Illustrating the Bohr Correspondence Principle ©

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Prerequisites: This worksheet is intended as a follow-up activity for a traditional lecture on the solution of the Schrodinger equation for particle confined to a 1-dimensional box (PIB) in undergraduate Physical Chemistry. Students must be familiar with basic Mathcad operations.

Goal: The goal of this document is to introduce the Bohr Correspondence Principle.

Introduction: Quantum Mechanics was invented because classical (Newtonian) mechanics fails in the "world of the very small". However, in order for Quantum Mechanics to be accepted, it should not contradict classical mechanics in cases where classical mechanics is known to be valid. This is known as Bohr's Correspondence Principle. In this document, we will illustrate this principle.

Performance Objectives: After completing the work described in this document you should be able to:
1. describe how the PIB wavefunction changes as the quantum number n increases
2. explain the mathematical basis for the restrictions on the quantum number n
3. explain (using the PIB, harmonic oscillator, and hydrogen atom as examples) how QM becomes constent with CM in the limit of very large quantum numbers in terms of probability density and energy quantization.

Part 1. Getting acquainted with the PIB wavefunctions

The general expression for wavefunctions of a particle confined to a box of length L (where the potential energy is zero inside, and infinite outside) is given by

$\psi(x) = 0$ when x<0 and x>L, outside the box

$\psi(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n \cdot \pi \cdot x}{L}\right)$ when $0 \le x \le L$, inside the box

The quantum number, n, is restricted to nonzero integers. We will now exmaine plots of ψ and ψ^2. First, we define n=1 and L=1

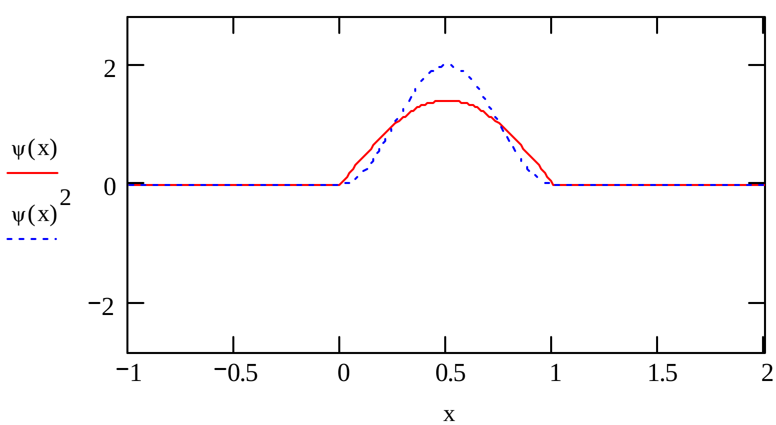
$n := 1$ $L := 1$

Then, we define ψ. The expression (0<x<L) is a "boolean expressions" and they evaluate to 1 (if true) or 0 (if false). Complete the expression for ψ in Eq. 1 below

$$\psi(x) := \left(\sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n \cdot \pi \cdot x}{L}\right)\right) \cdot (0 < x < L) \qquad \text{Eq. 1}$$

Now, we plot ψ and ψ^2 vs. x from x=-L to x=2L in steps of 0.01L

$x := -L, -0.99 \cdot L .. 2 \cdot L$



EXPLORATIONS

1. Change n to 2, 3, and 10. Describe how the plots change as n increases. Use the word "node" in your description. A node is a location where ψ changes sign.

The number of nodes increases as n increases; number of nodes = n-1. Then nodes are evenly spaced.

2. Change n to zero and examine the graph. Explain why n=0 is not acceptable. Hint: Since ψ^2 is the probability density function, what should the integral of ψ^2 from x=-infinity to x=+infinity, and what is the value of this integral if n=0?

Setting n=0 makes ψ (and ψ^2) zero everywhere. This makes the integral of ψ^2 from x=-infinity to x=+infinity equal to zero; this would mean that the particle does not exist. The integral should be equal to 1 (certain)

3. Change n to a non-integer value. Examine the graph and explain why non-integer values of n are not acceptable. Hint: refer to your notes or textbook regarding the justification for restricting the values of n.

When n is not an integer, the function is not continuous at x=L. This is not an acceptable function for ψ..

Part 2. Comparing probabilities: CM vs. QM

Classical Mechanics (CM), which is based on Newton's Laws, predicts that the probability of finding the particle is uniform throughout the box. Explain why using the following equation: F = -dV/dx = ma, where F=force, V=potential energy, m=mass, a=acceleration.

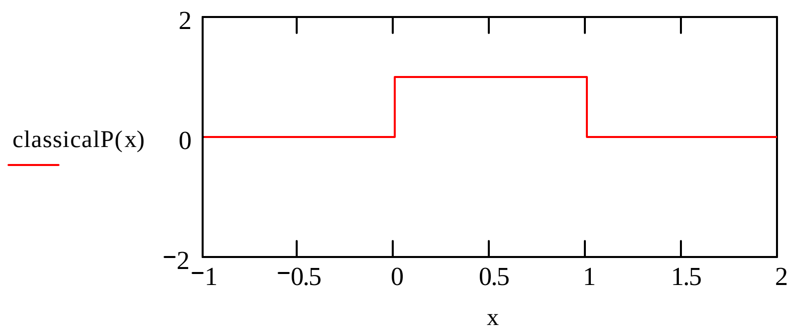
If V=0 inside the box, the there is no force acting on the particle; -dV/dx=0. It should be moving at constant speed (a=0) until it hits the wall, then it turns around and moves at the same constant speed again (with no energy transferred between wall and particle) until it hits the other wall. This means the likelihood of finding the particle is uniform throughout the box.

Use your intuition to answer the following questions. According to CM, what is the probability of finding the particle
a. in the left-half of the box? *1/2*
b. in the right-half of the box? *1/2*
c. in any quarter of the box? *1/4*

Here's the "probability density function" for the particle according to classical mechanics: (cf. Example B-3, page 67 of Reference 1)

$$\text{classicalP}(x) := \frac{1}{L} \cdot (0 \le x \le L)$$

$$x := -L, -0.999 \cdot L .. 2 \cdot L$$



The probability density function allows us to calculate the probability of finding the particle in any section of the box. We do this by integrating it with respect to x, using the left and right edges of the section as limits. For example, according to CM, the probability of finding the particle between x=0.5L and x=0.7L is

$$\int_{0.5 \cdot L}^{0.7 \cdot L} \text{classicalP}(x)\, dx = 0.2$$

Note that the section from 0.5L to 0.7L spans one-fifth of the box, and CM says the probability of finding the particle there is 0.2, which is one-fifth.

Complete the following general formula for the probability of finding the particle between x=a and x=b. [Assume a and b are between x=0 and x=L]

$$\text{classicalProb}(a,b) := \int_a^b \text{classicalP}(x)\,dx$$

Verify that this formula agrees with the intuitive answers you gave above. Plug in specific values of a and b to answer the questions.

A probability density function must be "normalized". This means the integral over all possible values of x is 1, i.e., it is certain (probability=1) that the particle will be in any one of all the possible locations. Complete the expression below to verify that the probability density function we have above is, in fact, normalized.

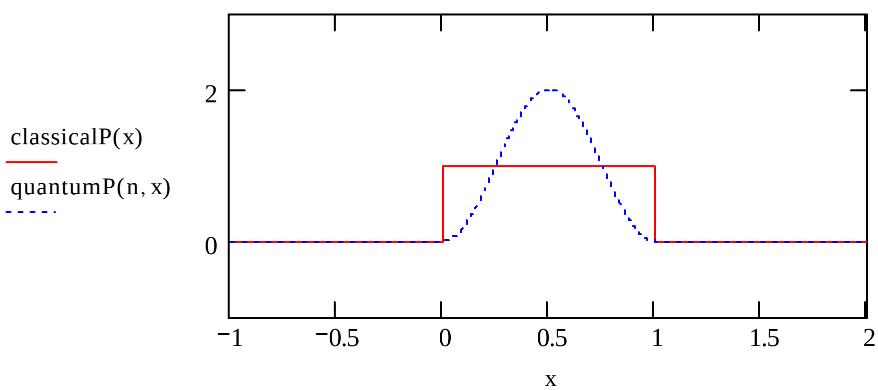
$$\text{classicalProb}(0,L) = 1$$

In Quantum Mechanics (QM), we postulate that ψ^2 is the probability density function. The probability density function therefore depends not just on the location but also on the quantum state (i.e., on the quantum number n). Complete the expression below for the probability density function for quantum state n, according to QM.

$$\text{quantumP}(n,x) := \left(\sqrt{\frac{2}{L}}\cdot\sin\left(\frac{n\cdot\pi\cdot x}{L}\right)\right)^2\cdot(0 \le x \le L)$$

Shown below is a plot of the probability density function for quantum state n=1. The probability density function according to CM is also shown for comparison. Increase the value of n (try 2, 3, 4, etc.) and observe how the QM probability density function compares with the classical probability density function. Does it look like the two will ever be the same? *No*

$x := -L, -0.999\cdot L .. 2\cdot L \qquad n := 1$

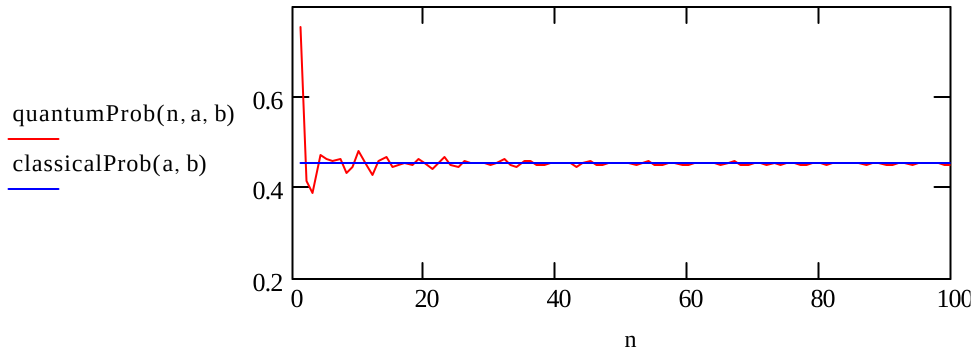


Now , let's examine the probability of finding the particle in a specific section of the box. Complete the following formula for the probability of finding the particle from x=a to x=b, if the particle is in quantum state n.

$$\text{quantumProb}(n,a,b) := \int_a^b \text{quantumP}(n,x)\,dx$$

The plot below shows a comparison of the QM and CM predictions for the probability of finding the particle in a section of the box. Pick ***any*** section; for starters, use a=0.1293L and b=0.6817L; then try others.

$a := 0.2293 \cdot L \qquad b := 0.6817 \cdot L \qquad n := 1, 2 .. 100$



Based on the plot, for what values of n do you expect QM to agree with CM? What values of n show a significant difference in the behavior of the quantum and classical systems?

I would expect agreement at large values of n. Significance difference in the behavior is observed at small values of n.

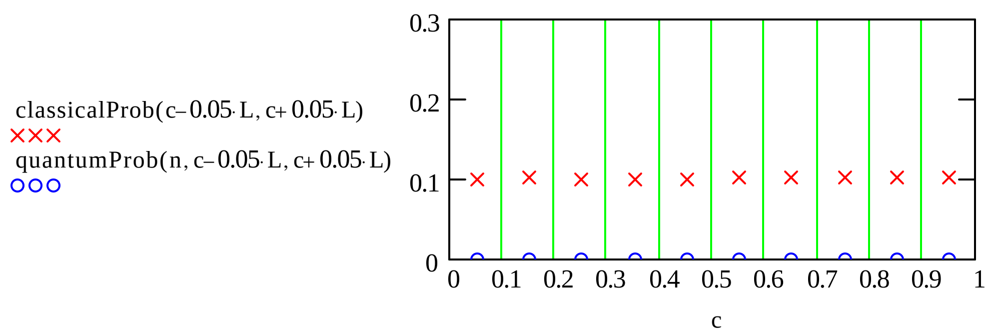
Here's another way to compare CM and QM. Let us divide our box into ten sections. Let c=centers of each section; these would be 0.05L, 0.15L, 0.25L, etc.

$c := 0.05L, 0.15 \cdot L .. 0.95L$

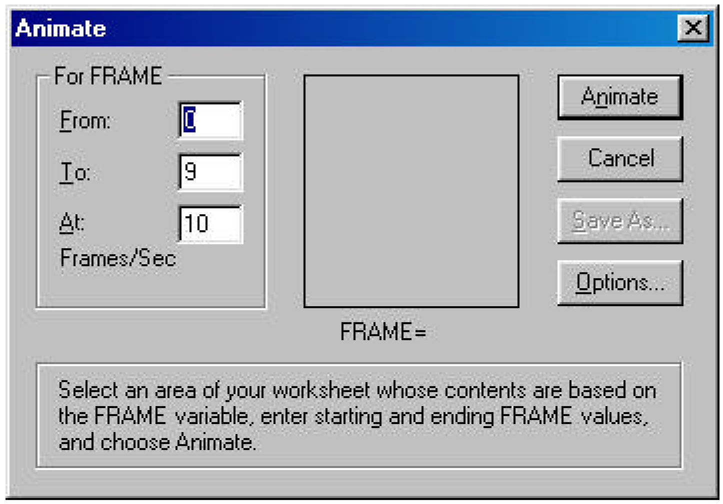
In the plot below, we show the classical probability of finding the particle in each tenth section by drawing an x in the middle of the section; note that the probability for each section according to CM is 1/10. Complete the label on the vertical axis to show the QM prediction, then create an animation as n advances from 1 to 100; 3 frames per second. Note that n as shown below is initially equal to zero (which is not allowed; remember why?); the FRAME variable assumes a zero value and changes only while you're generating an animation.

$n := \text{FRAME}$

$n = 0$



Now, let's generate an animation to see how the QM compares with CM predictions as n goes from 1 to 100. Go through the Mathcad menu to bring up the animation dialog box, which looks like the figure shown below. (This depends on the Mathcad version you're using. In Mathcad 2000 and 2001, click on View, Animate...) In the **For FRAME** boxes, enter From **1** to **100** at **2** Frames per second. Select the part of the Mathcad document that you want to track as the FRAME variable advances from 1 to 100 (you may need to drag the dialog box out of the way), then click Animate to generate the animation. For other versions of Mathcad please refer to the manual for instructions.



Observe the animation. For what values of n is QM more likely to agree with CM: very small or very large? Relate your observations here to those you made while exploring the graph in the previous page. You may find it helpful to read the discussion on page 85 of reference 1.

Agreement between QM and CM is better at very large n values. In the earlier exploration, the graph showed that the QM probability of finding the particle in any given section of the box tends to agree with CM if n is very large. In the animation, this was illustrated for ten equal sections of the box.

Part 3. The quantum state of an average He atom in a 1-Liter box at 298K

The allowed energies for a PIB are

$$E = \frac{n^2 \cdot h^2}{8 \cdot mass \cdot L^2}$$

where h=Planck's constant=$6.63x10^{-34}$ J s

Imagine He atoms in a 1-Liter cubic box at 298K. The edge of the box would be 10 cm or 0.1 m long. This is a length that is considered "macroscopic". Let us calculate n for an average atom in this box. For simplicity, we will consider the motion in only one dimension, i.e., treat the atom as a PIB. First we define the length of the box.

$$L := 0.1m$$

Then we calculate the mass of a He atom in kg. A mole of atomic mass units is equivalent to a gram (10^{-3} kg). Complete the equations below

$$g := 10^{-3} \cdot kg \qquad amu := \frac{1}{6.02 \cdot 10^{23}} \cdot g \qquad mass := 4 \cdot amu \qquad mass = 6.645 \times 10^{-27} kg$$

Define the value for Planck's constant:

$$s := sec \qquad J := kg \cdot m^2 \cdot s^{-2} \qquad h := 6.63 \cdot 10^{-34} \cdot J \cdot s$$

Kinetic Molecular Theory, which is based on classical mechanics, predicts that the average translational energy of a molecule along any axis is $(1/2)k_B$ T, where k_B is Boltzmann's constant and T is the absolute temperature. Let's calculate E for the motion of an average He atom along an axis at room temperature (298K) according to Kinetic Molecular Theory. First, we calculate Boltzmann's constant which is equal to the gas constant (R) divided by Avogadro's Number

$$kB := \frac{8.314}{6.02 \cdot 10^{23}} \cdot \frac{J}{K}$$

Then, we define the temperature $T := 298 \cdot K$

Enter the formula for E, according to Kinetic Molecular Theory

$$E := \frac{1}{2} \cdot kB \cdot T \qquad E = 2.058 \times 10^{-21} J$$

The formula for E according to Quantum Mechanics is

$$E = \frac{n^2 \cdot h^2}{8 \cdot mass \cdot L^2}$$

Use Mathcad's symbolic processor to solve for n (just take the positive root), and paste the result below.

$$n := \frac{2}{h} \cdot \sqrt{mass} \cdot L \cdot \sqrt{2} \cdot \sqrt{E}$$

Bohr's Correspondence Principle states that "in cases where classical mechanics is known to be valid, Quantum Mechanics should predict the same result." Explain how your calculations illustrate Bohr's Correspondence Principle.

$$n = 1.577 \times 10^{9}$$

> *For an average He atom at 298K in a 0.1m box, $n=1.6x10^9$, which is a very large number. Physically, we can imagine dividing the 0.1-m (or 4-inch) length into 1.577 billion equal segments and the probability of finding the particle in each segment is equal. In other words, QM agrees with CM as it should in this case (where CM is known to be valid) -- the probability density is essentially uniform throughout the box*

Go back above where we defined the value of L, and change the length of the box to something on the atomic scale, say $1x10^{-10}$ m. What happens to the value of the average quantum number, n? Based on these results, under what kind of conditions does the behavior of a quantum mechanical system differ considerably from a classical system?

> *With the size of the box reduced to 10^{-10} m, we find n=1.577 (i.e., approximatley 2) Based on what we learned in Part 2, we do not expect to have a uniform probability of finding the particle throughout the entire box. In the realm of small dimensions, QM differs significantly from CM.*

Above, you saw how the probability density function according to QM essentially agrees with CM as we approach macroscopic dimensions (where CM is known to be valid). There is another way we can illustrate the Bohr correspondence principle:

1. Change the length of the box back to 0.1m. How many energy allowed energy levels are there between 0 and 1/2 k_B T? *about 1.6 billion*
2. Change th length of the box back to 10^{-10} m. This time, how many allowed energy levels are there between 0 and 1/2 kB T? *only 1*
3. Explain how do your answers in #1 and #2 suggest consistency of QM with CM as we approach macroscopic dimensions.

In #1 (a macroscopic box), there are 1.6 billion allowed energy levels between 0 and 1/2 kBT, compared to only 1 in #2 (the atomic-size box). We could say that #1 agrees more with CM, which does not put a restriction on energy values.

Part 4. The Harmonic Oscillator

A detailed classical-mechanical treatment of a harmonic oscillator can be found in almost every introductory Physics textbook as well as undergraduate Physical Chemistry textbooks. Here, we provide a brief description. A harmonic oscillator is defined as a particle that is subject to a force given by

$$F = -k(x-x_o)$$

where k is a positive constant (called the force constant) and x is the location of the particle; x_o is called the equilibrium position of the particle. When $x=x_o$, then F=0, i.e., there is no net force acting on the particle. To simplify our explorations, we will set up our coordinate system so that $x_o=0$. In this case,

$$F = -k\,x$$

Newton's second law says: F = ma, where m=mass of particle and a=acceleration. This essentially says that if there is a net force acting on a particle, it either speeds up or slows down. If the force is directed opposite to the direction of motion, the particle slows down. If the force is directed in the same direction as the motion, the particle speeds up. Recall that acceleration is the rate of change in velocity; a=dv/dt, where v=velocity and t=time. Also, v=dx/dt. Therefore, for a harmonic oscillator:

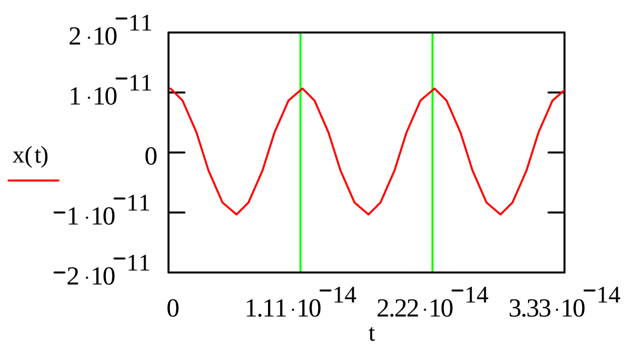
$$F = -kx = m\,d^2x/dt^2$$

Integrating this differential equation twice, and assuming that the particle is initially at rest and located at x=A, we find that the trajectory is

$$x(t) = A\cos(2\pi\nu t), \text{ where } \nu = (1/2\pi)(k/m)^{1/2}$$

Note that when time advances by an amount equal to $1/\nu$, the argument of the cosine function changes by 2π. Since a cosine function goes through one cycle (i.e., goes from +1 down to -1, then back up to +1) when its argument changes by 2π,.we could say that the particle travels from x=A going left towards x=-A, then back going right to x=A during a time interval equal to $1/\nu$;. The quantity $1/\nu$ is called the period of the oscillation (τ); $\tau = 1/\nu$. ν is called the frequency of the oscillation. The particle moves through the same cycle again and again. We refer to A and -A as the **classical turning points**; at these points the particle stops and reverses direction. A is also referred to as the amplitude of the oscillation. Suppose the trajectory of a particle is as shown in the plot below.

Note to teacher: to reveal details of calculations used to generate the plot, expand the hidden area below by double-clicking on the line. If you do not want students to see these, lock the area. Please check the Mathcad Help for details.



1. Estimate the period and amplitude of oscillation from the plot.

A is approximately 10^{-11}, and the period is $1.11x10^{-14}$

2. Recall that velocity is just the derivative, dx/dt and that the derivative is the slope of the tangent to the curve. The steepness of the slope is a measure of the speed. A negative slope means the particle is moving in the -x direction and a positive slope means the particle is moving in the +x direction. Examine the plot carefully and answer the following:

a. What is the value of the derivative at the turning points? *zero; x(t) is at either a maximum or minimum at the turning point*

b. Based on your answer to (a), what is the speed of the particle at the turning points? *zero, the derivative dx/dt is equal to the velocity.*

c. The slope changes sign (+ to -, or - to +) as the plot passes a turning point. Physically what does this mean? *The slope is equal to the derivative, dx/dt, which tells us the velocity. A positive slope means the particle is moving towards A, a negative slope means the particle is moving towards -A. Physically the changes tell us that the particle stops at the turning point, then starts moving in the opposite direction.*

d. At what location (x value) is the slope steepest? Physically, what does this mean?
The slope is steepest at x=0 (the "equilibrium position"). This means that the particle is moving fastest at x=0.

3. Shown below is a plot that we can use to generate an animation of the motion of the harmonic oscillator (represented by a blue circle). For comparison, a particle moving at constant speed (i.e., PIB, red x) and taking the same amount of time for one round-trip is also shown. Generate the animation over three periods and describe the motion of the oscillator. Note that time (t) is defined such that the time interval between frames is 1% of the period of oscillation.

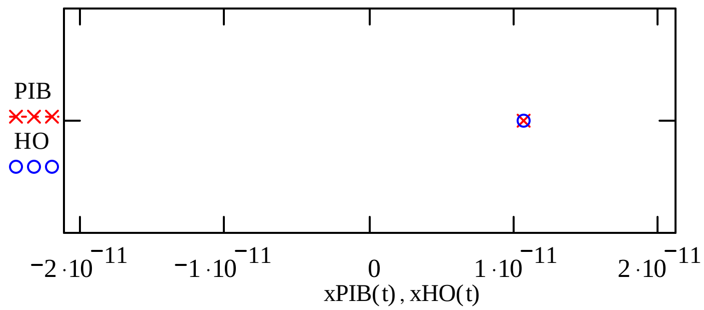
Examine the animation carefully. Recall that the probability density function for a PIB is uniform throughout its range of motion. Can you say the same of a harmonic oscillator? Classically, where is the most probable location of the oscillator: at the equilibrium position, at the turning points, or somwhere in between? Discuss in terms of the equations, plots, and animations your observations.

To generate the animation over three periods, I specify FRAME=1 to 300 since each frame represents 1% of a period. The motion of the harmonic oscillator can be described as follows:
1. it starts slower than the PIB from the turning point, but we can tell it is speeding up because it catches up with the PIB (which is moving at constant speed) halfway towards the other turning point.
2. at the halfway point towards the other turning point, its moving faster than the PIB, but it must be slowing down because the PIB eventually catches up with it and both reach the other turning point at the same time.
3. the return trip is similar: speeds up towards the middle, then slows down as it approaches the other turning point.
Conclusion: the most probable location of the harmonic oscillator is at the turning points, where it is moving the slowest.

Note to teacher: details of the calculation used to generate the graph are given in the hidden area below.

$t := FRAME \cdot 0.01 \cdot \tau$

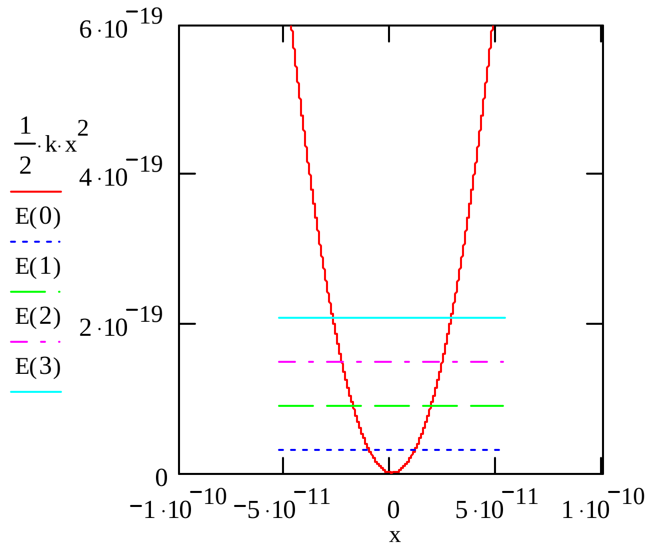
$t = 0.00\,\tau$



4. The force acting on a harmonic oscillator at any given location does not depend on time. This means that, if left alone, its energy will forever remain constant. Classically, the total energy is given by $E = 1/2\ k\ A^2$
where A is the amplitude of the oscillation. At the turning point, all the energy is potential (since the velocity at the turning point is zero; kinetic energy is zero). As the oscillator moves from one turning point to the other, potential energy is converted to kinetic energy. At the equilibrium position, all the energy is kinetic. As the particle passes through the equilibrium position, it starts to slow down and the kinetic energy is again being transformed back to potential energy. It can be shown that the potential (and kinetic) energy of the particle depends only on the location:

Potential Energy = $1/2\ k\ x^2$

For the harmonic oscillator that we have been studying above, the potential energy function, which is parabolic in shape, is shown below: The 4 lowest allowed energies, according to QM are overlayed as horizontal lines. The classical turning points corresponding to these energy levels occur at distances where the horizontal lines cross the parabola.



Refer to a Physical Chemistry textbook (for example, see Figure 5.8, page 171 of Reference 1) and examine plots of the wavefunctions (ψ) or probability density function (ψ^2) for the lowest-energy quantum states of a harmonic oscillator. Look for plots that are overlayed over a plot of the potential energy function and vertically centered on a horizontal line representing the total energy. How do the QM probability density functions differ from the classical prediction? Examine what happens to the QM probability density functions as energy increases. Explain how the trends illustrate the Bohr correspondence principle.

For the lowest quantum state (v=0), the most probable location is at x=0. However, at higher energies (larger v values), the magnitude of the probability density functions at the turning points ar larger. This suggests that as v gets larger, it becomes more and more likely that the oscillator can be found at the turning points, which would be more consistent with the classical expectation for the more probable location. This follows the same pattern as in the PIB, the higher the quantum number, the more likely QM tends to agree with CM. It can also be noted from the plot of the potential energy function that the "box" for the particle is larger -- the turning points are farther apart -- as v increases.

Part 5. Hydrogen atom energies

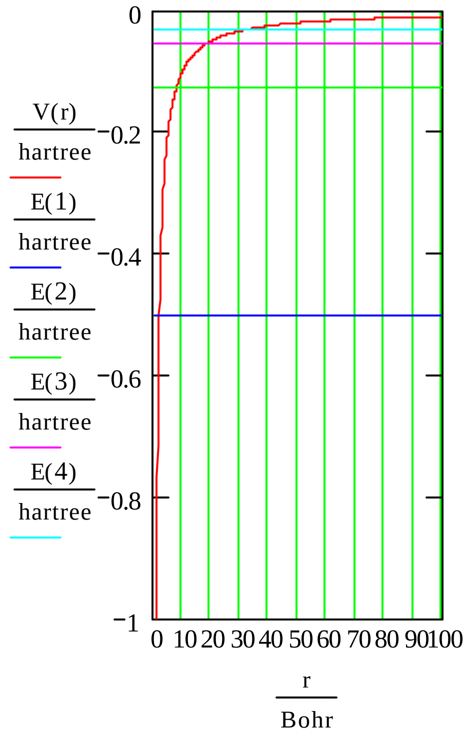
Shown on the right is a plot of the potential energy of the electron in a hydrogen atom, V(r), as a function of its distance from the nucleus. The distance (r) is in Bohr; 1 Bohr is 52.9 pm. The energy unit is hartree; 1 hartree=27.2 eV.

$V(r)=-1/r$

QM calculations tell us that the allowed energies for the electron are given by

$E(n) = -1/2n^2$

where n is called the principal quantum number. The first four allowed energy levels are indicated by horizontal lines in the plot.



1. Consider an electron in a 3s orbital (i.e., n=3). Calculate the distance, rmax, where, according to CM, the energy is all potential (kinetic energy=0).

$E(n) := \frac{-1}{2 \cdot n^2}$ $\qquad E(3) = -0.056\,\text{hartree}$

$rmax := \frac{-1}{E(3)}$ $\qquad rmax = 18\,\text{Bohr}$

2. In #1, you should have gotten 18 Bohr. According to CM, it is not possible for an electron in the 3s orbital to be farther than 18 Bohr away from the nucleus; explain why. [For n=3, we say that r>18 Bohr is a "classically-forbidden region" and r<18 Bohr is the "classically-allowed region"].

If r>18 Bohr, then the plot shows that the potential energy would be higher than the total energy.

3. For n=10000, how far away from the nucleus can an electron move away from the nucleus. Compare the size of the classically allowed region for n=3 and n=10000.

$rmax := \frac{-1}{E(10000)}$ $\qquad rmax = 2 \times 10^8\,\text{Bohr}$

The radius of the classically allowed region for n=10000 is 200 million times larger than for n=3.

4. The energy level spacing between the n=2 and n=3 quantum states is

$$E(3) - E(2) = 0.069\,\text{hartree}$$

Calculate the energy level spacing between n=10000 and n=10001. How does this and your answer to #3 illustrate the Bohr correspondence principle?

$$E(10001) - E(10000) = 9.999 \times 10^{-13}\,\text{hartree}$$

The spacing between adjacent energy levels of the electron is much, much smaller at very large n. This is more like the classical expectation -- continuous energy. In #3, we saw that for n=10000, the classically allowed region is very large. Again, QM tends to agree better with CM when the particle is not confined to very small regions.

NOTE: CM predicts that the an electron moving away from nucleus with energy equal to E(3) could only go as far as 18 Bohr. On its way back, however, CM predicts the electron to crash into the nucleus (i.e., unable to reverse direction). The nuclear model of the atom, as suggested by Rutherford's alpha scattering experiment, is classically unstable.

REFERENCE

1. D.A. McQuarrie and J. D. Simon, Physical Chemistry: A Molecular Approach, University Science Books, Sausalito, CA (1997).