Quantum Chemistry

Corrections 2B

1. One can use numerical matrix based methods to solve the Schrodinger equation. The accuracy of this method depends on the number discretization steps used.

a. Using the Matlab code provided, investigate how the accuracy of the numerical solutions of the energy for the particle-in-a-box problem depend on the number of discretization steps, N. In the calculations use:

Mass of the particle:	***m=me (mass of an electron)***
Size of the box:	***a=1.0 Å***
Minimum x value for discretization:	***xmin=-0.5 Å***
Maximum x value for discretization:	***xmax=1.5 Å***
Value of the potential:	***$V0=1\cdot 10^{12}$ eV (representing infinity)***

Plot the time it takes to perform the calculations and the relative deviation from the exact results for the energy levels n=1,2 and 5 for the values of N=20,21,50,51,100,101,102,200,201,500,501,1000,1001, 2000,2001, 5000 and 5001 (depending on your computer you can try even larger values)

Discuss the results, paying special attention to the differences between similar values of N.

You can use the functions tic and toc to measure calculation time. Put tic when you want to start counting, toc when you want to stop. These functions are already included in the script.

Next, we only want values for n=1,2,5. Hence, we change the n in the for loop to n=[1 2 5]

```
%------------ WRITE RESULTS TO SCREEN -------------------------------
------
disp('Quantum State       Eigenvalue              Exact Energy
Energy difference       Rel. energy difference  ');

for n = [1 2 5]
    fprintf('    %0.0f    \t      ',n);                          %
Quantum state
    fprintf('   %#5.8f \t      ',Eval(n,n));                     %
Calculated eigenvalue
    fprintf('   %#5.8f \t      ',E(n));                          %
Exact eigenvale
    fprintf('   %#5.8f \t      ',Eval(n,n)-E(n));                %
Calculate absolute deviation from exact result
    fprintf('   %#5.8f \t   \n',(Eval(n,n)-E(n))/E(n));          %
Calculate relative deviation from exact result
end
```

Next, we perform the calculation for different N which we can change in line 25.

```
%------------ SET PARAMETERS FOR CALCULATIONS -----------------------
------
N=501;                                       % Number of data points.
NOTE: number of intervals equals N-1
```

```
xmin=-0.5;                            % Minumum x value for the
calculation
xmax=+1.5;                            % Maximum x value for the
calculation
m=me;                                 % mass for calculation
a=1.0;                                % size of box (in
Angstroms)
V0=1.0*10^12;                         % potential outside box
(in eV), V0=10^12 for infinite
```

We can then read out the results, which for N=2001 should give you:

```
Quantum State    Eigenvalue        Exact Energy     Energy difference    Rel. energy difference
  1           37.60298441         37.60301591          -0.00003150        -0.00000084
  2           150.41156650        150.41206363         -0.00049713        -0.00000331
  5           940.05605398        940.07539768         -0.01934369        -0.0000205
```

And an elapsed time (which depends on your computer) in my case of 0.115077 seconds. Note that the elapsed time increases overall with N.

<u>Things you should notice:</u>

The immediate observation you can make, is that for higher n the error in Energy increases.

As one would expect, for larger N, the calculation becomes more precise. That is, the Energy Difference and Rel. Energy get smaller. Here the results for n=20

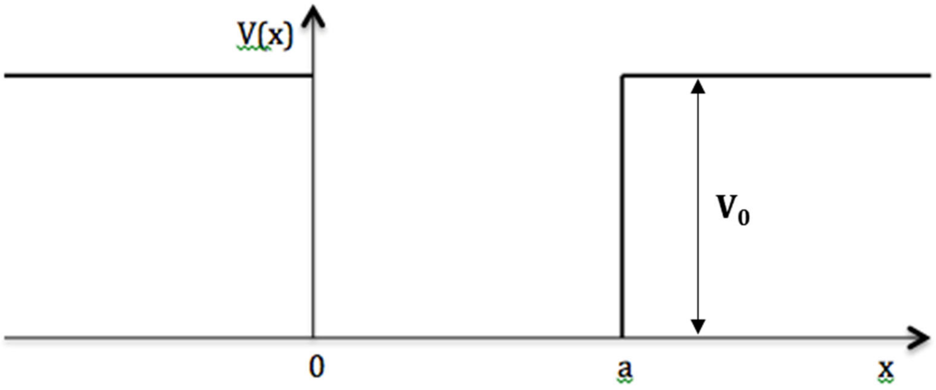
```
Quantum State    Eigenvalue        Exact Energy     Energy difference    Rel. energy difference
  1           27.85675192         37.60301591          -9.74626399        -0.25918836
  2           109.17021919        150.41206363         -41.2418444        -0.27419240
  5           589.83158881        940.07539768         -350.2438088       -0.37256991
```

If you run N=2000, you can notice a much larger error than for N=2001 which is of numerical origin.

```
Quantum State    Eigenvalue        Exact Energy     Energy difference    Rel. energy difference
  1           37.49037265         37.60301591          -0.11264326        -0.00299559
  2           149.96112133        150.41206363         -0.45094230        -0.00299805
  5           937.24085259        940.07539768         -2.83454509        -0.00301523
```

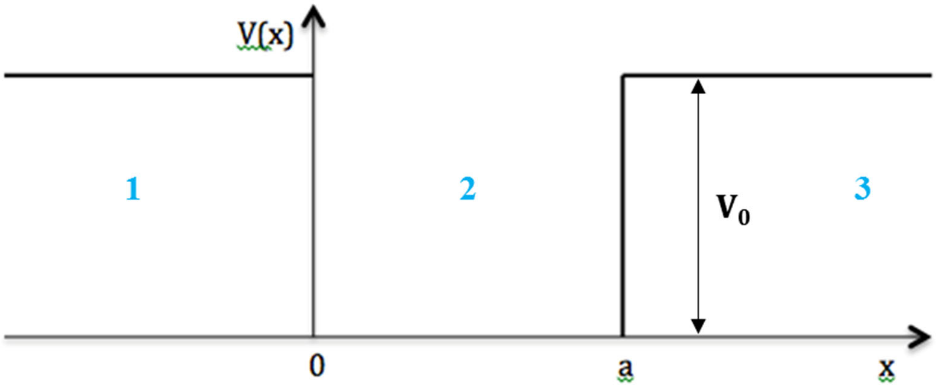
1. ***Consider a square well potential of the form:***

$$\begin{cases} V(x) = V_0 & for\ 0 \leq x \leq a \\ V(x) = 0 & for\ x < 0\ \ and\ \ x > a \end{cases}$$



The potential above is a good approximation for the potential of an electron solvated in liquid helium. In this case one finds that the electron is bound to the liquid by $V_0 = 1.1\ eV$ and resides in a cavity void of helium with a=34 Å. This is also known as an electron bubble.

a. ***Separate the problem into 3 regions and write down the Hamiltonian for each of these using classical observables.***



Following classical mechanics, we know that the Hamiltonian can be written as:

$$H_{CLASS} = E_{KIN} + E_{POT}$$

$$H_{CLASS} = \frac{p^2}{2m} + V(x)$$

And so, by looking at the three different regions that this problem presents,

$$\begin{cases} REGION\ 1. \quad V(x) = V_0 \quad H_{CLASS} = \frac{p^2}{2m} + \ V_0 \\ REGION\ 2. \quad V(x) = 0 \quad H_{CLASS} = \frac{p^2}{2m} \\ REGION\ 3. \quad V(x) = V_0 \quad H_{CLASS} = \frac{p^2}{2m} + \ V_0 \end{cases}$$

b. ***Write down the Hamiltonian operator for each of these regions.***

By replacing the classical observables by their respective operators of quantum mechanics,

$$\hat{p} = -i\hbar \frac{d}{dx}$$

we obtain:

$$\hat{H}_{QUANT} = \frac{-\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2} + \hat{V}(x,t)$$

And since we know the value of the potential for the three different regions,

$$\begin{cases} REGION\ 1. \quad V(x) = V_0 \quad \hat{H}_{QUANT} = \dfrac{-\hbar^2}{2m}\dfrac{\hat{\partial}^2}{\partial x^2} + V_0 \\ REGION\ 2. \quad V(x) = 0 \quad \hat{H}_{QUANT} = \dfrac{-\hbar^2}{2m}\dfrac{\hat{\partial}^2}{\partial x^2} \\ REGION\ 3. \quad V(x) = V_0 \quad \hat{H}_{QUANT} = \dfrac{-\hbar^2}{2m}\dfrac{\hat{\partial}^2}{\partial x^2} + V_0 \end{cases}$$

Region 1.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

Region 2.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$$

Region 3.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

c. ***Find the general solutions (eigenfunctions) to the Schrödinger equations for each region***

The general Schödinger equation is

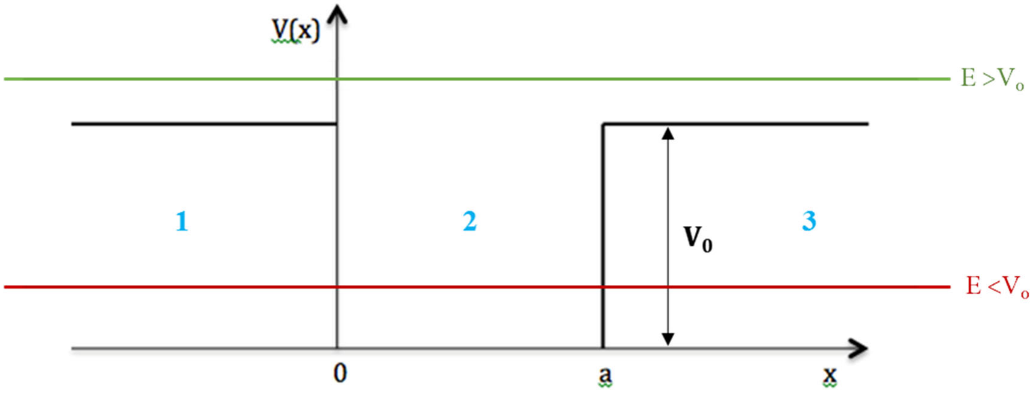
$$\hat{H}\psi = E\psi$$

$$\left[\frac{-\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2} + V(x,t)\right]\psi(x,t) = E\psi(x,t)$$

And since our potential is time independent,

$$\frac{\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2}\psi(x) + (E - V(x))\,\psi(x) = 0$$

That we should apply to each of the three regions in order to get the general solutions. However, as we can already guess, the solutions would depend on the sign of the term $(E - V(x))$, having this two different cases:



If $E > V_0$, we are in the case of unbound states, where the eigenvalues of the energy are a continumm (no discrete-no quantum). In this case, the wave function would be oscillatory, having a higher frequency when it traves between (0,a) since its energy would be purely kinetic. However, in this exercise we are interested on the bound states ($\boldsymbol{E < V_0}$), when the electron is confined inside the well/cavity. In this case, in region 1 & 3, total energy of the particle is lower than the energy "it should have" (classically) to be able to stay in those regions. Therefore, classically, the probability of finding the particle in this region would be zero. However, following quantum mechanical calculations we will find a non-zero probability. The solution for the different regions is:

$REGION\ 1.$

$$\left[\frac{-\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2} + V_0\right]\psi_1(x) = E\psi_1(x)$$

$$\frac{\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2}\psi_1(x) + (E - V_0)\psi_1(x) = 0$$

$$(E - V_0) < 0$$

$$\alpha^2 = \frac{2m}{\hbar^2}(V_0 - E) > 0$$

$$\frac{\partial^2\psi_1}{\partial x^2} - \alpha^2\psi_1 = 0$$

$$\psi_1(x) = A\, e^{\alpha x} + A'\, e^{-\alpha x}$$

$REGION\ 2.$

$$\frac{\hbar^2}{2m}\frac{\hat{\partial}^2}{\partial x^2}\psi_2(x) + E\psi_2(x) = 0$$

$$E > 0$$

$$\beta^2 = \frac{2m}{\hbar^2}E > 0$$

$$\frac{\partial^2\psi_2}{\partial x^2} + \beta^2\psi_2 = 0$$

$$\psi_2(x) = D\, e^{i\beta x} + D'\, e^{-i\beta x}$$

$$or$$

$$\psi_2(x) = B\, sin(\beta x) + B' \cos(\beta x)$$

$$with\ B = i(D - D') \quad and\ B' = (D + D') \quad \text{(Using Euler's formula)}$$

$REGION\ 3.$

Following the same procedure as in region 1,

$$\psi_3(x) = C\, e^{\alpha x} + C'\, e^{-\alpha x}$$

And so, we obtain:

$$\begin{cases} REGION\ 1. & \psi_1(x) = A\, e^{\alpha x} + A'\, e^{\alpha x} \\ REGION\ 2. & \psi_2(x) = B\, sin(\beta x) + B' \cos(\beta x) \\ REGION\ 3. & \psi_3(x) = C\, e^{\alpha x} + C'\, e^{-\alpha x} \end{cases}$$

But, by looking at the solution of $\psi_1(x)$ and $\psi_3(x)$ we can see that both eigenfunctions diverge when $x \to -\infty$ and $x \to +\infty$, and since the square of the wave function is proportional to the probability of finding the particle at any point, this result means that the it is more likely to find the particle at infinity. Therefore, this result makes no sense in this problem because we are trying to find wave functions for particles that stay in (or close to) the well. This restriction implies that:

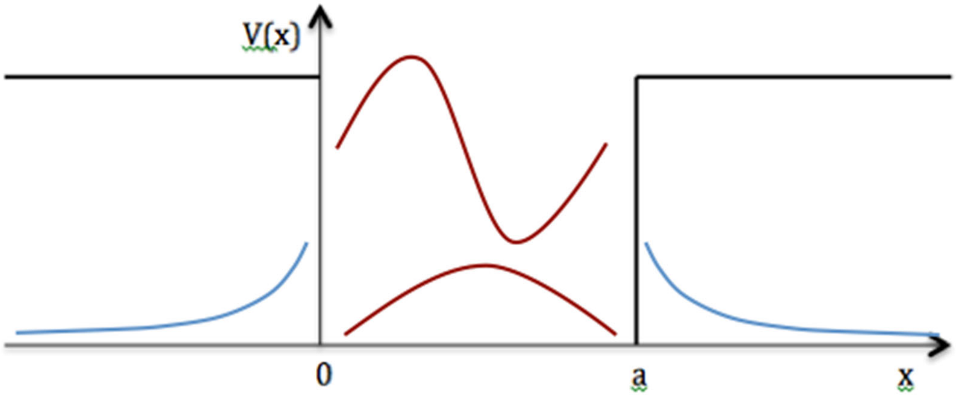
$$\psi_1(x) = A\, e^{\alpha x} \qquad A' = 0$$
$$\psi_3(x) = C'\, e^{-\alpha x} \qquad C = 0$$

so the eigenfunctions are:

$$\begin{cases} REGION\ 1. & \psi_1(x) = A\, e^{\alpha x} \\ REGION\ 2. & \psi_2(x) = B\, sin(\beta x) + B' \cos(\beta x) \\ REGION\ 3. & \psi_3(x) = C'\, e^{-\alpha x} \end{cases}$$

d. Draw the eigenfunctions for each region.

With the information that we can take from the general solutions of the eigenfuncions in the three different regions, we can sketch the following (i.e. increasing exponential in region 1, an oscillatory function in region 2 and a decreasing exponential in region 3).
Moreover, from theory we know that the first state of a quantum system does not have any node (point of the space in which the probability of finding the particle is zero), so we can already guess that the first eigenfunction will be a cosine wave.



e. Write down the boundary conditions for this problem.

Both the wavefunction and the first derivative need to be continuous everywhere, and so, we pay special attention at the boundaries, with in our case are x=0 and x=a;

$$\psi_1(0) = \psi_2(0) \qquad \& \qquad {\psi_1}'(0) = {\psi_2}'(0)$$
$$\psi_2(a) = \psi_3(a) \qquad \& \qquad {\psi_2}'(a) = {\psi_3}'(a)$$

+ the ones we found before:

$$A' = 0$$
$$C = 0$$

f. Discuss now this problem and its solutions relate to the particle-in-a-box problem having infinite potential outside the box.

Let's compare the infinite with the finite well potential.

In the first case, as you have seen in class, the particle is confined into the well. It is impossible for the particle (electron) to escape, since the energy necessary to go out of the box is infinite. However, in the second case the well is not infinitely deep, and this fact changes the result quite a lot.

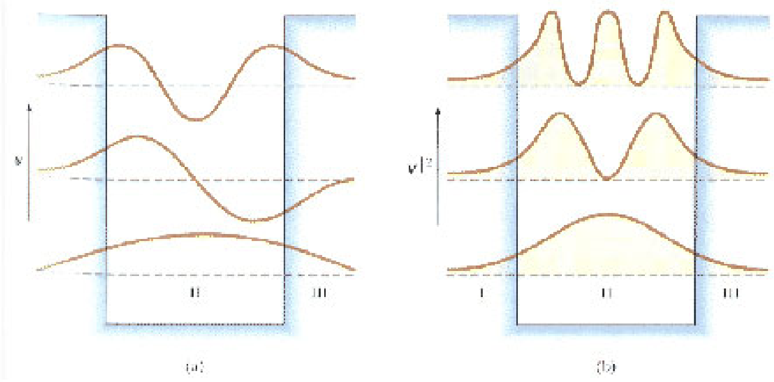
Let's start thinking in terms of classical physics and let's imagine that the electron has, for example, half of necessary energy to jump out of the well. In this case, the solutions (from classical physics) would be the same as the ones for the infinite well: if the electron is moving, it will arrive to the barrier, it would bounce on the wall and it would go back (following the same path it was doing before reach the wall). It does not matter the amount of energy that the electron has if it is lower than the barrier: from classical mechanics, it cannot jump.

But, let's look at this problem for the quantic point of view keeping in mind the corpuscular/wave duality. And again, let's imagine that the electron has half of the energy to jump out of the well. From the corpuscular nature, when the electron arrives to the barrier, it will bounce; but from the wave nature, the result is different. If the wave does not have enough energy to penetrate into the "forbidden region", it will reflect, but part of the wave will be able to penetrate slightly into the region of higher energy. In order to understand this effect physically, we can assume that the "forbidden" region is formed by an absorbent material. If the potential well is infinite, this material would have an infinite absorbance coefficient and therefore, before the wave can travel any distance through this material, it gets completely absorbed. However, if the potential well is finite, a new "magnitude" appears: the energy difference between the well and the electron's one. If this difference is large, the wave is absorbed by the material quickly (similar to the infinite case), although not infinitively quickly. It is something similar to what the Coyote and the Road Runner do when they walk through the vacuum before fall into the precipice.
If, however, this energy difference is small, the intensity of the wave would decrease slowly, travelling more through the "absorbent medium".

The mathematical result fits well with this explanation: out of the well, we obtain a wave whose amplitude decreases exponentially with distance. If the "energy difference" is large, the decrease in the exponential is abrupt (it almost does not feel that it has entered into the barrier), and if it is small, the amplitude decreases slowly.

But then, if there is a non-zero probability of finding the wave outside the well, THERE IS A NON-ZERO PROBABILITY of finding the ELECTRON OUTSIDE THE WELL, something that it cannot be imagined following Newton mechanics, being this THE MAIN DIFFERENCE BETWEEN THE FINITE AND INFINITE POTENTIAL WELL.

g. ***Now, without solving the resulting coupled equations, draw the eigenfunctions for the 3 lowest energy levels.***



h. ***Use Matlab to solve the Schrodinger equation numerically and determine the energy levels of butadiene assuming an ionization energy of 12 eV. Calculate the corresponding transition wavelength and wavenumber and compare the results to those found for a box with infinite walls.***

2h) We just change the barrier height to 12 eV.

```
%------------ SET PARAMETERS FOR CALCULATIONS -----------------------
------
N=501;                                       % Number of data points.
NOTE: number of intervals equals N-1
xmin=-0.5;                                   % Minumum x value for the
calculation
xmax=+6.28;                                   % Maximum x value for
the calculation
m=me;                                        % mass for calculation
a=5.78;                                       % size of box (in
Angstroms)
V0=12;                                       % potential outside box
(in eV), V0=10^12 for infinite
```

Remember to change the size of the box to the length of the butadiene molecule (5.78 Angstrom) as well as x $_{max}$.

Quantum State	Eigenvalue	Exact Energy	Energy difference	Rel. energy difference
1	0.86322231	1.12555573	-0.26233342	-0.23307013
2	3.44862257	4.50222290	-1.05360033	-0.23401781
3	7.74349593	10.13000153	-2.38650560	-0.23558788
4	13.72706598	18.00889161	-4.28182563	-0.23776175
5	21.37136400	28.13889314	-6.76752914	-0.24050445

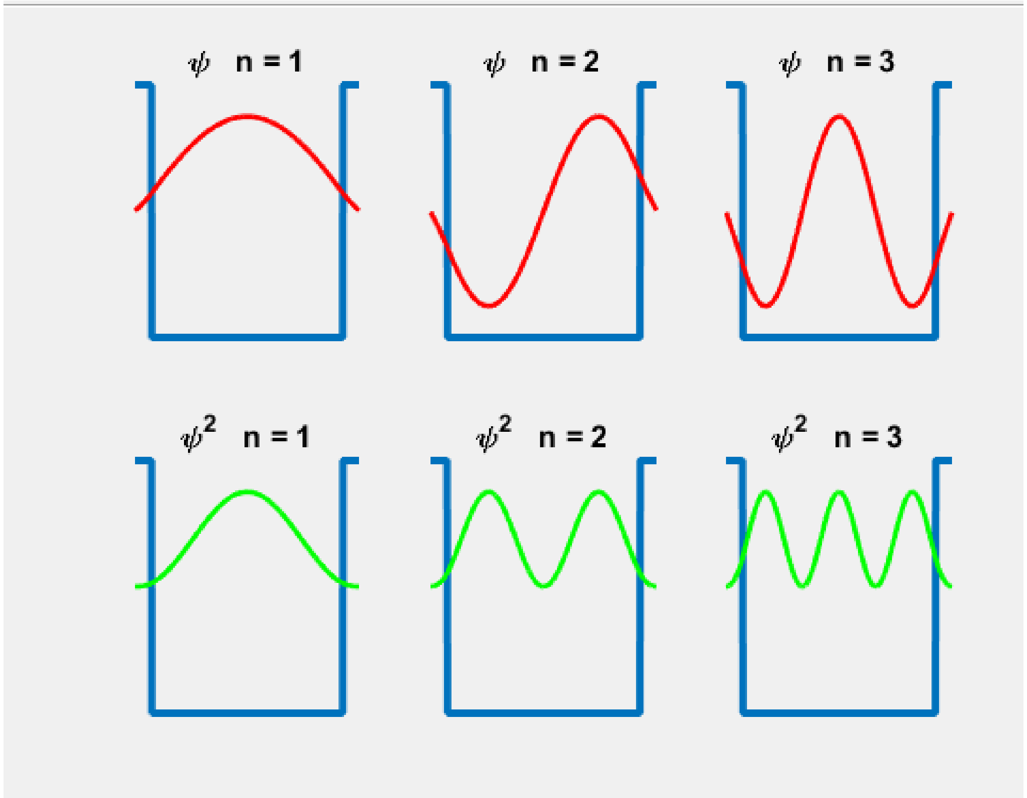
Find the energy difference between two quantum levels and then use the following equations to calculate the transition wavelength and wavenumber:

$$E = h\nu = \frac{hc}{\lambda} \qquad \tilde{\nu} = \frac{1}{\lambda}$$

respectively.

The conclusion that you can draw is that the finite well has lower energy levels than the infinite well. This is because the wavefunction in the finite potential well extends into the classically forbidden region, so the corresponding wavelengths are longer than those in the infinite well, resulting in lower energies.

Finite well:

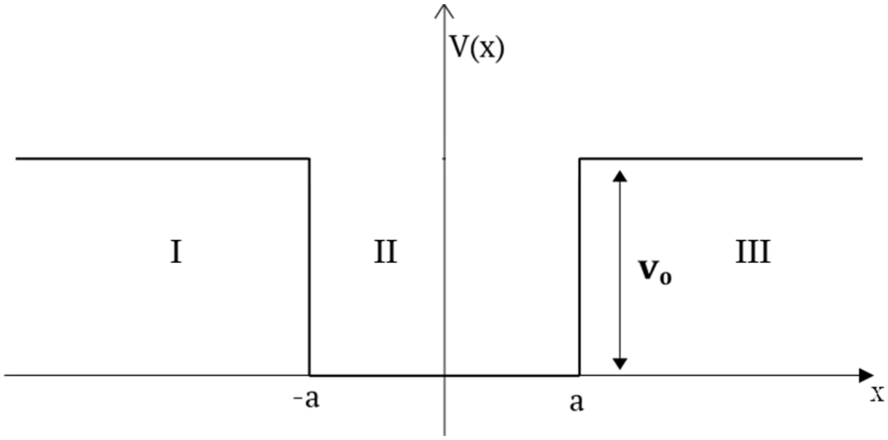


i. OPTIONAL: Solve the problem mathematically.

In order to have a symmetric potential for reflections as x → -x, we redefine the well and we move it to be symmetric with respect to 0,

$$\begin{cases} V(x) = 0 & for - a \leq x \leq a \\ V(x) = V_0 & for\ x < -a\ \ and\ \ x > a \end{cases}$$

so now the potential looks like:



We will discuss now each region:

Region 1: outside the box

$$V(x) = V_0 \quad \& \quad 0 < E < V_0$$

The Schrödinger equation for this region is:

$$\frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi_1 = 0 \qquad \text{where} \qquad \frac{2m}{\hbar^2}(E - V_0) < 0$$

so in order to find the general solutions for this equation we define:

$$\rho^2 = \frac{2m}{\hbar^2}(V_0 - E) > 0$$

Which simplifies the Schrödinger equation as:

$$\frac{\partial^2 \psi_1}{\partial x^2} = \rho^2 \psi_1$$

that has as solutions:

$$\psi_1(x) = B_1 e^{\rho x} + B_1' e^{-\rho x}$$

Region 3: outside the box

$$V(x) = V_0 \quad \& \quad 0 < E < V_0$$

Which as the same solutions as Region I:

$$\psi_3(x) = B_3 e^{\rho x} + B_3' e^{-\rho x}$$

Region 2: inside the box

$$V(x) = 0 \quad \& \quad 0 < E < V_0$$

The Schrödinger equation for this region is:

$$\frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2} E \psi_2 = 0 \qquad \text{where} \qquad \frac{2m}{\hbar^2} E > 0$$

So we can define the quantity:

$$k^2 = \frac{2m}{\hbar^2} E > 0$$

and find the solutions for the Schrödinger equation (as done for the particle in the infinite potential energy barrier):

$$\frac{\partial^2 \psi_2}{\partial x^2} = -k^2 \psi_2$$

That has as solutions,

$$\psi_2(x) = A_2 e^{ikx} + A_2' e^{-ikx}$$

Now, in order to solve the problem, we have to discuss the boundary conditions for the problem:

As it has been discussed in the section c, the eigenfunctions cannot diverge, and therefore:

$$\psi_1(x) = B_1 e^{\rho x} \qquad B_1' = 0$$

$$\psi_3(x) = B_3' e^{-\rho x} \qquad B_3 = 0$$

And we also should apply the requirement that the eigenfunction and its first derivative need to be continuous anywhere. So applying it to the boundaries:

$$\boldsymbol{A}\quad\begin{cases}\psi_1(-a)=\psi_2(-a)\\ \psi_1'(-a)=\psi_2'(-a)\end{cases}$$

$$\boldsymbol{B}\quad\begin{cases}\psi_2(a)=\psi_3(a)\\ \psi_2'(a)=\psi_3'(a)\end{cases}$$

- Let's start solving ***A*:**

$$\begin{cases}B_1e^{-\rho a}=A_2e^{-ika}+A_2'e^{ika}\\ \rho B_1e^{-\rho a}=ikA_2e^{-ika}-ikA_2'e^{ika}\end{cases}$$

Now, by multiplying the first equation for ik,

$$\begin{cases}ikB_1e^{-\rho a}=ikA_2e^{-ika}+ikA_2'e^{ika}\\ \rho B_1e^{-\rho a}=ikA_2e^{-ika}-ikA_2'e^{ika}\end{cases}$$

And summing and subtracting both we get:

$$(ik+\rho)B_1e^{-\rho a}=2ikA_2e^{-ika}$$

$$(ik-\rho)B_1e^{-\rho a}=2ikA_2'e^{ika}$$

So solving for A_2 and A_2':

$$\boldsymbol{A}\quad\begin{cases}A_2=\dfrac{ik+\rho}{2ik}e^{(ik-\rho)a}B_1\\ A_2'=\dfrac{ik-\rho}{2ik}e^{-(ik+\rho)a}B_1\end{cases}$$

- Let's now solve ***B*:**

$$\begin{cases}A_2e^{ika}+A_2'e^{-ika}=B_3'e^{-\rho a}\\ ikA_2e^{ika}-ikA_2'e^{-ika}=-\rho B_3'e^{-\rho a}\end{cases}$$

As we did above, we multiply the first equation for ik and sum and subtract the two of them and then we write A_2 and A_2' in function of B_3':

$$\boldsymbol{B}\quad\begin{cases}A_2=\dfrac{ik-\rho}{2ik}e^{-(ik+\rho)a}B_3'\\ A_2'=\dfrac{ik+\rho}{2ik}e^{(ik-\rho)a}B_3'\end{cases}$$

At this point we can equal the solutions for A_2 and A_2' found in ***A*** with the ones found in ***B***:

A $$\begin{cases} A_2 = \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_1 \\ A_2' = \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_1 \end{cases}$$ **B** $$\begin{cases} A_2 = \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_3' \\ A_2' = \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_3' \end{cases}$$

$$\begin{cases} \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_1 = \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_3' \\ \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_1' = \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_3' \end{cases}$$

For both equations, we can write the ratio B_3'/B_1 in function of k and ρ :

$$\begin{cases} \dfrac{B_3'}{B_1} = \dfrac{ik+\rho}{ik-\rho} e^{2ika} \\ \dfrac{B_3'}{B_1} = \dfrac{ik-\rho}{ik+\rho} e^{-2ika} \end{cases}$$

so then:

$$\frac{ik+\rho}{ik-\rho} e^{2ika} = \frac{ik-\rho}{ik+\rho} e^{-2ika}$$

$$e^{4ika} = \left(\frac{ik-\rho}{ik+\rho}\right)^2 = \left(\frac{\rho-ik}{\rho+ik}\right)^2 \quad (*)$$

In which ρ and k depend on the energy,

In order to solve (*) we have to do its square root, so then we have to solve:

(1) $$e^{2ika} = \frac{\rho-ik}{\rho+ik}$$

(2) $$e^{2ika} = -\frac{\rho-ik}{\rho+ik}$$

- Let's start solving **(1)** multiplying for $\rho+ik$,

$$e^{2ika} = \frac{\rho+ik}{\rho+ik} \cdot \frac{\rho-ik}{\rho+ik} = \frac{\rho^2+k^2}{(\rho+ik)^2}$$

$$(\rho+ik)^2 = (\rho^2+k^2)e^{-2ika}$$

It is easier to solve this equation if we think in terms of complex numbers:

$$z = x + iy = re^{i\varphi} = \sqrt{x^2 + y^2}\, e^{i\varphi}$$

$$\varphi = arctg\frac{y}{x}$$

$$\frac{y}{x} = tg\varphi$$

By analogy we can write:

$$\rho + ik = \sqrt{\rho^2 + k^2}\, e^{-ika}$$

$$tg(-ka) = \frac{k}{\rho} > 0$$

That for the properties of tg and cotg can be rewritten as:

$$tg(ka) = -\frac{k}{\rho} < 0$$

$$cotg(ka) = -\frac{\rho}{k}$$

In order to solve this equation we can use the following property of cotg:

$$1 + cotg^2(ka) = \frac{1}{\sin^2(ka)}$$

$$1 + \frac{\rho^2}{k^2} = \frac{1}{\sin^2(ka)}$$

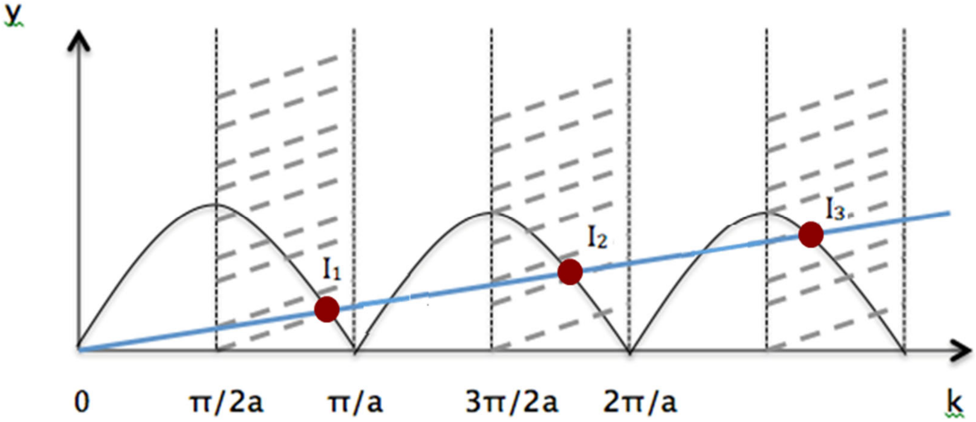
$$\left|\sin(ka)\right| = \frac{k}{\sqrt{\rho^2 + k^2}} = \frac{k}{k_0}$$

with $k_0 = \sqrt{\rho^2 + k^2} = \sqrt{\frac{2m}{\hbar^2}\left[(V_0 - E) + E\right]} = \sqrt{\frac{2m}{\hbar^2}V_0}$ that now is a number!

We have simplified the equation that now depends on the square root of the E. So now, the system that we need to solve is:

$$\begin{cases} \left|\sin(ka)\right| = \dfrac{k}{k_0} \\ tg(ka) < 0 \end{cases}$$

We can solve it graphically: the solutions (proportional to the energy of the system) will be the intersection points between the curve $\left|\sin(ka)\right|$ and the line $\frac{k}{k_0}$ in the regions where $tg(ka) < 0$.



- Let's now solve **(2)** multiplying for $(\rho - ik)$ following the same method we used above:

$$e^{2ika} = \frac{(k+i\rho)^2}{k^2+\rho^2}$$

$$k + i\rho = \sqrt{k^2+\rho^2}\, e^{ika}$$

$$tg(ka) = \frac{\rho}{k} > 0$$

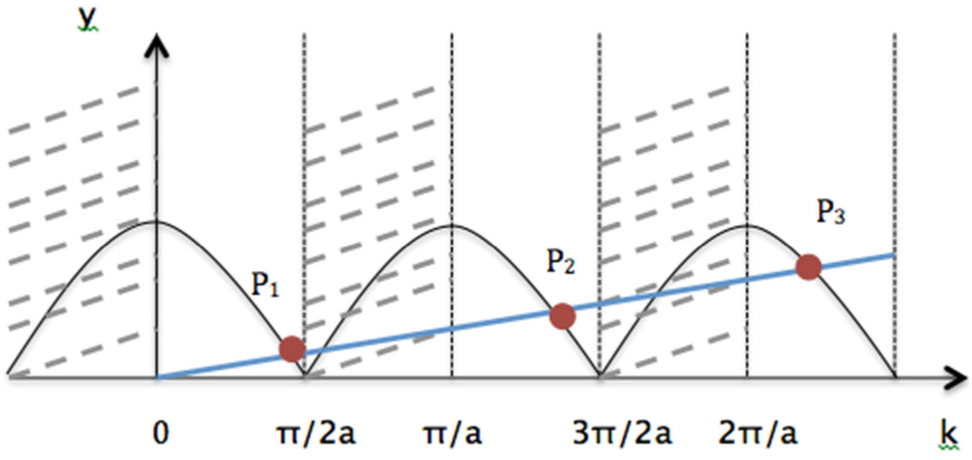
this time we will use the following property of the tangent :

$$1 + tg^2(ka) = \frac{1}{\cos^2(ka)}$$

$$1 + \frac{\rho^2}{k^2} = \frac{1}{\cos^2(ka)}$$

$$\begin{cases} |\cos(ka)| = \dfrac{k}{\sqrt{k^2+\rho^2}} = \dfrac{k}{k_0} \quad \text{with} \quad k_0 = \sqrt{\dfrac{2mV_0}{\hbar^2}} \\ tg(ka) > 0 \end{cases}$$

Which we can again solve graphically: the solutions (proportional to the energy of the system) will be the intersection points between the curve $|\cos(ka)|$ and the line $\frac{k}{k_0}$ in the regions where $tg(ka) < 0$.



And, in order to combine both solutions, we can substitute the following expressions:

$$\textbf{(1)}\quad e^{2ika} = \frac{\rho - ik}{\rho + ik}$$

$$\textbf{(2)}\quad e^{2ika} = -\frac{\rho - ik}{\rho + ik}$$

into the equations:

$$\boldsymbol{A}\begin{cases} A_2 = \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_1 \\ A_2' = \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_1 \end{cases} \qquad \boldsymbol{B}\begin{cases} A_2 = \dfrac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_3' \\ A_2' = \dfrac{ik+\rho}{2ik} e^{(ik-\rho)a} B_3' \end{cases}$$

In order to find the coefficients.

- Let's start from plugging the equation **(2)** in the expression for A_2 of system ***A***:

  $$\rho + ik = -(\rho - ik)e^{-2ika}$$
  $$A_2 = -\frac{(\rho - ik)}{2ik} e^{ika} e^{-2ika} e^{-\rho a} B_1 = \frac{ik-\rho}{2ik} e^{-(ik+\rho)a} B_1 = A_2'$$

  Similarly, by plugging the equation **(2)** in the expression for A_2' of system ***A***, we can find that:

  $$B_1 = B_3'$$

  So then the wavefunctions look like:

$$\begin{cases} \psi_1(x) = B_1 e^{\rho x} \\ \psi_2(x) = A_2 e^{ikx} + A_2 e^{-ikx} = 2A_2\cos(kx) \\ \psi_3(x) = B_1 e^{-\rho x} \end{cases}$$

Being these functions *EVEN* functions $\psi(-x) = \psi(x)$.

- However, if now we plug the equation **(1)** in the expression for A_2 and A_2' of system ***B*** and we would find that:

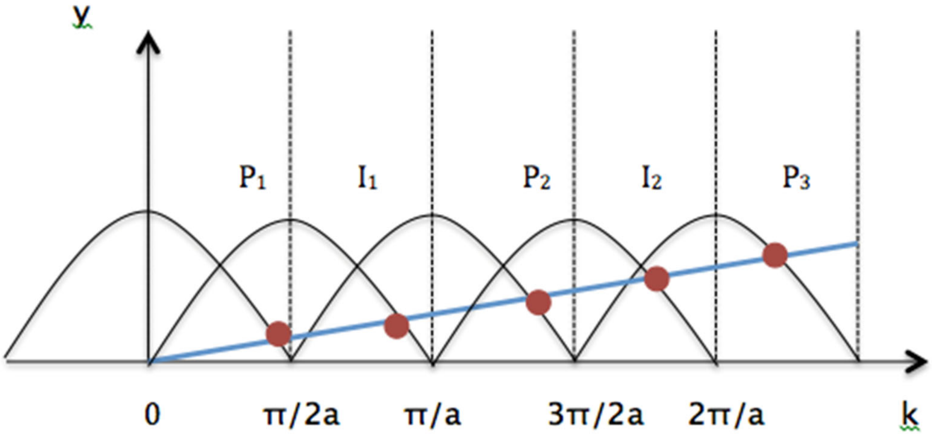
$$A_2 = -A_2'$$
$$B_1 = -B_3'$$

And in this case, the wavefunctions look like:

$$\begin{cases} \psi_1(x) = B_1 e^{\rho x} \\ \psi_2(x) = A_2 e^{ikx} - A_2 e^{-ikx} = 2iA_2\sin(kx) \\ \psi_3(x) = -B_1 e^{-\rho x} \end{cases}$$

And these functions are ODD functions $\psi(-x) = -\psi(x)$.

Finally, if we couple the solutions that we found above, we have a sequence of odd and even energy levels:



P_1 even (cos) → E_1
I_1 odd (sin) → E_2
P_2 even (cos) → E_3
I_2 odd (sin) → E_4
P_3 even (cos) → E_5