

# Application of Shooting Method to Solve the Schrödinger Equation

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## Abstract

In this work the numerical solution of the eigenvalue problems are obtained through the shooting algorithm, which is applied to solve to the time-independent Schrödinger Equation for the one dimensional harmonic oscillator and the radial wavefunctions of the hydrogen atom. The results are discussed and compared to the respective analytical solutions of obtained via pure mathematical handling and physical argumentation.

## Introduction

A wide variety of situations in physics happens to be expressed by second order differential equations, which are not always solvable. In such cases, the numerical approach is necessary in order to study the system.

As a subclass of second order differential equation, there are the eigenvalue problems, which involves the determination of the eigenvalues to which the solutions of the equation of the problem obeys the boundary conditions, i.e., the spatial restrictions of the problem [6].

The problem treated in this work is the quantum harmonic oscillator which is an example of both eigenvalue determination and root solving problem; as it will be better explained in the following sections [4].

First, one solves the harmonic oscillator analytically via Fröbenius method [5], in which one rewrites the wavefunction as a power series. As this new wavefunction is substituted in the Schrödinger equation, a recursion relation between the series terms appears so that one can analyze the even and odd terms, whose parity relates to the states parity. The solution of the radial part of the Schrödinger equation for the hydrogen atom are the so called hydrogen atom radial wavefunctions and they represent the behavior of the wavefunction given a  $n$  and a  $l$ . These are obtained in the same way the harmonic oscillator both analytical and numerical solutions.

In the numerical resolution of this problem, one uses the shooting method together with the bisection method as a root solver in order to obtain both the eigenvalues and wavefunctions subject to the initial and boundary conditions [2].

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## The Shooting Algorithm

Consider, for instance, the time-independent one dimensional Schrödinger equation,

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

Let  $V(x)$  remain undefined and  $\psi(x)$  be the eigenstate of the problem, one can then rewrite the the above equation such that

$$-\frac{\hbar}{2m} \frac{d^2\psi(x)}{dx^2} + [V(x) - E] \psi(x) = 0 \quad (2)$$

Now one need to solve the above equation for the eigenvalues  $E$  and the eigenstates  $\psi(x)$  for and  $V(x)$ .

The idea is to expand the second order derivatives by using the finite difference method, hence

$$\lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \frac{df}{dx} \quad (3)$$

Which,

$$\frac{df}{dx} \approx \frac{\Delta f}{\Delta x} = \frac{f(x + \delta x) - f(x - \delta x)}{2\delta x} = \quad (4)$$

$$\frac{d^2f}{dx^2} \approx \frac{1}{2\delta x} \left( \frac{df}{dx} \Big|_{x+\delta x} - \frac{df}{dx} \Big|_{x-\delta x} \right) \quad (5)$$

Now applying the difference method one obtains

$$\frac{d^2f}{dx^2} \approx \frac{f(x + \delta x) - 2f(x) + f(x - \delta x)}{(\delta x)^2} \quad (6)$$

Now substituting the above expression in the Schrödinger equation [7], one obtains

$$-\frac{\hbar}{2m} \left[ \frac{\psi(x + \delta x) - 2\psi(x) + \psi(x - \delta x)}{(\delta x)^2} \right] + [V(x) - E] \psi(x) = 0 \quad (7)$$

Hence,

$$\psi(x + \delta x) - 2\psi(x) + \psi(x - \delta x) = \frac{2m}{\hbar^2} (\delta x)^2 [V(x) - E] \psi(x) = 0 \quad (8)$$

Simplifying the expression, one has that

$$\psi(x + \delta x) = \frac{2m}{\hbar^2}(\delta x)^2 [V(x) - E] \psi(x) - \psi(x - \delta x) \quad (9)$$

The above expression says that if one knows the  $\psi(x - \delta x)$  and  $\psi(x)$ ,  $\psi(x + \delta x)$  can be determined for any eigenenergy  $E$ . The Shooting Method is the iterative raffle of initial conditions and eigenenergies and the correct matching with the problem's initial conditions[].

Starting with the two known values of  $\psi(x)$  a third value is predicted, which is to be used in the next iteration allowing the prediction of a fourth value; this procedure is successively applied by a choosen energy  $E$ . The solutions must satisfy the boundary conditions below;

$$\psi(x \rightarrow \infty) \rightarrow 0; \frac{\partial}{\partial x} \psi(x \rightarrow \infty) \rightarrow 0$$

For a symmetric  $V(x)$ , so are problem's eigenstates. Suppose a state with odd parity [7], the first excited state of a symmetric quantum well, seen in figure (), it must be zero at the middle of the well, due to its parity. This way, a small displacement along the  $x$  direction,  $\psi(x)$  must have a finite value, whose magnitude is not significant due to the normalization of  $\psi$ . Starting with the following boundary conditions:

$$\psi(0) = 0; \psi(\delta x) = 1$$

Now it is necessary to find  $E$  [3], which is the value that guarantees the  $\psi(x)$  satisfies the boundary conditions above. Since  $E$  is unknown,  $\psi$  is a function of  $x$  and  $E$ . Now, one must look for solutions that obeys

$$\psi(\infty, E) = 0$$

Whose values can be determined via any root solver.

In the case where the eigenstate has even parity, the wave function has a non-zero value at  $x=0$ . Hence,  $\psi(0) = 1$  is a nice choice. Also,  $\psi(x)$  is symmetric, i.e.,  $\psi(\delta x) = \psi(-\delta x)$ , which when substituted into (), yields:

$$\psi(\delta x) = \left( \frac{2m}{\hbar^2}(\delta x)^2 [V(x) - E] + 2 \right) \cdot 1 - \psi(\delta x) \quad (10)$$

So,

$$\psi(\delta x) = \frac{1}{2} \left( \frac{2m}{\hbar^2}(\delta x)^2 [V(x) - E] + 2 \right) \quad (11)$$

## The Analytical Solution for the Quantum Harmonic Oscillator

The potential associated to this system is,

$$V(x) = \frac{1}{2} m \omega^2 x^2 \quad (12)$$

And the the problem consists on solving the the time-independent Schrödinger Equation:

$$-\frac{\hbar}{2m} \frac{d^2 \psi(x)}{dx^2} + \frac{1}{2} m \omega^2 x^2 \psi(x) = E \psi(x) \quad (13)$$

Which can be rewritten in a more convenient form by defining

$$\epsilon = \sqrt{\frac{m\omega}{\hbar}} x \quad (14)$$

and

$$K = \frac{2E}{\hbar\omega} \quad (15)$$

Hence,

$$\frac{d^2 \psi}{d\epsilon^2} = (\epsilon^2 - K) \psi \quad (16)$$

Which, by considering  $\epsilon \gg K$  reduces to

$$\frac{d^2 \psi}{d\epsilon^2} \approx \epsilon^2 \psi \quad (17)$$

Whose solution is,

$$\psi(\epsilon) = A e^{-\frac{\epsilon^2}{2}} + B e^{\frac{\epsilon^2}{2}} \quad (18)$$

The second term must be zero, once  $\psi(\epsilon) = h(\epsilon) e^{-\frac{\epsilon^2}{2}}$ ,

$$\frac{d\psi}{d\epsilon} = \left( \frac{dh}{d\epsilon} - h\epsilon \right) e^{-\frac{\epsilon^2}{2}} \quad (19)$$

So,

$$\frac{d^2 \psi}{d\epsilon^2} = \left( \frac{d^2 h}{d\epsilon^2} - 2\epsilon \frac{dh}{d\epsilon} + (\epsilon^2 - 1)h \right) e^{-\frac{\epsilon^2}{2}} \quad (20)$$

And finally gives

$$\frac{d^2 \psi}{d\epsilon^2} - 2\epsilon \frac{dh}{d\epsilon} + (K - 1)h = 0 \quad (21)$$

Solving this differential equation through the Frobenius Method

$$h(\epsilon) = \sum_{j=0}^{\infty} a_j \epsilon^j = 0 \quad (22)$$

Differentiating the equation,

$$\frac{dh(\epsilon)}{d\epsilon} = \sum_{j=0}^{\infty} j a_j \epsilon^{j-1} = 0 \quad (23)$$

Again,

$$\frac{d^2 h(\epsilon)}{d\epsilon^2} = \sum_{j=0}^{\infty} (j+1)(j+2) a_{j+2} \epsilon^j = 0 \quad (24)$$

Putting (22)-(24) back in (21) yields

$$\sum_{j=0}^{\infty} [(j+1)(j+2) a_{j+2} - 2j a_j + (K-1) a_j] \epsilon^j = 0 \quad (25)$$

From which one obtains the following recursion formula,

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)} a_j \quad (26)$$

Because of the  $j+2$  index it is necessary to split the solution into its even and odd terms, i.e., terms whose index and power are even and odd [5].

In order to normalize the solutions, one sees that for a large  $j$  the recursion formula (15) reduces to,

$$a_{j+2} \approx \frac{2}{j} a_j \quad (27)$$

Which implies that for a given constant  $C$  such that

$$a_j = \frac{C}{(j/2)!} \quad (28)$$

The solution becomes

$$h(\epsilon) = C \sum_{j=0}^{\infty} \frac{1}{(j/2)!} \epsilon^j = C \sum_{j=0}^{\infty} \frac{1}{(j)!} \epsilon^{2j} = C e^{\epsilon^2} \quad (29)$$

As the solution has to be truncated at a given term, which can be even or odd, (15) requires that  $K = 2n+1$ .

When substituted in (4) results that

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega \quad (30)$$

Where  $n \in \mathbb{N}$

## The Harmonic Oscillator Numerical Solution

As a lot of the numerical implementation of the problem has already been discussed in the explanation of the method.

Here the first two excited states are discussed in deep detail as well as the ground state [7].

In order to ease the check of the results, one might use  $\hbar = \omega = 1$ , without any restriction.

## The Implementation of Shooting Method

The piece of code below shows the details in the implementation of shooting method with the bisection method as the root solver.

The code was written in Python and can be run on python2.7 interpreter. The code generates the figures used in this article [8].

```
E_precision = 0.000001

lower_bound = 0.0
upper_bound = 4.0

E = upper_bound
dE = 1

while dE > E_precision:

    for i in lin[0:-1]:

        if i==0:
            psi[i+1]=f0[i]+dx*dpsi_0
        else:
```

```
psi[i+1] = -psi[i-1]+psi[i]*\
(2-dx**2*(2*E-x[i]**2))
```

```
#Here Bisection Method is Applied
```

```
if psi[i]>5:
    lower_bound = E
    E = lower_bound + \
    (upper_bound-lower_bound)/2
    break
elif psi[i]<-5:
    upper_bound = E
    E = upper_bound - \
    (upper_bound-lower_bound)/2
    break
```

```
dE = upper_bound-lower_bound
```

What it does is basically to use the initial guess for the energy to check if the this energy permits the wave function to obey the boundary conditions[autarkaw].

## Ground State

As the ground state is even, i.e., symmetric with respect to  $x=0$ ,  $\psi'(0) = 0$  and one choosing the  $\psi(0) = 1$ .

It is important to mention that the choice of  $\psi(0)$  is irrelevant since  $\psi(x)$  will be normalized.

The values of  $\psi'(0)$  and  $\psi(0)$  suffice to determine the ground state energy by choosing defining a gap within which the ground state energy can be found. The length of the gap is directly related to the uncertainty of the calculation.

Increasing  $x$  by  $\delta x$  along the domain, the shooting is run with the initial guess  $E_0$ . This value is improved iteratively with the root solver, which in this case is the bisection method.

If  $\psi(x \rightarrow \infty) \rightarrow \infty$  then the initial guess for  $E_0$  is wrong and must be corrected, in this case it is raised; On the other hand, if  $\psi(x \rightarrow \infty) \rightarrow -\infty$ , the initial guess for  $E_0$  is lowered.

This procedure is held until the chosen accuracy for the bisection method is reached.

The input used to determine the eigenenergy corresponding to the ground state was already show in the code above resulting on

```
E0: 0.50028181076
```

With 0.06% of relative error from the analytical ground state energy  $E_0 = (0 + \frac{1}{2}) = 0.5$ .

## First Excited State

As the first excited state is odd,  $\psi'(0)$  can assume any value but  $\psi(0)$  has to be zero.

Obviously  $E_0 < E_1$ , this suggests that a good choice for the lower bound for the first excited state is  $E_0$  but the

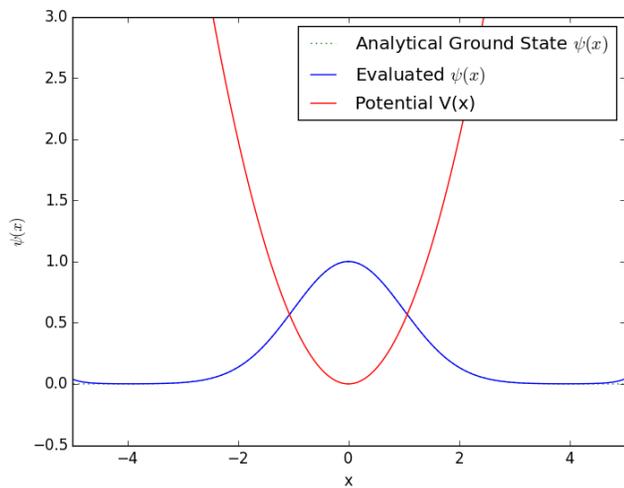


Figure 1: Comparison of the Exact solution and the Wavefunction for the ground state through Shooting Method ran with the above input parameters

choice of the upper bound is not a simple task since the only condition it has to obey is that  $E_1 > E_0$ .

However it is not easy to determine the upper bound of the first excited state, it must equal the lower bound of the second excited state.

The input used here was:

```
lower_bound = E
upper_bound = 4.0
E1=lower_bound
```

Which resulted on an eigenenergy of:

```
E1: 1.50000014392
```

And a relative error of 0.00009% over then first excited state energy in (30), 1.5 .

### Second Excited State

The second excited state is even and the condition  $E_1 < E_2$  is a the best choice. Due to the parity of state the same initial conditions used for the ground state can be used here.

```
lower_bound = E
upper_bound = 4.0
E1=lower_bound
```

From which, one obtains:

```
E2: 2.50070469402
```

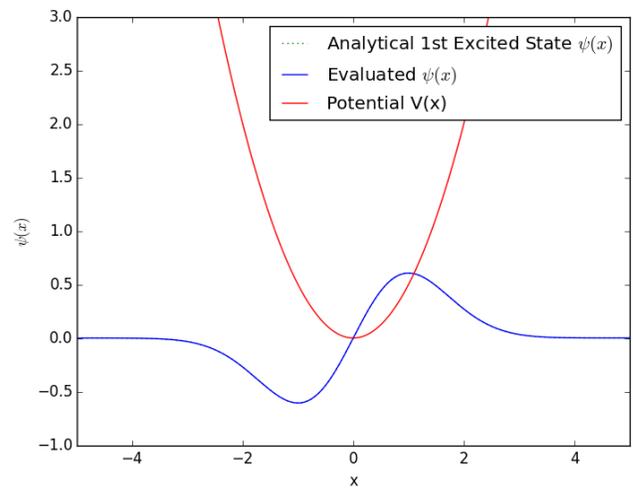


Figure 2: Comparison of the Exact solution and the Wavefunction for the first excited state through Shooting Method ran with  $lower\_bound = E$ ,  $upper\_bound = 4.0$  and  $E1 = lower\_bound$

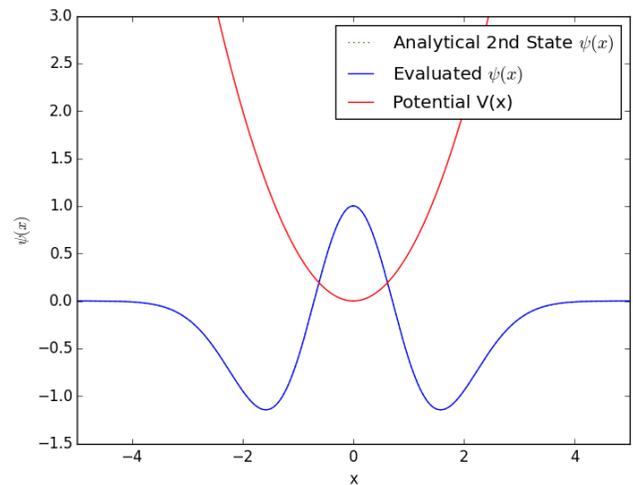


Figure 3:

Whose relative error is 0.03% with respect to the second excite state energy, 2.5.

As one can see in figures 1-3, the agreement of the analytical solution and the calculated is impressive with a small deviation in the edges.

### Schrödinger's Equation Radial Part Obtention

The solution of the angular part of the Schrödinger equation was already simulated as posted on the Quantum Mechanics' *Drive*, within a python implementation that used *scipy.special* module (which is an excellent package since it accomplishes all special functions used in physics and its simplicity in the usage) to calculate the spherical harmonics and *Mayavi* for the visualization. Here, the solution of the radial part of the Schrödinger equation is obtained both

analytically and through computer simulation.

First, one may start by deriving the exact solution. After applying the Laplacian operator and using the separation of variables one obtains

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) R(r) - \frac{2mr^2}{\hbar^2} [V(r) - E] \quad (31)$$

As the radial part of the Schrödinger equation. Now using the reduced mass and substituting the hydrogen atom potential it reduces to

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[ -\frac{e^2}{r} - E \right] - l(l+1) = 0 \quad (32)$$

By simplifying,

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) R(r) + \left[ \frac{2\mu e^2}{r\hbar^2} + \frac{2\mu r^2 E}{\hbar^2} - l(l+1) \right] R(r) = 0 \quad (33)$$

Now defining

$$y(r) = rR(r) \Rightarrow R(r) = \frac{y(r)}{r} \quad (34)$$

It follows that

$$\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R(r) = r^2 \frac{d^2 y(r)}{dr^2} \quad (35)$$

Hence () gives

$$\frac{d^2 y(r)}{dr^2} + \left[ \frac{2\mu e^2}{r\hbar^2} + \frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r^2} \right] y(r) = 0 \quad (36)$$

In order to simplify the expression one might use

$$\left( \frac{\epsilon}{2} \right)^2 = -\frac{2\mu E}{\hbar^2}$$

$$\frac{d^2 y(r)}{dr^2} + \left[ \frac{2\mu e^2}{r\hbar^2} - \frac{e^2}{4} - \frac{l(l+1)}{r^2} \right] y(r) = 0 \quad (37)$$

$$\frac{d^2 y(r)}{dr^2} = \epsilon^2 \frac{d^2 y(x)}{dx^2} \quad (38)$$

So the radial equation assumes the form of

$$\frac{d^2 y(x)}{dx^2} + \left[ -\frac{1}{4} + \frac{2\mu e^2}{\hbar^2 \epsilon x} - \frac{l(l+1)}{x^2} \right] y(x) = 0 \quad (39)$$

where

$$l(l+1) = \frac{k^2 - 1}{4}$$

and

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j + k + 1}{2} \quad (40)$$

Which implies in the solution in the form of

$$y_j^k = e^{-\frac{\epsilon}{2} x} x^{\frac{(k+1)}{2}} L_j^k(x) \quad (41)$$

where  $L_j^k(x)$  are the Laguerre polynomials

This final solution could be written in a more friendly and equivalent manner,

$$R_{n,l}(r) = \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na_0}} \left( \frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2r}{na_0} \right) \quad (42)$$

As seen in [10].

## Implementation of the solution

In this work, the radial solutions were obtained via shooting method [code site] in the same way the harmonic oscillator was solved.

The piece of code below expresses the shooting algorithm usage

```
" evaluation from r=infty to r=0"

# initial condition
u0 = array([0., 1.])

# integration of Sch. equation
ub = integrate.odeint(Schoedinger_deriv, \
    u0, r_mesh, args=(1, eps, Z))
u_at_0 = ub[-1, 0] + (ub[-2, 0] - ub[-1, 0]) * \
    (0.0 - r_mesh[-1]) / (r_mesh[-2] - r_mesh[-1])
```

One can see that from the initial guess of the eigenenergy it takes the integration process as seen in [9] in order to determine the numerical solution.

In order to ease and fasten the physical approach, the usage of the python module called *sympy.physics.hydrogen* within the library *sympy* the radial function are obtained by calling the *R\_nl* that receives n, l and r as arguments [11]. This way, one would not be determining the radial solutions since the Laguerre polynomials are already implemented and used in calculation via analytical expression of *R\_nl* (42).

## Results of the Numerical Calculation

Running the code for a couple of values of n and l, one obtained the curves seen in figure 4.

As one can see, the results obtained are in agreement with the ones available in the literature [1].

By looking at the legend, n=1 represents the 1s orbital radial wavefunction as well as for n=2 and n=3 one has the p orbitals.

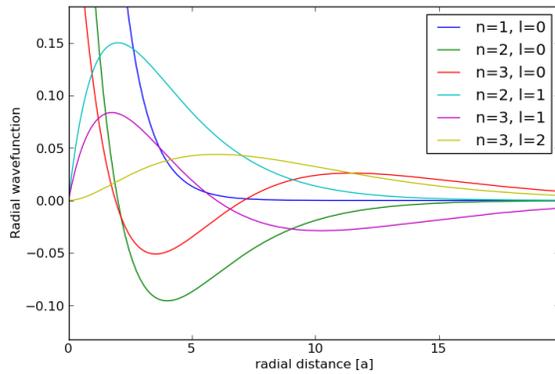


Figure 4: Radial Wavefunction Obtained Numerically from `sympy.physics.hydrogen.R_nl`

## Conclusions

As demonstrated above, the analytical solution of the harmonic oscillator subject to a one dimensional parabolic potential, the eigenenergies are given by:

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega \quad (43)$$

By using a very simple implementation one obtained excellent results which differ from the exact solution by on average 0.03%; such an impressive agreement.

The results of the computer program are in accordance with the demonstrates in (30). One can also see the agreement on the plots, where analytical and numerical solutions slightly differ only close to the boundaries; which are due to the extremely high precision and computational representation of the numbers .

Also, the analytical solution for the radial wavefunctions (42) where obtained numerically through the shooting method. The obtained radial solutions are in agreement with the analytical result.

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