

Numerical Solution of a Potential—Final Project

1 Introduction

The purpose is to determine the lowest order wave functions of and energies a potential which describes the vibrations of molecules fairly well. Consider the vibrations of diatomic HBr (Hydrogen Bromide). It is a gas room temperature and is useful in several respects [1] For simplicity, we will consider Bromine nucleus fixed (it has nearly 80 times the mass of hydrogen) and consider the oscillations of the hydrogen nucleus. The potential for the hydrogen nucleus has the following phenomenological form

$$V(x) = V_o(1 - e^{-x/a})^2, \quad (1)$$

where x is the displacement of the hydrogen nucleus from equilibrium. For $V_o = 50 \hbar^2/Ma^2$ a graph of the potential is shown below. We will solve for the energies and wave functions in this potential. For small fluctuations around the equilibrium (i.e. small quantum number n) a harmonic oscillator approximation is valid, and the energies are given by the simple harmonic oscillator (see below). However for larger fluctuations around equilibrium (large quantum number n) the shape of the potential matters and the harmonic approximation is poor. The graph below shows the energies for this potential and the energies in a corresponding harmonic approximation. One sees that as n becomes large the harmonic approximation starts to fail.

For actual hydrogen bromide the parameters are: $a \simeq 1.1a_o \simeq 0.58 \text{ \AA}$ and $V_o \simeq 4.83\text{eV} \simeq 433 \hbar^2/Ma^2$ [2]. Because V_o is rather large (relative to \hbar^2/Ma^2), the energies are quite close to the harmonic approximation until the quantum number is rather large. We will therefore use $V_o \simeq 50 \hbar^2/Ma^2$ in our analytical and numerical work unless otherwise directed.

2 Analysis

1. For what range of energies do we expect discrete energies and for what range do we expect continuous energies.. Describe classically what would happen if the nucleus were to be given a kick (e.g. by light) of energy E in the discrete case and the continuous case. Why is V_o called the dissociation energy?
2. Near the minimum, we can approximate the full potential with a simple harmonic potential. Show that near $x = 0$

$$V(x) \simeq \frac{1}{2}kx^2, \quad (2)$$

where $k \simeq 2V_o/a^2$. Show that allowed energies of the molecular vibrations are approximately

$$E = \hbar\omega_o(n + \frac{1}{2}), \quad (3)$$

and determine ω_o in terms of V_o and a .

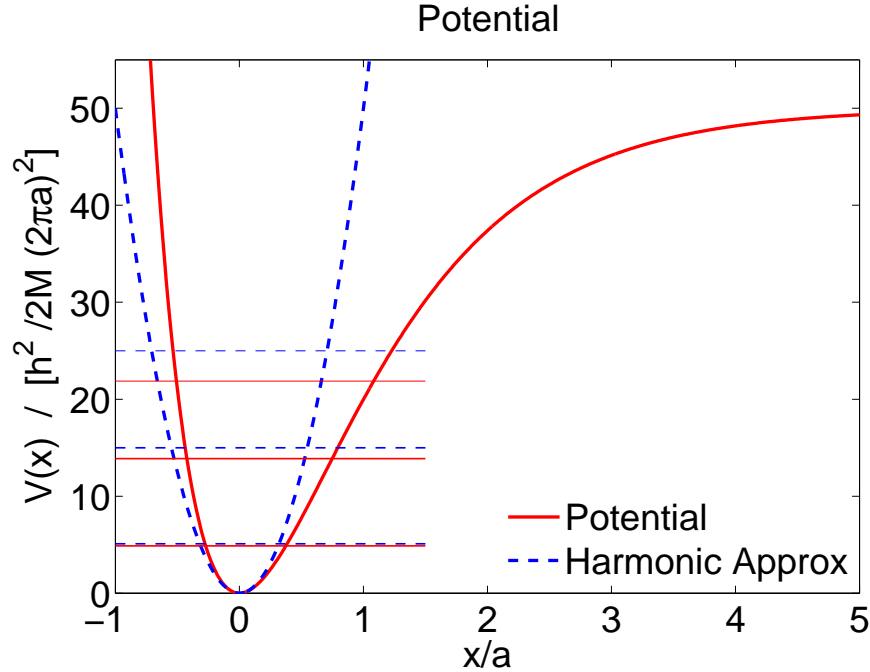


Figure 1: The potential and its harmonic oscillator approximation. The horizontal lines show the allowed energies for the full potential and the the allowed energies in the harmonic oscillator approximation

3. Show that the classical turning points of the potential occur at

$$x_{\mp} = -a \log \left(1 \pm \sqrt{E/V_o} \right) .$$

4. Write the potential as as a harmonic oscillator + corrections. Show that

$$V(x) \simeq \frac{1}{2} k x^2 + \delta V(x) \quad \text{with} \quad \delta V(x) \simeq -V_o \left(\frac{x}{a} \right)^3 \quad (4)$$

and show that in a first approximation $\delta V(x)$ does not change the ground state energy.

5. Expanding to higher order, we estimate that higher order corrections are of order

$$\delta E \sim V_o \left(\frac{x}{a} \right)^4 . \quad (5)$$

Estimate that $x^4 \sim L^4$ where L is the size of the harmonic oscillator wave function which we estimated in class [3]. Use this to estimate that higher order corrections are of order

$$\delta E \sim \hbar \omega_o \left(\frac{\hbar \omega_o}{V_o} \right) \quad (6)$$

Thus the full energy is

$$E_n = \hbar\omega_o\left(n + \frac{1}{2}\right) + O(\delta E) \quad (7)$$

where δE records *anharmonic corrections*.

6. Use classical reasoning and the harmonic oscillator approximation to gain intuition about the dynamics of HBr. For this part only use the parameters of the real Hydrogen Bromide molecule.

(a) For the parameters of Hydrogen Bromide what is the typical energy spacing $\hbar\omega_o$ in eV. What range of the electromagnetic spectrum does this correspond to (e.g. x-ray, visible, infrared, microwave, radio, etc). How does this molecular vibration energy compare to electronic excitation energies in hydrogen?

(b) Estimate the % correction to the energy due to anharmonic terms?

(c) Assume that the vibrational energy is $\hbar\omega_o$, what is the maximum displacement of the molecule from equilibrium in units of the Bohr radius. You should find it is smaller.

(d) Assume that the vibrational energy is $\hbar\omega_o$, determine the maximum velocity of the nucleus and compare it the velocity of an electron in the lowest Bohr orbit.

(e) This is a comment. It is useful to realize that during the time it takes the hydrogen nucleus to make one vibration. The electron circling the hydrogen has made many many orbits $N \sim 50$. Thus the nucleus is making small, slow, vibrations on electronic scales. This is why it is a good approximation to treat it separately from the electrons.

7. Watch this absolutely great you-tube-video which explains how the vibrational frequencies of different molecular bonds can be measured. Include a schematic of the experimental setup in your report. A typical output from a spectrometer is shown in Fig. 2

8. Now introduce a set of dimensionless variables. The dimensionful constants of this problem are

$$\hbar, M, a, V_o$$

Choose to measure distance in units of a , energies in units of (\hbar^2/Ma^2) and mass in terms of M . Define

$$x = \frac{x}{a} \quad v_o = \frac{V_o}{(\hbar^2/Ma^2)} = 50 \quad \epsilon = \frac{E}{(\hbar^2/Ma^2)} \quad (8)$$

(a) Show that the Schrödinger equation

$$\left[\frac{-\hbar^2}{2M} \frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E\Psi(x) \quad (9)$$

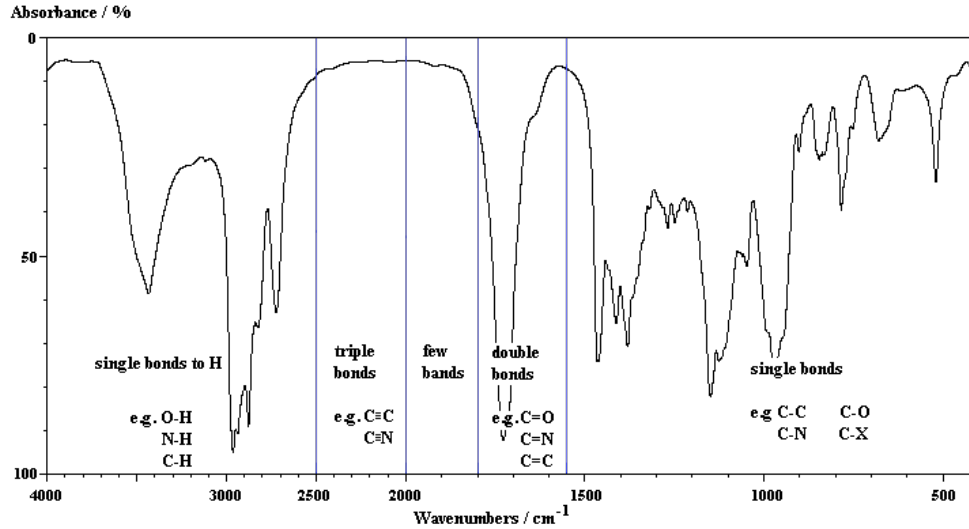


Figure 2: A typical result from a spectrometer in the ??? part of the electromagnetic spectrum. The units on the x axis are wavenumber, $k = 2\pi/\lambda = E/\hbar c$ of the photon

becomes in terms of these dimensionless variables.

$$\frac{d^2\bar{\psi}}{dx^2} = -2(\epsilon - v(x))\bar{\psi} \quad (10)$$

where

$$v(x) = v_o(1 - e^{-x})^2 \quad (11)$$

We will solve this numerically on the computer

(b) Show that the discrete energies in the harmonic oscillator approximation are

$$\epsilon_n = \frac{E}{\hbar/Ma^2} = \sqrt{2v_o} \left(n + \frac{1}{2} \right) \quad (12)$$

and that the turning points are

$$x_{\mp} = -\log(1 \pm \sqrt{\epsilon/v_o}) \quad (13)$$

3 Numerical Analysis

1. On the web site for the course you will find a link to a `matlab` program which solves the simple harmonic potential `sho.m`.

$$V(x) = \frac{1}{2}kx^2. \quad (14)$$

A ultrabrief intro to `matlab` is also on the web site. The numerical procedure to solve for this potential was discussed in lecture and the lecture is available online [3]. The energies of the oscillator

$$\epsilon = \frac{E}{\hbar\omega_o} = n + \frac{1}{2}. \quad (15)$$

First run the simple harmonic oscillator program. Read through it and understand how it works. Change the energy and see that you can reproduce what you expect for the first excited state and the second excited state. You will need to change the limits on the graphs of the wave functions in order to make a good plot of these wave functions. You do not need to include your experiments in your report. A sample figure produced by `sho.m` is shown in Fig. 3

2. Modify this program to solve for the energies and wave functions of the current potential. Here is some advice:
 - (a) First, construct a grid from $x = -1.2 \dots 4$ rather than $-5 \dots 5$ as was used in the harmonic oscillator.
 - (b) Set the energy to the lowest order energy of the harmonic oscillator approximation to get started, $\epsilon = \sqrt{2v_o}\frac{1}{2}$
 - (c) You should adjust the ranges of the graphs so that both the potential and the wave function are clearly visible:
 - i. For the potential graph my ranges are $x = -1 \dots 4$ and $y = 0 \dots v_o$, i.e. I make the range up to v_o
 - ii. For wave function graph my ranges are $x = -1 \dots (x_+ + 1.3)$, i.e. I make a plot a unit and a half beyond the turning point.
 - (d) After modifying the code you should find for $\epsilon = 0.5\sqrt{2v_o}$ a graph that looks as shown in Fig. 4. If you can not do this step you will have to ask me or your TA for help.
 - (e) $\epsilon_{\text{high}} = 0.5\sqrt{2v_o}$ is not the correct energy; it is too high. Change the energy to $\epsilon_{\text{low}} = 0.4\sqrt{2v_o}$. This is also is not the allowed energy; it is too low. You should realize that the correct energy is in between these values – Why?.
 - (f) Now manually search for the correct energy using a bisection search procedure:
 - i. Try halfway between ϵ_{low} and ϵ_{high} .

$$\epsilon_* = \frac{\epsilon_{\text{low}} + \epsilon_{\text{high}}}{2}$$

- ii. If ϵ_* is too high, then the real energy is in between ϵ_{low} and ϵ_* . Set $\epsilon_{\text{high}} = \epsilon_*$ and go back to step one.
- iii. If ϵ_* is too low, then the real energy is between ϵ_* and ϵ_{high} . Set $\epsilon_{\text{low}} = \epsilon_*$ and go back to step one.

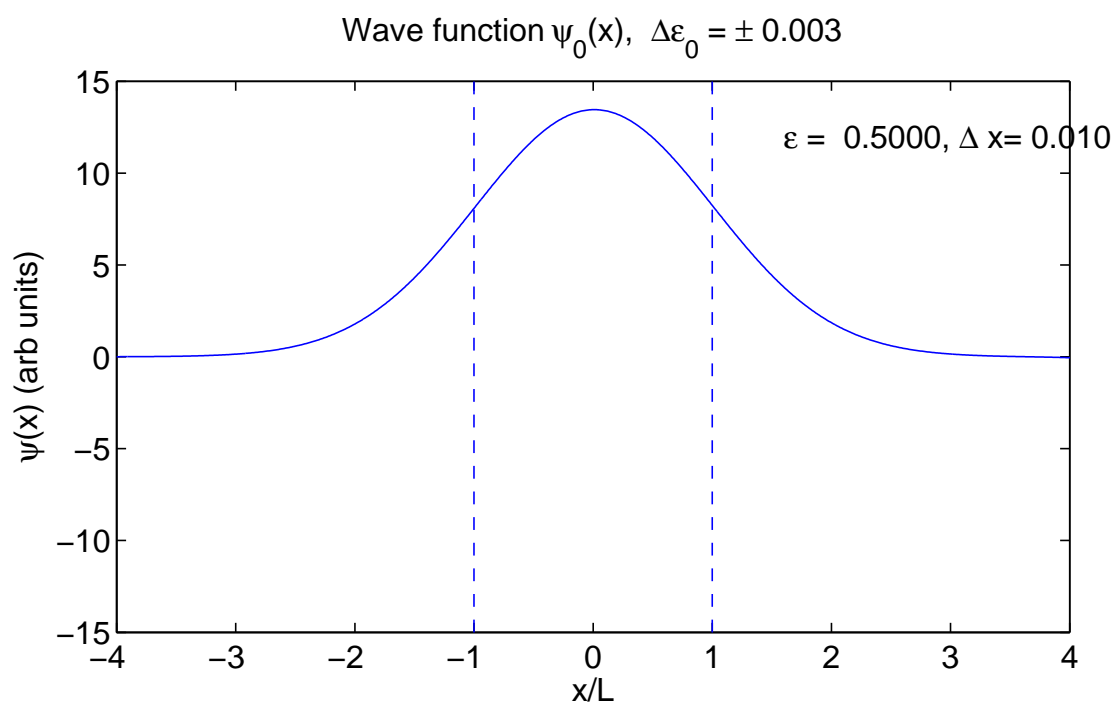
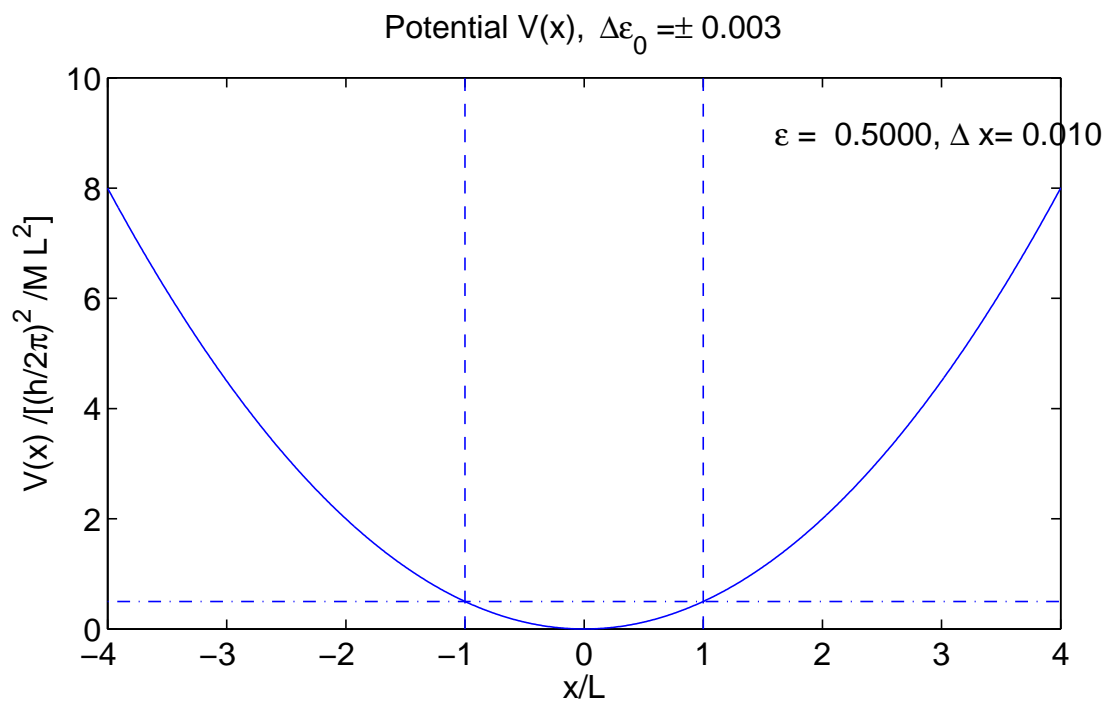


Figure 3: Sample figure produced by `sho.m`.

(g) In this way, I tried the following sequence¹ of $[\epsilon_{\text{low}}, \epsilon_{\text{high}}]$:

$$[0.4, 0.5], [0.45, 0.5], [0.475, 0.5], [0.4874, 0.5], [0.4874, 0.49375], [0.4874, 0.49062], \\ [0.4874, 0.4890], [0.4874, 0.4882], [0.4874, 0.4879]$$

I conclude from the last bin that

$$\epsilon_{0*} \simeq (0.4877 \pm 0.0003)\sqrt{2v_o}$$

(h) For this part (question 2.), include two plots one for the last $\epsilon_{0,\text{low}}$, one for the last $\epsilon_{0,\text{high}}$. For inclusion with part 4. also make a graph of your final estimate of $\epsilon_{0*} \simeq \epsilon_0$.

3. Change your grid spacing from $\Delta x = 0.01$ to $\Delta x = 0.005$, and see how the first excited state changes. Record a graph of showing ϵ_{low} and ϵ_{high} in this case.
4. Now change the grid spacing back to $\Delta x = 0.01$. Find the first four excited states following the same procedure to a precision of better than 0.25%. Include in your report one graph ($\epsilon_{n,*}$ say) for each energy, from $n = 0, 1, 2, 3, 4$. Be sure that in the title of your graph you record your final energy and the uncertainty in the energy.

4 Summary & Your Report

1. Your report should consist of the answers to all of the questions of Sect. 2.
2. A total of 9 graphs from Sect. 3
 - ϵ_{low} and ϵ_{high} for $\Delta x = 0.01$
 - ϵ_{low} and ϵ_{high} for $\Delta x = 0.005$
 - Graphs for $\epsilon_{0*}, \dots, \epsilon_{4*}$.

The axes of each graph should be clearly labeled. A short title should be given to explain what the graph is about: Also record ϵ , n , and Δx and any other relevant data. Feel free to label graphs by hand if you find it easier and quicker.

3. Also provide a short summary based on the following remarks: In fact the energies for this potential are known analytically

$$E_n = \hbar\omega_o \left(n + \frac{1}{2} \right) - \hbar\omega_o x_e \left(n + \frac{1}{2} \right)^2 \quad (16)$$

where ω_o is $\sqrt{k/M}$ as computed in Sect. 2, and the x_e is a dimensionless parameter which measures the deviation from the harmonic oscillator

$$x_e = \frac{\hbar\omega_o}{4V_o} \quad (17)$$

¹ $\epsilon_1 = 0.4875\sqrt{2v_o}$ is very close to the actual energy. $0.4874\sqrt{2v_o}$ was chosen as it was clearly below the actual energy.

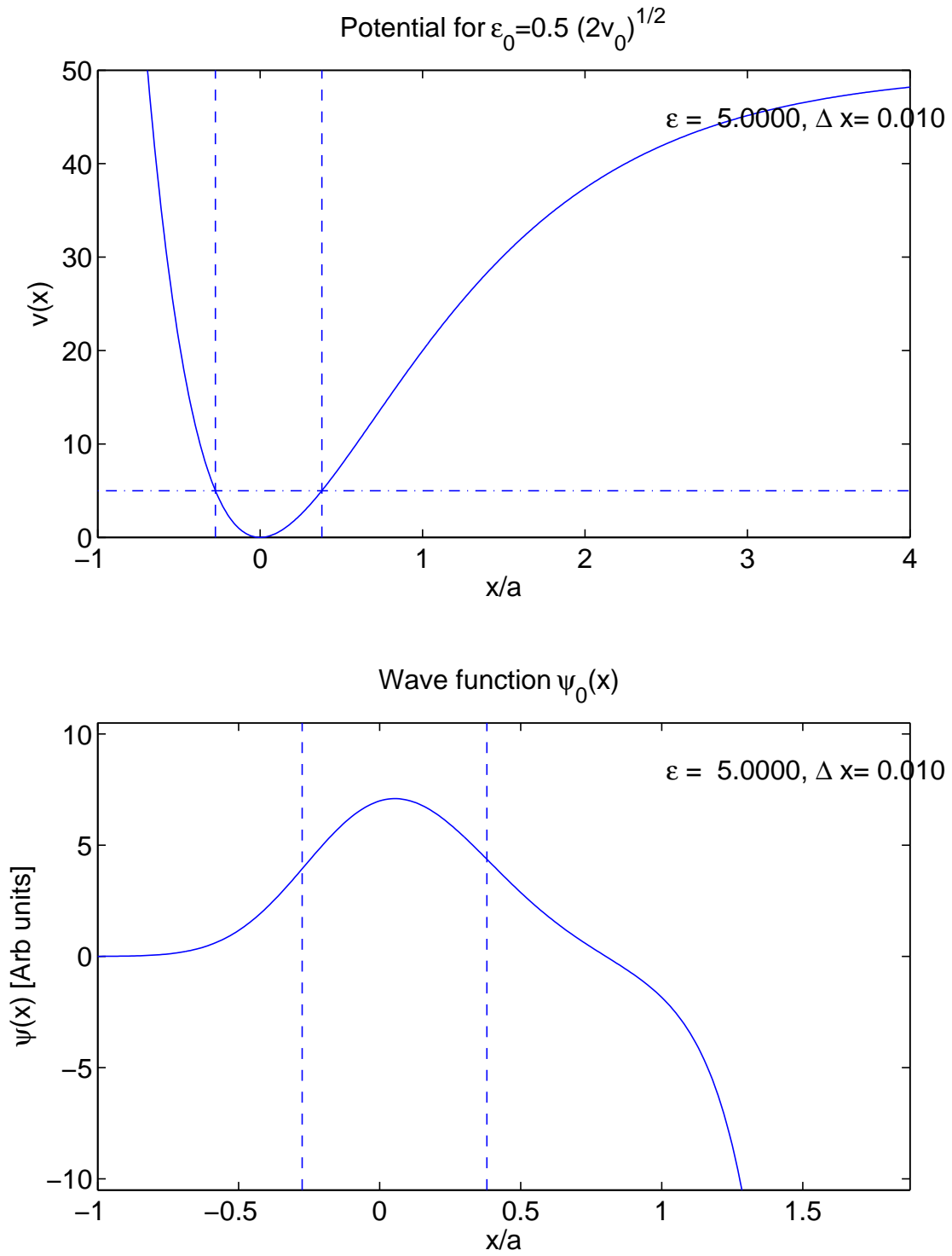


Figure 4: Sample figure for the potential of we are studying $V(x) = V_0(1 - e^{-x/a})^2$.

What is x_e for the potential we are considering, what is it for HBr , and why is it called the anharmonicity parameter. (Hint examine Eq. 16 and use the results of question 5.) Summarize your results for the energies in a table, showing the computed energies (and their uncertainties), the estimate for the energy based on the simple harmonic oscillator approximation, and the exact energy based on Eq. 16. Very briefly discuss how your energies and wave functions differ from the harmonic oscillator wave functions.

References

- [1] See for example, http://en.wikipedia.org/wiki/Hydrogen_bromide.
- [2] See for example, <http://www.nist.gov/pml/data/msd-di/index.cfm>. The more pedagogical page, <http://hyperphysics.phy-astr.gsu.edu/hbase/tables/diatomic.html>, may be useful.
- [3] See `120.pdf` and `120_slides.pdf`.