Lecture Quantum Physics
Examples of One-Dimensional Potentials

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1 Dirac Delta Function Potential

We start by considering the Dirac delta function, which can be used as a model potential. We recall that the delta function is defined as

$$\delta(x) = \lim_{b\to\infty} \sqrt{\frac{b}{\pi}} e^{-bx^2} \tag{1}$$

i.e. we can think of it as the limit of infinitely thin Gaussian curves. It has been normalized such that

$$\int_{-\infty}^{\infty} \delta(x) dx = 1 \tag{2}$$

and it satisfies

$$\delta(x) = \begin{cases} 0 & x \neq 0 \\ \infty & x = 0 \end{cases} \tag{3}$$

The Dirac delta have the very useful property that they pick out one value from a function with which it is multiplied and integrated over, i.e. we have

$$\int_{\infty}^{\infty} f(x)\delta(x) dx = f(0) \tag{4}$$

or more generally

$$\int_{\infty}^{\infty} f(x)\delta(x-a) dx = f(a) \tag{5}$$

where $f(x)$ can be any well-behaved function.

We now consider the delta function potential, which we define to be

$$\frac{2m}{\hbar^2} V(x) = -\frac{\alpha}{a}\delta(x) \tag{6}$$

where a has units of length and α is unitless and determines the strength of the potential. We note that the Dirac delta function has units of $1/[L]$, which can be seen from the normalization condition demanding that $\delta(x)dx$ is unit less, and knowing that dx has units of length. We have that since $\hbar$ has units of $[M][L]^2[T]^{-1}$. Knowing that energy has units of $[M][L]^2[T]^{-2}$ we get that $\frac{2m}{\hbar}V(x)$ has units of $1/[L]^2$.

We now consider the boundary conditions of the wave function There are in this case only two regions, namely $x < 0$ and $x > 0$. The Schrödinger equation being a second-order differential equation we would like to demand the wavefunction being continuous everywhere. We consider the integral from infinitesimally above $x = 0$ to infinitesimally above of both the wavefunction and its first derivative. We start with the derivative

$$\int_{0^-}^{0^+} \frac{d^2\psi}{dx^2} = (\frac{d\psi}{dx})_{0^+} - (\frac{d\psi}{dx})_{0^-} \tag{7}$$

$$= \frac{2m}{\hbar^2} \int_{0^-}^{0^+} [V(x) - E]\psi(x)dx \tag{8}$$

using the Schrödinger equation. We use that the area of integration is infinitesimally small and the intgrand is not infinite to obtain

$$\frac{2mE}{\hbar^2} \int_{0^-}^{0^+} \psi(x)dx = 0 \tag{9}$$

Furthermore, we have

$$\frac{2m}{\hbar^2} \int_{0^-}^{0^+} V(x)\psi(x)dx = - \frac{\alpha}{a} \int_{0^-}^{0^+} \delta(x)\psi(x)dx = -\frac{\alpha}{a}\psi(0) \tag{10}$$

We therefore have

$$(\frac{\partial\psi}{\partial x})_{0^+} - (\frac{\partial\psi}{\partial x})_{0^-} = -\frac{\alpha}{a}\psi(x) \tag{11}$$

where we see that the first derivative has a discontinuity at zero. We also see why the derivative is generally continuous for non-singular potentials.

We now solve Schrödinger's equation for the Dirac delta potential. We have for $x \neq 0$ that

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \tag{12}$$

We are searching bound states ($E < V_0$) we have the solution

$$\psi = Ae^{i\kappa x} + Be^{-i\kappa x} \tag{13}$$

where

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}} \tag{14}$$

As for the square wells we demand the wavefunction to be continuous which gives that $A = B$

$$\psi(x) = \begin{cases} Ae^{i\kappa x} & x \leq 0 \\ Ae^{-i\kappa x} & x \geq 0 \end{cases} \tag{15}$$

We substitute the wavefunction into our condition for the derivatives' continuity and we find

$$-2\kappa A = -\frac{\alpha}{a}A \tag{16}$$

or equivalently

$$\sqrt{\frac{-2mE}{\hbar^2}} = \frac{\alpha}{2a} \tag{17}$$

This gives the energy of the bound state

$$E = -\frac{\hbar^2\alpha^2}{8ma^2} \tag{18}$$

So we have found that the Dirac delta only take one bound state. This is very reasonable considering its shape, and that there are no other shapes which we could conceive of which could be viable wavefunctions for this systems, up to an overall phase. This is because we must demand the wavefunction being exponentially dampened away from $x = 0$.

2 Molecular Binding

2.1 Double Square Well

Having seen that the finite square well can be a model system for a particle trapped by a simple atom such as Hydrogen, we shall now run with this and consider a double finite square well, which we can think of as modelling a simple molecule such as an Hydrogen molecule ion H_2^+. By studying this simple toy system, we can gain insights into why molecules can exist. We can see straight away that for bound states the wavefunctions must be oscillatory inside of the wells and decrease exponentially away from the wells.

This is quite a bit more involved to solve compared to the square wells, since we have five different regions and eight boundary conditions for the wavefunctions and its derivatives. However we can exploit the symmetry of the problem and note that the potential is an even function $V(-x) = V(x)$. We also know that the ground state is even and knowing the shape of the solutions inside of the wells we can sketch the shape of the ground state and the first excited state.

Classically one might expect that the electron would be trapped in the vicinity of either on or the other protons, but here we see that the electron is equally likely to be at both protons, due to the symmetry of potential and therefore also of the wavefunctions. Furthermore, there is also a non-vanishing probability of finding the electron in the region between the protons. It is this sharing of the electron between the wells which make the molecule stable by increasing the binding, or actually by making it more energy efficient for the electron to be close to the protons.

2.2 Delta Function Well

We shall simplify the potential even further, and instead of the double square well consider the Dirac delta function well. We define the following potential

$$\frac{2m}{\hbar^2}V(x) = -\frac{\alpha}{a}[\delta(x-a) - \delta(x+a)] \tag{19}$$

That is, two delta functions which are separated by a distance $2a$. The wavefunction must now satisfy

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \tag{20}$$

for the ($E < 0$) bound solutions. We again define

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}} \tag{21}$$

Since $E < 0$ we have that $\kappa \in \mathbb{R}_+$. We have the exponential functions solving the Schrödinger equations for $V(x) = 0$. We note that for the $E > 0$ we would get complex exponentials and oscillatory solutions. We use that we must demand that the exponentials which diverge for $|x| \to \infty$ must be discarded, which gives us

$$\psi(x) = \begin{cases} Ce^{\kappa x} & x < -a \\ A\cosh(\kappa x) & x \in (-a, a) \\ Ce^{-\kappa x} & x > a \end{cases} \tag{22}$$

where we have

$$\cosh(\kappa x) = \frac{e^{\kappa x} + e^{-\kappa x}}{2} \tag{23}$$

We now apply boundary conditions. We only need to do it explicitly for $x = a$, since the system is symmetric. Continuity of the wavefunction gives

$$A\cosh(\kappa x) = Ce^{-\kappa x} \tag{24}$$

For the first derivative we once again have a discontinuity

$$(\frac{\partial\psi}{\partial x})_{0^+} - \ (\frac{\partial\psi}{\partial x})_{0^-} = -\frac{\alpha}{a}\psi(x) \tag{25}$$

We insert the wavefunctions and get

$$-\kappa Ce^{-\kappa x} - \kappa A\sinh(\kappa x) = -\frac{\alpha}{a}A\cosh(\kappa x) \tag{26}$$

where

$$\sinh(\kappa x) = \frac{e^{\kappa x} - e^{-\kappa x}}{2} \tag{27}$$

Substituting the continuity equation for the wavefunction itself into the condition for the discontinuity of the derivative and dividing by $\cosh(\kappa x)$ we obtain

$$\tanh(\kappa x) = \frac{\alpha}{\kappa a} - 1 \tag{28}$$

where

$$tanh(\kappa x) = \frac{sinh(\kappa x)}{\cosh(\kappa x)} \tag{29}$$

We have now found the equation determining the allowed energies, and we see that it is an transcendental equation which must be solved graphically in a manner similar to for the finite square well, where we must determine where the curve $\frac{\alpha}{\kappa a} - 1$ and $\tanh(\kappa x)$ intersect. Since we know that the tangent hyperbolicus functions is always less than one we can say with certainty the crossing will occur somewhere such that

$$\frac{\alpha}{\kappa a} - 1 < 1 \tag{30}$$

Inserting from the definition of κ we now find

$$E < -\frac{\hbar^2\alpha^2}{8ma^2} \tag{31}$$

We now compare this with the single Dirac delta potential and we see that the double delta potential well has lower energy. This means that it is energetically preferable for system to organize into a molecule than single atoms.

It is not guaranteed that the double wells such as delta wells and the double square wells have excited states. We stated previously that the double well will have an excited state, but for the delta well it will depend on the strength of the potential α whether or not there are excited states. The hydrogen molecule does not have any excited states.

3 Scattering

Until now we have mostly considered potentials which have, at least some, bound states which have discrete energy spectra. We shall now begin studying one-particle systems for which the Schrödinger equation takes solutions fir which the particle is not confined to a given region of space. For such systems there exists a continuum of allowed energies, since there are no constraining condition on the energies. That is, the energies are no longer quantized. We generate physically acceptable solutions in such systems by superposition of several solutions to form wave packets, which will be normalizable. These solutions will also be dynamic, i.e. be evolving in time, since they consists of superpositions of energy eigenstates.

We consider as a start the step potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases} \tag{32}$$

Initially we start by assuming the energy is larger than the potential, i.e. $E > V_0$. We then have to the left of the step barrier

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \qquad x < 0 \tag{33}$$

For notational simplicity we define

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{34}$$

and we then have the solutions on the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad x < 0 \tag{35}$$

Here we note the importance of using complex exponentials instead of trigonometric functions, since we can then associate them with incoming and outgoing waves.

We now consider the right side of the potential barrier, where we have the Schrödinger equation

$$\frac{d^2\psi}{dx^2} = -\sqrt{\frac{2m(E - V_0)}{\hbar^2}} \qquad x > 0 \tag{36}$$

where we define

$$k_0 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} = \sqrt{k^2 - \frac{2mV_0}{\hbar^2}} \tag{37}$$

Since we know $E > V_0$ we have the solutions

$$\psi(x) = Ce^{ik_0x} + De^{-ik_0x} \qquad x > 0 \tag{38}$$

We now use the requirement that the wavefunction must be continuous and have continuous first derivatives. We consider the potential problematic point at $x = 0$. Continuity of the wavefunction gives

$$A + B = C + D \tag{39}$$

and the first derivatives

$$ik(A - B) = ik_0(C - D) \tag{40}$$

We now see that we have only two equations for four unknowns. Which means we are free to chose some of the constants as we please, or on the basis of physical considerations, since there are many configurations of constants which satisfy the equations. We therefore choose $D = 0$. Which gives

$$\psi(x) = Ce^{ik_0x} \qquad x > 0 \tag{41}$$

We may now easily solve the remaining equations by expressing B and C in terms of A

$$B = \frac{k - k_0}{k + k_0}A \tag{42}$$

$$C = \frac{2k}{k + k_0}A \tag{43}$$

Where we note that this solution works for any value of k, i.e. for any energy. Thus the energy is continuous as there are no constrains which compels it to be quantized. In this case we cannot determine the constant A from normalization conditions but since the wavefunction doesn't go to zero as x goes to infinity, it is not normalizable. We will therefore consider the probability current instead, which describes the probability of reflection and transmission and is given as

$$j_x = \frac{\hbar}{2mi}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right) \tag{44}$$

We have the wavefunction

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik_0 x} & x > 0 \end{cases} \tag{45}$$

Which gives the probability current

$$j_x = \begin{cases} \frac{\hbar k}{m}(|A|^2 - |B|^2) & x < 0 \\ \frac{\hbar k_0}{m}|C|^2 & x > 0 \end{cases} \tag{46}$$

Here the positive term represent current in the positive x-direction and the negative in the direction towards negative values of x. Each term is equal to the probability density multiplied by the velocity of propagation $\hbar k/m$ left of the origin and $\hbar k_0/m$ right of the origin. This is also why we chose to set $D = 0$, as such a term would imply a probability current coming in from the right. This is unphysical when we consider a scattering experiment with particles coming in from the left. We now define the reflection coefficient R, the probability of reflection, as the ratio of the magnitude of reflected and incoming current

$$R = \frac{j_{ref}}{j_{inc}} = \frac{\frac{\hbar k}{m}|B|^2}{\frac{\hbar k}{m}|A|^2} = \frac{|B|^2}{|A|^2} \tag{47}$$

Similarly, we define the transmission coefficient

$$T = \frac{j_{trans}}{j_{inc}} = \frac{\frac{\hbar k_0}{m}|B|^2}{\frac{\hbar k}{m}|A|^2} = \frac{k_0|B|^2}{k|A|^2} \tag{48}$$

Where we note that the transmission coefficient is taking into account that the particle moves with a different velocity for $x > 0$ and this is why the transmission coefficient is not just the ratio of $|B|^2$ to $|A|^2$. We substitute for the expressions we found previously for A and B and find

$$R = \frac{(k - k_0)^2}{(k + k_0)^2} \tag{49}$$

and

$$T = \frac{4kk_0}{(k + k_0)^2} \tag{50}$$

Where we can find comfort in conforming that

$$R + T = 1 \tag{51}$$

These result seem strange from a classical point of view, since a particle approaching the potential step would slow down without being reflected. However, from a wave mechanics-point of view this makes sense, knowing that a wave propagating on a rope would partly be reflected and partly transmitted if there were a discontinuity in density and thus in the speed of reflection.

We stated previously that a way of generating physically viable solutions is to superimpose solutions to Schrödinger's equation to a normalizable solution, just as we've already seen for the free particle. For $E > V_0$ this superposition can be written as

$$\psi(x,t) = \begin{cases} \int_{-\infty}^{\infty} \left[A(k)e^{i(kx - \frac{Et}{\hbar})} + B(k)e^{-i(kx + \frac{Et}{\hbar})}\right] & x < 0 \\ \int_{-\infty}^{\infty} C(k)e^{i(k_0 x - \frac{Et}{\hbar})}dx & x > 0 \end{cases} \tag{52}$$

Where each of the terms signify a wave packet travelling in a given direction in both of the regions. We once again see why we set $D = 0$ even though the equations still would hold for $D0$, but on physical grounds we don't want a wave travelling towards the origin from the right, as this doesn't make sense in the scattering scenario we are considering.

We shall now consider the case where the energy is less than that of the potential step, i.e. $E < V_0$, where we have, as before, the same general form of the elementary solutions

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{\kappa x} + De^{-\kappa x} & x > 0 \end{cases} \tag{53}$$

where we define

$$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \tag{54}$$

Again we set $D = 0$, since we want a normalizable function and the corresponding term diverge as $|x| \to \infty$. Continuity of the wavefunction and its derivatives now yield

$$A + B = C \tag{55}$$

and

$$ik(A - B) = -\kappa C \tag{56}$$

We rearrange to get

$$\frac{B}{A} = \frac{k - i\kappa}{k + i\kappa} \tag{57}$$

We then get

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{B^* B}{A^* A} = (\frac{k - i\kappa}{k + i\kappa})(\frac{k + i\kappa}{k - i\kappa}) = 1 \tag{58}$$

Thus 100% of the incident wave is reflected. This might seem counter-intuitive, since the we have a non-zero wavefunction to the right of the step. This can however be seen to hold form the probability current where we have

$$j_x = \begin{cases} \frac{\hbar k}{m}(|A|^2 - |B|^2) & x < 0 \\ 0 & x > 0 \end{cases} \tag{59}$$

So we have the transmission coefficient vanishing in this expression, i.e. $T = 0$ and we thus also have the probability conserved as $R + T = 1$ as we want.

4 Tunnelling

We shall no consider the case where a particle with energy $E \in (0, V_0)$ is incident on an energy barrier defined as

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \in (0, a) \\ 0 & x > 0 \end{cases} \tag{60}$$

We thus consider the case where the potential barrier is larger than the energy, which in classical mechanics would imply that the transmission probability would be zero. In quantum mechanics we have a non-zero transmission probability and we call this phenomena tunnelling. For a particle incident on the barrier from the left the wavefunction is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{\kappa x} + Ge^{-\kappa x} & x \in (0, a) \\ Ce^{ikx} & x > a \end{cases} \tag{61}$$

where we once again defined

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{62}$$

and

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{63}$$

Boundary conditions from the continuity of the wavefunction gives

$$A + B = F + G \qquad\qquad \text{at } x = 0 \tag{64}$$

and

$$Fe^{\kappa a} + Ge^{-\kappa a} = Ce^{ika} \qquad \text{at } x = a \tag{65}$$

Continuity of the first derivative gives

$$ik(A - B) = \kappa(F - G) \qquad\quad \text{at } x = 0 \tag{66}$$

and

$$\kappa(Fe^{\kappa a} - Ge^{-\kappa a}) = ikCe^{ika} \qquad \text{at } x = a \tag{67}$$

We now determine the transmission coefficient, which we know is defined as $T = |A|^2/|C|^2$. Since we have that

$$T = \frac{j_{trans}}{j_{inc}} = \frac{|C|^2}{|A|^2} \tag{68}$$

We can use our four equations to determine the four unknowns. We start by eliminating B from the first and the third and we get

$$2ikA = (ik - \kappa)F + (ik + \kappa)G \tag{69}$$

and eliminating F from the second and forth gives

$$2\kappa FGe^{\kappa a} = (\kappa + ik)Ce^{ika} \tag{70}$$

and G from the second and forth equations

$$2\kappa Fe^{-\kappa a} = (\kappa - ik)Ce^{ika} \tag{71}$$

Substituting the expressions for F and G in the two latter subsidiary equations into the first one gives

$$2ikA = (ik - \kappa)\big[\frac{\kappa - ik}{2\kappa}Ce^{ika+\kappa a}\big] + (ik + \kappa)\big[\frac{\kappa + ik}{2\kappa}Ce^{ika-\kappa a}\big] \tag{72}$$

This is equivalent to

$$\frac{A}{C} = \frac{e^{ika}}{4ik\kappa}\big[(-\kappa^2 + k^2 + 2ik\kappa)e^{\kappa a} + (\kappa^2 - k^2 + 2ik\kappa)e^{-\kappa a}\big] \tag{73}$$

$$= \frac{e^{ika}}{2ik\kappa}\big[(k^2 - \kappa^2)\sinh(\kappa a) + 2ik\kappa\cosh(\kappa a)\big] \tag{74}$$

Which then gives

$$\frac{|A|^2}{|C|^2} = \frac{1}{4k^2\kappa^2}\big[(k^2 - \kappa^2)^2\sinh(\kappa a)^2 + 4k^2\kappa^2\cosh^2(\kappa a)\big] \tag{75}$$

$$= 1 + \frac{(k^2 + \kappa^2)^2}{4k^2\kappa^2}\sinh^2(\kappa a) \tag{76}$$

where we have used that

$$\cosh^2(x) - \sinh^2(x) = 1 \tag{77}$$

This gives us

$$T = \left[1 + \frac{(k^2+\kappa^2)^2}{4k^2\kappa^2}\sinh^2(\kappa a)\right]^{-1} \tag{78}$$

Tunnelling is a very commonly occurring thing on a microscopic scale so this tunnelling transmission probability is often very large for e.g. electrons, but for macroscopic objects the transmission probability is minuscule.

For a thick barrier the expression can be simplified slightly. If a is very small compared to the energy of the particle, such that $\kappa a \gg 1$. In this case we have

$$\sinh(\kappa a) = \frac{e^{\kappa a} - e^{-\kappa a}}{2} \approx \frac{1}{2}e^{\kappa a} \gg 1 \tag{79}$$

and therefore we have

$$T = \left(\frac{4k\kappa}{k^2+\kappa^2}\right)^2 e^{-\kappa a} \tag{80}$$

We see here that the transmission is very sensitive to the thickness of the barrier a and the value of κ which depends on $V_0 - E$, since there is an exponential dependence on it.

If e.g. for a certain value of E and V_0 and with $a = 1nm$ we have $e^{-2\kappa a} = 10^{-10}$, which means that there may certainly be some tunnelling since there are so many electrons per cubic centimeters (typically 10^{22}). However, if we were to have $a = 5nm$ instead of the one nanometer barrier we would have $T = 10^{-50}$, which would mean that no electrons will be able to tunnel.

This is how Scanning Tunnelling Microscopes work. They exploit that there is a 2% change in current through the tip of the microscope probe when the distance changes by $0.001nm$. The tip is then dragged over the surface to the imaged and traces out the contours of the surface and thereby creates a sort of image of it.

4.1 Field Emission of Electrons: Tunnelling through a Non-Square Barrier

For $\kappa a \gg 1$

$$\ln(T) \approx \ln\left(\left(\frac{4k\kappa}{k^2+\kappa^2}\right)^2\right) - 2\kappa a \tag{81}$$

$$\approx C - 2\kappa a \tag{82}$$

where C is some constant. Where we have used that in the last step the logarithmic term will not change much compared to the one which is linear in energy. If the barrier varies slowly with position compared with κ^{-1} we can approximate it as a series of square barriers, which are thick enough for us to make the "thick barrier"-approximation. We write the approximation as

$$\ln(T) \approx C - 2\int\sqrt{\frac{2m[V(x)-E]}{\hbar^2}}dx \tag{83}$$

for the whole barrier, where the limits of integration includes the region where $V(x) > E$. This should be fairly accurate close to the classical turning points, where $V(x) \approx E$ and thus κ is roughly zero.

An application of this is field emission of electrons. We have already discussed the photoelectric effect, where we had that the energy needed for ejecting the most energetic electrons is the work function W. Another way of liberating these electrons is by changing the shape of the potential well and thereby allow the electrons to tunnel out. If some negative charge is put on the metal the surface near the metal will have a constant electric field of magnitude $\mathcal{E}$ which is proportional to the surface charge density. Since the force $e\mathcal{E}$ is presumed to be constant the potential energy in the vicinity of the surface is $W - e\mathcal{E}x$, where x is the perpendicular distance from the surface and W is the potential energy at the surface. The transmission is then roughly given by

$$T = Ce^{-2\sqrt{\frac{2m}{\hbar^2}}\int_0^L \sqrt{W - e\mathcal{E}x}dx} \tag{84}$$

where C is a constant and $L = W/e\mathcal{E}$ is the distance the most energetic electrons must tunnel before reaching a region outside the metal where $E > V$. Performing the integral gives

$$T = Ce^{-\frac{4\sqrt{2m}}{3\hbar e\mathcal{E}}W^{\frac{3}{2}}} \tag{85}$$

This is called the Fowler-Nordheim relation. It was one of the first predictions of quantum mechanics.