9: NUMERICAL SOLUTIONS FOR SCHRÖDINGER'S EQUATION

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CHAPTER OVERVIEW

9: Numerical Solutions for Schrödinger's Equation

Numerically solving the Schrödinger equation is a complex problem that stems from the large number of points needed on a grid and the requirement to satisfy boundary conditions.

9.1: Introduction to Numerical Solutions of Schödinger's Equation

Solving Schrödinger's equation is the primary task of chemists in the field of quantum chemistry. However, exact solutions for Schrödinger's equation are available only for a small number of simple systems. Therefore the purpose of this tutorial is to illustrate one of the computational methods used to obtain approximate solutions.

Mathcad offers the user a variety of numerical differential equation solvers. We will use Mathcad's ordinary differential equation solver, Odesolve, because it allows one to type Schrödinger's equation just as it appears on paper or on the blackboard; in other words it is pedagogically friendly. In what follows the use of Odesolve will be demonstrated for the one-dimensional harmonic oscillator. All applications of Odesolve naturally require the input of certain parameters: integration limits, mass, force constant, etc. Therefore the first part of the Mathcad worksheet will be reserved for this purpose.

- Integration limit: x_{max} := 5
- Effective mass: μ := 1
- Force constant: k := 1

The most important thing distinguishing one quantum mechanical problem from another is the potential energy term, $V(x)$. It is entered below.

Potential energy:

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

Entering the potential energy separately, as done above, allows one to write a generic form for the Schrödinger equation applicable to any one-dimensional problem. This creates a template that is easily edited when moving from one quantum mechanical problem to another. All that is necessary is to type in the appropriate potential energy expression and edit the input parameters. This is the most valuable feature of the numerical approach - you don't need a new mathematical tool or trick for each new problem, a single template works for all one-dimensional problems after minor editing.

Mathcad's syntax for solving the Schrödinger equation is given below. As it may be necessary to do subsequent calculations, the wavefunction is normalized. Note that seed values for an initial value for the wavefunction and its first derivative are required. It is also important to note that the numerical integration is carried out in atomic units:

$$h/2\pi = me = e = 1.$$

Given

$$\frac{-1}{2\mu}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

with $\psi(-x_{max}) = 0$ and $\psi'(-x_{max}) = 0.1$.

$$\psi = Odesolve(x, x_{max})$$

Normalize wavefunction:

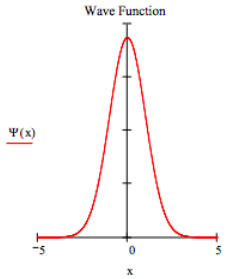
$$\psi(x) = \frac{\psi(x)}{\sqrt{\int_{-x_{max}}^{x_{max}} \psi(x)^2 dx}}$$

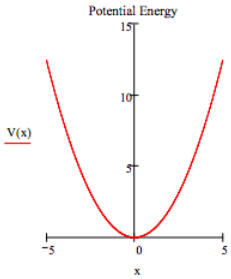
Numerical solutions also require an energy guess. If the correct energy is entered the integration algorithm will generate a wavefunction that satisfies the right-hand boundary condition. If the right boundary condition is not satisfied another energy guess is made. In other words it is advisable to sit on the energy input place holder, type a value and press F9 to recalculate.

Energy guesses that are too small yield wavefunctions that miss the right boundary condition on the high side, while high energy guesses miss the right boundary condition on the low side. Therefore it is generally quite easy to bracket the correct energy after a few guesses.

Enter energy guess: E ≡ .5

Of course the solution has to be displayed graphically to determine whether a solution (an eigenstate) has been found. The graphical display is shown below. It is frequently instructive to also display the potential energy function.






```
%matplotlib inline

from scipy.integrate import odeint
import matplotlib.pyplot as plt
import numpy as np


mu=1
k=1
E=.5
xmax=-5

def psi(y,x):
    psi1, psi2_dx2 = y
    return [psi2_dx2, ((2*mu)/(-1))*(E*psi1 - (1/2)*x**2*psi1)]

x0 = [0.0, 0.1]
val = np.linspace(-5,5,101)
sol = odeint(psi, x0, val)
#plot, legends, and titles
plt.plot(val,sol[:,0],color = "red",label = " ")
plt.title("Wave Function")
leg = plt.legend(title = "(x)  ", loc = "center", bbox_to_anchor=[-.11,.5],frameon=Fa

plt.show()
```

run | restart | restart & run all

```
%matplotlib inline

import matplotlib.pyplot as plt
import numpy as np
import math

# initialize constants k and create x array
k = 1
x = np.linspace(-5,5,100)

# set boundaries
plt.xticks([-5,5])
```

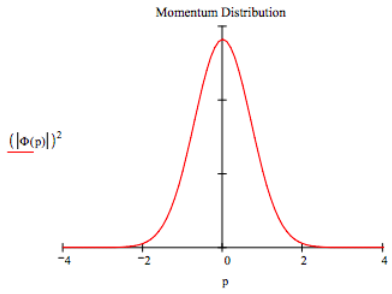
```
plt.yticks([0,5,10,15])

# plot
plt.plot(x,(.5)*k*(x**2), color = "red",label = " ")

# add titles and legend
plt.title("Potential Energy")
leg = plt.legend(title = "\u03A8  ", loc = "center", bbox_to_anchor=[-.11,.5],frameon=

plt.show()
```

run | restart | restart & run all

It is quite easy, as shown below, to generate the momentum-space wavefunction by a Fourier transform of its coordinate-space counterpart.

$$p := -4, -3.9..5$$

$$\Phi(p) = \frac{1}{\sqrt{2\pi}} \int_{-x_{max}}^{x_{max}} e^{-ipx} \psi(x) dx$$




```
%matplotlib inline

import numpy as np
import matplotlib.pyplot as plt
from scipy.integrate import odeint
import scipy.integrate as integrate
import math

#set constants
mu=1
k=1
E=.5
xmax=5

#create ode
def psi(y,x):
    psi1, psi2_dx2 = y
    return [psi2_dx2, ((2*mu)/(-1))*(E*psi1 - (1/2)*x**2*psi1)]

#create space
x0 = [0.0, 0.001]
val = np.linspace(-xmax,xmax,101)
```

```
#solve ode using odeint
sol = odeint(psi, x0, val)

#format plot
fig = plt.figure()
ax = fig.add_subplot(1, 1, 1)

#show tick marks to the left and lower axes only
plt.yticks([])
plt.axis(xmin = -4,xmax = 4,ymin = 0,ymax = 30)

#move left yaxis passing through origin
ax.spines["left"].set_position("center")

#eliminate upper and right axes
ax.spines["right"].set_color("none")
ax.spines["top"].set_color("none")

#plot graph
plt.plot(val,sol[:,0],color = "red",label = " ")


#add titles and legend
plt.title("Momentum Distribution")
leg = plt.legend(title = "(|\u03A6(p)|\u00b2)", loc = "center", bbox_to_anchor=[-.10,

plt.show()
```

run | restart | restart & run all

9.2: Particle in an Infinite Potential Well

Numerical Solutions for Schrödinger's Equation

Integration limit: $x_{max} := 1$ Effective mass: $\mu := 1$

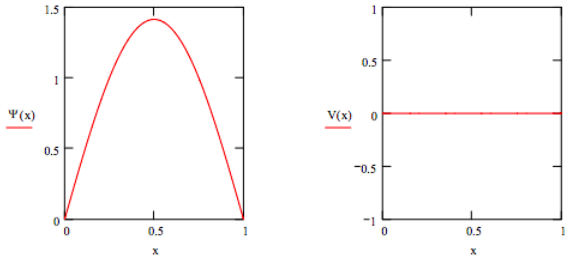
Potential energy: V(x) := 0

Numerical integration of Schrödinger's equation:

Given: $\frac{1}{2\mu}\frac{d^2}{dx^2}\Psi(x) + V(x)\Psi(x) = E\Psi(x)\ \ \Psi(0) = 0\ \ \Psi'(0) = 0.1$

$\Psi := Odesolve(x, x_{max})$ Normalize wave function: $\Psi(x) := \frac{\Psi(x)}{\sqrt{\int_0^{x_{max}} \Psi(x)^2 dx}}$

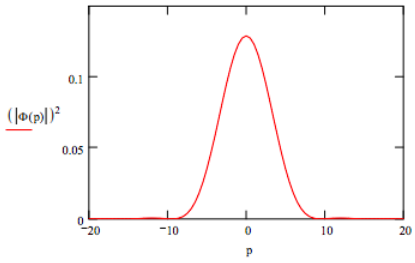
Enter energy guess: E = 4.934



Fourier transform coordinate wave function into momentum space:

p := -20, -19.5 .. 20

$\Phi(p) := \frac{1}{2\mu}\int_0^{x_{max}} exp(-i \cdot p \cdot x) \cdot \Psi(x) dx$



9.3: Particle in a Gravitational Field

The Unhindered Quantized Bouncing Particle

- Integration limit: $z_{max} = 3$
- Mass: $m = 2$
- Acceleration due to gravity: $g = 1$

The first 10 roots of the Airy function are as follows:

a_1 = 2.33810	a_2 = 4.08794	a_3 = 5.52055	a_4 = 6.78670	a_5 = 7.94413
a_6 = 8.02265	a_7 = 10.04017	a_8 = 11.00852	a_9 = 11.93601	a_{10} = 12.82877

Calculate energy analytically by selecting the appropriate Airy function root:

$$\text{i} = 1 \quad \text{E} = \frac{mg^2}{2}^{\frac{1}{3}} a_1 \quad \text{E} = 2.338$$

Generate the associated wavefunction numerically: Potential energy: $V(z) = mgz$

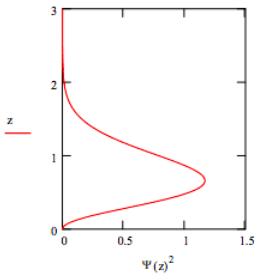
Given $\frac{-1}{2 \cdot m} \frac{d^2}{dz^2} \psi(z) + V(z)\psi(z) \equiv E\psi(z)$

$$\psi(0.0) = 0.0$$

$$\psi'(0.0) = 0.1$$

Given, $\psi = Odesolve(z, z_{max})$

Normalize wavefunction: $\psi(z) = \frac{\psi(z)}{\sqrt{\int_0^{z_{max}} \psi(z)^2 dz}}$



9.4: Particle in a One-dimensional Egg Carton

Numerical Solutions for Schrödinger's Equation

Integration limit: x_{max} = 10 Effective mass: μ = 1

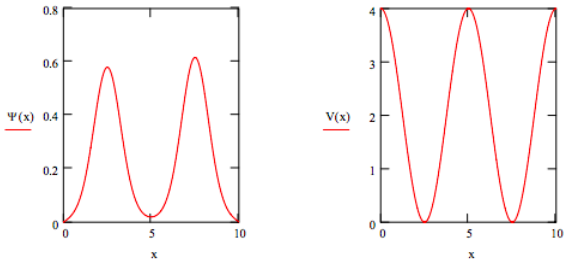
Potential energy: V_o = 2 atoms = 2 $V(x) = V_o(\cos(atoms 2\pi \frac{x}{x_{max}}) + 1)$

Numerical integration of Schrödinger's equation:

Given $\frac{-1}{2\mu}\psi(x) + V(x)\psi(x) = E\psi(x)$ $\psi(0) = 0$ $\psi' = 0.1$

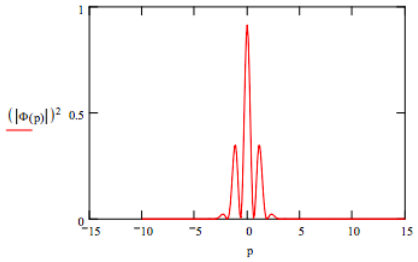
$\psi = Odesolve(x, x_{max})$ Normalize wave function: $\psi(x) = \frac{\psi(x)}{\sqrt{\int_0^{x_{max}} \psi(x)^2 dx}}$

Enter energy guess: E = 0.83583



Fourier transform coordinate wave function into momentum space.

p = -10, -9.9 .. 10 $\Phi(p) = \frac{1}{\sqrt{2\pi}} \int_0^{x_{max}} exp(-ipx)\psi(x)\, dx$



9.5: Particle in a Finite Potential Well

Numerical Solutions for the Finite Potential Well

Schrödinger's equation is integrated numerically for the first three energy states for a finite potential well. The integration algorithm is taken from J. C. Hansen, J. Chem. Educ. Software, 8C2, 1996.

Set parameters:

n = 100	xmin = -3	xmax = 3	$\Delta = \frac{xmax - xmin}{n-1}$
μ = 1	lb = -1	rb = 1	V_0 = 4

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

i = 1 .. n	j = 1 .. n	x_i = xmin + (i - 1) Δ

$$V_{i,i} = if[(x_i \geq lb)(x_i \leq rb), 0, V_0] \quad T_{i,j} = if[i = j, \frac{\pi^2}{6\mu\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}]$$

Form Hamiltonian energy matrix: H = TV

Find eigenvalues: E = sort(eigenvals(H))

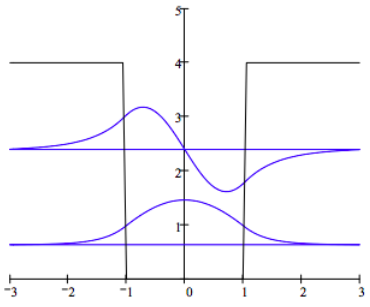
Display three eigenvalues: m = 1 .. 3

E_m =

0.63423174
2.39691438
4.4105828

Calculate associated eigenfunctions: k = 1 .. 2 ψ(k) = eigenvec(H, E_k)

Plot the potential energy and bound state eigenfunctions: $V_{pot1} := V_{i,i}$



9.6: Particle in a Semi-infinite Potential Well

Numerical Solutions to Schrödinger's Equation for the Particle in the Semi-infinite Box

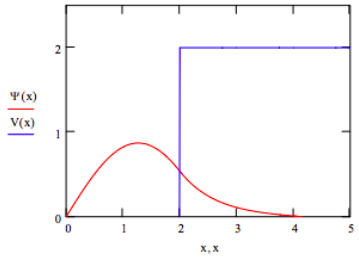
Parameters go here: $x_{min} = 0 \;\; x_{max} = 5 \;\; m = 1 \;\; lb = 2$

Potential energy $V(x) = if[(x \geq lb), V_0, 0]$

Given $\frac{d^2}{dx^2}\psi(x) = 2m(V(x) - E)\psi(x) \;\; \psi(x_{min}) = 0 \;\; \psi'(0) = 0.1$

$\psi := Odesolve(x, x_{max}) \;\; \psi = \frac{\psi(x)}{\sqrt{\int_{x_{min}}^{x_{max}} \psi(x)^2 dx}}$

Enter energy guess: E = 0.766

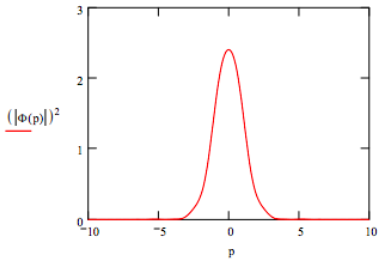


Calculate the probability that the particle is in the barrier: $\int_2^5 \psi(x)^2 dx = 0.092$

Calculate the probability that the particle is not in the barrier: $\int_0^2 \psi(x)^2 dx = 0.908$

Calculate and display the momentum distribution:

Fourier transform: p = -10,-9.9 .. 10 $\Phi(p) = \int_{-x_{min}}^{x_{max}} exp(-1px)\psi(x)\, dx$



9.7: Particle in a Slanted Well Potential

Numerical Solutions for Schrödinger's Equation for the Particle in the Slanted Box

Parameters go here: $x_{max} = 1$ $\mu = 1$ $V_0 = 2$

Potential energy $V(x) = V_0 x$

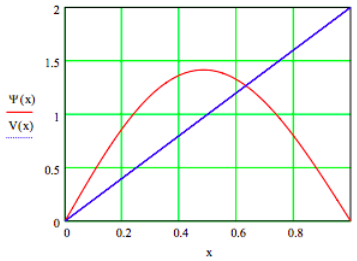
Given

$$\frac{-1}{2\mu}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

with these boundary conditions: $\psi(0) = 0$ and $\psi'(0) = 0.1$

$\psi = Odesolve(x, x_{max})$ Normalize wavefunction: $\psi(x) = \frac{\psi(x)}{\sqrt{\int_0^{x_{max}} \psi(x)^2 dx}}$

Enter energy guess: E = 5.925



Calculate most probably position: x = 0.5 Given $\frac{d}{dx}\psi(x) = 0$ Find (x) = 0.485

Calculate average position: $X_{avg} = \int_0^1 \psi(x)(x)\psi(x)dx$ $X_{avg} = 0.491$

Calculate potential and kinetic energy:

$V_{avg} = V_0 X_{avg}$ $V_{avg} = 0.983$

$T_{avg} = E - V_{avg}$ $T_{avg} = 4.942$

9.8: Numerical Solutions for a Particle in a V-Shaped Potential Well

Schrödinger's equation is integrated numerically for a particle in a V-shaped potential well. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,* 8C2**, 1996.

Set parameters:

$$n = 100 \quad xmin = -4 \quad xmax = 4 \quad \Delta = \frac{xmax - xmin}{n-1} \quad \mu = 1 \quad Vo = 2$$

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i = 1 .. n \quad j = 1 .. n \quad x_i = xmin + (i - 1)\,\Delta$$

$$V_{i,i} = V_o\,|x_i| \quad T_{i,j} = \text{if}\left[i = j, \frac{\pi^2}{6\mu\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

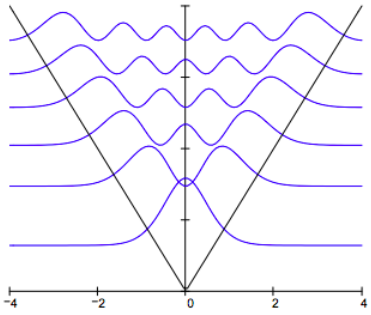
Calculate eigenvalues: E = sort(eigenvals(H))

Selected eigenvalues: m = 1 .. 6

E_m =

1.284
2.946
4.093
5.153
6.089
7.030

Display solution:



For $V = ax^n$ the virial theorem requires the following relationship between the expectation values for kinetic and potential energy: $\langle T \rangle = 0.5n\langle V \rangle$. The calculations below show the virial theorem is satisfied for this potential for which n = 1.

$$\begin{pmatrix} \text{"}Kinetic\ Energy\text{"} & \text{"}Potential\ Energy\text{"} & \text{"}Total\ Energy\text{"} \\ \psi(1)^T T \psi(1) & \psi(1)^T V \psi(1) & E_1 \\ \psi(2)^T T \psi(2) & \psi(2)^T V \psi(2) & E_2 \\ \psi(3)^T T \psi(3) & \psi(3)^T V \psi(3) & E_3 \end{pmatrix}$$

$$= \begin{pmatrix} \text{"}Kinetic\ Energy\text{"} & \text{"}Potential\ Energy\text{"} & \text{"}Total\ Energy\text{"} \\ 0.428 & 0.857 & 1.284 \\ 0.982 & 1.964 & 2.946 \\ 1.365 & 2.728 & 4.093 \end{pmatrix}$$

9.9: Numerical Solutions for the Harmonic Oscillator

Schrödinger's equation is integrated numerically for the first three energy states for the harmonic oscillator. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,* 8C2**, 1996.

Set parameters:

Increments: n = 100

Integration limits: xmin = -5

xmax = 5

$$\Delta = \frac{xmax - xmin}{n - 1}$$

Effective mass: μ = 1

Force constant: k = 1

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i = 1 \,..\, n \quad j = 1 \,..\, n \quad x_i = xmin + (i - 1)\,\Delta$$

$$V_{i,\,j} = if\left[i = j,\ \frac{1}{2}k(x)^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 3

E_m =

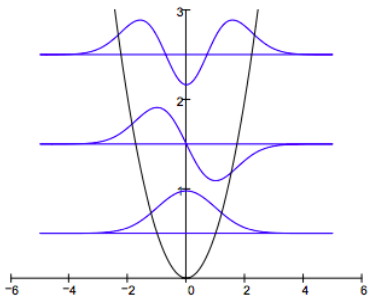
0.5000
1.5000
2.5000

Calculate associated eigenfunctions:

k = 1 .. 3

$$\psi(k) = eigenvec(H, E_k)$$

Plot the potential energy and selected eigenfunctions:



For $V = ax^n$ the virial theorem requires the following relationship between the expectation values for kinetic and potential energy: <T> = 0.5n<V>. The calculations below show the virial theorem is satisfied for the harmonic oscillator for which n = 2.

$$\begin{pmatrix} \text{"}Kinetic\ Energy\text{"} & \text{"}Potential\ Energy\text{"} & \text{"}Total\ Energy\text{"} \\ \psi(1)^T T \Psi(1) & \psi(1)^T V \psi(1) & E_1 \\ \psi(2)^T T \Psi(2) & \psi(2)^T V \psi(2) & E_2 \\ \psi(3)^T T \Psi(3) & \psi(3)^T V \psi(3) & E_3 \end{pmatrix}$$

$$= \begin{pmatrix} \text{"}Kinetic\ Energy\text{"} & \text{"}Potential\ Energy\text{"} & \text{"}Total\ Energy\text{"} \\ 0.2500 & 0.2500 & 0.5000 \\ 0.7500 & 0.7500 & 1.5000 \\ 1.2500 & 1.2500 & 2.5000 \end{pmatrix}$$

9.10: Numerical Solutions for a Double-Minimum Potential Well

Schrödinger's equation is integrated numerically for a double minimum potential well: $V = bx^4 - cx^2$. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

Increments: n = 100

Integration limits: xmin = -4

xmax = 4

$$\Delta = \frac{xmax - xmin}{n - 1}$$

Effective mass: μ = 1

Constants: b = 1 c = 6

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i = 1 \,..\, n \quad j = 1 \,..\, n \quad x_i = xmin + (i - 1)\,\Delta$$

$$V_{i,\,j} = if\left[i = j,\ b(x_i)^4 - c(x_i)^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix:

$$H = T + V$$

Calculate eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 5

E_m =

-6.64272702
-6.64062824
-2.45118605
-2.3155705
0.41561275

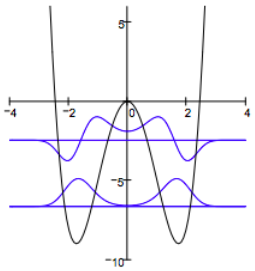
Calculate selected eigenvectors:

k = 1 .. 4

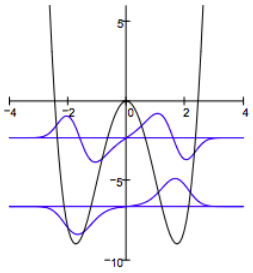
$$\psi(k) = eigenvec(H, E_k)$$

Display results:

First two even solutions:



First two odd solutions:



9.11: Numerical Solutions for the Quartic Oscillator

Schrödinger's equation is integrated numerically for the first three energy states for the quartic oscillator. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

Increments: n = 100

Integration limits: xmin = -3

xmax = 3

$$\Delta = \frac{xmax - xmin}{n - 1}$$

Effective mass: μ = 1

Force constant: k = 1

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i = 1 \,..\, n \quad j = 1 \,..\, n \quad x_i = xmin + (i - 1)\,\Delta$$

$$V_{i,\,j} = if\left[i = j,\ k(x_i)^4,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 3

E_m =

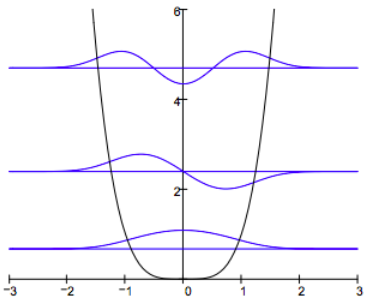
0.6680
2.3936
4.6968

Calculate associated eigenfunctions:

k = 1 .. 3

$$\psi(k) = eigenvec(H, E_k)$$

Plot the potential energy and selected eigenfunctions:



For $V = ax^n$ the virial theorem requires the following relationship between the expectation values for kinetic and potential energy: <T> = 0.5n<V>. The calculations below show the virial theorem is satisfied for the harmonic oscillator for which n = 4.

$$\begin{pmatrix} \text{"}\,Kinetic\ Energy\,\text{"} & \text{"}\,Potential\ Energy\,\text{"} & \text{"}\,Total\ Energy\,\text{"} \\ \psi(1)^T T \psi(1) & \psi(1)^T V \psi(1) & E_1 \\ \psi(2)^T T \psi(2) & \psi(2)^T V \psi(2) & E_2 \\ \psi(3)^T T \psi(3) & \psi(3)^T V \psi(3) & E_3 \end{pmatrix}$$

$$= \begin{pmatrix} \text{"}\,Kinetic\ Energy\,\text{"} & \text{"}\,Potential\ Energy\,\text{"} & \text{"}\,Total\ Energy\,\text{"} \\ 0.4453 & 0.2227 & 0.6680 \\ 1.5958 & 0.7979 & 2.3936 \\ 3.1312 & 1.5656 & 4.6968 \end{pmatrix}$$

9.12: Numerical Solutions for Morse Oscillator

Schrödinger's equation is integrated numerically for the first three energy states for the Morse oscillator. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

n = 300

xmin = -2

xmax = 12

$$\Delta = \frac{xmax - xmin}{n - 1}$$

μ = 1

D = 2

β = 2

x_e = 0

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

i = 1 .. n j = 1 .. n x_i = xmin + (i - 1) Δ

$$V_{i,\,j} = if\left[i = j,\ D[1 - exp[\beta(x_i - x_e)]]^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 3

E_m =

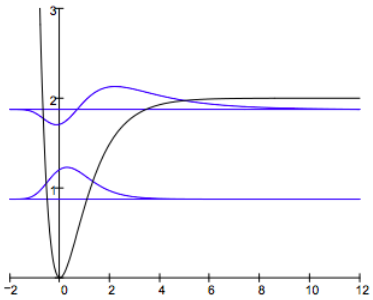
0.8750
1.8750
2.0596

Calculate associated eigenfunctions:

k = 1 .. 3

$$\psi(k) = eigenvec(H, E_k)$$

Plot the potential energy and selected eigenfunctions:



For $V = ax^n$, the virial theorem requires the following relationship between the expectation values for kinetic and potential energy:

$$< T >= 0.5n < V >.$$

The calculations below show that virial theorem is not satisfied for the Morse oscillator. The reason is revealed in the following series expansion in x. The expansion contains cubic, quartic and higher order terms in x, so the virial theorem **does not** apply to the quartic oscillator.

$$D(1 - exp(-\beta x))^2 \text{ converts to the series } D\beta^2 x^2 + (-D)\beta^3 x^3 + \tfrac{7}{12} D\beta^4 x^4 + O(x^5)$$

$$\begin{pmatrix} \text{" } Kinetic\ Energy \text{"} & \text{" } Potential\ Energy \text{"} & \text{" } Total\ Energy \text{"} \\ \psi(1)^T T \psi(1) & \psi(1)^T V \psi(1) & E_1 \\ \psi(2)^T T \psi(2) & \psi(2)^T V \psi(2) & E_2 \end{pmatrix}$$

$$= \begin{pmatrix} \text{" } Kinetic\ Energy \text{"} & \text{" } Potential\ Energy \text{"} & \text{" } Total\ Energy \text{"} \\ 0.3750 & 0.5000 & 0.8750 \\ 0.3754 & 1.4996 & 1.8750 \end{pmatrix}$$

9.13: Numerical Solutions for the Lennard-Jones Potential

Merrill (Am. J. Phys. **1972**, *40*, 138) showed that a Lennard-Jones 6-12 potential with these parameters had three bound states. This is verified by numerical integration of Schrödinger's equation. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

- n = 200
- $x_{min} = 0.75$
- $x_{max} = 3.5$
- $\Delta = \frac{xmax - xmin}{n-1}$
- μ = 1
- σ = 1
- ε = 100

Numerical integration algorithm:

$$i = 1 \,..\, n \quad j = 1 \,..\, n \quad x_i = xmin + (i - 1)\,\Delta$$

$$V_{i,\,j} = if\left[i = j,\ 4\varepsilon\left[\left(\frac{\sigma}{x_i}\right)^1 2 - \left(\frac{\sigma}{x_i}\right)^6\right], 0\right]$$

$$T_{i,\,j} = if\left[i = j, \frac{\pi^2}{6\mu\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 4

E_m =

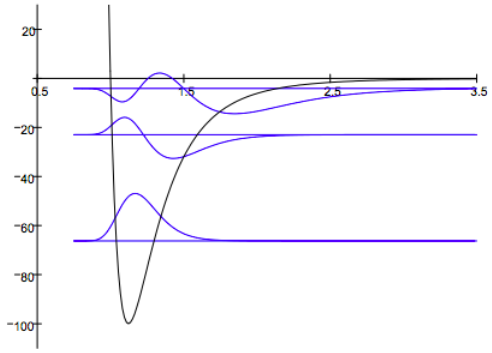
-66.269
-22.981
-4.132
1.096

Calculate eigenvectors:

k = 1 .. 3

$$\psi(k) = eigenvec(H, E_k)$$

Display results:



9.14: Numerical Solutions for the Double Morse Potential

Schrödinger's equation is integrated numerically for the first four energy states for the double Morse oscillator. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

n = 200

xmin = -10

xmax = 10

$$\Delta = \frac{xmax - xmin}{n - 1}$$

μ = 1

D = 2

β = 1

x_0 = 1

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

i = 1 .. n j = 1 .. n x_i = xmin + (i - 1) Δ

$$V_{i,\,j} = if\left[i = j,\ D\left[1 - exp\left[-\beta\left(\left|x_i\right| - x_0\right)\right]\right]^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display four eigenvalues: m = 1 .. 4

E_m =

0.8092
0.9127
1.8284
1.8975

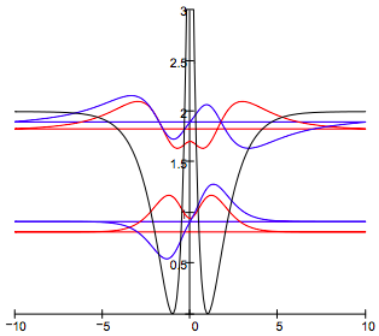
Calculate associated eigenfunctions:

k = 1 .. 4

$$\psi(k) = eigenvec(H, E_k)$$

Plot the potential energy and bound state eigenfunctions:

$$Vpot_i = V_{i,\,i}$$



9.15: Particle in a Box with an Internal Barrier

Numerical integration of Schrödinger's equation:

Potential energy:

$$V(x) = \begin{cases} V_0 \; if \; (x \geq lb)(x \leq rb) \\ 0 \; otherwise \end{cases}$$

Given:

$$\frac{-1}{2\mu}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

$$\psi(0) = 0$$

$$\psi'(0) = 0.1$$

$$\psi = \text{Odesolve}(x, x_{max})$$

Normalize wave function:

$$\psi(x) = \frac{\psi(x)}{\sqrt{\int_0^x \psi(x)^2 dx}}$$

Integration limit: $x_{max} = 1$

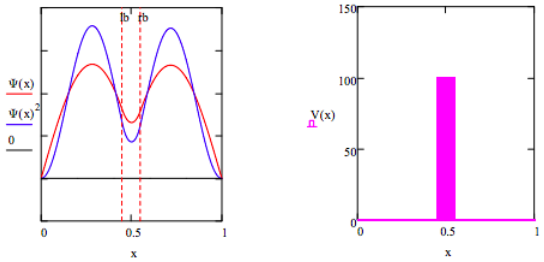
Effective mass: $\mu = 1$

Barrier height: $V_0 = 100$

Barrier boundaries: lb = 0.45

rb = 0.55

Enter energy guess: E = 15.45



Calculate potential energy: $PE = \int_0^1 V(x)\psi(x)^2 dx$ PE = 4.932 $\int_0^1 \psi(x)^2 dx = 1.00$

Calculate kinetic energy: $KE = E - PE$ E = 10.518

Ratio of potential energy to total energy: $\frac{PE}{E} = 0.319$

Calculate probability in barrier: $\frac{PE}{V_0} = 0.049$

$$P = \int_{lb}^{rb} \psi(x)^2 dx = 0.049$$

1. Find the first four energy levels, sketch ψ^2 for each state, and fill in the table below. KE, PE and the probability in the electron is in the barrier are calculated above.

E	KE	PE	P
15.45	10.518	4.932	0.049
20.30	19.827	0.473	0.0047
62.20	47.745	14.455	0.145
80.80	78.968	1.832	0.018

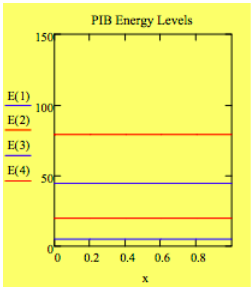
2. Interpret the results for energy in light of the fact that a 100 E_h (2720 eV) potential barrier of finite thickness exists in the center of the box.

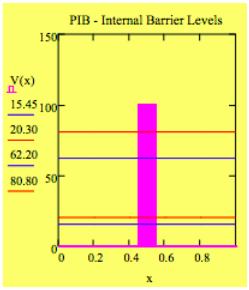
This is an excellent example of quantum mechanical tunneling. For the first four energy states the particle has probability of being found in the tunnel in spite of the fact that its energy is less than the barrier energy.

3. Explain the obvious bunching of energy states in pair in terms of the impact of the internal barrier. In other words why is the probability of being in the potential barrier larger for the n = 1 and 3 states than it is for the n = 2 and 4 states.

The PIB energy levels without an internal barrier are: $E(n) = \frac{\pi^2}{2}n^2$

The bunching can be seen by comparing the two energy manifolds. The n = 2 and 4 states have nodes at the middle of the box where the internal barrier is situated. Thus their potential energy does not increase as much as the n = 1 and 3 states which do not have nodes in the barrier.





4. Find the ground state energy for particle masses of 0.5 and 1.5. Record your results in the table below and interpret them.

$Mass$	E	T	V	P
0.5	23.95	14.411	9.539	0.095
1.0	15.45	10.518	4.932	0.049
1.5	11.55	8.684	2.866	0.029

The higher the mass the lower the energy because in quantum mechanics in $E \sim \frac{1}{mass}$. The greater the mass the lower the probability that tunneling will occur. This is due to the fact that the deBroglie wavelength is inversely proportional to mass.

5. Find the ground state energy for a m = 1 particle for barrier heights 50 and 150 Eh. Record your results in the table below and interpret them.

V_0	E	T	V	P
50	11.97	7.203	4.767	0.095
100	15.45	10.518	4.932	0.049
150	17.32	13.024	4.296	0.029

The higher the barrier energy the higher the ground-state energy and the lower the tunneling probability.

6. On the basis of your calculations in this exercise describe quantum mechanical tunneling. In your answer you should consider the importance of particle mass, barrier height and barrier width. Perform calculations for widths of 0.05 and 0.15 in atomic units.

Tunneling is inversely proportional to mass, barrier height and barrier width.

$Width$	E	T	V	P	$\frac{P}{Width}$
0.05	11.65	7.326	4.324	0.043	0.860
0.10	15.45	10.518	4.932	0.049	0.490
0.15	18.35	13.317	5.033	0.050	0.333

9.16: Another Look at the in a Box with an Internal Barrier

The purpose of this tutorial is to explore the impact of the presence of a large (100 E_h) thin (0.10 a_0) internal barrier on the solutions to the particle-in-a-box (PIB) problem. Schrödinger's equation is integrated numerically for the first five energy states. (Integration algorithm taken form J. C. Hansen, *J. Chem. Educ. Software*, **8C2**, 1996.)

For the one-bohr PIB the energy eigenvalues are:

m = 1 .. 5

$E_m = \frac{m^2\pi^2}{2}$

E^T = (4.935 19.739 44.413 78.957 123.37)

Set parameters:

n = 100

xmin = 0

xmax = 1

$\Delta = \frac{xmax - xmin}{n-1}$

μ = 1

Vo = 100

lb = .45

rb = .55

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

$$i = 1 .. n \quad j = 1 .. n \quad x_i = xmin + (i - 1)\,\Delta$$

Potential energy:

$$V_{i\,j} = if[(x_i \geq lb)(x_i \leq rb), Vo,\ 0]$$

Kinetic energy:

$$T_{i,\,j} = if\left[i = j, \frac{\pi^2}{6\mu\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

$$V_{i,\,j} = if\left[i = j,\ D\left[1 - exp\left[-\beta(|x_i| - x_0)\right]\right]^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j, \frac{\pi^2}{6\mu\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display selected eigenvalues: m = 1 .. 5

E_m =

15.011
19.589
60.453
78.268
137.903

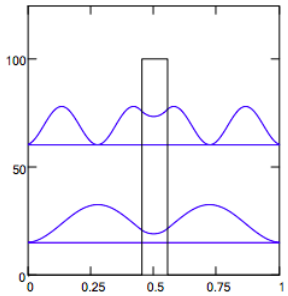
Calculate selected eigenvectors:

k = 1 .. 4

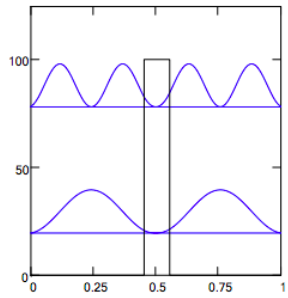
$$\psi(k) = eigenvec(H, E_k)$$

Display probability distributions and energy level manifold in the presence of the internal potential barrier:

n = 1 and n = 3 states:



n = 2 and n = 4 states:



It is clear from the numeric and graphic display of the energy manifold that the presence of the internal barrier causes a bunching of the energy eigenstates for the four lowest levels. This is frequently called "inversion doubling" because of an identical effect that appears in the analysis of the ammonia umbrella inversion. This gives the impression that a second set of quantized energy levels is created by the internal barrier. However, the correct explanation for this bunching is evident in the display of the four lowest wave functions. The presence of the barrier raises all energy levels relative to the simple PIB, but the n = 2 and n = 4 states have nodes in the barrier, thus reducing the barrier's effect on raising the energy. Thus the odd states are raised in energy more than the even states, causing the bunching.

9.17: Particle in a Box with Multiple Internal Barriers

Integration limit: x_{max} = 1

Effective mass: μ = 1

Barrier height: V_0 = 100

Potential energy:

$$V(x) = \begin{cases} V_0 \text{ if } (x \geq .185)(x \leq .215) + (x \geq .385)(x \leq .415) + (x \geq .585)(x \leq .615) + (x \geq .785)(x \leq .815) \\ 0 \text{ otherwise} \end{cases}$$

Numerical integration of Schrödinger's equation:

Given

$$\frac{-1}{2\mu}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

$$\psi(0) = 0$$

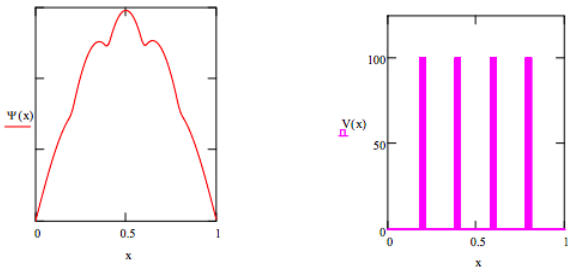
$$\psi'(0) = 0.1$$

$$\psi = Odesolve(x, x_{max}$$

Normalize wave function:

$$\psi(x) = \frac{\psi(x)}{\sqrt{\int_0^{x_{max}} \psi(x)^2 dx}}$$

Enter energy guess: E = 18.85



Calculate kinetic energy:

$$T = \int_0^1 \psi(x)\frac{-1}{2}\frac{d^2}{dx^2}\psi(x)dx = 5.926$$

Calculate potential energy:

$$V = E - T = 12.924$$

Tunneling probability:

$$\frac{V}{V_0} \times 100 = 12.924$$

9.18: Particle in an Infinite Spherical Potential Well

Reduced mass: μ = 1

Angular momentum: L = 2

Integration limit: r_{max} = 1

Solve Schrödinger's equation numerically. Use Mathcad's ODE solve block:

Given

$$\frac{-1}{2\mu}\frac{d^2}{dr^2}\psi(r) - \frac{1}{r\mu}\frac{d}{dr}\psi(r) + \left[\frac{L(L+1)}{2\mu r^2}\right]\psi(r) = E\psi(r) \quad \psi(.0001) = .1 \quad \psi'(.0001) = 0$$

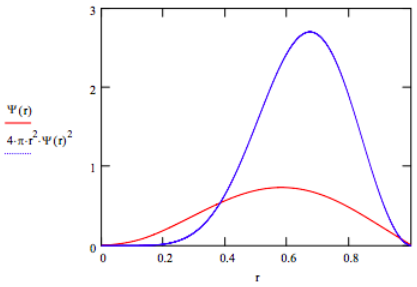
$$\psi = Odesolve(r, r_{max})$$

Normalize the wavefunction:

$$\psi(r) = \left(\int_0^{r_{max}} \psi(r)^2 4\pi r^2 dr\right)^{\frac{-1}{2}} \psi(r)$$

Energy guess: E = 16.51

r = 0, .001 .. r_{max}



9.19: Numerical Solutions for the Two-Dimensional Harmonic Oscillator

Reduced mass: μ = 1

Angular momentum: L = 2

Integration limit: r_{max} = 5

Force constant: k = 1

Energy guess: E = 3

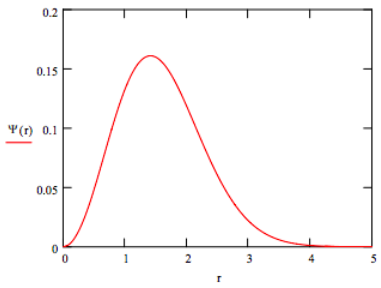
Solve Schrödinger's equation numerically. Use Mathcad's ODE solve block:

Given

$$\frac{-1}{2\mu}\frac{d^2}{dr^2}\psi(r) - \frac{1}{2\mu}\frac{d}{dr}\psi(r) + \left(\frac{L^2}{2\mu r^2} + \frac{1}{2}kr^2\right)\psi(r) = E\psi(r) \quad \psi(.001) = 1 \quad \psi'(.001) = 0.1$$

$$\psi = Odesolve(r, r_{max}, .001)$$

$$\psi(r) = \left(\int_0^{r_{max}} \psi(r)^2 4\pi r^2 dr\right)^{\frac{-1}{2}} \psi(r)$$



9.20: Numerical Solutions for the Three-Dimensional Harmonic Oscillator

Reduced mass: μ = 1

Angular momentum: L = 0

Integration limit: r_{max} = 6

Force constant: k = 1

Solve Schrödinger's equation numerically. Use Mathcad's ODE solve block:

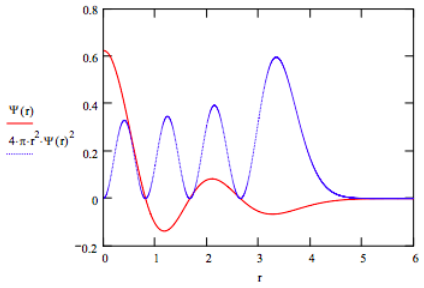
Given

$$\frac{-1}{2\mu}\frac{d^2}{dr^2}\psi(r) - \frac{1}{r\mu}\frac{d}{dr}\psi(r) + \left[\frac{L(L+1)}{2\mu r^2} + \frac{1}{2}kr^2\right]\psi(r) = E\psi(r) \quad \psi(.001) = 1 \quad \psi'(.001) = 0.1$$

$$\psi = Odesolve(r, r_{max})$$

$$\psi(r) = \left(\int_0^{r_{max}} \psi(r)^2 4\pi r^2 dr\right)^{\frac{-1}{2}} \psi(r)$$

Energy guess: E = 7.5



9.21: Numerical Solutions for the Hydrogen Atom Radial Equation

Reduced mass: μ = 1

Angular momentum: L = 0

Integration limit: r_{max} = 18

Nuclear charge: Z = 1

Solve Schrödinger's equation numerically. Use Mathcad's ODE solve block:

Given

$$\frac{-1}{2\mu}\frac{d^2}{dr^2}\psi(r) - \frac{1}{r\mu}\frac{d}{dr}\psi(r) + \left[\frac{L(L+1)}{2\mu r^2} + \frac{1}{2}kr^2\right]\psi(r) = E\psi(r) \quad \psi(.0001) = .1 \quad \psi'(.0001) = 0.1$$

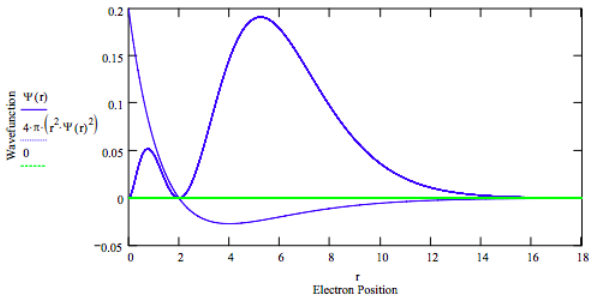
$$\psi = Odesolve(r, r_{max})$$

Normalize wave function:

$$\psi(r) = \left(\int_0^{r_{max}} \psi(r)^2 4\pi r^2 dr\right)^{\frac{-1}{2}} \psi(r)$$

Energy guess:

E = -.125 r = 0, .001 .. r_{max}



Calculate average position:

$$\int_0^{r_{max}} \psi(r) r \psi(r) 4\pi r^2 dr = 5.997$$

Calculate kinetic energy:

$$\int_0^{r_{max}} \psi(r)\left[\frac{-1}{2\mu}\frac{d^2}{dr^2}\psi(r) - \frac{1}{r\mu}\frac{d}{dr}\psi(r) + \left[\frac{L(L+1)}{2\mu r^2}\right]\psi(r)\right] 4\pi r^2 dr = 0.125$$

Calculate potential energy:

$$\int_0^{r_{max}} \psi(r)\frac{-Z}{r}\psi(r) 4\pi r^2 dr = -0.25$$

9.22: Numerical Solutions for a Modified Harmonic Potential

This tutorial deals with the following potential function:

$$V(x,d) = \begin{cases} \frac{1}{2}k(x-d)^2 \; if \; x \geq 0 + d \leq 0 \\ \infty \; otherwise \end{cases}$$

If d = 0 we have the harmonic oscillator on the half-line with eigenvalues 1.5, 3.5, 5.5, ... for k = μ = 1. For large values of d we have the full harmonic oscillator problem displaced in the x-direction by d with eigenvalues 0.5, 1.5, 2.5, ... for k = μ = 1. For small to intermediate values of d the potential can be used to model the interaction of an atom or molecule with a surface.

Integration limit: x_{max} = 10

Effective mass: μ = 1

Force constant: k = 1

Potential energy minimum: d = 5

Potential energy:

$$V(x,d) = \frac{k}{2}(x-d)^2$$

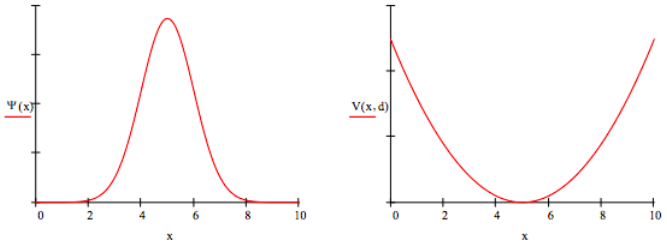
Integration algorithm:

Given

Normalize wavefunction:

$$\psi(x) = \frac{\psi(x)}{\sqrt{\int_0^{x_{max}} \psi(x)^2 dx}}$$

Energy guess: E = 0.5



Calculate average position:

$$X_{avg} = \int_0^{x_{max}} \psi(x) x \psi(x) dx = 5$$

Calculate potential and kinetic energy:

$$V_{avg} = \int_0^{x_{max}} \psi(x) V(x,d) \psi(x) dx = 0.25$$

$$T_{avg} = E - V_{avg} = 0.25$$

Exercises:

- For d = 0, k = μ = 1 confirm that the first three energy eigenvalues are 1.5, 3.5 and 5.5 E_h. Start with x_{max} = 5, but be prepared to adjust to larger values if necessary. xmax is effectively infinity.
- For d = 5, k = μ = 1 confirm that the first three energy eigenvalues are 0.5, 1.5 and 2.5 Eh. Start with x_{max} = 10, but be prepared to adjust to larger values if necessary.

- Determine and compare the virial theorem for the exercises above.
- Calculate the probability that tunneling is occurring for the ground state for the first two exercises. (Answers: 0.112, 0.157)
