to do this, we developed the method of separation of variables and found a complete, albeit formal, solution of the TDSE:

$$\Psi(x, t > 0) = \sum_n e^{-iE_n t/\hbar} \psi_n(x)(\psi_n, \Psi(x, t = 0)).$$

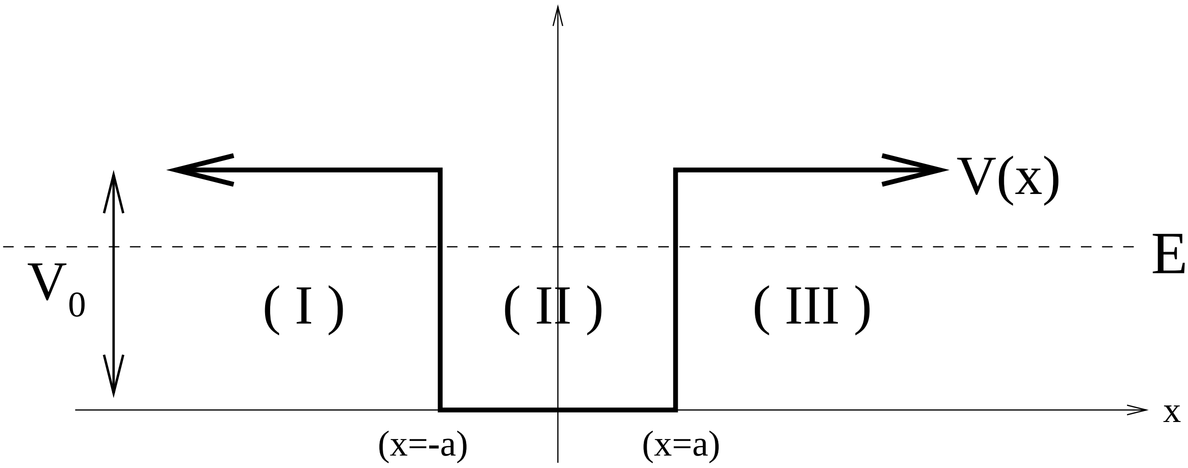
This "complete" solution to the TDSE, however, is written in terms of the solutions $(\psi_n(x), E_n)$ of yet another equation, the time independent Schrödinger equation (TISE):

$$\hat{H}\psi_n(x) \equiv -\frac{\hbar^2}{2m}\partial_x^2 \psi_n(x) + V(x)\psi_n(x) = E_n \psi_n(x). \tag{1}$$

The final link which will allow us to predicting quantum phenomena is to learn how to solve this final equation, the TISE.

Learning this is best done by working through examples in detail. We shall begin in Section 1 with the solution of the TISE in finite square well. We will begin with one of the more complicated examples because by working with it, we will touch on most of the issues faced in the solution of the TISE.

In a later set of notes, we will discuss the solution of two special limiting cases of the finite square well, the infinite square well and the attractive delta potential. We will show how the solutions for these systems may be obtained either through taking the appropriate limit of our solutions to the finite square well or by solving the TISE in these potentials directly.



1 Finite Square Well

The finite square well problem consists of a particle of mass m subject to the potential function in Figure 1.

Keep in mind that no physical potential could exhibit the discontinuities which we see in this potential at the interface of regions I and II ($x = -a$) or the interface between region II and III ($x = a$). At some sufficiently small length scale, any physical potential will look smooth and continuous. You should think of the square well potential as an idealization of a smooth potential which happens to vary continuously but very rapidly from $V = V_0$ to $V = 0$ in small regions near $x = -a$ and $x = a$. Mathematically, you should consider the potential in Figure 1 as the result of a limiting process where the steepness of the change in the potential at the interfaces of the regions is taken to approach infinity.

The time independent Schrödinger equation (1) for the that the pure energy states $\psi(x)$ of energy E of a particle of mass m may be rearranges into the following more convenient form,

$$\frac{d^2}{dx^2}\psi(x) = \frac{2m}{\hbar^2}(V(x) - E)\psi(x). \tag{2}$$

We will begin by considering the possibility of a state "bound" within the well. This state will have energy E as sketched in the figure. We must have that $E > 0$, the minimum potential in the system, but for a bound state we must also insist that $E < V_0$, so that particle has insufficient energy to travel to large distances from the well.

The TISE holds in each of the three regions I, II, III of the figure. We shall treat each of these regions separately, proceeding from left to right beginning with region I.

1.1 Region I

In this region, $V(x) - E = V_0 - E > 0$ is a constant. To remind ourselves that this constant is positive, we shall rewrite (2) as

$$\frac{d^2}{dx^2}\psi(x) = \kappa^2\psi(x), \tag{3}$$

where κ is a real constant defined by

$$\frac{\hbar^2\kappa^2}{2m} = V_0 - E, \tag{4}$$

By convention we always choose κ itself to be positive. (3) is a second order linear differential equation with constant coefficients. Such linear, constant coefficient differential equations always possesses solutions of the form $Ae^{\alpha x}$ for some constants α and A. The above equation is satisfied so long as $\alpha^2 = \kappa^2$. There are thus have two linearly independent solutions $A'e^{\kappa x}$ and $B'e^{-\kappa x}$. Because the TISE is linear, we may add these two solutions to produce a more general solution $A'e^{\kappa x} + B'e^{-\kappa x}$. Finally, because (3 is a second order equation, there are at most two linearly independent solutions and thus we have found the most general solution to the TISE in region I:

$$\psi_I(x) = A'e^{\kappa x} + B'e^{-\kappa x}. \tag{5}$$

The behavior of any physical state in region I must be of the form (5). However, the converse of this statement is not true. Just because a function obeys the TISE in region I does not mean that it is a *physically acceptable* solution. For instance, if $B' \neq 0$ in 5, then $\psi_I(x)$ would *grow exponentially* as $x \to -\infty$, meaning that as we go further and further to the left of the well, the probability of finding the particle becomes greater and greater. $\int_{-\infty}^{x_0} dx\, \mathcal{P}(x) \to \infty$ for all $x_0 < 0$ meaning that there is an infinite weight of finding the particle at a infinite distance from the well. Physically, we see that if $B' \neq 0$, $\psi(x)$ cannot represent the state of the particle in the system we are studying. Mathematically, we must reject this solution because the probability cannot be normalized. These considerations lead us to the first restriction which we place on allowable wavefunctions on physical grounds,

$$\textit{Boundary Condition I: We Reject Exponentially Growing Solutions at } \pm\infty. \tag{6}$$

We thus insist that for any physically acceptable solution, $B' = 0$. To reduce the complexity of the algebra, we define $A \equiv A'e^{\kappa a}$ so that our final form for the behavior of the wavefunction in region I is

$$\psi_I(x) = Ae^{\kappa(x-a)}. \tag{7}$$

One may arrive at (7) directly by observing that it is the only solution which obeys the TISE for region I (3) and is consistent with the boundary condition (6).

1.2 Boundary Between Region I and Region II

While we know that any physical state obeys the TISE in each of the three regions I, II and III, we must be careful in how we connect our solutions across the interfaces at $x = -a$ and $x = a$. Because $\mathcal{P}(x) = |\psi(x)|^2$ is a physically measurable quantity we expect it and thus $\psi(x)$ always to be continuous. It is not necessary to add this as an additional *physical* requirement, because this continuity is a consequence of the TISE. Recall that the finite square well potential represents an idealization of a smooth potential which happens to vary extremely rapidly at the interfaces between the regions. In all physical cases where the potential is "smooth" (continuous with all of its derivatives continuous, a so called "C^∞" function), the solutions to the TISE will also be smooth. All we must then determine is the behavior of the solutions of the TISE, as we make the walls of the well steeper and steeper.

The best way to predict this behavior of the wavefunctions is to apply the mean value theorem of calculus. The mean value theorem states that for any function $f(x)$ whose derivative exists over the range between two points b_1 and b_2, there exists a third point c between b_1 and b_2 for which

$$f(b_2) - f(b_1) = f'(c)(b_2 - b_1).$$

To apply this theorem in our case, we take $f(x) = \frac{d}{dx}\psi(x)$ in (2). In any case where $V(x)$ is continuous (although perhaps very steep) for any two points $b_1 < -a < b_2$ straddling the interface at $x = -a$,

$$\frac{d}{dx}\psi(b_2) - \frac{d}{dx}\psi(b_1) = (\frac{2m}{\hbar^2}(V(c) - E)\psi(x))(b_2 - b_1),$$

for some point c in the range $b_1 < c < b_2$. Because $V(x)$ remains finite in the range $b_1 < x < b_2$, as we take the limit $b_1 \to -a^-$ and $b_2 \to -a^+$, the left hand side of the above equation will approach zero and thus $\frac{d}{dx}\psi(-a^+) - \frac{d}{dx}\psi(-a^-) \to 0$, and we have proven that the derivative $\psi'(x)$ remains continuous even if the potential possesses a *finite* discontinuity.

A similar argument may be applied to $\psi(x)$ to show that whenever $\psi'(x)$ is finite, the wavefunction itself is also continuous. Taken together, these two facts give our second boundary condition:

$$\text{Boundary Condition II: For Finite } V(x),\ \psi(x) \text{ and } \psi'(x) \text{ are continuous across all boundaries: } \Delta\psi = \Delta\psi' = 0. \tag{8}$$

This tells us how to connect solutions across the interface at $x = -a$ and continue our solution from region I into region II.

1.3 Region II

The solution in region II must solve the differential equation (2) and match the appropriate boundary conditions. The boundary conditions at $x = -a$, as discussed in the previous section, are that the slope and value of the wavefunction at $x = -a$ must match those of the wavefunction in region I,

$$\begin{aligned} \psi_I(-a) &= A = \psi_{II}(-a) \\ \psi'_I(-a) &= \kappa A = \psi'_{II}(-a) \end{aligned} \tag{9}$$

In region I the TISE reads

$$\frac{d^2}{dx^2}\psi_{II}(x) = -\frac{2m}{\hbar^2}E\psi_{II}(x) \equiv -k^2\psi_{II}(x), \tag{10}$$

where we have introduced a new constant

$$\frac{\hbar^2 k^2}{2m} \equiv E, \tag{11}$$

with a minus sign in (10) to remind us of the sign of the left hand side of (2).

Just as in region I, this is a second order linear differential equation with constant coefficients, and so again, this equation must also have solutions of the form $Ae^{\alpha x}$. In this case $\alpha^2 = -k^2 \Rightarrow \alpha = \pm ik$. The general solution to (10) is thus $\psi_{II}(x) = A''e^{ikx} + B''e^{-ikx}$, where A'' and B'' are the two independent constant parameters. Again, it is good form to write the solution as centered at the boundary $\psi_{II}(x) = A'e^{ik(x+a)} + B'e^{-ik(x+l)}$, where $A' \equiv e^{-ika}A''$ and $B' \equiv e^{-ika}B''$. In this case, one final redefinition of constants is convenient. Because the TISE is a real differential equation, we expect it to possesses two linearly independent *real* solutions. We bring this out explicitly by writing new constants $A_{II} \equiv A' + B'$ and $B_{II} \equiv i(A' - B')$ giving us the form

$$\psi_{II}(x) = A_{II}\cos\left(k(x+a)\right) + B_{II}\sin\left(k(x+a)\right) \tag{12}$$

Again, one may arrive at 12 directly. In a classically *allowed* region (where we define k's instead of κ's), the solutions are always sinusoidal and direct substitution verifies that (12) solves (10).

With the most general solution to the differential equation region II, it remains only to adjust the coefficients so that the boundary conditions are matched. With the function written in this form, the algebra of this is simple,

$$\psi_{II}(-a) = A_{II}$$

and

$$\psi'_{II}(-a) = kB_{II}.$$

Comparing this with with the value and slope carried across, "injected" from region I (9) we have $A_{II} = A$, $B_{II} = \frac{\kappa}{k}A$. With the constants determined, we have the final solution in region II,

$$\psi_{II}(x) = A\left(\cos k(x+a) + \frac{\kappa}{k}\sin k(x+a)\right).$$

1.4 Boundary Between Region II and Region III

The same logic applies here as with the boundary between regions I and II. Again the slope and value of the wavefunction must be continuous across the boundary, this time at $x = a$. The value and slope injected from region II into region III is then just

$$\psi_{II}(a) = A\left(\cos 2ka + \frac{\kappa}{k}\sin 2ka\right) = \psi_{III}(a)$$

and

$$\psi'_{II}(a) = A\left(-k\sin 2ka + \kappa\cos 2ka\right) = \psi'_{III}(a).$$

1.5 Region III

The TISE in this region is precisely the same as it was in region I. Using the same definition for κ (4) , the general solution in region III is of the form $A'e^{\kappa(x-a)} + B'e^{-\kappa(x-a)}$. To ease the algebra we again centered the solution about the boundary $x = a$. To further reduce the algebra, we introduce our final "trick." Taking linear combinations we define new constants $A_{III} \equiv A' + B'$ and $B_{III} \equiv A' - B'$, so that

$$\psi_{III}(x) = A_{III}\cosh\kappa(x-a) + B_{III}\sinh\kappa(x-a). \tag{13}$$

Again, one may arrive at 13 directly. In a classically *forbidden* region (where we define κ's instead of k's), the solutions are always sinusoidal and direct substitution verifies that (13) solves (3).

Matching the boundary conditions with this form is straight forward, we find

$$\psi_{III}(a) = A_{III} = \psi_{II}(a) = A\left(\cos 2ka + \frac{\kappa}{k}\sin 2ka\right)$$

$$\psi'_{III}(a) = \kappa B_{III} = \psi'_{II}(a) = A\left(-k\sin 2ka + \kappa\cos 2ka\right).$$

The solution in region III as propagated from region I through region II then reads

$$\psi_{III}(x) = A\left((\cos 2ka + \frac{\kappa}{k}\sin 2ka)\cosh\kappa(x-a) + (-\frac{k}{\kappa}\sin 2ka + \cos 2ka)\sinh\kappa(x-a)\right). \tag{14}$$

1.6 Discussion of solution

Note that by the matching of boundary conditions of value and slope at each of the interfaces, *the entire solution at a given energy E is determined by the solution in one of the regions* (in this case, the solution in region where we started). This is just a reflection of the fact that the solution of a *second* order differential equation is completely determined by any two conditions, in this case the value and slope of the solution at any point. The entire solution we have built up is

$$\psi(x) = \begin{cases} Ae^{\kappa(x+a)} & x < -a \qquad \text{(Region I)} \\ A\left(\cos k(x+a) + \frac{\kappa}{k}\sin k(x+a)\right) & -a < x < a \qquad \text{(Region II)} \\ A\left((\cos 2ka + \frac{\kappa}{k}\sin 2ka)\cosh\kappa(x-a)\right. & \\ \left.\quad +(-\frac{k}{\kappa}\sin 2ka + \cos 2ka)\sinh\kappa(x-a)\right) & a < x \qquad \text{(Region III)} \end{cases} \tag{15}$$

First note that there a single degree of freedom A left. This freedom is just a constant multiplying the overall solution. This degree of freedom cannot be determined from the TISE alone because the TISE is a linear equation and any solution to it may be multiplied by an overall constant. Ultimately, A will be determined by the physical condition of normalization of $\psi(x)$ as a quantum mechanical wavefunction. For the solution to be normalizable, we must also avoid exponentially growing solutions in region III. Because, the differential equation completely determines the form of $\psi(x)$ once we set the behavior in region I, we are only be able to meet the condition that there is no growing part to our solution in region III when k and κ have a very special relationship. Because $k \equiv \sqrt{2mE}/\hbar$ and $\kappa \equiv \sqrt{2m(V_0 - E)}/\hbar$ are ultimately defined in terms of E, it is precisely this relationship between k and κ which will determine the physically allowed eigenenergies of our system, the energies of the pure energy states of the system.

1.7 Eigenenergies

To find the allowed energies, we must impose the condition on (6) that $\psi(x \to \infty)$ show no exponentially growing behavior. To explore the exponential behaviors of the solution in region III, we expand the hyperbolic functions in $\psi_{III}(x)$ in their exponential components,

$$\begin{aligned}\psi_{III} &= A\left((\cos 2ka + \frac{\kappa}{k}\sin 2ka)\cosh\kappa(x-a) + (-\frac{k}{\kappa}\sin 2ka + \cos 2ka)\sinh\kappa(x-a)\right)\\ &= A\left((2\cos 2ka + \frac{\kappa}{k}\sin 2ka - \frac{k}{\kappa}\sin 2ka)e^{\kappa(x-a)}/2 + (\frac{\kappa}{k}\sin 2ka + \frac{k}{\kappa}\sin 2ka)e^{-\kappa(x-a)}/2\right).\end{aligned}$$

The first term gives rise to exponential growth as $x \to \infty$ and so its prefactor must be zero,

$$0 = 2\cos 2ka + \frac{\kappa}{k}\sin 2ka - \frac{k}{\kappa}\sin 2ka \tag{16}$$

To simplify this condition, we expand the double angle trigonometric functions and multiplying through by $k\kappa$. (Note that this may introduce an extraneous root at $k = 0$) The eigensolution condition on k and κ then becomes

$$\begin{aligned}0 &= k\kappa\cos^2 ka - k\kappa\sin^2 ka + \kappa^2\sin ka\cos ka - k^2\sin ka\cos ka\\ &= (k\cos ka + \kappa\sin ka)(\kappa\cos ka - k\sin ka),\end{aligned} \tag{17}$$

Having succeeded in factoring our expression in the last step, we have simplified the condition considerably. Unfortunately, the factors still represent fairly complex transcendental equations for the energy E. To proceed, we must resort to a numerical or graphical solution method for each of the two roots of (17).

$$k/\kappa = -\tan ka \qquad \text{Odd solutions} \tag{18}$$

$$k/\kappa = \cot ka \qquad \text{Even solutions.} \tag{19}$$

We will see later that these roots represent either the odd or even solutions, respectively.

The graphical solution proceeds as follows. First we note that k is related to E through (11)

$$??k \equiv \sqrt{\frac{2m}{\hbar^2}E}, \tag{20}$$

so that working with either k or E is nearly equivalent. Next, κ and k share the relationship,

$$\kappa \equiv \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} = \sqrt{\frac{2m}{\hbar^2}V_0 - k^2} \equiv \sqrt{Q_0^2 - k^2}, \tag{21}$$

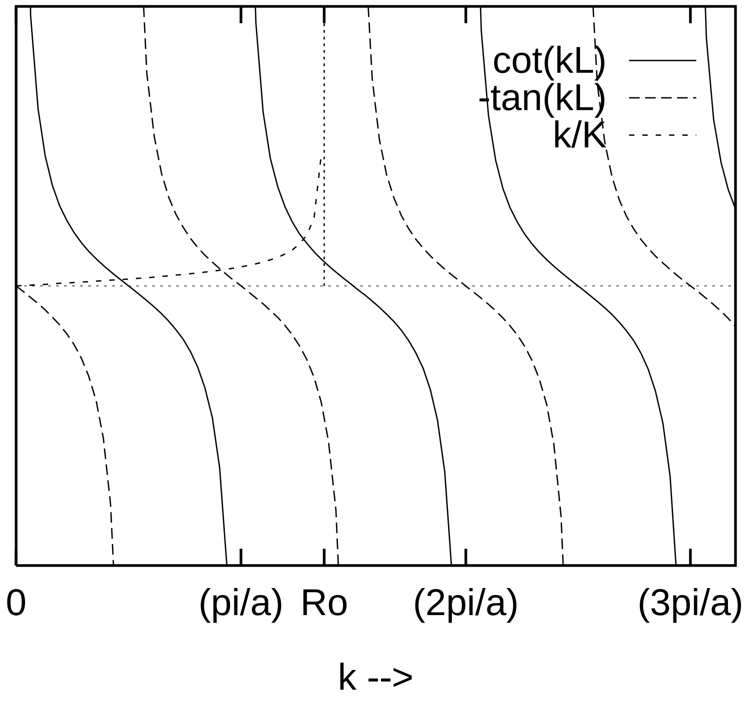
where we have defined

$$Q_0 \equiv \sqrt{\frac{2m}{\hbar^2}V_0}.$$

Plotting the three functions $k/\sqrt{Q_0^2 - k^2}$, $\tan ka$ and $\cot ka$ on the same graph, the solutions to (18) and (19) may be read off as the k values of the intersections of the curves in Figure 1.7.

The first intersection (at $k = 0$) is an extraneous root we introduced when we multiplied by $k\kappa$. This must extraneous root, because when we let $k \to 0$ in (16), which is the value of the prefactor to the exponentially growing solution in region III, we get $2 + 2\kappa a > 0$, which would lead to exponentially growing solutions. The only extraneous root we introduced was for $k = 0$, all remaining intersections of the curves in the figure then represent allowable eigensolultions to the TISE.

From the figure we learn several things. First, we see that there is always at least one allowed energy, corresponding to the intersection of the $k/\sqrt{Q_0^2 - k^2}$ curve with the first branch of the $\cot ka$ curve. This occurs for $k < \pi/2a$ and is always the first, lowest energy (ground state) solution. After



that, $k/\sqrt{Q_0^2 - k^2}$ heads toward $+\infty$ at $k = Q_0$, and there may or may not be further solutions according to whether $Q_0 > \pi/a$, which would then allow an intersection with the next branch.

For the case in the figure $Q_0 \approx 1.4\pi/a$ and so there are three allowed pure energy states, one at $k \approx 0.5\pi/a$, $k \approx 0.9\pi/a$ and one at $k \approx 1.2\pi/a$. We see that in general there are $N = [2Q_0/(\pi a)]+1 \equiv \left[\sqrt{8m^2V_0/(\pi^2\hbar^2a^2)}\right] + 1$ allowed eigenenergies, where $[x]$ is the notation for taking the integer part of a real number x.

For the lower bound states, the curve $k/\sqrt{Q_0^2 - k^2}$ stays relatively close to the k-axis so that the solutions are at approximately $k = \frac{\pi}{2a}n$ for $n = 1, 2, ...$, correspondingly precisely to the Bohr-Sommerfeld solutions

$$E_n = \frac{\hbar^2\pi^2}{2m(2a)^2}n^2$$

for a particle in a box of size $2a$ and matching, as we shall discuss shortly, the eigenenergies for the infinite square well, $V_0 \to \infty$. This is physically reasonable, if the solutions have energies E far below V_0, these states act as through V_0 were infinite.

Finally, note that as E (or equivalently k) increases the k/κ curve intersects alternately the two curves $\cot ka$ and $-\tan ka$ so that the $\cot ka$ root corresponds to even numbered excited solutions (we regard the ground state as $n = 0$) $-\tan ka$ root corresponds to the odd numbered solutions.

1.8 Wavefunctions

Substituting the expressions for k/κ for the even (19) or odd (18) states into the form for the wavefunction (15) gives,

$$\psi(x) = \begin{cases} Ae^{\kappa(x+a)} & x < -a \qquad \text{(Region I)} \\ A\frac{\cos kx}{\cos ka} & -a < x < a \qquad \text{(Region II)} \\ Ae^{\kappa(x-a)} & a < x \qquad \text{(Region III)} \end{cases} ,$$

for even solutions and

$$\psi(x) = \begin{cases} Ae^{\kappa(x+a)} & x < -a \qquad \text{(Region I)} \\ -A\frac{\sin kx}{\sin ka} & -a < x < a \qquad \text{(Region II)} \\ -Ae^{\kappa(x-a)} & a < x \qquad \text{(Region III)} \end{cases} ,$$

for odd solutions, respectively.

Note that the even solutions are indeed even functions $\psi(x) = \psi(-x)$ and the odd solutions are odd functions of x, $\psi(x) = -\psi(-x)$.