

Energies and Wavefunctions for Several One-Dimensional Potentials

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Abstract

This module allows students to calculate energies and wavefunctions for several one-dimensional potentials. Potentials include: Particle in a finite box, Particle in a box with a barrier, Harmonic oscillator, Morse oscillator, and a Double-minimum potential. Students learn how changing the potential affects the wavefunctions and their energies by comparing a particle in a box with a particle in a finite box and comparing harmonic and Morse oscillators. In addition, students explore how barriers affect wavefunction tunneling by looking at two double minima potentials. The potentials used are models for a variety of physical systems, including an O-H stretch vibration and inversion of ammonia. The Schrodinger Equation is solved using a particle in a box basis set and the Variational method. As the approach used is quite general, the module can be readily modified to allow students to calculate wavefunctions and energies of arbitrary one-dimensional potentials.

Prior to working with this document, students should have been introduced to the Schrodinger equation and the concepts of wavefunctions and energies of states. It is useful, but not essential, for students to have had some exposure to linear algebra (eigenvalue equations).

Goals

For students to gain an intuitive feel for the wavefunctions of a one-dimensional potential and how modifying the potential affects the wavefunctions and energies of the system.

Objectives

After working through the module students should be able to:

1. Predict the number of nodes in the ground state, first excited state, etc. wavefunction.
2. Identify regions where the wavefunction tunnels (is found in the classically forbidden region), and identify how the potential affects the extent of tunneling and the energy spacing between states below the barrier.
3. Identify some differences between the Morse and harmonic potentials and how these affect the wavefunctions and their energies.
4. Complete an analysis of one additional potential function following the model presented in this template.

Introduction

This document allows students to calculate energies and wavefunctions for a variety of potentials. The Schrodinger Equation is solved numerically, using the variational method and the particle in a box basis set. The variational method is widely used in electronic structure calculations and to find energy levels of highly vibrationally excited molecules, and for many other calculations. Several articles introduce students to the variational method by using it to calculate energies for simple one-dimensional potentials such as the particle in a box, comparing the variational results with the analytical solutions [1-6]. The variational method is most useful, however, in solving the Schrodinger equation for potentials for which there are no analytical solutions, or where the solution is very difficult [7-9]. Although the Schrodinger equation can also be solved using other techniques [10-12], they cannot match the generality, precision and ease of use of the variational method. This document offers a brief introduction to the variational method (Grubbs [5] and Dunn [6] give a more detailed introductions, also using Mathcad), then uses it to introduce students to features of the wavefunctions and energies of a variety of potentials, some of which cannot be solved analytically. This document could be incorporated in the curriculum in the Quantum portion of undergraduate Physical Chemistry, as an extension to the discussion offered by most texts. It is especially useful in an introductory Quantum mechanics class, where the properties of wavefunctions can be explored in detail. Again, references [5,6] complement this document, as they give a good discussion of the variational method, along with an introduction to basis sets and eigenvalue problems.

References

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Contents (Links are underlined. Double click to jump to that section)

This document first defines constants and functions to implement the Variational method. It then solves the Schrodinger equation for several potentials:

- Particle in a Finite Box
- Particle in a Finite Box with a Barrier
- Harmonic and Morse Oscillators
- Double Minimum Potential

introducing and asking questions about features of the wavefunctions and energies for each potential.

Text in this document is color-coded:

- Mathcad comments are in **black**.
- Scientific comments are in **blue**.
- Questions and exercises for students are in **red**.
- Links are **underlined**. Double-click to bring up a window with more information or to change a parameter.

Define constants

This program does all calculations internally in atomic units....

mass in electron masses (1 e-mass = 1/1822.882 amu)

energy in hartree (1 hartree = 27.211608 eV)

distances in bohr (1 bohr = 1 a0 = 0.52917706 Angstrom)

$\hbar \equiv 1$

in atomic units, \hbar is one

$\text{cm_to_har} \equiv 8065.479 \cdot 27.211608$

convert cm^{-1} to hartree

$\text{amu} \equiv 1822.882$

1 amu, in electron masses

$a_0 \equiv 0.52917706$

1 Bohr, in Angstroms

$N_{\text{tot}} := 40$

Number of basis functions. More basis functions gives more accurate result, but the calculation takes longer.

$j := 1 .. N_{\text{tot}}$

$k := 1 .. N_{\text{tot}}$

$j_0 := 0 .. N_{\text{tot}} - 1$

$k_0 := 0 .. N_{\text{tot}} - 1$

Definition of functions

This section defines the functions required to solve the Schrodinger equation using the Variational method.

For a description of the Variational method and details on its implementation [double click here](#) First level physical chemistry students should study the contents of this link before proceeding with the remainder of the main document.

$$\phi(n, x, \text{start}, \text{end}) := \begin{cases} A \leftarrow \text{end} - \text{start} \\ \sqrt{\frac{2}{A}} \cdot \sin\left[n \cdot \pi \cdot \frac{(x - \text{start})}{A}\right] \end{cases}$$

The basis functions are the particle in a box wavefunctions with quantum number **n**. The box extends from **start** to **end**.

$$S(j, k, \text{start}, \text{end}) := \int_{\text{start}}^{\text{end}} \phi(j, x, \text{start}, \text{end}) \cdot \phi(k, x, \text{start}, \text{end}) dx$$

Overlap integral

Confirm that the basis functions are orthogonal and normalized. If they are, then the overlap integral **S** will be 1 if **j=k** and will be zero otherwise, and the matrix **Smat** (below) will be the identity matrix.

$$x_i := \frac{-5}{a_0} \quad x_f := \frac{15}{a_0}$$

$$Smat_{j-1, k-1} := S(j, k, x_i, x_f)$$

$$Smat =$$

	0	1	2	3	4
0	1	0	0	0	0
1	0	1	0	0	0
2	0	0	1	0	0
3	0	0	0	1	0
4	0	0	0	0	1

The basis set is orthogonal and normalized

$$T(j, k, \mu, \text{start}, \text{end}) := \begin{cases} A \leftarrow \text{end} - \text{start} \\ \frac{\pi^2 \cdot k^2}{2 \cdot \mu \cdot A^2} \quad \text{if } j = k \\ 0 \quad \text{otherwise} \end{cases}$$

Kinetic Energy Integral. If **j=k**, it is the energy of the particle in a box of length **A**, otherwise it is zero.

$$U(j, k, V, \text{start}, \text{end}) := \int_{\text{start}}^{\text{end}} \phi(j, x, \text{start}, \text{end}) \cdot V(x) \cdot \phi(k, x, \text{start}, \text{end}) dx$$

Potential Energy Integral

$$H(j, k, V, \mu, \text{start}, \text{end}) := T(j, k, \mu, \text{start}, \text{end}) + U(j, k, V, \text{start}, \text{end})$$

Hamiltonian (Kinetic Energy + Potential Energy)

Calculate wavefunction at given value of x by summing contributions of all basis functions. In this expression, *vec* is the eigenvector that corresponds to the wavefunction being calculated. The eigenvector will be calculated using Mathcad's *eigenvec* function.

$$\text{wavefcn}(\text{vec}, \text{Ntot}, x, \text{start}, \text{end}) := \sum_{i=1}^{\text{Ntot}} \text{vec}_{i-1} \cdot \phi(i, x, \text{start}, \text{end})$$

Solve Schrodinger Equation for various potentials

Particle in a Finite Box

$$\mu := 1.0$$

Mass of particle (currently set at 1 electron)

$$\text{height} := \frac{35000}{\text{cm_to_har}}$$

Box height (currently 35000 cm⁻¹)

$$\text{left} := \frac{0}{a0} \quad \text{right} := \frac{10.0}{a0}$$

left and right positions of box in Angstroms

$$V_{\text{FiniteBox}}(r) := \begin{cases} \text{height} & \text{if } r > \text{right} \\ \text{height} & \text{if } r < \text{left} \\ 0.0 & \text{otherwise} \end{cases}$$

Define the potential for a finite box

$$V(r) := V_{\text{FiniteBox}}(r)$$

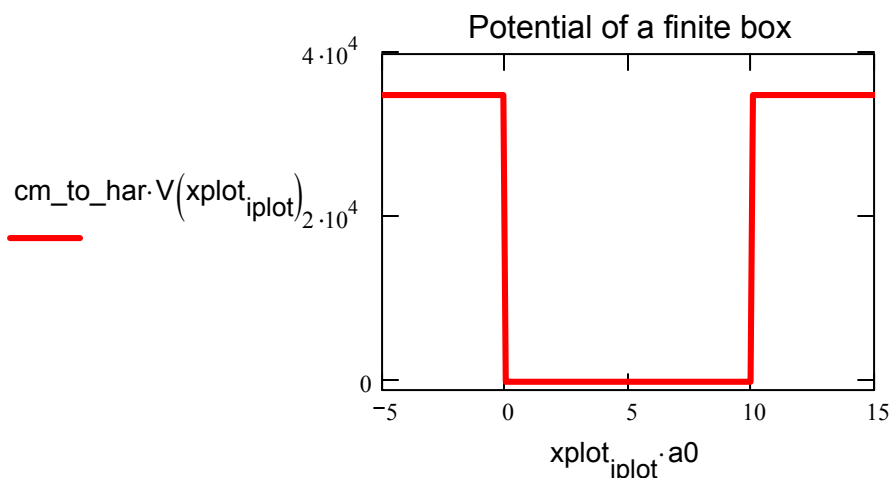
Define range to use for calculation and plots. Should extend beyond edges of box.

$$\text{nplot} := 200$$

$$\text{xi} := \text{left} - \frac{5}{a0} \quad \text{xf} := \text{right} + \frac{5}{a0}$$

Range to use for calculation

$$\text{dxplot} := \frac{\text{xf} - \text{xi}}{\text{nplot} - 1} \quad \text{iplot} := 0 .. \text{nplot} - 1 \quad \text{xplot}_{\text{iplot}} := \text{xi} + \text{iplot} \cdot \text{dxplot}$$



Calculate the Hamiltonian Matrix

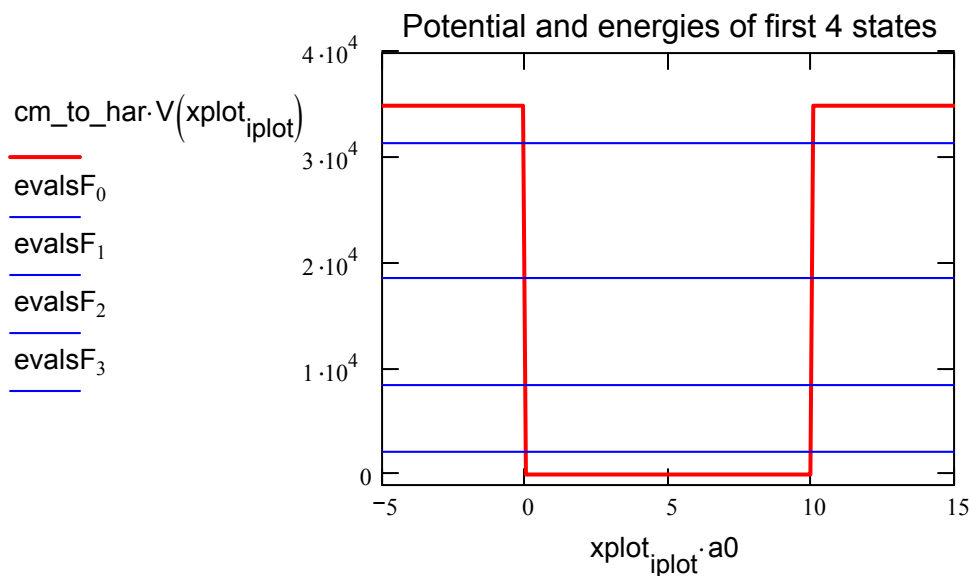
$$HF_{j-1, k-1} := H(j, k, V, \mu, xi, xf) \cdot cm_to_har$$

Find the eigenvalues (energies) of the Hamiltonian matrix

$$evalsF := \text{sort}(\text{eigenvals}(HF))$$

	0
0	2144.37
1	8483.58
2	18649.62
3	31444.92

**Energies
(eigenvalues) in cm^{-1}**



Make sure xi is small enough and xf is large enough to extend beyond the edges of the box

Describe the energy levels of a particle in a finite box. Is there zero-point energy? Are the energy levels equally spaced? Would you expect the fifth state to have an energy above the barrier? Would you expect states above the barrier to have quantized (discrete) energies?

Note for experts: the method we've used to solve the Schrodinger equation does not accurately calculate energies of unbound (continuum) states - this is discussed in more detail below.

Next, we'll compare finite particle in a box energy levels to those of a box with infinitely high walls (i.e., the standard particle in a box).

Do you think that the particle in a finite box energy levels will be lower or higher than those of the standard particle in a box? Why?

$$\text{infheight} := \frac{10^6}{\text{cm_to_har}}$$

the height of the "infinite" box (a very large number)

$$V_{\text{InfiniteBox}}(r) := \begin{cases} \text{infheight} & \text{if } r > \text{right} \\ \text{infheight} & \text{if } r < \text{left} \\ 0.0 & \text{otherwise} \end{cases}$$

define the potential for a standard particle in an infinite box

$$V_l(r) := V_{\text{InfiniteBox}}(r)$$

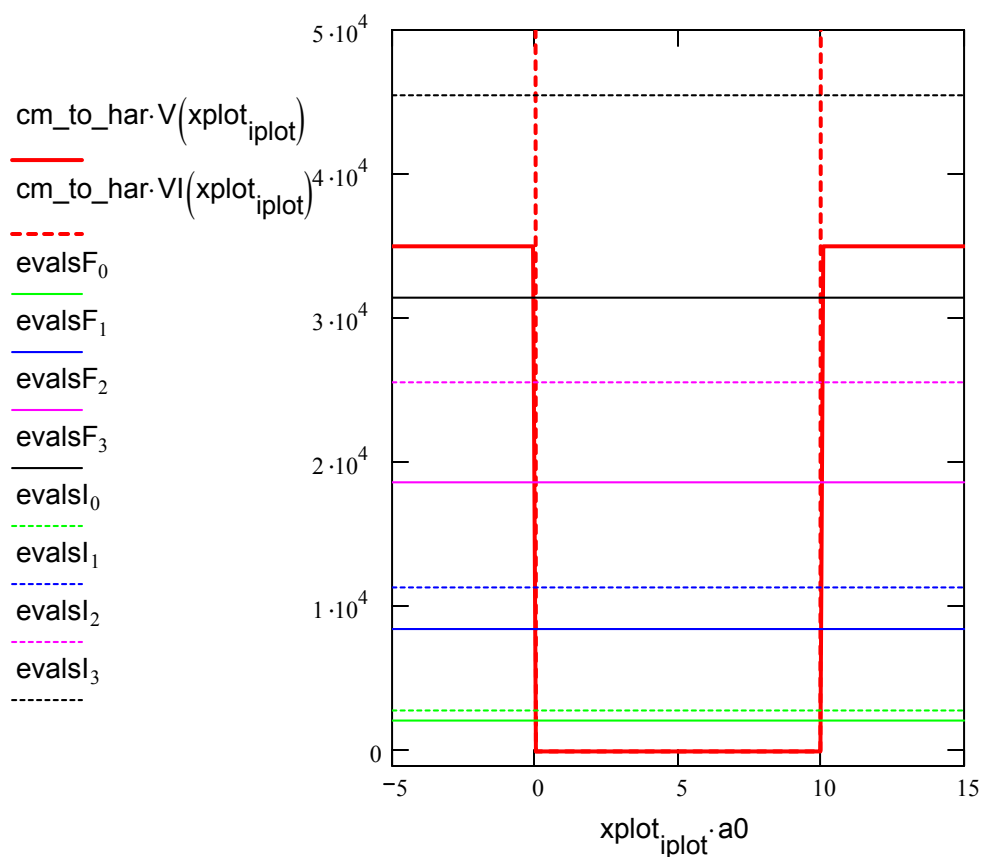
$$H_{l_{j-1}, k_{j-1}} := H(j, k, V_l, \mu, x_l, x_f) \cdot \text{cm_to_har}$$

calculate the Hamiltonian for a standard particle in a box extending from "left" to "right"

$$\text{evals}_l := \text{sort}(\text{eigenvals}(H_l))$$

Diagonalize the Hamiltonian matrix to find energy values (eigenvalues) and wavefunctions (eigenfunctions)

POTENTIAL AND ENERGIES OF FIRST 4 STATES FOR PARTICLE IN A BOX (dashed lines) AND PARTICLE IN A FINITE BOX (solid lines)



Which are lower, the energy levels of the finite or infinite particle in a box ?
Does this difference become more or less pronounced for states at high energies ?

To see why this occurs, let's compare the wavefunctions for the two potentials.

Set up array for plotting wavefunction

nwfplot := 200

iwfp := 0 .. nwfplot - 1

$dwf := \frac{xf - xi}{nwfplot - 1}$

Number of points at which to plot wavefunction - choose larger number for smoother wavefunctions

$xwf_{iwfp} := xi + iwfp \cdot dwf$

Plot particle in a box and particle in a finite box wavefunctions with quantum number qn

qn := 0

select quantum number to plot

$evectF := \text{eigenvec}(HF, \text{evals}F_{qn})$

Mathcad's eigenvec function calculates the eigenvector that corresponds to the desired eigenvalue

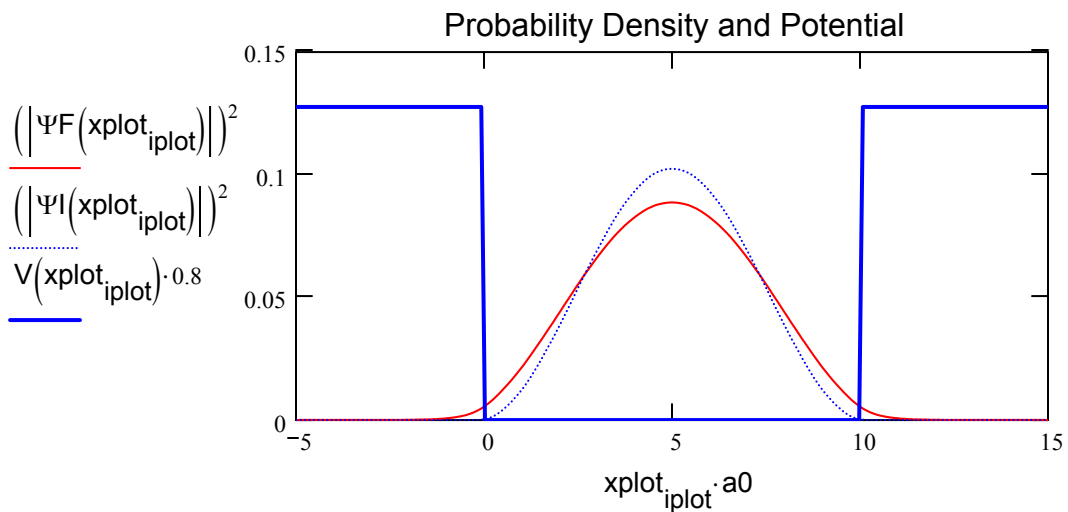
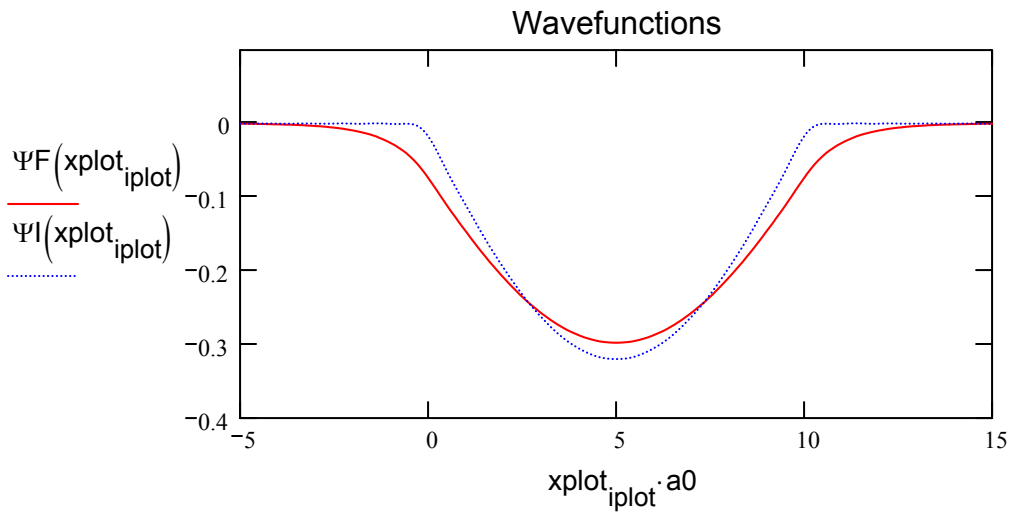
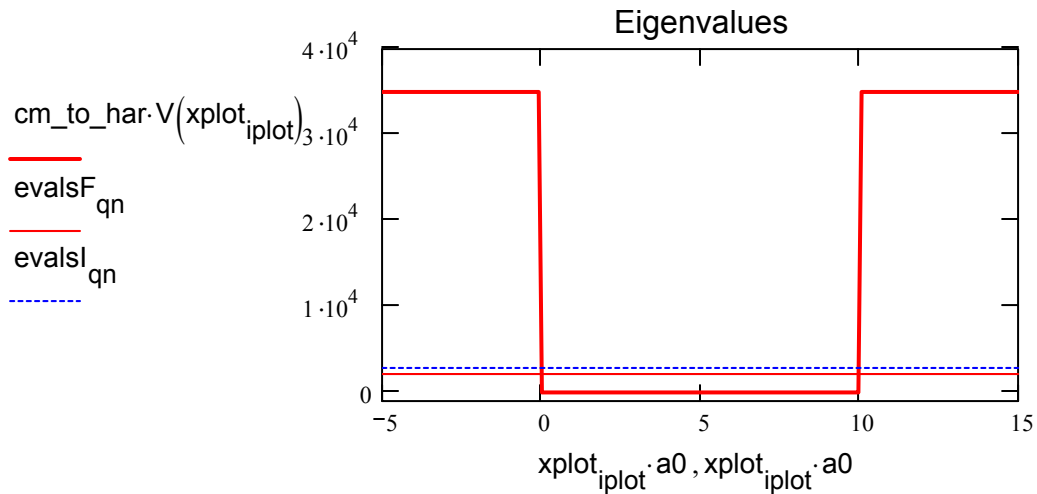
$\Psi F(x) := \text{wavefcn}(evectF, N_{tot}, x, xi, xf)$

$evectI := \text{eigenvec}(HI, \text{evals}I_{qn})$

The wavefcn function calculates the value of the desired wavefunction at each value of x - ΨF is for a finite box; ΨI for an infinite box

$\Psi I(x) := \text{wavefcn}(evectI, N_{tot}, x, xi, xf)$

The next three plots show the energies, wavefunctions, and probability densities for a particle in finite box (solid red line) and infinite box (dashed blue line). Which has the lower energy? How do the wavefunctions differ - what feature of the wavefunction might lead to the lower energy?



Again, make sure that **xi** is small enough and **xf** is large enough that the wavefunctions are very close to zero at the edges.

The box goes from 0 to 10 Angstroms, and the particle in an infinite box wavefunction (dashed lines) stays in the box, but the wavefunction for the particle in a finite box has some probability of being outside the box, especially for states at higher energy. The particle in a finite box wavefunction tunnels - it has some probability of being in a region where its energy is less than the potential. As a result, the finite box wavefunction is broader and has less curvature and hence less kinetic energy. This more than compensates for the slightly higher average potential energy of the finite box wavefunction, so, overall, the finite box has lower energy than the infinite box. The extent of tunneling increases for wavefunctions with higher quantum numbers (try it !), making the energy difference between the two wavefunctions even larger.

[Double-click here to change the quantum number](#)

How does making the walls of the finite box higher affect the energies of the states? How does it affect the probability that the wavefunction will be outside the box?

Vary the quantum number of the wavefunction you're plotting - how does the number of nodes in the wavefunction (the number of times it crosses through zero) depend on the quantum number ?

With three simple rules (and no math) you can figure out qualitatively what a wavefunction will look like, even for complicated potentials.

1. The ground state wavefunction has zero nodes, the first excited state has one node, and so on (this is true for bound states of one-dimensional potentials). You just saw this above.
2. If the energy of the wavefunction is below the potential, the wavefunction will decay approximately exponentially. For an example, look at the shape of the wavefunction for the particle in a finite box in the region outside the box (where it tunnels).
3. If the energy of the wavefunction is above the potential, the wavefunction will oscillate (roughly like a sine wave); the higher the energy is above the potential, the more rapidly it will oscillate.

For an explanation of #1 see p. 73 of [9].

[For an explanation of #2 and #3 double-click here](#)

Particle in a Finite Box with a Barrier

$$\text{height} := \frac{35000}{\text{cm_to_har}}$$

Box height in cm^{-1}

$$\text{barrier} := \frac{15000}{\text{cm_to_har}}$$

Barrier height in cm^{-1}

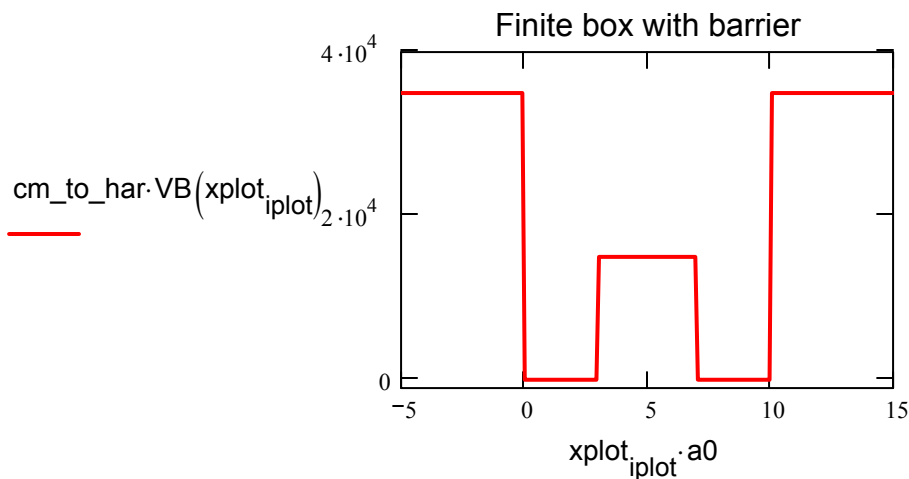
$$\text{leftbarrier} := \frac{3.0}{a0} \quad \text{rightbarrier} := \frac{7.0}{a0}$$

Barrier position

$$V_{\text{FBOXwithBarrier}}(r) := \begin{cases} \text{height} & \text{if } r > \text{right} \\ \text{height} & \text{if } r < \text{left} \\ \text{barrier} & \text{if } \text{leftbarrier} < r < \text{rightbarrier} \\ 0.0 & \text{otherwise} \end{cases}$$

Potential of a finite box with a barrier in the middle

$$VB(r) := V_{\text{FBOXwithBarrier}}(r)$$

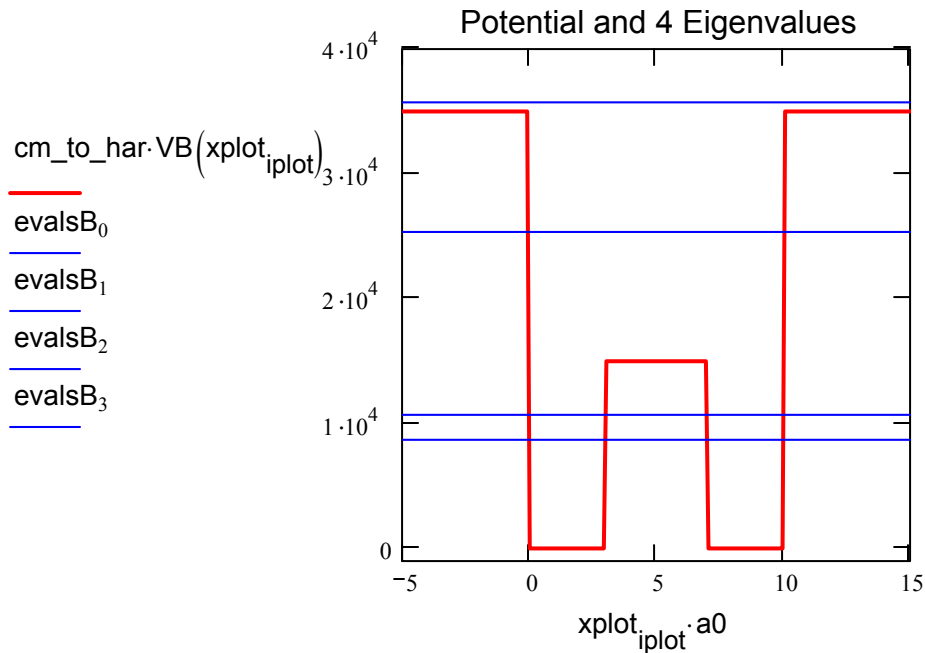


$$HB_{j-1, k-1} := H(j, k, VB, \mu, xi, xf) \cdot \text{cm_to_har}$$

Calculate the Hamiltonian for the Finite Box with Barrier potential

$$\text{evalsB} := \text{sort}(\text{eigenvals}(\text{HB}))$$

Diagonalize the Hamiltonian matrix to find energy values (eigenvalues) and wavefunctions (eigenfunctions)



Make sure \mathbf{xi} is small enough and \mathbf{xf} is large enough to extend beyond the edges of the box

In the particle in an infinite box and particle in a finite box, the spacing between energy levels increases as you go to higher energies (as long as you're in the box). Is this the case for the particle in a box with a barrier? Can you think of a reason why the two lowest states have similar energies?

Examining the wavefunctions for the two lowest energy states may explain why they have similar energies.

Plot wavefunctions for states with quantum numbers $qn1$ and $qn2$. In Mathcad, the lowest state has quantum number 0.

$qn1 := 0$ $qn2 := 1$ **select quantum numbers to plot**

$vecB := \text{eigenvec}(HB, evalsB_{qn1})$

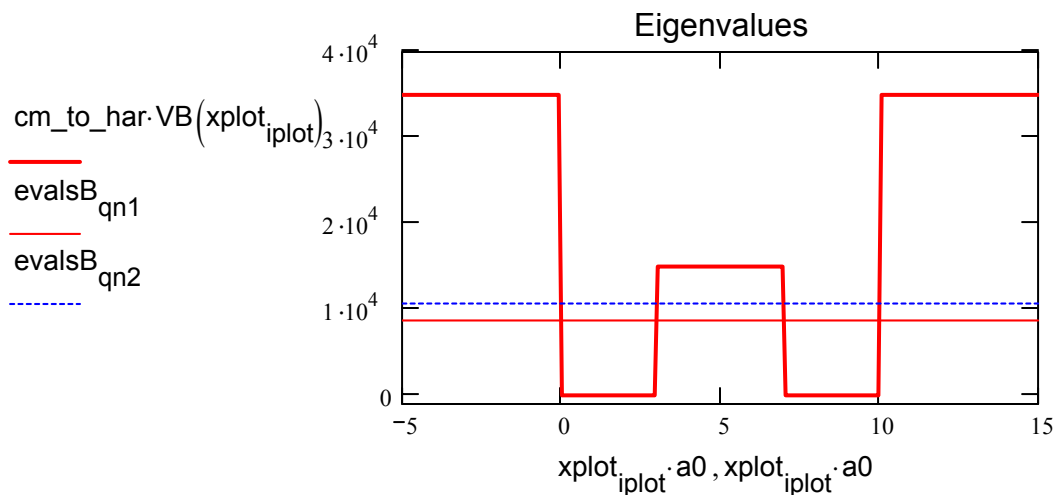
Mathcad's eigenvec function calculates the eigenvector that corresponds to the desired eigenvalue.

$\Psi B1(x) := \text{wavefcn}(vecB, Ntot, x, xi, xf)$

$vecB := \text{eigenvec}(HB, evalsB_{qn2})$

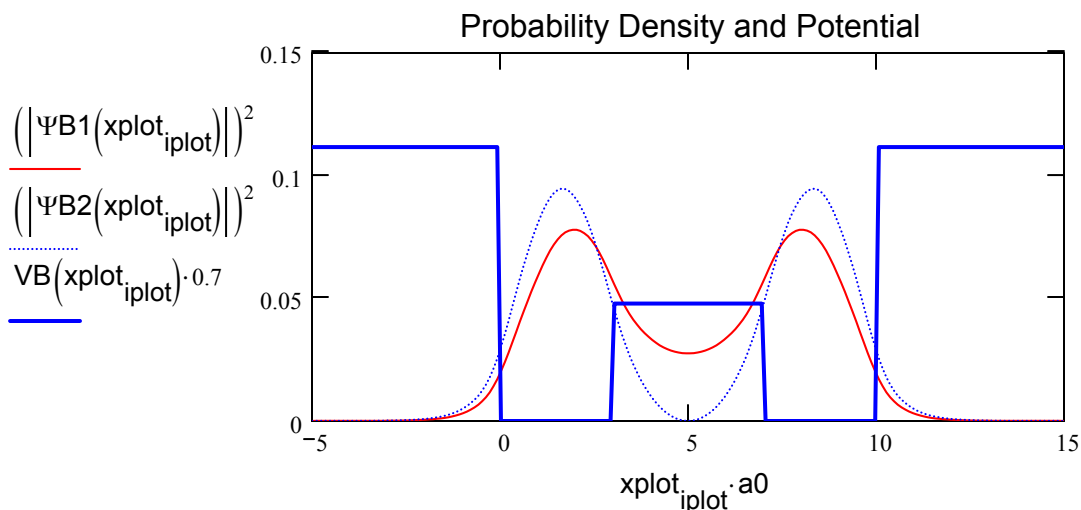
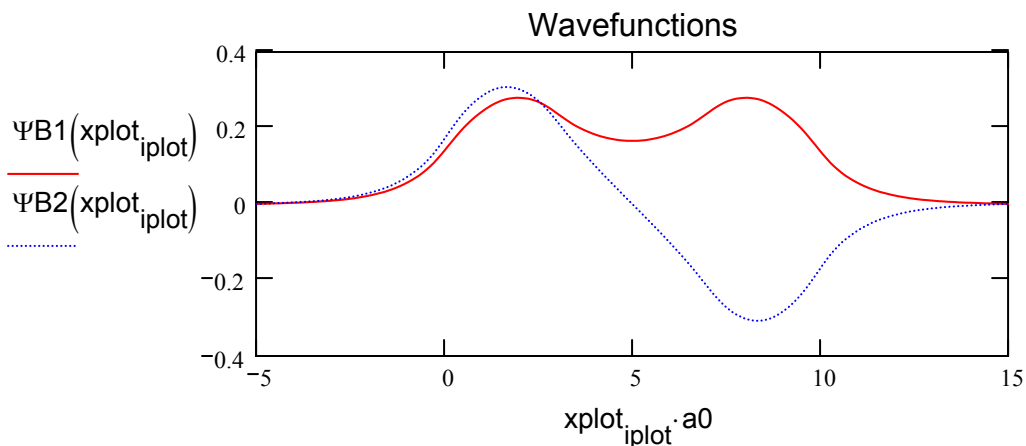
The wavefcn function calculates the value of the desired wavefunction at each value of x .

$\Psi B2(x) := \text{wavefcn}(vecB, Ntot, x, xi, xf)$



Here are the energy levels, wavefunctions and probability densities for the two lowest states. Note that the energy of the ground state is below the height of the barrier, but the wavefunction has some probability of being inside the barrier. This is another example of quantum tunneling.

By looking at the wavefunctions can you explain why these states have similar energies? How about the probability densities?



Again, make sure that r_i is small enough and r_f is large enough that the wavefunctions are very close to zero at the edges

Change the barrier height (it's the variable "barrier" above) and see how this affects the wavefunctions with quantum numbers 0 and 1. As you increase the barrier, how does this change the energy spacing between these two states? How does it change their probability densities?

Double click to change barrier

Plot the wavefunction with quantum number 4. Its energy is above the edges of the box. It is no longer bound - it's a free particle. The wavefunction will now extend to the edges of the region calculated (even if you extend this region by decreasing r_i and increasing r_f).

Double click to change quantum number

You may have noticed that if you change the values of r_i and r_f the energies of the unbound states change. This is because the method we've used to solve Schrodinger equation is not very good at calculating unbound (continuum) states. Since we use a particle in a box basis set, all of the wavefunctions are confined to a box that extends from r_i to r_f . Usually, this is not a problem (as the wavefunction for a bound state would not extend beyond this range, anyhow) but wavefunctions for unbound states do extend outside this range and are artificially confined.

Comparison of Harmonic Oscillator and Morse Oscillator

Compare energy levels and wavefunctions for these two potentials

Parameters given are approximately those of an O-H stretch in OH radical or in water.

$$r_i := \frac{1.0}{a_0} \quad \text{Bond length (1.0 Angstrom to start)}$$

$$m_1 := 16 \cdot \text{amu} \quad m_2 := 1 \cdot \text{amu} \quad \text{masses of O and H atom}$$

$$\mu := \frac{m_1 \cdot m_2}{m_1 + m_2} \quad \text{reduced mass of molecule}$$

Harmonic Oscillator parameters

$$\omega := \frac{3600}{\text{cm_to_har}} \quad \text{Vibrational frequency}$$

$$k_2 := \mu \cdot \omega^2 \quad \text{force constant}$$

$$V_{\text{HarmOsc}}(r, k_2, r_i) := \frac{1}{2} \cdot k_2 \cdot (r - r_i)^2 \quad \text{Potential of a harmonic oscillator}$$

$$V_{\text{harm}}(r) := V_{\text{HarmOsc}}(r, k_2, r_i) \quad \text{Harmonic potential}$$

Morse Oscillator parameters

$$\omega_i := \frac{3760}{\text{cm_to_har}} \quad \text{Frequency} \quad \text{These values of } \omega_i \text{ and } \omega_{\text{exe}} \text{ give a fundamental frequency (the } n=0 \text{ to } n=1 \text{ energy difference) of } 3600 \text{ cm}^{-1}, \text{ which is the same as for the harmonic oscillator.}$$

$$\omega_{\text{exe}} := \frac{80}{\text{cm_to_har}} \quad \text{Anharmonicity}$$

$$D_{\text{ei}} := \frac{\omega_i^2}{4 \cdot \omega_{\text{exe}}} \quad \text{Dissociation energy}$$

$$k_{2i} := \mu \cdot \omega_i^2 \quad a_i := \left(\frac{k_{2i}}{2 \cdot D_{\text{ei}}} \right)^{\frac{1}{2}}$$

$$V_{\text{Morse}}(r, D_{\text{ei}}, a_i, r_i) := D_{\text{ei}} \cdot \left[1 - e^{-a_i \cdot (r - r_i)} \right]^2 \quad \text{Morse potential}$$

$$VMorse(r) := VMorse(r, Dei, ai, ri)$$

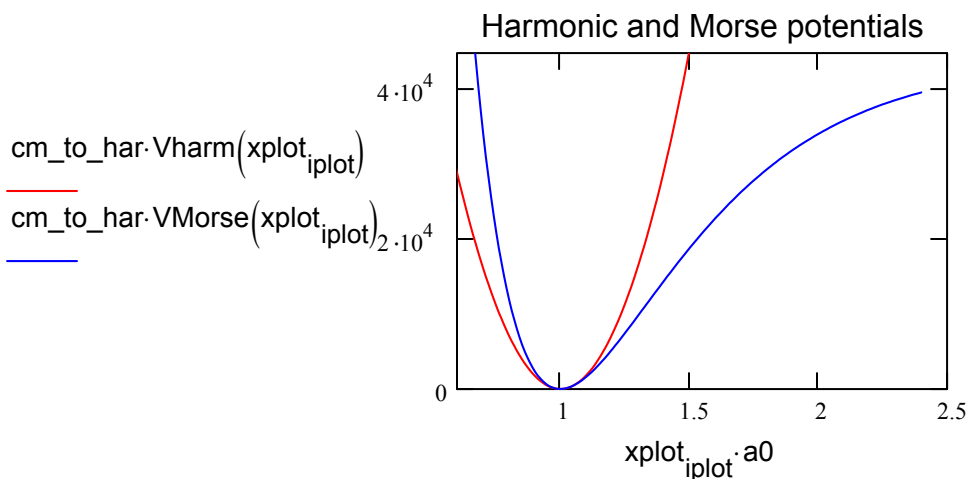
$$xi := \frac{0.4}{a0}$$

$$xf := \frac{2.4}{a0}$$

Range to use for calculation. This should be wide enough that the wavefunction is nearly zero outside this range.

$$dxplot := \frac{xf - xi}{nplot - 1}$$

$$xplot_{iplot} := xi + iplot \cdot dxplot \quad iplot := 0 .. nplot - 1$$



For small displacements (near the minimum) the two potentials are similar. The Morse potential is more repulsive at small bond lengths and more attractive at large bond lengths.

Compare energy levels of Morse and harmonic oscillator

Although the harmonic oscillator can be solved analytically (the solutions are given in most physical chemistry texts), we'll solve it using the same method we've used for the other potentials - numerically, using the Variational method

$$HH_{j-1, k-1} := H(j, k, Vharm, \mu, xi, xf) \cdot cm_to_har$$

Calculate the Hamiltonian for a harmonic oscillator

$$evalsH := sort(eigenvals(HH))$$

Diagonalize the Hamiltonian matrix to find energy values (eigenvalues) and wavefunctions (eigenfunctions)

$$HM_{j-1, k-1} := H(j, k, VMorse, \mu, xi, xf) \cdot cm_to_har$$

Do the same for the Morse oscillator

$$evalsM := sort(eigenvals(HM))$$

**Energies (eigenvalues) in cm^{-1}
for Harmonic potential**

evalsH =

	0
0	1800
1	5400
2	9000
3	12600
4	16200

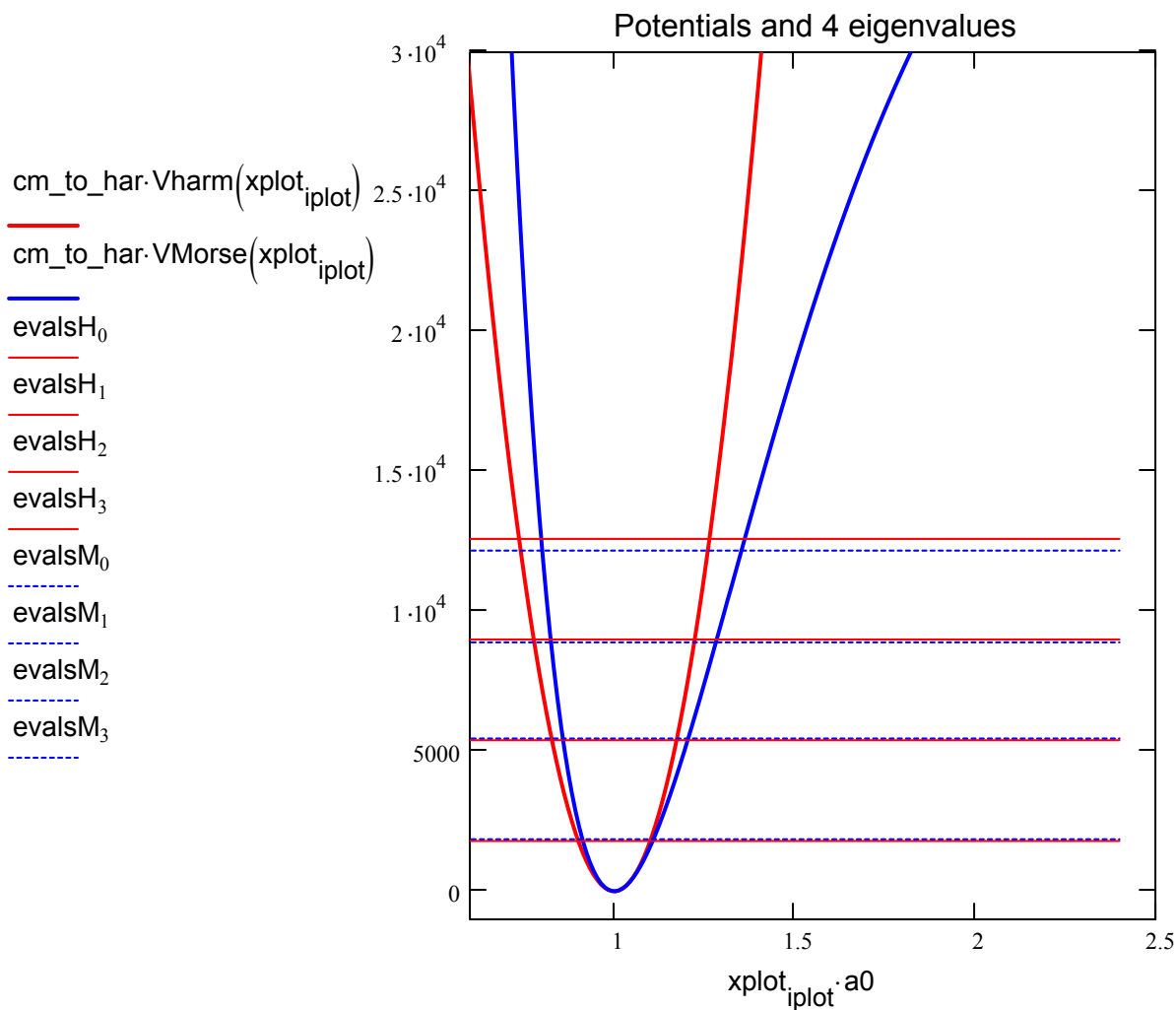
**Energies (eigenvalues) in cm^{-1}
for Morse potential**

evalsM =

	0
0	1860
1	5460
2	8900
3	12180
4	15300

Calculate the energy levels of a harmonic and a Morse oscillator with the frequency and anharmonicity given above.

How do the results of the Variational calculation compare to the exact results ? Write your answer in your note book.



CALCULATE AND PLOT WAVEFUNCTIONS

Calculate range over which to display wavefunction - plot from xi to xf

$$i_{wfp} := 0 .. nwfplot - 1 \quad dwf := \frac{xf - xi}{nwfplot - 1} \quad xwf_{i_{wfp}} := xi + i_{wfp} \cdot dwf$$

Plot harmonic oscillator and Morse oscillator wavefunctions with quantum number qn

$$qn := 0$$

select quantum number to plot

$$evecH := \text{eigenvec}(HH, \text{evalsH}_{qn})$$

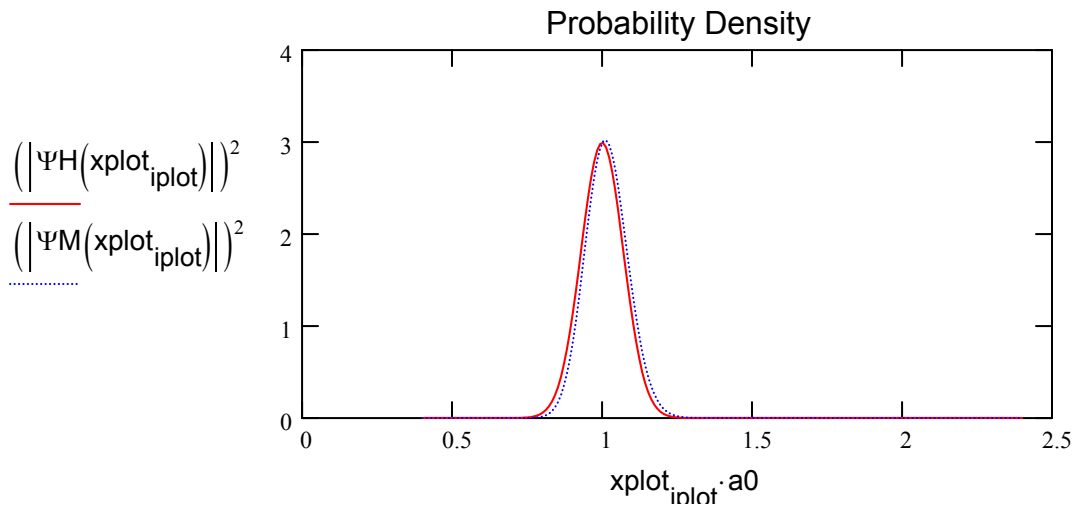
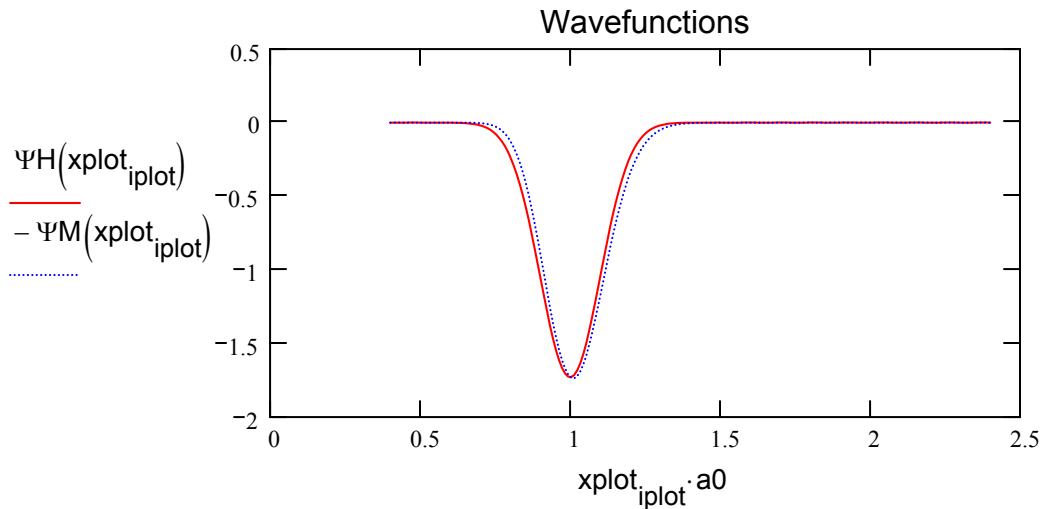
$$\Psi H(x) := \text{wavefcn}(evecH, N_{tot}, x, xi, xf)$$

$$evecM := \text{eigenvec}(HM, \text{evalsM}_{qn})$$

$$\Psi M(x) := \text{wavefcn}(evecM, N_{tot}, x, xi, xf)$$

Wavefunction for harmonic oscillator
Mathcad's eigenvec function calculates the eigenvector that corresponds to the desired eigenvalue and the wavefcn function calculates the value of the desired wavefunction at each value of x

Wavefunction for Morse oscillator



Again, make sure that r_i is small enough and r_f is large enough that the wavefunctions are very close to zero at the edges

Note that the ground state wavefunctions and energies for the harmonic and Morse oscillators are very similar.

Qualitatively predict what the $n=8$ wavefunction for the harmonic oscillator will look like:

How many nodes will the $n=8$ wavefunction have ?

(see rule #1 above)

How rapidly will the wavefunction oscillate near $x=1$ Angstrom ? What about near the 0.6 and 1.4 Angstrom ?

(see rule #3 above)

Double click to review the 3 simple rules

Qualitatively, how will the Morse oscillator wavefunction with $n=8$ differ from the harmonic oscillator wavefunction ?

Plot the wavefunctions with quantum number 8. Compare your predictions with the actual wavefunctions. How do the harmonic and Morse oscillator wavefunctions differ ?

Double click to change quantum number

Double Minimum Potential

This type of potential is found in molecules like ammonia, which have two equivalent configurations (pyramidal) separated by a barrier (at the planar configuration).

Double Minimum parameters (for NH₃)

$$\text{barrier2} := \frac{800}{\text{cm_to_har}} \quad \text{Barrier height (in cm}^{-1}\text{)}$$

$$\text{spacing} := \frac{0.6}{a_0} \quad \text{Spacing between the two minima}$$

$$k_2 := \frac{-8 \cdot \text{barrier2}}{\text{spacing}^2} \quad k_4 := \frac{\text{barrier2} \cdot 16}{\text{spacing}^4} \quad r_i := 0$$

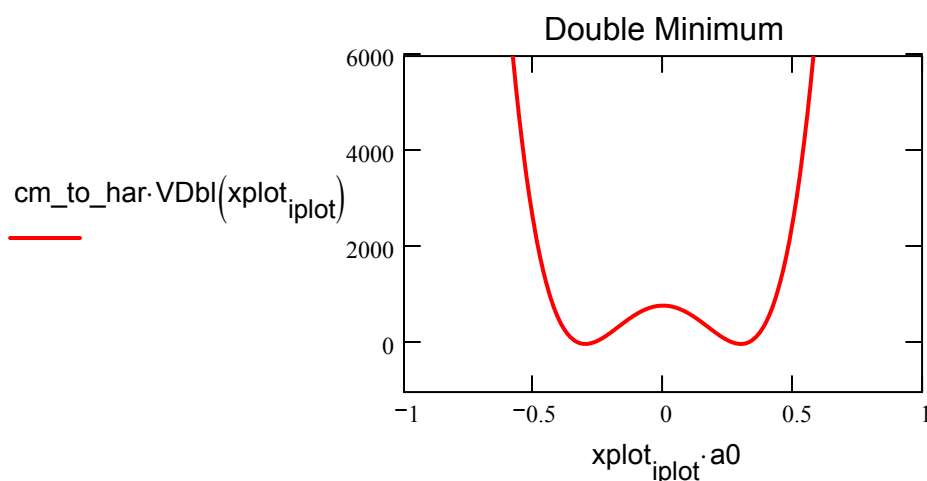
$$V_{\text{Double}}(r, k_2, k_4, \text{barrier2}, r_i) := k_2 \cdot (r - r_i)^2 + k_4 \cdot (r - r_i)^4 + \text{barrier2}$$

$$V_{\text{DbI}}(r) := V_{\text{Double}}(r, k_2, k_4, \text{barrier2}, r_i)$$

$$x_i := \frac{-0.58}{a_0} \quad x_f := \frac{0.58}{a_0}$$

$$\mu := 3.0 \cdot \text{amu} \quad \text{reduced mass for vibration (3 hydrogens are moving)}$$

$$dx_{\text{plot}} := \frac{x_f - x_i}{n_{\text{plot}} - 1} \quad x_{\text{plot}_i} := x_i + i_{\text{plot}} \cdot dx_{\text{plot}} \quad i_{\text{plot}} := 0 .. n_{\text{plot}} - 1$$



The two minima correspond to trigonal pyramidal NH₃. The local maximum between them corresponds to planar NH₃, which is a saddle point.

Use the variational method to solve the Schrodinger equation for this double minimum potential and answer the questions below.

Tip: Copy the Mathcad code for a similar potential from above, paste it below, then edit it. Use the finite box with a barrier code (as it's the most similar to what you want to do), copying from the first plot of the potential to the plots of the energy levels, wavefunctions and probability densities. Replace $V_B(r)$ with $V_{Dbl}(r)$ (make sure to also replace V_B in the function $H()$ which calculates the Hamiltonian and in the plots). In the final plot (probability densities and potential, you'll be able to see the potential better if you multiply it by 100, rather than 0.7).

[Double click to go to finite box with barrier potential](#)

Plot the ammonia (double minimum) potential along with the energies of the states with quantum number 0 and 1.

In a second graph, plot the wavefunctions for the states with quantum number 0 and 1.

In a third graph, plot the potential and probability density for the wavefunctions with quantum number 0 and 1.

[Double click to change barrier height](#)

Is the energy of the ground state above or below the height of the barrier ?

**Does the ground state wavefunction show tunneling ?
Where ?**

Due to the barrier, the energies of the two lowest states are very similar.

How does increasing the barrier height affect their splitting ?

How does increasing the barrier height affect the probability that the ground state wavefunction will be at $x=0$ (planar NH_3) ?

Now that you're an expert, feel free to solve the Schrodinger equation for your own potential by modifying one of the potentials above (or writing your own). Some possibilities:

- The potential between two inert-gas molecules is often described by the Lennard-Jones potential $V(x) = a x^{-12} - b x^{-6}$. (values for a and b can be found in your Physical Chemistry text, be sure to use the correct masses for the atoms and to convert a and b so that V and x have units of hartree and bohr, respectively).

- You can carry out an ab initio calculation (using Gaussian, Spartan, Hyperchem or a similar program) to calculate the potential (the energy) of a diatomic molecule at several bond lengths (10 or so is good) and then calculate vibrational energies on this potential. Express the potential energy in hartree (with the bottom of the well at an energy of zero) and bond length in bohr and use the Mathcad functions interp() and lspline() to interpolate the energy values between the calculated points. Make sure you calculate energies to sufficiently large and small values of the bond length that the vibrational wavefunction is close to zero near the edges.

Double click for hints on using the Variational method with your own potential