What's in the box? A quantum or classical particle?

A theoretical analysis of the effects when stretching potential wells in the quantum mechanical and classical theory.

Finn ten Hove
Supervisor: Prof. Dr. R. Kleiss

Radboud Universiteit Nijmegen

High Energy Physics Department
Radboud University Nijmegen
The Netherlands
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Abstract

In this thesis the effects of stretching potential wells are examined. Specifically the change in the energy levels and the corresponding force applied on the barriers of the potential. This force can be measured from outside the well to determine how the particle behaves. Both the quantum mechanical and classical theory will be used to calculate this force. Comparing both results you could determine whether you can tell from outside the well if the particle inside behaves quantum or classical. It turns out there is a difference between quantum and classical particles in an (stretched) harmonic potential, finite square well and a stretched triangular potential. In these cases the quantum theory yields extra terms which create slight deviations from the classical theory. It is not possible to spot this difference for a infinite square well, spherical well and the normal triangular potential (not stretched). In the classical limit, for large energies, the quantum theory gives the same result as the classical theory for all potentials as you would expect to happen.

Contents

1 Introduction

We all know the famous quantum mechanical potentials like the infinite square well and harmonic potential and the corresponding wave functions and energy levels. These potentials become more interesting when you start to change the shape of the potential. In this thesis the effects of stretching a potential are examined. The potentials are stretched by adding a variable space of zero potential with size L within the two sides of a potential. By changing the size L the energies of the system change. Increasing L actually decreases the energy levels, this effect can be interpreted as the particle inside the potential performing work on the barriers. Associated with the work there is also a force that is applied onto the barriers. The energy levels and force of the stretched potentials will be calculated. The calculation will be done using the classical and the quantum mechanical theory. Both results will be compared to see if any differences occur. If there are differences between the theories it would be possible to determine from the outside whether the particle inside the potential well behaves quantum or classical. These calculations will be done for several potentials including: the infinite square well, the finite square well, harmonic potential well, triangular potential well and spherical well. These potential (except the spherical well) are only analysed in one dimension.

For every potential the corresponding wave functions need to be calculated first. This will be done by solving the Schrödinger Equation in the non-zero potential parts. The wave functions in the zero potential part are already known as the plane wave solutions $\psi(x) = Ae^{ikx} + Be^{-ikx}$. Here the classical dispersion relation is used: $E = \frac{\hbar^2 k^2}{2m}$. The wavenumber k will be used often to describe the energy. Next the boundary conditions need to be satisfied. These boundary equations will give the relations between the energy and size L of the potential. Often these relations are very hard to solve exact, so the actual values of the energy at a certain size L will be calculated numerically. Using the found equations an exact equation for the force can often be found by differentiating the equations with respect to the energy and the size L.

2 Infinite Square Well

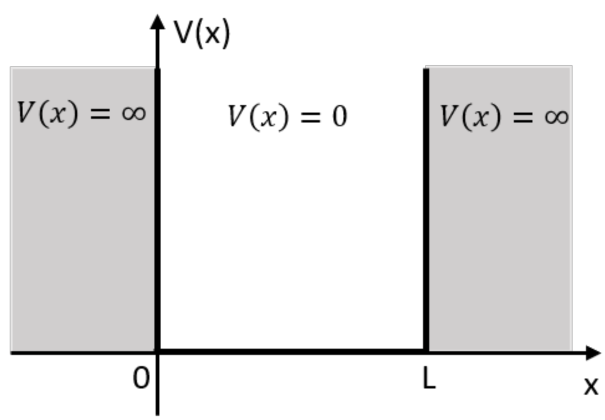

Figure 1: The schematic figure of an infinite square well potential of size L.

Consider an infinite square well as seen in figure 1. The energy levels of this potential are already well known and given by[1]:

$$E_n = \frac{\hbar^2 \pi^2}{8mL^2} n^2 \tag{2.1}$$

Using the energy levels we can calculate the quantum mechanical "force" on the barriers. The force a particle exerts on the walls of the potential well is given by the derivative with respect to the distance:

$$F_n = -\frac{dE_n}{dL} = \frac{\hbar^2 \pi^2 n^2}{8m} \frac{2}{L^3} = \frac{2E_n}{L} \tag{2.2}$$

In the classical approach the particle transfers momentum on the wall ($\Delta p = 2p$) and collides with the wall again after a certain time $\Delta t = 2L/v$ for a particle moving with velocity v. The force is given by:

$$F = \frac{\Delta p}{\Delta t} = \frac{2pv}{2L} = \frac{mv^2}{L} = \frac{2}{L}E \tag{2.3}$$

Thus the quantum and classical approach give the same result for the force. In both cases the force decreases with L^{-3} so it rapidly decreases when L gets larger.

3 Matching the boundary conditions

In this thesis the shapes of the different potentials have some similarities, allowing us to solve the boundaries without knowing the actual shape of the potential and the corresponding wave function. Consider a potential

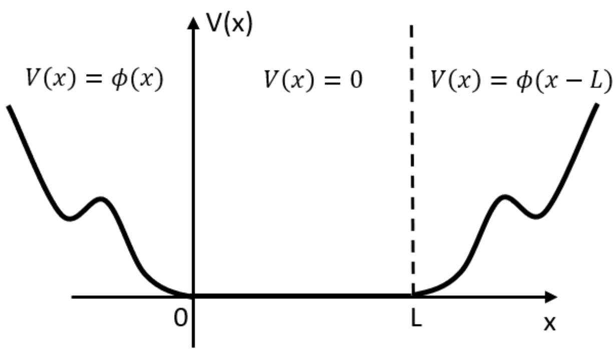

Figure 2: An arbitrary potential consisting of two parts ($x < 0$ and $x > L$) being described by a function ϕ and in the middle a potential of zero.

consisting of three parts, see figure 2. The potential is symmetric (around $x = \frac{L}{2}$) and is described by a certain function $\phi(x)$. In between these potentials ($0 < x < L$) the potential is equal to 0, so a free particle described by a standing wave. This gives us the wave functions:

$$\begin{aligned} \psi_1(x) &= A f_1(x) && \text{for } x < 0 \\ \psi_2(x) &= B_1 e^{ikx} + B_2 e^{-ikx} && \text{for } 0 < x < L \\ \psi_3(x) &= c f_3(x - L) && \text{for } x > L \end{aligned} \tag{3.1}$$

Here f_1 and f_3 are arbitrary functions that are solutions to the Schrödinger Equation in the region were they exist. Now matching the boundary conditions gives us the following equations:

$$Af_1(0) = B_1 + B_2 \tag{3.2}$$
$$Af_1'(0) = ik(B_1 - B_2) \tag{3.3}$$
$$Cf_3(0) = B_1e^{ikL} + B_2e^{-ikL} \tag{3.4}$$
$$Cf_3'(0) = ik(B_1e^{ikL} - B_2e^{-ikL}) \tag{3.5}$$

Because of the symmetry of the potential we can split the solutions for the wave functions in two types; even and odd solutions. First consider the even solutions where we assume that $\psi_1(0) = \psi_3(L)$. Combining equations 3.2 and 3.4 gives:

$$B_1 + B_2 = B_1e^{ikL} + B_2e^{-ikL}$$

Rearranging yields a relation between B_1 and B_2:

$$B_2 = B_1\frac{1 - e^{ikL}}{e^{-ikL} - 1} = B_1e^{ikL}$$

Filling this result in equation 3.2, it gives:

$$Af_1(0) = B_1(1 + e^{ikL})$$

Using equation 3.4 it gives:

$$\begin{aligned} Af_1'(0) &= ikA\frac{1 - e^{ikL}}{1 + e^{ikL}}f_1(0) \\ \frac{f_1'(0)}{f_1(0)} &= ik \cdot -i\ \tan(kL/2) \\ \frac{\psi_1'(0)}{\psi_1(0)} &= k\ \tan(\frac{kL}{2}) \end{aligned} \tag{3.6}$$

Now consider the odd solutions with $\psi_1(0) = -\psi_3(L)$. The process remains the same and combining equations 3.2 and 3.4 gives:

$$B_2 = -B_1e^{ikL}$$

This gives again the relation between A and B_1 and using equation 3.4 you end up with:

$$\begin{aligned} Af_1'(0) &= ikA\frac{1 + e^{ikL}}{1 - e^{ikL}}f_1(0) \\ \frac{f_1'(0)}{f_1(0)} &= ik\frac{i}{\tan(kL/2)} \\ \frac{\psi_1'(0)}{\psi_1(0)} &= \frac{-k}{\tan(kL/2)} \end{aligned} \tag{3.7}$$

The boundary conditions yield two equations (3.6 and 3.7) which will give a solution for the energy of the system. To find these energies it is only necessary to determine the wave function and its derivative in the region $x < 0$ as long as the potential is symmetric.

4 Harmonic Potential Well

Consider an harmonic potential well with spacing L as seen in figure 3. The potential consists of two harmonic parts which have a potential proportional to x^2 and in the middle a free potential.

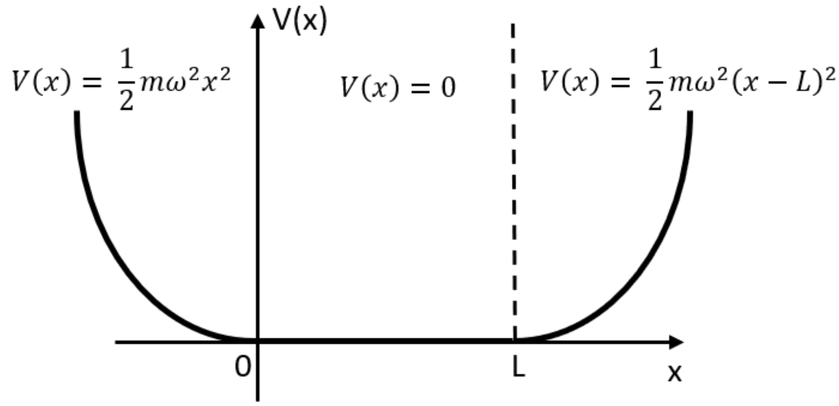

Figure 3: An harmonic potential, however the two sides of the potential are spaced out by a potential of zero of length L.

The shape of the potential is described by the mass m of the particle inside it and $\omega = \sqrt{\frac{c}{m}}$ were c is a constant describing the strength of the potential. So the potential is described by the following expression:

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2x^2 & \text{for } x < 0 \\ 0 & \text{for } 0 < x < L \\ \frac{1}{2}m\omega^2(x-L)^2 & \text{for } x > L \end{cases}$$

4.1 The classical approach

Consider first the classical approach. A classical particle for x > L will follow a harmonic path given by $x(t) = L + A\sin\omega t$. A is the amplitude and is given by the maximum deviation from x=L. This deviation follows from $V(x = A) = E$ and gives $A = \sqrt{\frac{2E}{m\omega^2}}$. The time spent in the harmonic part of the system is given by the time t_h when the position is L again after t=0. This gives $t_h = \frac{\pi}{\omega}$. The time spent in the middle part without a potential is $t_0 = \frac{L}{v}$. Here v is given by the derivative of the x(t) at L. So $v = \dot{x}(t = 0) = A\omega$. Then force is given by the change of momentum over time:

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv}{2t_h + 2t_0} = \frac{mv}{\frac{\pi}{\omega} + \frac{L}{v}} = \frac{mv^2}{\pi\frac{v}{\omega} + L} = \frac{2E}{L + \pi\sqrt{\frac{2E}{m\omega^2}}} \tag{4.1}$$

For a harmonic potential, meaning L=0, in the classical approach the force is given by:

$$F = \frac{1}{\pi}\sqrt{2m\omega^2E} \tag{4.2}$$

4.2 The quantum approach

In the quantum approach the potential consists of three parts. This gives the wave function for a particle with energy E between x=0 and x=L:

$$\psi(x) = B_1 e^{ikx} + B_2 e^{-ikx} \text{ with } k = \frac{\sqrt{2mE}}{\hbar} \tag{4.3}$$

For $x < 0$ and $x > L$ the potential is harmonic, therefore the Schrödinger Equation becomes:

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x) \tag{4.4}$$

Now substitute $\eta = \frac{E}{\hbar\omega}$ and $\xi = \sqrt{\frac{2m\omega}{\hbar}}x \equiv \sqrt{2}\alpha x$ and rearranging gives:

$$\frac{d^2\psi}{d\xi^2} - \left(\frac{\xi^2}{4} - \eta\right)\psi(\xi) = 0 \tag{4.5}$$

This equation can be solved by the first Kummer function [2] and an exponent, which gives the following wave function:

$$\psi(\xi) = \left[AM\left(\frac{-\eta}{2} + \frac{1}{4}, \frac{1}{2}, \frac{\xi^2}{2}\right) + B\xi M\left(\frac{-\eta}{2} + \frac{3}{4}, \frac{3}{2}, \frac{\xi^2}{2}\right)\right] e^{-\xi^2/4} \tag{4.6}$$

Here A and B are arbitrary constants and need to be determined. For convenience set $\frac{-\eta}{2} + \frac{1}{4} = a$. The constants A and B follow from the fact that $\psi(\xi)$ has to go to zero if $\xi \to \infty$. In this limit the Kummer functions can be approximated by $M(a,b,\xi^2/2) \approx \frac{\Gamma(b)}{\Gamma(a)} e^{\xi^2/2} (\frac{\xi^2}{2})^{a-b}$ and this gives the following equation:

$$\begin{aligned}
\psi(\xi) &\approx \left[A\frac{\Gamma(1/2)}{\Gamma(a)} e^{\xi^2/2}\left(\frac{\xi^2}{2}\right)^{a-1/2} + B\xi\frac{\Gamma(3/2)}{\Gamma(a+1/2)} e^{\xi^2/2}\left(\frac{\xi^2}{2}\right)^{a+1-3/2}\right] e^{-\xi^2/4} \\
&= \left[A\frac{\Gamma(1/2)}{\Gamma(a)} + B\xi\frac{\Gamma(3/2)}{\Gamma(a+1/2)}\left(\frac{\xi^2}{2}\right)^{-1/2}\right]\left(\frac{\xi^2}{2}\right)^{a-1/2} e^{\xi^2/4} \\
&= \left[A\frac{\sqrt{\pi}}{\Gamma(a)} + B\frac{\sqrt{\pi/2}}{\Gamma(a+1/2)}\frac{\xi}{\sqrt{\xi^2}}\right]\left(\frac{\xi^2}{2}\right)^{a-1/2} e^{\xi^2/4}
\end{aligned} \tag{4.7}$$

Because this equation needs to go to zero and using the fact that $\xi < 0$ (so $\frac{\xi}{\sqrt{\xi^2}} = -1$) it yields the following expression for B:

$$B = \sqrt{2}A\frac{\Gamma(a+1/2)}{\Gamma(a)} \tag{4.8}$$

This gives the full expression for ψ, which is:

$$\psi(\xi) = A\left[M\left(a, \frac{1}{2}, \frac{\xi^2}{2}\right) + \sqrt{2}\frac{\Gamma(a+1/2)}{\Gamma(a)}\xi M\left(a + \frac{1}{2}, \frac{3}{2}, \frac{\xi^2}{2}\right)\right] e^{-\xi^2/4} \equiv AH(\xi)e^{-\xi^2/4} \tag{4.9}$$

Then the wave functions in the harmonic parts of the potential are given by:

$$\psi(\xi) = \begin{cases} AH(\xi)e^{-\xi^2/4} \text{ for } x < 0 \\ CH(\xi - \sqrt{2}\alpha L)e^{-(\xi-\sqrt{2}\alpha L)^2/4} \text{ for } x > L \end{cases} \tag{4.10}$$

The derivatives are:

$$\psi'(\xi) = \begin{cases} A\left[H'(\xi)e^{-\xi^2/2} - \frac{\xi}{2}H(\xi)e^{-\xi^2/2}\right] & \text{for } x < 0 \\ C\left[H'(\xi-\sqrt{2}\alpha L)e^{-(\xi-\sqrt{2}\alpha L)^2/2} - \frac{\xi-\sqrt{2}\alpha L}{2}H(\xi-\sqrt{2}\alpha L)e^{-(\xi-\sqrt{2}\alpha L)^2/2}\right] & \text{for } x > L \end{cases} \tag{4.11}$$

The derivative of the Kummer function $M(a,b,x)$ is given by $\frac{a}{b}M(a+1,b+1,x)$ which give the derivative of H:

$$H'(\xi) = 2a\xi M\left(a+1,\frac{3}{2},\frac{\xi^2}{2}\right) + \sqrt{2}\frac{\Gamma(a+1/2)}{\Gamma(a)}M\left(a+\frac{1}{2},\frac{3}{2},\frac{\xi^2}{2}\right) + \sqrt{2}\frac{\Gamma(a+1/2)}{\Gamma(a)}\frac{2a+1}{3}\xi M\left(a+\frac{3}{2},\frac{5}{2},\frac{\xi^2}{2}\right) \tag{4.12}$$

Using that $M(a,b,0) = 1$ and equation 3.6 gives the energy values for the even solutions. Here use that $\eta = \frac{E}{\hbar\omega} = \frac{\hbar^2 k^2}{2\hbar m\omega} = \frac{k^2}{2\alpha^2}$

$$\begin{aligned} k\tan\left(\frac{kL}{2}\right) &= \frac{\psi'(0)}{\psi(0)}\frac{d\xi}{dx} = \frac{H'(0)}{H(0)}\sqrt{2}\alpha = 2\alpha\frac{\Gamma(a+1/2)}{\Gamma(a)} \\ \sqrt{\frac{\eta}{2}}\tan\left(\sqrt{\frac{\eta}{2}}\alpha L\right) &= \frac{\Gamma(3/4-\eta/2)}{\Gamma(1/4-\eta/2)} \end{aligned} \tag{4.13}$$

Equation 3.7 gives the odd solutions:

$$\begin{aligned} k\frac{1}{\tan(\frac{kL}{2})} &= -\frac{\psi'(0)}{\psi(0)}\frac{d\xi}{dx} = -\frac{H'(0)}{H(0)}\sqrt{2}\alpha = -2\alpha\frac{\Gamma(a+1/2)}{\Gamma(a)} \\ \sqrt{\frac{\eta}{2}}\frac{1}{\tan(\sqrt{\frac{\eta}{2}}\alpha L)} &= -\frac{\Gamma(3/4-\eta/2)}{\Gamma(1/4-\eta/2)} \end{aligned} \tag{4.14}$$

η is the value that represents the energy of the particle. Therefore the equation can be solved to find the energy as a function of L.

4.3 Deriving the quantum mechanical force

Using equations 4.13 and 4.14 we can calculate the force. This can be done by differentiating the equation with respect to the energy and L. For the even solutions the equation we got from the boundary conditions (expressed in k) has the following form:

$$f(k,L) = 2\alpha\frac{\Gamma(\frac{3}{4}-\frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4}-\frac{k^2}{4\alpha^2})} - k\tan\left(\frac{kL}{2}\right) \equiv g(k) - k\tan\left(\frac{kL}{2}\right) = 0 \tag{4.15}$$

Now use that for a function f(k,L) which is always zero the following needs to hold too:

$$\begin{aligned} df(k,L) &= \frac{\partial f}{\partial L}dL + \frac{\partial f}{\partial E}dE = 0 \\ \frac{\partial f}{\partial L}dL &= -\frac{\partial f}{\partial E}dE \\ \frac{\partial f}{\partial L}\frac{\partial E}{\partial f} &= -\frac{dE}{dL} = F \end{aligned} \tag{4.16}$$

Then the force is given by:

$$\begin{aligned} F &= \frac{\partial f}{\partial L}\frac{\partial E}{\partial f} = \frac{\partial E}{\partial k}\frac{\partial f}{\partial L}(\frac{\partial f}{\partial k})^{-1} \\ &= \frac{\hbar^2 k}{m}\frac{-k^2/2}{\cos^2(kL/2)}\left(-\tan(kL/2) - \frac{kL}{2\cos(kL/2)} + \frac{dg(k)}{dk}\right)^{-1} \\ &= \frac{\hbar^2 k^3}{2m}\left(\frac{1}{2}\sin(kL) + \frac{kL}{2} - \cos^2(kL/2)\frac{dg(k)}{dk}\right)^{-1} \\ &= \frac{\hbar^2}{m}\frac{k^2}{L + \sin(kL)/k - \frac{2\cos^2(kL/2)}{k}\frac{dg(k)}{dk}} \end{aligned} \tag{4.17}$$

For the odd solutions we can apply the same strategy which gives:

$$f(k,L) = 2\alpha\frac{\Gamma(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})} + \frac{k}{\tan(\frac{kL}{2})} \equiv g(k) + \frac{k}{\tan(\frac{kL}{2})} = 0 \tag{4.18}$$

The force for the odd solutions is given by:

$$\begin{aligned} F &= \frac{\partial f}{\partial L}\frac{\partial E}{\partial f} \\ &= \frac{\hbar^2 k}{m}\frac{-k^2/2}{\sin^2(kL/2)}\left(1/\tan(kL/2) - \frac{kL}{2\sin^2(kL/2)} + \frac{dg(k)}{dk}\right)^{-1} \\ &= \frac{\hbar^2 k^3}{2m}\left(-\frac{1}{2}\sin(kL) + \frac{kL}{2} - \sin^2(kL/2)\frac{dg(k)}{dk}\right)^{-1} \\ &= \frac{\hbar^2}{m}\frac{k^2}{L - \sin(kL)/k - \frac{2\sin^2(kL/2)}{k}\frac{dg(k)}{dk}} \end{aligned} \tag{4.19}$$

To get the final expression for the force we need the derivative of the function g, which is given by:

$$\begin{aligned} \frac{dg(k)}{dk} &= 2\alpha\frac{d}{dk}\frac{\Gamma(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})} \\ &= \frac{-k}{\alpha}\left[\frac{\Gamma'(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})} - \frac{\Gamma'(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})^2}\Gamma'(\frac{1}{4} - \frac{k^2}{4\alpha^2})\right] \\ &= \frac{-k}{\alpha}\frac{\Gamma(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})}\left[\psi^{(0)}(\frac{3}{4} - \frac{k^2}{4\alpha^2}) - \psi^{(0)}(\frac{1}{4} - \frac{k^2}{4\alpha^2})\right] \end{aligned} \tag{4.20}$$

Where $\psi^{(0)}(x) = \frac{\Gamma'(x)}{\Gamma(x)}$ which is the polygamma function. Now use the boundary solutions to substitute $\frac{\Gamma(\frac{3}{4} - \frac{k^2}{4\alpha^2})}{\Gamma(\frac{1}{4} - \frac{k^2}{4\alpha^2})}$. Then combining everything back together the even force becomes:

$$F = \frac{\hbar^2}{m}\frac{k^2}{L + \sin(kL)/k - \frac{k\sin(kL)}{2\alpha^2}(\psi^{(0)}(\frac{3}{4} - \frac{k^2}{4\alpha^2}) - \psi^{(0)}(\frac{1}{4} - \frac{k^2}{4\alpha^2}))} \tag{4.21}$$

And the force for the odd solutions:

$$F = \frac{\hbar^2}{m} \frac{k^2}{L - \sin(kL)/k + \frac{k\sin(kL)}{2\alpha^2}(\psi^{(0)}(\frac{3}{4} - \frac{k^2}{4\alpha^2}) - \psi^{(0)}(\frac{1}{4} - \frac{k^2}{4\alpha^2}))} \tag{4.22}$$

If you look at the force found by the classical theory (equation 4.2) and insert the equation for the energy, you will get $\frac{\hbar^2}{m}\frac{k^2}{L+\pi k/\alpha^2}$. The quantum theory thus yields a much more complex equation with extra terms in the denominator.

The different behaviour of the quantum mechanical solution can easily be seen in figure 4 where the energy levels and corresponding forces are plotted for the classical and quantum theory. The quantum force is slightly different than the classical force and seems to be oscillating around the classical force with increased frequency for higher energies. When the energy becomes very large the $sin(kL)/k$ term disappears. The term with the polygamma functions is difficult to determine in the high energy limit because the polygamma functions are not defined when the argument goes to negative infinity.

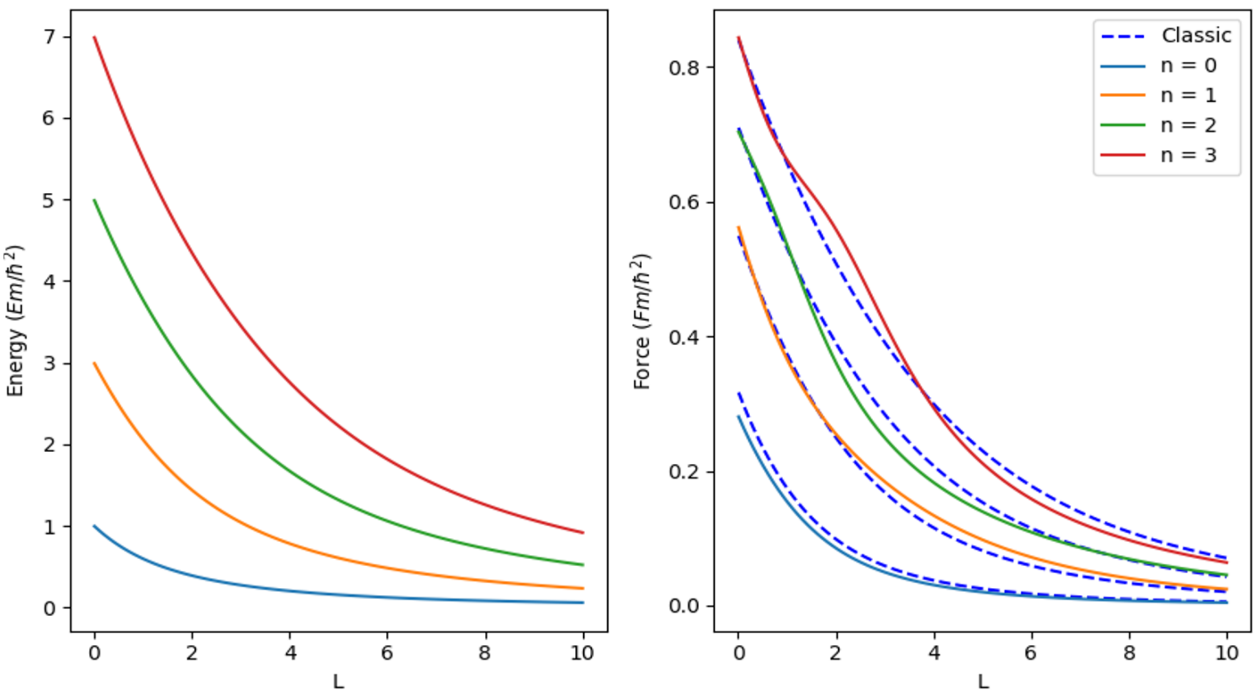

Figure 4: The energy levels and corresponding forces of the harmonic potential well. On the left the energy is plotted as $\frac{Em}{\hbar^2}$ and on the right the force as $\frac{Fm}{\hbar^2}$. The blue dotted lines are the results of the classical equations corresponding with each energy level. For the calculation of the classical force the quantum mechanical energy levels have been used.

4.4 Solving the even solutions at L = 0

An interesting limit is when L goes to zero, which yields the normal harmonic oscillator. An expansion to the first order at L=0 for the even solutions gives:

$$\frac{\alpha L \eta}{2} = \frac{\Gamma(3/4 - \eta/2)}{\Gamma(1/4 - \eta/2)} \tag{4.23}$$

Assume the energy values are close to the even energies of the normal harmonic oscillator $E = \hbar\omega(2n + 1/2)$ and the definition for η give $\eta = 2n + \frac{1}{2} - \epsilon$. Where ϵ is very small. These value for η can also be derived from the fact that $\Gamma(1/4 - \eta/2)$ has to diverge to infinity when L goes to zero. Then the equation becomes:

$$\frac{\alpha L}{2}(2n + \frac{1}{2} - \epsilon) = \frac{\Gamma(-n + 1/2 - \epsilon/2)}{\Gamma(-n + \epsilon/2)} \tag{4.24}$$

For the gamma functions we can use the following approximations:

$$\Gamma(-n + 1/2 - \epsilon/2) \approx \Gamma(-n + 1/2) = \frac{(-2)^n \sqrt{\pi}}{(2n-1)!!} = \frac{(-4)^n n! \sqrt{\pi}}{(2n)!} \tag{4.25}$$

$$\Gamma(-n + \epsilon/4) \approx \frac{2(-1)^n}{n!\epsilon} \tag{4.26}$$

Filling this back in the original equation and assuming ϵ is also negligible at the left hand side:

$$\begin{aligned} \frac{\alpha L}{2}(2n + \frac{1}{2}) &= \frac{\sqrt{\pi}}{2} \frac{4^n (n!)^2}{(2n)!} \epsilon \\ \epsilon &= \alpha L \frac{2n + 1/2}{\sqrt{\pi}} \frac{(2n)!}{4^n (n!)^2} \end{aligned} \tag{4.27}$$

This gives us the final equation for the force applied by the even solutions:

$$F = -\frac{dE}{dL} = -\hbar\omega \frac{d\eta}{dL} = \hbar\omega \frac{d\epsilon}{dL} = \sqrt{\hbar m \omega^3} \frac{2n + \frac{1}{2}}{\sqrt{\pi}} \frac{(2n)!}{4^n (n!)^2} \tag{4.28}$$

4.5 Solving the odd solutions at L = 0

Doing an expansion for equation 4.14 around L=0 yields:

$$\frac{1}{\alpha L} = -\frac{\Gamma(3/4 - \eta/2)}{\Gamma(1/4 - \eta/2)} \tag{4.29}$$

Performing the same approximation for $\eta = 2n + \frac{3}{2} - \epsilon$ for the odd energy levels. This follows from $E = \hbar\omega(2n + 1 + \frac{1}{2})$.

$$\frac{1}{\alpha L} = -\frac{\Gamma(-n + \epsilon/2)}{\Gamma(-n - 1/2)} = -\frac{\Gamma(-n + \epsilon/2)}{\Gamma(-(n+1) + 1/2)} = -\frac{2(-1)^n}{n!\epsilon} \frac{(2n+2)!}{(-4)^{n+1}(n+1)!\sqrt{\pi}} = \frac{2n+1}{\sqrt{\pi}} \frac{(2n)!}{4^n (n!)^2 \epsilon} \tag{4.30}$$

Similar to the even solutions this gives for ϵ:

$$\epsilon = \alpha L \frac{2n+1}{\sqrt{\pi}} \frac{(2n)!}{4^n (n!)^2} \tag{4.31}$$

Then the force is given by:

$$F = -\frac{dE}{dL} = \hbar\omega \frac{d\epsilon}{dL} = \sqrt{\hbar m \omega^3} \frac{2n+1}{\sqrt{\pi}} \frac{(2n)!}{4^n (n!)^2} \tag{4.32}$$

4.6 Comparing with the classical and quantum result at L = 0

Consider the even solutions given by equation 4.28. For large energies and thus large n, the system becomes classical. The factorials can be approximated using Stirling's formula[3].

$$\frac{4^n(n!)^2}{(2n)!} = \sqrt{\pi n} \tag{4.33}$$

Then the force in the classical approximation becomes for the even solutions:

$$F = \sqrt{\hbar m\omega^3}\frac{2n+1/2}{\pi\sqrt{n}} \approx \frac{2\sqrt{\hbar m\omega^3}}{\pi}\sqrt{n} \tag{4.34}$$

When doing the same approximation for the odd solutions you will get exactly the same equation. For large values of n the energy can be approximated by $E = \hbar\omega(2n+1/2) \approx 2\hbar\omega n$ which is the same for both even and odd solutions. Filling this in the equation we found using the classical theory (equation 4.2) we get $F = \frac{1}{\pi}\sqrt{2m\omega^2 E} = \frac{2\sqrt{\hbar m\omega^3 n}}{\pi}$ which is the same as the classical limit of the quantum theory. Which confirms the validity of the found quantum mechanical solution.

The dependence of the force on n, which is the energy level of the system, is plotted in figure 5. For small difference there is a difference in the force between the quantum odd and even and the classical solutions. For large n the three solutions get closer to each other and eventually become the same function as was found before using Stirling's formula.

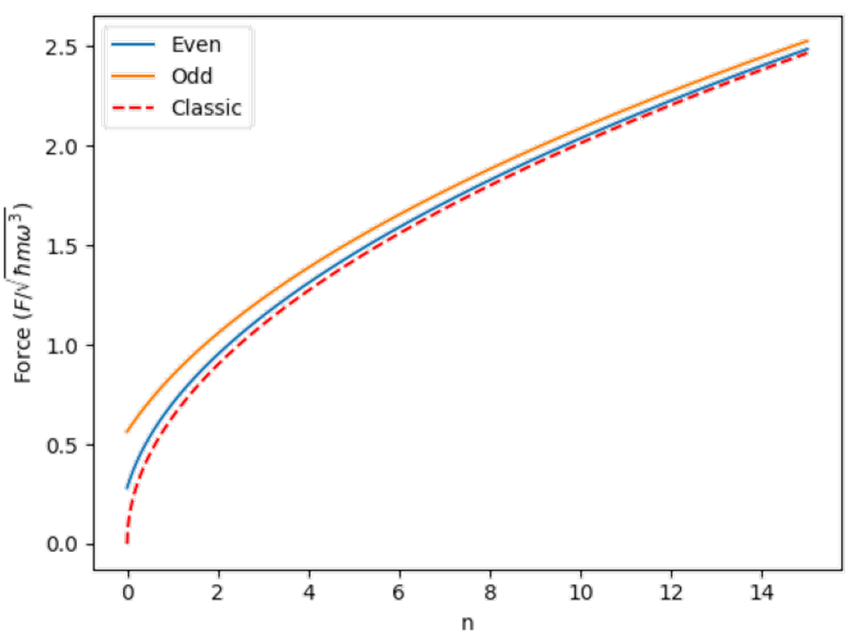

Figure 5: The force of the harmonic potential for L = 0 plotted against the the energy level (n) for the even, odd and classical solutions.

5 Triangular Potential Well

Next we consider a triangular potential. There are two parts that are proportional to x and the angle is described by a constant a. In the middle there is a potential of zero as seen in figure 6. The potential can be described by the following expression:

$$V(x) = \begin{cases} a|x| = -ax & \text{for } x < 0 \\ 0 & \text{for } 0 < x < L \\ a(x-L) & \text{for } x > L \end{cases}$$

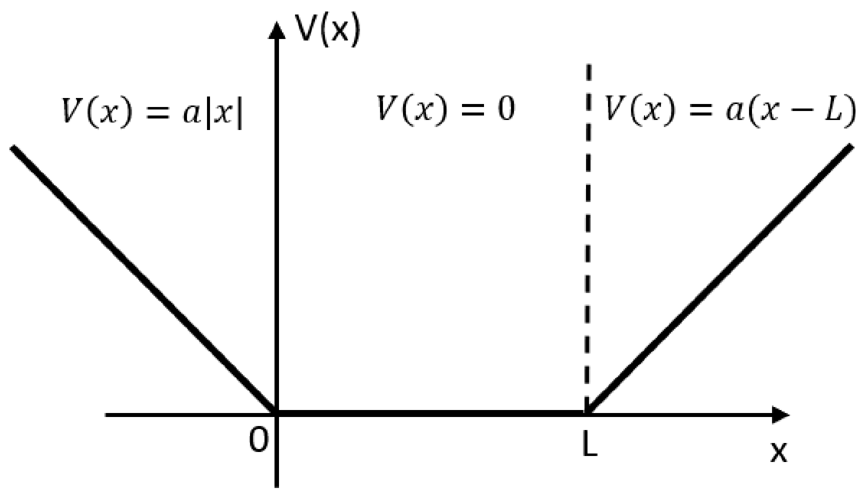

Figure 6: A triangular or linear potential described on a constant a spaced out by a potential equal to zero of length L.

5.1 The classical approach

The time the particle spends in the linear part of the potential follows from the equation for the velocity $v(t) = v_0 - \frac{a}{m}t$. So the time is given by $-v_0 = v_0 - \frac{a}{m}t_l$. This gives a time of $t_l = \frac{2mv_0}{a}$ and the time spent in the zero potential part in $t_0 = \frac{L}{v_0}$. This yields the average force applied on one of sides of the barrier by the particle. Using the fact that it applies a constant force of a on the barriers in the triangular parts.

$$F = a\frac{t_l}{2t_0 + 2t_l} = \frac{a}{2}\frac{2mv_0/a}{L/v_0 + 2mv_0/a} = \frac{mv_0^2}{L + 2mv_0^2/a} = \frac{2E}{L + 4E/a} \tag{5.1}$$

5.2 The quantum approach

We start by constructing the Schrödinger Equation for both sides of the potential. For $x < 0$ we get the following equation:

$$\begin{aligned} \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + a|x|\psi(x) &= E\psi(x) \\ \frac{d^2\psi}{dx^2} - \left(\frac{2am}{\hbar^2}|x| - \frac{2mE}{\hbar^2}\right)\psi(x) &= 0 \\ \frac{d^2\psi}{dx^2} - \left(\alpha|x| - k^2\right)\psi(x) &= 0 \end{aligned} \tag{5.2}$$

Where $k^2 = \frac{2mE}{\hbar^2}$ and $\alpha = \frac{2am}{\hbar^2}$. The solutions of this differential equations are the so called Airy functions [2] and give the following wave function:

$$\psi_1(x) = A_1 \cdot Ai\left(\frac{\alpha|x| - k^2}{\alpha^{2/3}}\right) + A_2 \cdot Bi\left(\frac{\alpha|x| - k^2}{\alpha^{2/3}}\right) \tag{5.3}$$

Here Ai(x) is the first Airy function and Bi(x) the second. However as $x \to \infty$, $Ai(x) \to 0$ and $Bi(x) \to \infty$. therefore the second Airy function is not valid as the wave function so we set $A_2 = 0$. And replace $|x|$ to -x we get the final wave function:

$$\psi_1(x) = A \cdot Ai\left(\frac{-\alpha x - k^2}{\alpha^{2/3}}\right) \tag{5.4}$$

The right side of the potential gives due to symmetry a similar result. In this equation $|x|$ becomes (x-L) and therefore the wave function becomes:

$$\psi_3(x) = C \cdot Ai\left(\frac{\alpha(x - L) - k^2}{\alpha^{2/3}}\right) \tag{5.5}$$

Now again we use equations 3.6 and 3.7 to find even and odd solutions.

5.3 Solving the even equations

The even solutions are given by the following equation:

$$k\tan\left(\frac{kL}{2}\right) = \frac{\psi_1'(0)}{\psi_1(0)} = \frac{-\alpha^{1/3} Ai'\left(\frac{-k^2}{\alpha^{2/3}}\right)}{Ai\left(\frac{-k^2}{\alpha^{2/3}}\right)} \tag{5.6}$$

We call the above function f(k,L) and differentiate it to k and L separately to find an equation for the force.

$$f(k,L) = k\tan\left(\frac{kL}{2}\right) + \alpha^{1/3}\frac{Ai'\left(\frac{-k^2}{\alpha^{2/3}}\right)}{Ai\left(\frac{-k^2}{\alpha^{2/3}}\right)} = 0 \tag{5.7}$$

Then as done with the harmonic potential differentiating f(k,L) gives:

$$-\frac{dk}{dL} = \frac{\partial f}{\partial L}\frac{\partial k}{\partial f} = \frac{k^2/2}{\cos^2(kL/2)}\left[\tan(kL/2) + \frac{kL/2}{\cos^2(kL/2)} + \frac{2k}{\alpha^{1/3}}\left(\frac{Ai''(\frac{-k^2}{\alpha^{2/3}})}{Ai(\frac{-k^2}{\alpha^{2/3}})} - \frac{Ai'(\frac{-k^2}{\alpha^{2/3}})^2}{Ai(\frac{-k^2}{\alpha^{2/3}})^2}\right)\right]^{-1} \tag{5.8}$$

Now using the definition for the Airy functions $\frac{Ai''(x)}{Ai(x)} = x$ and substitute $(\frac{Ai'(x)}{Ai(x)})^2$ using f(k,L) the equation becomes:

$$\begin{aligned}
\frac{dk}{dL} &= \frac{k^2/2}{\cos^2(kL/2)}\left[\tan(kL/2) + \frac{kL/2}{\cos^2(kL/2)} + \frac{2k}{\alpha^{1/3}}(\frac{k^2}{\alpha^{2/3}} + \frac{k^2}{\alpha^{2/3}}\tan^2(kL/2))\right]^{-1} \\
&= \frac{k^2/2}{\cos^2(kL/2)}\left[\tan(kL/2) + \frac{kL/2}{\cos^2(kL/2)} + \frac{2k^3}{\alpha}(1+\tan^2(kL/2))\right]^{-1} \\
&= \frac{k^2/2}{\cos^2(kL/2)}\left[\tan(kL/2) + \frac{kL/2}{\cos^2(kL/2)} + \frac{2k^3}{\alpha}\frac{1}{\cos^2(kL/2)}\right]^{-1} \\
&= k^2/2\left[\cos^2(kL/2)\tan(kL/2) + kL/2 + \frac{2k^3}{\alpha}\right]^{-1} \\
&= \frac{k^2}{\sin(kL) + kL + 4k^3/\alpha}
\end{aligned} \tag{5.9}$$

Using this result the force applied on one of the barriers is given by:

$$F = -\frac{dE}{dL} = -\frac{dE}{dk}\frac{dk}{dL} = \frac{\hbar^2 k}{m}\frac{k^2}{\sin(kL) + kL + 4k^3/\alpha} = \frac{\hbar^2}{m}\frac{k^2}{L + \sin(kL)/k + 4k^2/\alpha} \tag{5.10}$$

5.4 Solving the odd equations

The odd solutions are given by the following equation:

$$\frac{-k}{\tan(kL/2)} = \frac{\psi_1'(0)}{\psi_1(0)} = \frac{-\alpha^{1/3}Ai'(\frac{-k^2}{\alpha^{2/3}})}{Ai(\frac{-k^2}{\alpha^{2/3}})} \tag{5.11}$$

Following the same method as for the even solutions we find:

$$\begin{aligned}
-\frac{dk}{dL} &= \frac{k^2/2}{\sin^2(kL/2)}\left[\frac{-1}{\tan(kL/2)} + \frac{kL/2}{\sin^2(kL/2)} + \frac{2k^3}{\alpha}\frac{1}{\sin^2(kL/2)}\right]^{-1} \\
&= \frac{k^2}{-\sin(kL) + kL + 4k^3/\alpha}
\end{aligned} \tag{5.12}$$

This gives the force for the odd solutions:

$$F = \frac{\hbar^2}{m}\frac{k^2}{L - sin(kL)/k + 4k^2/\alpha} \tag{5.13}$$

5.5 Analysing the limits of the solutions

A way to determine if the above solutions are valid we can look at some of the limits of the solutions.
The first limit is L=0 which gives us the normal triangular potential. This limit means the even and odd force becomes:

$$F = \frac{\hbar^2}{m}\frac{k^2}{4k^2/\alpha} = \frac{\hbar^2\alpha}{4m} = \frac{a}{2} \tag{5.14}$$

This is a logical solution as the force is the derivative of the potential which is in this case ofcourse the constant a. It is divided by 2 because this represents the force of one of the barriers. Comparing this with the classical solution for L=0 we find the exact same equation.
Another interesting limit is $a \to \infty$ which should yield the infinite square well solution. This means that $\alpha^{1/3} \frac{Ai'(\frac{-k^2}{\alpha^{2/3}})}{Ai(\frac{-k^2}{\alpha^{2/3}})} \to \infty$ because both the Airy function and its derivative constants when their arguments are 0. To make sure the equations hold, $\tan(kL/2) \to \infty$ for the even solutions. This means that $\cos(kL/2)$ has to go to zero, so only specific values of kL are allowed: $kL = (2n+1)\pi$. therefore the $\sin(kL)$ is always zero and the force becomes:

$$F = \frac{\hbar^2 k^2}{mL} = \frac{2E}{L} \tag{5.15}$$

Comparing this with the force in the infinite square well (equation 2.2) we see the result is the same, which confirms the validity of the found solution for the triangular well.

5.6 Comparing the classical and quantum result

Using the classical solution and the fact that $E = \frac{\hbar^2 k^2}{2m}$ and $E/a = k^2/\alpha$ we find:

$$F = \frac{2E}{L + 4E/a} = \frac{\hbar^2}{m} \frac{k^2}{L + 4k^2/\alpha} \tag{5.16}$$

Comparing this with equations 5.10 and 5.13 we can see that both results are actually very similar but have a small difference. The quantum mechanical solutions actually contain an extra term $\sin(kL)/k$ which means a slight shift in force. Which actually means for certain values of k the force is a bit higher or lower. The difference becomes clear if you plot the quantum and classical results in one graph. This can be seen in figure 7. The quantum solutions oscillate around the classical solutions with a frequency that is dependent of k. This oscillation is caused by the additional $\sin(kL)/k$ term. This term is suppressed for large energies (large values for k). In these limits the quantum solution approaches the classical theory. It also becomes clear that at L=0 the force has the same values for every energy level and in both the classical and quantum theory. This coincides with the value for the force found in equation 5.14.

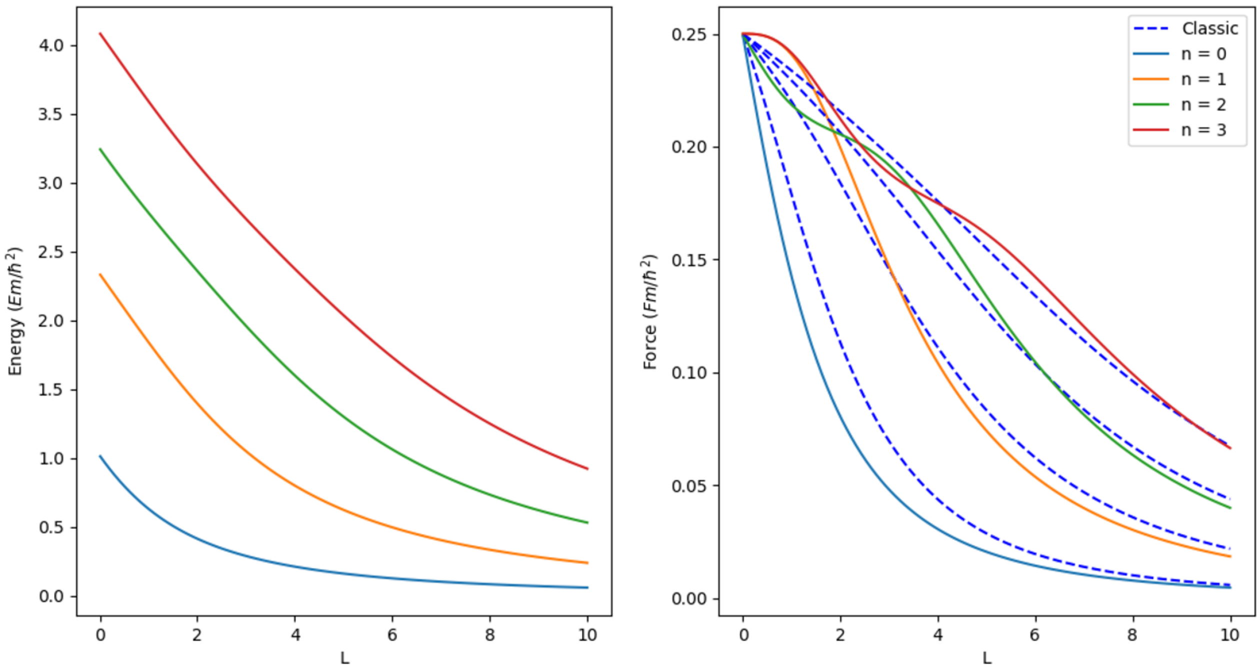

Figure 7: The energy levels and corresponding forces of the triangular well. On the left the energy is plotted as $\frac{Em}{\hbar^2}$ and on the right the force as $\frac{Fm}{\hbar^2}$. The blue dotted lines are the results of the classical equations corresponding with each energy level. For the calculation of the classical force the quantum mechanical energy levels have been used.

6 The Finite Square Well

Another interesting potential is the finite square well. This potential is of course very similar to the infinite square which gave the same result for the quantum and classical approach. However the height of the potential is not infinite in this case, but has a finite height V_0. The potential can be described by the following equations and figure 8.

$$V(x) = \begin{cases} V_0 & \text{for } x < 0 \\ 0 & \text{for } 0 < x < L \\ V_0 & \text{for } x > L \end{cases}$$

The classical approach will yield the same equation (2.2) for force and energy because we consider bound states and the particles are not influenced by the height of the potential. In the quantum mechanical theory the wave function can exist outside the potential well (in the regions $x < 0$ and $x > L$) so this will probably influence the end result. Consider the bound states ($E < V_0$) then the wave function for $x < 0$ is given by [4]:

$$\psi_1(x) = Ae^{\kappa x}, \ \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \tag{6.1}$$

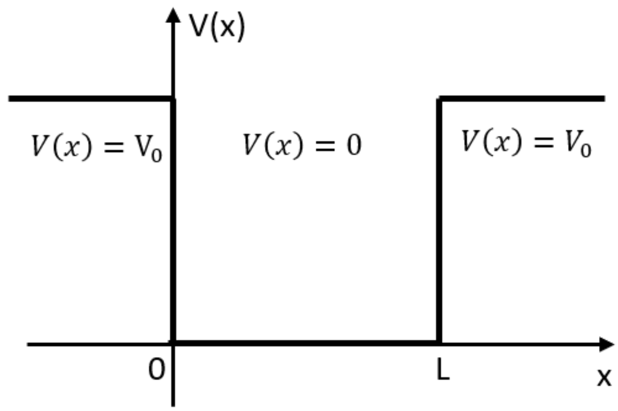

Figure 8: A finite square well of size L and potential step of V_0.

We can use the same equations for the boundary conditions as before which gives:

$$k\tan(kL/2) = \frac{\psi_1'(0)}{\psi_1(0)} = \kappa \tag{6.2}$$

Differentiating this function like was done for the other potentials we get the force on one of the walls:

$$\begin{aligned} F &= \frac{\partial f}{\partial L}\frac{\partial E}{\partial f} = \frac{k^2/2}{\cos^2(kL/2)}\left[(\tan(kL/2) + \frac{kL/2}{\cos^2(kL/2)})\frac{dk}{dE} - \frac{d\kappa}{dE}\right]^{-1} \\ &= k^2\left[(\sin(kL) + kL)\frac{dk}{dE} - 2\cos^2(kL/2)\frac{d\kappa}{dE}\right]^{-1} \\ &= k^2\frac{dE}{dk}\left[\sin(kL) + kL - 2\cos^2(kL/2)\frac{d\kappa}{dk}\right]^{-1} \end{aligned} \tag{6.3}$$

And as we know the relation between k, κ and the energy of the system we get:

$$\frac{d\kappa}{dk} = \frac{d}{dk}\sqrt{\frac{2mV_0}{\hbar^2} - k^2} = -\frac{k}{\sqrt{2mV_0/\hbar^2 - k^2}} \tag{6.4}$$

So the equation for the force becomes:

$$F = \frac{\hbar^2}{m}\frac{k^2}{L + \sin(kL)/k + \frac{2\cos^2(kL/2)}{\sqrt{2mV_0/\hbar^2 - k^2}}} \tag{6.5}$$

The result is very different from the infinite square well and thus the classical finite well. The equation contains two extra terms $\sin(kL)/k$ which also appeared in the other potentials and a term $\frac{2\cos^2(kL/2)}{\sqrt{2mV_0/\hbar^2 - k^2}}$ which increases and thus decrease the force if the energy of the particle is close to the height of the barrier. This term is always positive so decreases the force on the wall which is understandable as part of the wave actually goes through the barrier instead of being reflected.

For the odd solutions we can use a similar approach and we get using 3.7:

$$\frac{k}{\tan(kL/2)} = -\kappa \tag{6.6}$$

Using the same strategy as before we can calculate the force by the particle:

$$\begin{aligned} F &= \frac{\partial f}{\partial L}\frac{\partial E}{\partial f} = \frac{-k^2/2}{\sin^2(kL/2)}\left[\left(\frac{1}{\tan(kL/2)} - \frac{kL/2}{\sin^2(kL/2)}\right)\frac{dk}{dE} + \frac{d\kappa}{dE}\right]^{-1} \\ &= k^2\frac{dE}{dk}\left[-\sin(kL) + kL + 2\sin^2(kL/2)\frac{d\kappa}{dk}\right]^{-1} \\ &= \frac{\hbar^2}{m}\frac{k^2}{L - \sin(kL)/k + \frac{2\sin^2(kL/2)}{\sqrt{2mV_0/\hbar^2 - k^2}}} \end{aligned} \tag{6.7}$$

An important thing to note is that not all energy levels can exist for a certain length of the well. As the size decreases the energy of the levels increases, but energies higher than V_0 are not allowed. This gives a minimum size of the well for certain energy levels. This gives an upper limit for k: $\frac{\hbar^2 k_{max}^2}{2m} = V_0$ so $k_{max} = \sqrt{\frac{2mV_0}{\hbar^2}}$. In the boundary equation the right-hand side (κ) become zero, so $\tan(kL/2) = 0$ for the even solutions and $1/\tan(kL/2) = 0$ for the odd solutions. So for the even equations the maximum value for k is given by:

$$\begin{aligned} \sin(k_{max}L/2) &= 0 \\ k_{max}L &= 2n\pi \\ L_{min} &= \frac{2\pi n}{k_{max}} = \frac{2\pi n}{\sqrt{\frac{2mV_0}{\hbar^2}}} \end{aligned} \tag{6.8}$$

Similar for the odd solutions we find $L_{min} = \frac{2\pi n + \pi}{\sqrt{\frac{2mV_0}{\hbar^2}}}$. Here $n = 0, 1, 2...$ which are the energy levels of the system. So this minimal size of the well of course depends on the height of the barrier and on the height of the energy level. The ground state (n=0) does not have a minimum size and can always exist. With the equations for the energy (k) and the force for the even, odd and classical solutions we can numerically solve them and plot them in figure 9. An interesting difference between the classical and quantum theory becomes clear from the right plot. As L approaches its minimal allowed value the quantum force becomes zero, while the classical force becomes infinite. The behaviour of the quantum force is that the difference between the energy and potential becomes very small, which is equivalent to a particle in a well with a very small barrier but with a finite length (L). In this situation the wave function is allowed to exist outside the well for a very long extend. As L approaches zero the wave function exist almost entirely outside the well, resulting in a small force. So for high energies close to V_0 the big difference between the quantum and classical theory. However the limit $V_0 \to \infty$, which is an infinite square well, should yield the classical result. This means that κ is infinitely large and so for the even solutions $\cos(kL/2)$ should go to zero which causes the term with $\cos^2(kL/2)$ to vanish in the force. For the odd solutions the $\sin(kL/2)$ has to be zero. If the energy of the particle is large, but not close to V_0, the $sin(kL)/k$ term will disappear too, So in these limits the quantum mechanical theory behaves like the classical theory, as you would expect for high energies.

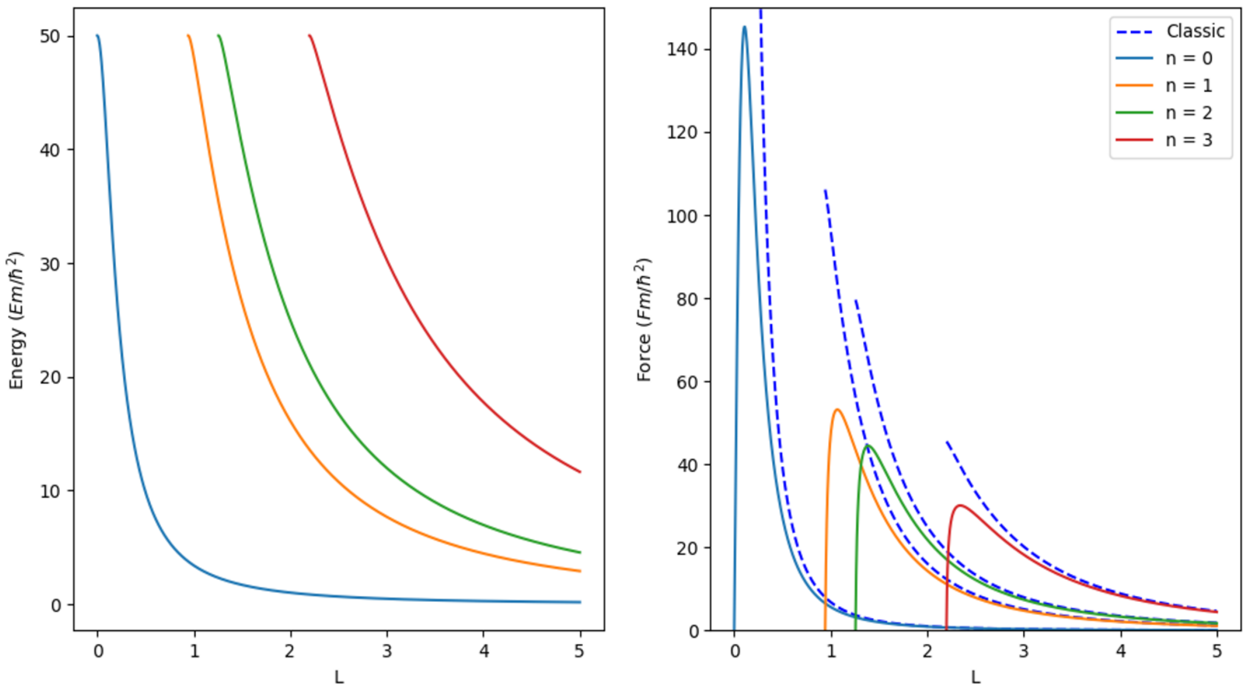

Figure 9: The energy levels and corresponding forces of the finite square well. On the left the energy is plotted as $\frac{Em}{\hbar^2}$ and on the right the force as $\frac{Fm}{\hbar^2}$. The blue dotted lines are the results of the classical equations corresponding with each energy level. For the calculation of the classical force the quantum mechanical energy levels have been used. The minimum length of the well for the energy levels is also taken into account.

7 Spherical Well

The spherical well is a 3-dimensional symmetric infinite well given by the following potential:

$$V(r) = \begin{cases} 0 & \text{for } 0 \leq r \leq L \\ \infty & \text{for } r > L \end{cases}$$

Because of symmetry we can split the Schrödinger Equation into a radial and spherical part. For this calculation only the radial part[5] is needed and is given by:

$$\frac{d^2R_{n,l}}{dr^2} + \frac{2}{r}\frac{dR_{n,l}}{dr} + \left(k^2 - \frac{l(l+1)}{r^2}\right)R_{n,l} = 0 \tag{7.1}$$

If we substitute $z = k \cdot r$ the radial part of the wave function becomes:

$$\begin{aligned} R_{n,l}(z) &= Aj_l(z) + By_l(z) \\ &= Az^l\left(\frac{-1}{z}\frac{d}{dz}\right)^l\left(\frac{\sin z}{z}\right) - Bz^l\left(\frac{-1}{z}\frac{d}{dz}\right)^l\left(\frac{\cos z}{z}\right) \end{aligned} \tag{7.2}$$

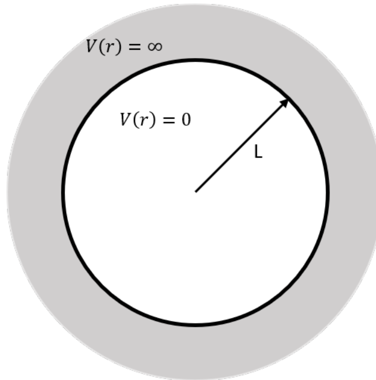

Figure 10: A 3-dimensional spherical well where the potential is zero within a radius L and infinite outside the boundary.

Where $j_l(z)$ and $y_l(z)$ are the spherical Bessel functions. The second term goes to infinity when $r \to 0$ so we set B=0. At the edge of the potential r=L we want $R_{n,l}(z)$ to go to zero too. So the zero of $R_{n,l}(z)$ is called $z_{n,l}$ which is equal to kL. The energy eigenvalues of the radial wave function are known and dependant on the zero. These energy eigenvalues are $E_{n,l} = \frac{\hbar^2 z_{n,l}^2}{2mL^2}$. therefore the force is given by:

$$F = -\frac{dE}{dL} = 2\frac{\hbar^2 z_{n,l}^2}{2mL^3} = \frac{2}{L}E_{n,l} \tag{7.3}$$

This is the same as the solution as the infinite square well. This is expected as this potential is very similar to the infinite well but in three dimensions
In the classical approach we can actually use the ideal gas law which is of course $PV = Nk_bT$. And the energy of the gas is given by $E = \frac{3}{2}k_bT$. Then the force follows from:

$$\begin{aligned} PV &= Nk_bT \\ \frac{F}{A}V &= \frac{2}{3}E \\ F &= \frac{A}{V}\frac{2}{3}E = \frac{2}{3}\frac{4\pi L^2}{4\pi L^3/3}E = \frac{2E}{L} \end{aligned} \tag{7.4}$$

Which is the same force as we found using the quantum mechanical approach.

8 Conclusion

When comparing the classical and quantum mechanical results it is possible to find differences between the two theories for certain potentials. In this case it could be possible to determine if the particle behaves quantum or classical. For other potentials there is no difference, making it impossible to distinguish how the particle behaves.

For the infinite square well and spherical well there are no differences in the force for the classical and quantum mechanical theory. Both giving the same equation for the force proportional to the energy and L^{-1}. This can be explained by the fact that the wave function has to be zero at the barriers giving that the product $k \cdot L$ must a constant.

For the triangular well there is a small difference, namely an extra $\sin(kL)/k$ term. This becomes apparent for small energies and small L. This term causes the quantum mechanical solution to oscillate around the classical one giving a higher or lower force depending on the value of L. However for L=0 this term vanishes and the quantum mechanical result becomes the same as the classical result.

For the harmonic potential two extra terms are found. Again one term dependant on $\sin(kL)/k$ and a term $\frac{k\sin(kL)}{2\alpha^2}(\psi^{(0)}(\frac{3}{4} - \frac{k^2}{4\alpha^2}) - \psi^{(0)}(\frac{1}{4} - \frac{k^2}{4\alpha^2}))$. These terms cause the quantum mechanical solutions to oscillate around the classical solutions, similar to the triangular well. For L=0 there is still a difference in the force in the quantum mechanical and classical theory.

The finite potential also has two extra terms $\frac{2\cos^2(kL/2)}{\sqrt{2mV_0/\hbar^2 - k^2}}$ and $\sin(kL)/k$ in the quantum mechanical solution for the even solutions. For the odd solutions the cosine becomes a sine. The first term is dominant for smaller V_0 and always decreases the force compared to the classical force. As L increases the energy of the particle approaches the height of the potential the terms becomes very large so the force becomes very small. This is a very big difference in behaviour as the classical force goes to infinity when L goes to zero.

So if you would measure the force exerted on the walls from outside the potential well, you would be able to determine for most of the potentials if the particle inside would behave classical or quantum. The only potentials were this can not be distinguished are the infinite square well, spherical well and the normal triangular well (L=0). For the potentials were there was a difference, there always appeared an additional $\sin(kL)/k$ term causing an oscillation around the classical solution. This term always appears in the quantum result because it follows from the $\tan(kL/2)$ term in the boundary conditions. In the classical limit of the quantum theory, which means k is large, the $\sin(kL)/k$ term disappears. Other terms added in the quantum theory also vanish giving the same result as the classical theory as you would expect for all the potentials.

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