Project 1: Semiclassical quantisation of molecular vibrations

Computational Physics PHYC30012
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Aim

In this project we aim to find the energies of molecular vibration of the hydrogen molecule in the Bohr semi-classical approximation. This essentially involves finding the roots of Equation 1 i.e. root-finding.

$$s(\varepsilon_n) = \gamma \int_{x_{in}}^{x_{out}} [\varepsilon_n - v(x)]^{1/2} \, dx - \left(n + \frac{1}{2} \right) \pi \qquad \text{(Equation 1)}$$

This is an integral which cannot be solved analytically, which is why we employ computational methods.

Analytic values for x_{in} and x_{out} are found by solving Equations 2 and 3. Other variables used in Equation 1 are defined as shown in Equations group 4, where V_0 is the potential at equilibrium, and a is the equilibrium position.

$$\varepsilon_n - v(x_{in}) = 0 \qquad \text{(Equation 2)}$$

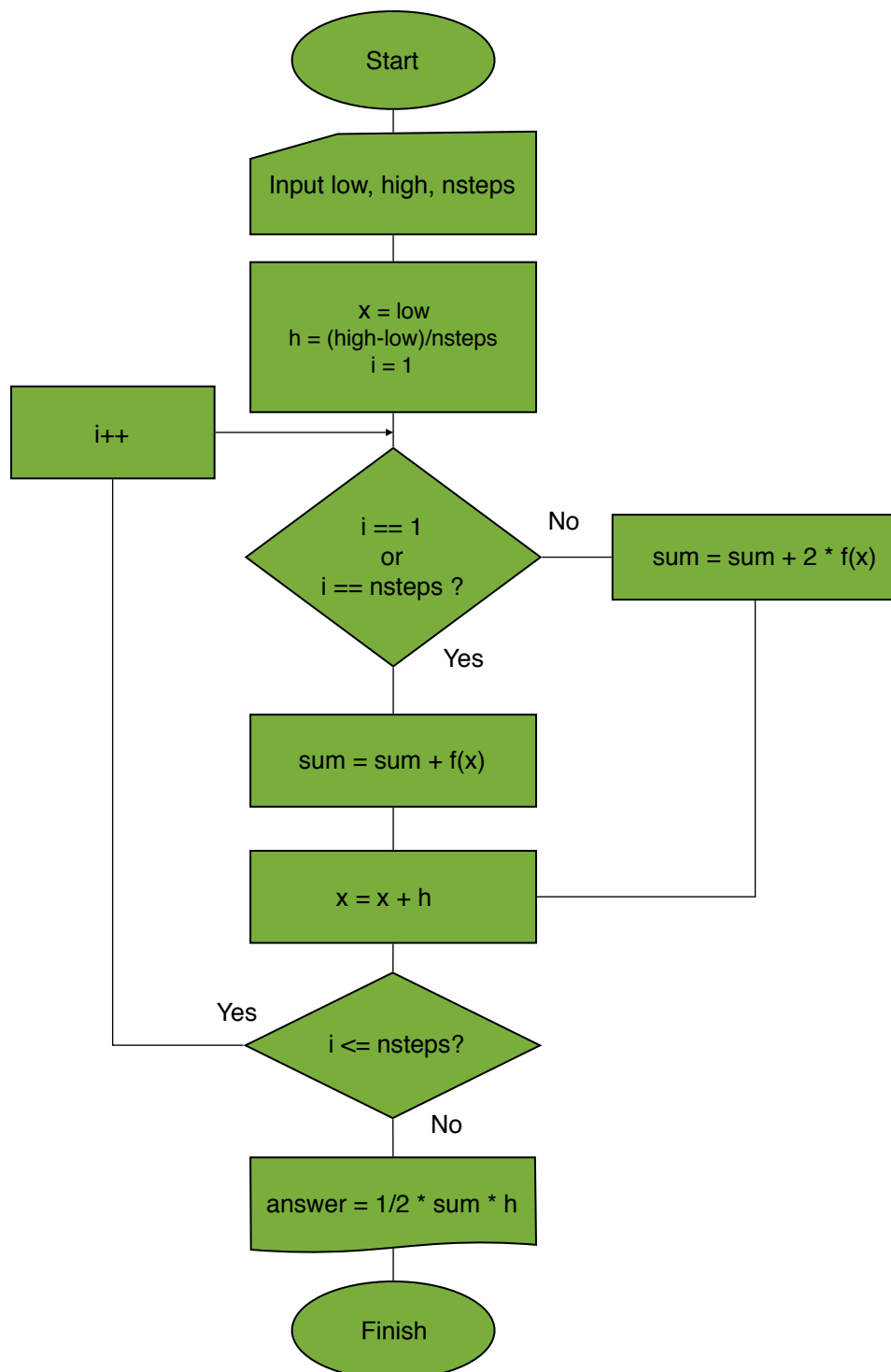$$\varepsilon_n - v(x_{out}) = 0 \qquad \text{(Equation 3)}$$

$$\varepsilon_n \equiv E_n / V_0 , \quad v(r) \equiv V(r)/V_0 , \quad x \equiv r/a \qquad \text{(Equations group 4)}$$

Method

1. First, methods were developed to computationally calculate integrations using three different types of quadrature method:
   1. Rectangular
   2. Trapezoidal and
   3. Simpson
2. The relative accuracies of these integration methods was explored for different step-sizes.
3. A scan function was implemented that, given an initial guess for x, would scan a given function f(x) to find values x_{i-1} and x_i for which f(x) straddles the x axis.
4. A root-finding function was then implemented which used these values x_{i-1} and x_i to find accurate roots of f(x) using the false position method.
5. The accuracy of the root-finding algorithm was explored for different values of the relevant parameters.
6. This root-finding function was then used to find the roots of a quadratic function and compare them to the analytically derived values. Refer to Appendix 1 for derivations.
7. The root-finding function was then used to find roots of the Morse potential for the hydrogen atom, and compare them to experimental values.
8. The plotting package cpgplot was used to plot the Morse potential and the experimental vibrational energy levels of the hydrogen molecule. Refer to Appendix 2.

Results

FIGURE 1 - A FLOW CHART FOR THE TRAPEZOIDAL RULE.

Start

Input low, high, nsteps

x = low
h = (high-low)/nsteps
i = 1

i++

i == 1
or
i == nsteps ?

No → sum = sum + 2 * f(x)

Yes

sum = sum + f(x)

x = x + h

i <= nsteps?

Yes

No

answer = 1/2 * sum * h

Finish

The results of the Trapezoidal and Simpson rules for numerical integration of Equation 5 are shown in Figure 2. The analytic value of this integral is 0.822467 (6 dp).
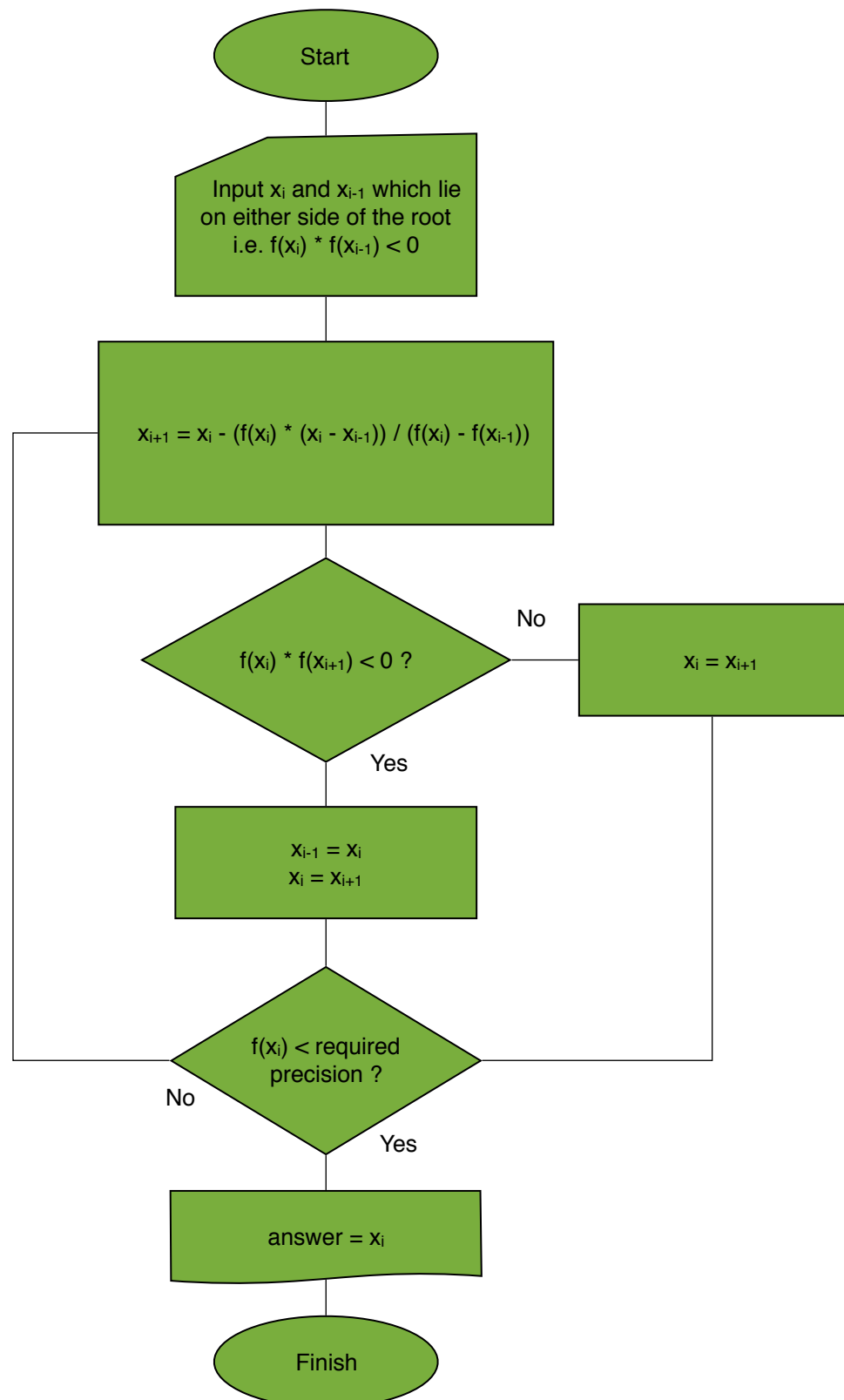
$$\int_0^1 \frac{\ln(1+x)}{x}\,dx = \frac{\pi^2}{12}$$ (Equation 5)

Step size	Trap Int	Abs Trap Diff	Trap Diff	Simp Int	Abs Simp Diff	Simp Diff
1.000000	0.500000	-0.322467	-39.207288 %	0.333333	-0.489134	-59.471525 %
0.100000	0.752407	-0.070060	-8.518318 %	0.728046	-0.094421	-11.480247 %
0.010000	0.815528	-0.006939	-0.843630 %	0.813206	-0.009261	-1.126041 %
0.001000	0.821774	-0.000693	-0.084282 %	0.821543	-0.000924	-0.112389 %
0.000100	0.822398	-0.000069	-0.008424 %	0.822375	-0.000092	-0.011234 %
0.000010	0.822460	-0.000007	-0.000839 %	0.822458	-0.000009	-0.001120 %
0.000001	0.822466	-0.000001	-0.000081 %	0.822466	-0.000001	-0.000109 %

FIGURE 2 - TABLE OF COMPUTATIONAL VALUES FOR THE INTEGRAL IN EQUATION 2 CALCULATED FOR DIFFERENT STEP SIZES USING THE TRAPEZOIDAL AND SIMPSON METHODS, AND COMPARED TO THE ANALYTIC VALUE.

We can clearly see that both integration styles increase rapidly in accuracy with reduction in step size. We can also see that Trapezoidal is more accurate than Simpson for all step sizes, with a smaller percentage error, despite the fact that theoretically the reverse is true. This may be due to programming error, or peculiarities due to the choice of integral.

FIGURE 3 - A FLOW-CHART FOR THE FALSE-POSITION ROOT-FINDING ALGORITHM.

Start

Input x_i and x_{i-1} which lie on either side of the root i.e. $f(x_i) * f(x_{i-1}) < 0$

$x_{i+1} = x_i - (f(x_i) * (x_i - x_{i-1})) / (f(x_i) - f(x_{i-1}))$

$f(x_i) * f(x_{i+1}) < 0$?

No

$x_i = x_{i+1}$

Yes

$x_{i-1} = x_i$
$x_i = x_{i+1}$

$f(x_i) <$ required precision ?

No

Yes

answer $= x_i$

Finish

Values of the non-zero root of Equation 6 using the false position algorithm are shown in Figure 4.

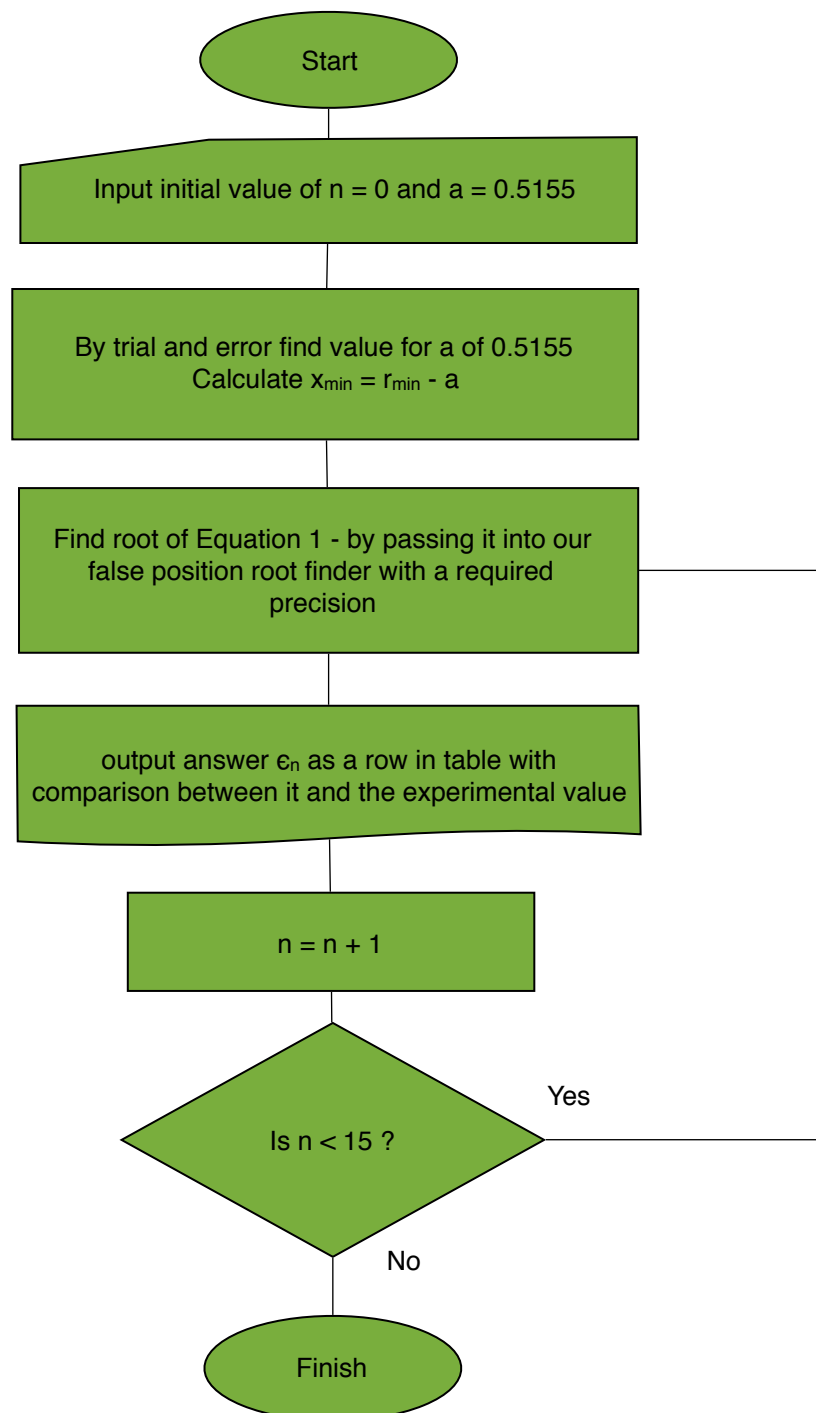$$f(x) = \int_0^x t^2\, dt - x \qquad \text{(Equation 6)}$$

Starting Pos	Step Size	Tolerance	Divisions in integral	Found Root	Abs diff cf analytic value	Perc Diff cf analytic value
	Roots found with False Position using the Simpson integration method:					
2	0.100000	0.010000	100000	1.731583	-0.000468	-0.027013 %
2	0.100000	0.010000	1000000	1.731551	-0.000499	-0.028835 %
2	0.100000	0.001000	100000	1.732078	0.000027	0.001555 %
2	0.100000	0.001000	1000000	1.732047	-0.000004	-0.000246 %
2	0.010000	0.010000	100000	1.730000	-0.002051	-0.118403 %
2	0.010000	0.010000	1000000	1.730000	-0.002051	-0.118403 %
2	0.010000	0.001000	100000	1.732080	0.000029	0.001696 %
2	0.010000	0.001000	1000000	1.732049	-0.000002	-0.000102 %
3	0.100000	0.010000	100000	1.731583	-0.000468	-0.027013 %
3	0.100000	0.010000	1000000	1.731551	-0.000499	-0.028835 %
3	0.100000	0.001000	100000	1.732078	0.000027	0.001555 %
3	0.100000	0.001000	1000000	1.732047	-0.000004	-0.000246 %
3	0.010000	0.010000	100000	1.730000	-0.002051	-0.118403 %
3	0.010000	0.010000	1000000	1.730000	-0.002051	-0.118403 %
3	0.010000	0.001000	100000	1.732080	0.000029	0.001696 %
3	0.010000	0.001000	1000000	1.732049	-0.000002	-0.000102 %
	Smallest difference between root found with False Position, and the analytic value:					
3	0.010000	0.001000	1000000	1.732049	-0.000002	-0.000102 %
	The root found using Rectangular Integration method with same values has a larger error, indicating that this method is less accurate than Simpson.					
3	0.010000	0.001000	1000000	1.732045	-0.000005	-0.000310%
	The root found using Trapezoidal integration method with same values also has a larger error, indicating that this method is less accurate than Simpson.					
3	0.010000	0.001000	1000000	1.732046	-0.000005	-0.000287%

FIGURE 4 - TABLE OF THE NON-ZERO ROOT OF EQUATION 6 FOUND COMPUTATIONALLY FOR DIFFERENT STEP SIZES, TOLERANCE AND NUMBER OF DIVISIONS IN THE INTEGRAL, USING FALSE POSITION ALGORITHM AND SIMPSON INTEGRATION METHOD, COMPARING THE BEST RESULT WITH THAT FOUND USING RECTANGULAR AND TRAPEZOIDAL METHODS.

As seen in Figure 4 above, the most accurate value for the root was found using Simpson with a starting position of 3, step size of 0.001, and number of steps of 1×10^6. This was also shown to be more accurate than the roots found using using Rectangular and Trapezoidal methods with the same values.

For the analytic turning points and vibrational energy levels for the quadratic potential, refer to Appendix 1.

FIGURE 5 - FLOWCHART FOR AN ALGORITHM TO NUMERICALLY SOLVE EQUATION 1 FOR THE VIBRATIONAL ENERGY LEVELS.

Start

Input initial value of n = 0 and a = 0.5155

By trial and error find value for a of 0.5155
Calculate $x_{min} = r_{min} - a$

Find root of Equation 1 - by passing it into our false position root finder with a required precision

output answer ϵ_n as a row in table with comparison between it and the experimental value

n = n + 1

Is n < 15 ?

Yes

No

Finish

We then tested our root finding methodology for the vibration energy levels by numerically solving Equation 1 using the quadratic potential of Equation 7, for various root finding tolerances and the number of divisions in the integral. The analytic solution depending on n is given in Equation 8.

$$v(x) = 4(x-1)(x-2)$$ (Equation 7)

$$\varepsilon_n = 4n+1$$ (Equation 8)

n	Tolerance	Divisions in integral	Found Root	Abs Diff	Perc Diff
0	0.010000	10000	1.000006	0.000006	0.000589 %
0	0.010000	100000	1.000000	0.000000	0.000015 %
0	0.001000	10000	1.000006	0.000006	0.000589 %
0	0.001000	100000	1.000000	0.000000	0.000015 %
1	0.010000	10000	5.000018	0.000018	0.000353 %
1	0.010000	100000	5.000000	0.000000	0.000009 %
1	0.001000	10000	5.000018	0.000018	0.000353 %
1	0.001000	100000	5.000000	0.000000	0.000009 %
2	0.010000	10000	9.000029	0.000029	0.000327 %
2	0.010000	100000	9.000001	0.000001	0.000009 %
2	0.001000	10000	9.000029	0.000029	0.000327 %
2	0.001000	100000	9.000001	0.000001	0.000009 %
3	0.010000	10000	13.000041	0.000041	0.000317 %
3	0.010000	100000	13.000001	0.000001	0.000008 %
3	0.001000	10000	13.000041	0.000041	0.000317 %
3	0.001000	100000	13.000001	0.000001	0.000008 %
	Smallest difference between root found with False Position, and the analytic value:				
3	0.001000	100000	13.000001	0.000001	0.000008 %

FIGURE 6 - TABLE OF COMPUTATIONAL VALUES FOR THE ROOTS OF THE QUADRATIC POTENTIAL, EQUATION 4, COMPARED TO THE ANALYTIC VALUE.

We found the best results were achieved by starting with a guess that is close to the analytic solution, and use the smallest practical step size.

For the derivation of the analytic turning points for the Morse potential, refer to Appendix 1.

We adjusted our program to compute vibrational energies for molecular Hydrogen. The value of a that fits the first energy level spacing E_0 is

$$a = 0.5155 \text{ Å} \qquad \text{(Equation 9)}$$

found through trial and error. We then used this value to solve for the higher energy levels.

Constants used

$V_o = 4.747$
$r_{min} = 0.74166 \text{ Å}$
$\gamma = 33.6567 \text{ x } a = 17.350028 \text{ (6 dp)}$

n	Comp E_n	Exper E_n	Abs Diff	Percent Diff
0	-4.477340	-4.477000	-0.000340	0.007600%
1	-3.961674	-3.962000	0.000326	-0.008218%
2	-3.477548	-3.475000	-0.002548	0.073325%
3	-3.024961	-3.017000	-0.007961	0.263884%
4	-2.603915	-2.587000	-0.016915	0.653857%
5	-2.214412	-2.185000	-0.029412	1.346075%
6	-1.856444	-1.811000	-0.045444	2.509355%
7	-1.530006	-1.466000	-0.064006	4.366029%
8	-1.235116	-1.151000	-0.084116	7.308047%
9	-0.971761	-0.867000	-0.104761	12.083180%
10	-0.739950	-0.615000	-0.124950	20.317115%
11	-0.539675	-0.400000	-0.139675	34.918773%
12	-0.370943	-0.225000	-0.145943	64.863603%
13	-0.233748	-0.094000	-0.139748	148.667573%
14	-0.128091	-0.017000	-0.111091	653.478459%

FIGURE 7 - TABLE OF COMPUTATIONALLY DERIVED VALUES OF E_N FOR THE HYDROGEN MOLECULE, ROOTS OF EQUATION 1 WHICH HAVE THEN BEEN SCALED BY MULTIPLICATION BY V_O = 4.747, COMPARED TO THE EXPERIMENTAL SPECTRUM.

When compared to the experimental energy spectrum for the hydrogen molecule, the computational results shown in Figure 7 started very close to the experimental spectrum with an error of 0.00760% (3 sf) for low values of n, increasing up to an error of 653% (3 sf) for n up to 15. This could either be due to error in implementing the algorithms, limitations of the computational mythology used, or limitations of the Morse potential itself in describing the experimental energy spectrum.

Conclusion

We have implemented a variety of computational methods for numerical integration. We found that the Simpson method for numerical integral calculation is usually more accurate than Rectangular and Trapezoidal, but not always.

We have also implemented a root-finding algorithm using the false-position method, which can compute physically useful results, as well as solve problems which are analytically intractable. Comparing the results of computational root-finding with analytic results has led to insight into how numerical calculation depends on various input factors e.g. starting position, step size, tolerance and number of divisions in the integral.

Comparing the results of computational root-finding of the energy levels of molecular vibration of the hydrogen molecule with experimental data shows that for low values of n, the false-position root-finding method gives accurate results. For higher values of n, the root-finding algorithm may in part be the reason for the discrepancies between the numerical and experimental results. Other sources of error here may include problems with programming implementation of algorithms, as well as limitations of the Morse potential in modelling the physical system.

Appendix 1

Derivation of the analytic turning points and vibrational energy levels for the quadratic potential, and of the analytic turning points for the Morse potential.

Comp.

Project 1. ie $v(x) = 4(x-1)(x-2)$

With $V(r) = 4V_0 \left(\frac{r}{a} - 1\right)\left(\frac{r}{a} - 2\right)$

$E_n - V(r_{in}) = 0$. ie $e_n(x_{in})$ $V(x_{in}) = 0$.

$\Rightarrow e_n(x_{in}) = 4(x_{in} - 1)(x_{in} - 2) \Rightarrow 4(x_{in} - 1)(x_{in} - 2) - e_n(x_{in}) = 0$

$E_n - V(r_{out}) = 0$ ie $e_n(x_{out}) = 4(x_{out} - 1)(x_{out} - 2)$

$4(x_{out} - 1)(x_{out} - 2) - e_n(x_{out}) = 0$

$$E_n - 4\left(\frac{r}{a} - 1\right)\left(\frac{r}{a} - 2\right) = 0$$

$$E_n - 4\left(\frac{r^2}{a^2} - 3\frac{r}{a} + 2\right) = 0.$$

$r_{in} = (\ ) + \sqrt{}$

$r_{out} = (\ ) - \sqrt{}$

Charting : draw.io.

$$E_n a^2 - 4(r^2 - 3ra + 2a^2) = 0.$$

$$\frac{E_n a^2}{4} - r^2 + 3ra - 2a^2 = 0.$$

$$r^2 - 3ra + \left(2a^2 - \frac{E_n a^2}{4}\right) = 0.$$

$$\Rightarrow r = \left(3a \pm \sqrt{9r^2 a^2 - 8a^2 + E_n a^2}\right)/2.$$

$$8x^2 + tx + a = 0$$

$$x = -\frac{t \pm \sqrt{t^2 - 4su}}{2s}$$

$$\Rightarrow r = \frac{30a}{2} \pm \sqrt{90a^2 - 32 + E_n a^2}$$

$$\text{ie } r_{in} = \frac{30a \pm \sqrt{90a^2 - 8a + E_n a^2}}{2}$$

$$r_{out} = \frac{30a + \sqrt{90a^2 - 8a + E_n a^2}}{2}$$

$$E_n a^2 - 4r^2 + 12ra - 8a^2 = 0.$$
$$4r^2 - 12ra + (8a^2 - E_n a^2) = 0.$$

$$\Rightarrow r = \frac{12a \pm 4\sqrt{144a^2 - 16(8a^2 - E_n a^2)}}{8}$$

$$= \frac{30a \pm \frac{1}{4}\sqrt{4(360a^2 - 4(8a^2 - E_n a^2)}}{2}$$

$$= \frac{30a \pm \frac{1}{2}\sqrt{360a^2 - 4(8a^2 - E_n a^2)}}{2}$$

$$= \frac{30a \pm \frac{1}{2}\sqrt{4(90a^2 - 8a^2 + E_n a^2)}}{2}$$

$$= \frac{30a \pm \sqrt{9a^2 - 8a^2 + E_n a^2}}{2} \qquad \checkmark\checkmark$$

$$= \frac{3a \pm \sqrt{a^2 + E_n a^2}}{2} = \frac{3a \pm \sqrt{a^2(1 + E_n)}}{2}$$

$$\text{ie } x = \frac{r}{a} = \frac{3 \pm \sqrt{1 + E_n}}{2}$$

$$\Rightarrow 4a^2 x^2 - 12a^2 x + a^2(8 - E_n) = 0.$$

$$\Rightarrow \text{Solve} \quad s(\varepsilon_n) = \int_{x_{in}}^{x_{out}} \left(\varepsilon_n - v(x)\right)^{1/2} dx - \left(n+\tfrac{1}{2}\right)\pi$$

$$= \int_{x_{in}}^{x_{out}} \left[\varepsilon_n - 4(x-1)(x-2)\right]^{1/2} dx - \left(n+\tfrac{1}{2}\right)\pi.$$

Integrand $I = \left[\varepsilon_n - 4x^2 + 12x - 8\right]^{1/2}$

$$= \left[-4x^2 + 12x + (\varepsilon_n - 8)\right]^{1/2}.$$

$$\Rightarrow \int_{x_{in}}^{x_{out}} I \, dx = \frac{\left[4 \times (-4) \times (\varepsilon_n - 8) - 144\right]\pi}{8 \times (-4)\sqrt{4}}$$

$$= \frac{\left(-16(\varepsilon_n - 8) - 144\right)\pi}{-32\sqrt{4}}$$

$$= \frac{\left(16\varepsilon_n - 8 \cdot 16 + 144\right)\pi}{32\sqrt{4}}$$

$$= \frac{\left(\varepsilon_n - 8 + 9\right)\pi}{2\sqrt{4}} = \frac{(\varepsilon_n + 1)\pi}{2\sqrt{4}} = \frac{(\varepsilon_n + 1)\pi}{4}.$$

$$\Rightarrow s(\varepsilon_n) = \frac{(\varepsilon_n + 1)\pi}{4} - \left(n + \tfrac{1}{2}\right)\pi = 0.$$

$$\Rightarrow (\varepsilon_n + 1)\pi = 4\left(n + \tfrac{1}{2}\right)\pi$$

$$\varepsilon_n + 1 = 4\left(n + \tfrac{1}{2}\right)$$

$$\underline{\varepsilon_n = 4n + 2 - 1 = 4n + 1.}$$

(c) $\quad V_{Morse}(r) = V_0\left[\left(1 - e^{-(r - r_{min})/a}\right)^2 - 1\right]$

Turning points: $\varepsilon_n - V(r_{\text{m}}) = 0$ ~~~~~~~~~~~~~~

$$\epsilon_n = \frac{E_n}{V_0} = V_0\left[\left(1 - e^{-(r - r_{min})/a}\right)^2 - 1\right]$$

$$E_n - V_0\left[\left(1 - e^{-(r - r_{min})/a}\right)^2 - 1\right] = 0.$$

$$\left(1 - e^{-(r - r_{min})/a}\right)^2 = \epsilon_n + 1.$$

$$1 - e^{-(r - r_{min})/a} = \pm\sqrt{\epsilon_n + 1}.$$

$$e^{-(r - r_{min})/a} = 1 \pm \sqrt{\epsilon_n + 1}.$$

$$-(r - r_{min})/a = \ln\left(1 \pm \sqrt{\epsilon_n + 1}\right)$$

$$r - r_{min} = -a\ln\left(1 \pm \sqrt{\epsilon_n + 1}\right)$$

$$r = r_{min} - a\ln\left(1 \pm \sqrt{\epsilon_n + 1}\right).$$

$$x = \frac{r}{a} \Rightarrow r = xa$$

$$\Rightarrow x = \frac{1}{a}\left[r_{min} - a\ln\left(1 \pm \sqrt{\epsilon_n + 1}\right)\right].$$

Also $V_{Morse}(x) = \left[\left(1 - e^{-(x - r_{min}/a)}\right)^2 - 1\right].$

$$= \left(1 - e^{-(x - r_{min}/a)}\right)^2 - 1.$$

$$x = x_{min} - \ln\left(1 \pm \sqrt{\epsilon_n + 1}\right)$$

Appendix 2

A plot made using scientific plotting package cpgplot of the Morse potential and the experimental vibrational energy levels of the hydrogen molecule.

Experimental vibrational energy levels of the Hydrogen molecule