AMIRKABIR
University of Technology

Numerical Solution of The Schrodinger Equation for Hydrogen Atom

Amir M. Gholizad

January 2021

CONTENTS

Preface

Solving The Schrodinger Equation has always been an interesting subject to work on for physicists. But using analytical solutions for such a complicated PDE, might need high mathematical skills. Another way to achieve satisfying answers is to get help from Computers! Computers can do dozens of rough calculations in a fraction of a second. In this project, we are going to apply numerical methods to the Schrodinger equation and visualize different energy states for a Coulombic potential.

$$\hat{H}\,\psi = E\,\psi$$

Schrodinger Equation

The time-independent Schrodinger equation in spherical coordinates, (r, θ, φ), takes the form

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \qquad [1]$$

knowing the form of Laplacian in spherical coordinates

$$\nabla^2 = \left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{1}{r^2 \sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{d^2}{d\varphi^2}\right) \qquad [2]$$

Schrodinger Equation

we get

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)+\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi}{d\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{d^2\psi}{d\varphi^2}\right)-\frac{e^2}{r}\psi=E\psi \qquad [3]$$

We are going to look for solutions that are separable into products:

$$\psi(r,\theta,\varphi)=R(r).P(\theta).Q(\varphi) \qquad [4]$$

Putting this into Equation 3 and multiplying both sides by $\frac{r^2 sin^2(\theta)}{R\cdot P\cdot Q}$, we achieve

$$\sin^2\theta\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)\right]+\frac{1}{Q}\frac{d^2Q}{d\varphi^2}+\frac{2\mu}{\hbar^2}(E-V(r))r^2\sin^2\theta=\circ \qquad [5]$$

Schrodinger Equation

Left hand side of the Equation 5 is made of two functions, one the function of θ and r and the other function of φ. Summation of these two functions can't lead to zero as it is in right hand side. So each function must be equal to a constant number, as we call it, m^2

$$\frac{1}{Q}\frac{d^2Q}{\partial\varphi^2} = -m^2 \quad or \quad \frac{d^2Q}{\partial\varphi^2} = -m^2 Q \qquad [6]$$

The other function becomes

$$sin^2\theta\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{P\,sin\,\theta}\frac{d}{d\theta}\left(sin\,\theta\frac{dP}{d\theta}\right)\right] + \frac{2\mu}{\hbar^2}(E - V(r))r^2 sin^2\theta = m^2 \qquad [7]$$

Schrodinger Equation

Now we notice that the Equation 7 also is made of two function with two independent variables. These functions also must be equal to a constant number, in this case, k. By putting the Coulombic potential (in CGS system) into $V(r)$ we have

$$\frac{1}{P\,sin\,\theta}\frac{d}{d\theta}\left(sin\,\theta\,\frac{dP}{d\theta}\right)-m^2\,sin^2\,\theta=-k \qquad [8]$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{r}\right)R-\frac{kR}{r^2}=\circ \qquad [9]$$

After doing some algebraic simplifications we get

$$\frac{d^2P}{d\theta^2}=P\left(\left(\frac{m}{sin\,\theta}\right)^2-k\right)-\frac{1}{tan\,\theta}\frac{dP}{d\theta} \qquad [10]$$

Schrodinger Equation

and

$$\frac{d^2u}{dr^2} = \left(\frac{1}{n^2 a_\circ^2} - \frac{2}{r a_\circ} + \frac{k}{r^2}\right) u \qquad [11]$$

Which u and $a_\circ$ are

$$u(r) = r \cdot R(r) \qquad [12]$$

$$a_\circ = \frac{\hbar^2}{\mu e^2} \equiv Bohr\ radius \qquad [13]$$

$$\lambda^2 \equiv \frac{-2\mu E}{\hbar^2} = \frac{1}{n a_\circ} \qquad [14]$$

These changings of variables are very important to make the original equation solvable.

RK-4 Method

In numerical analysis, the Runge–Kutta methods are a family of implicit and explicit iterative methods, which include the well-known routine called the Euler Method, used in temporal discretization for the approximate solutions of ordinary differential equations. These methods were developed around 1900 by the German mathematicians Carl Runge and Wilhelm Kutta.

The most widely known member of the Runge–Kutta family is generally referred to as "RK-4", the "classic Runge–Kutta method" or simply as “The Runge–Kutta method".

RK-4 is capable of solving only first order ODEs, but after applying some modifications, we can turn a second order ODE to two first order ODEs and solve them with RK-4 method.

RK-4 Method

For a second order ODE like $\frac{d^2y}{dt^2} = f_2(y,t)$, we can say

$$\frac{d^2y}{dt^2} = \frac{d}{dt}\left(\frac{dy}{dt}\right) \qquad [15]$$

Now we define

$$\frac{dy}{dt} \equiv x \equiv f_1(x,y,t) \qquad [16]$$

Finally we achieve a system of first order ODEs which is solvable

$$\frac{dy}{dt} = f_1(x,y,t) \qquad [17]$$

$$\frac{dx}{dt} = f_2(x,y,t) \qquad [18]$$

RK-4 Method

After getting ready our first order ODEs, we may now use the RK-4 algorithm to solve them. First we need to have an interval such as $[a, b]$,which is the interval that we want to use for plotting the answer. Then we will need the initial value of each equation $(y_{\circ} = y(a), x_{\circ} = \frac{dy}{dx}|_{x=a})$.

Now that we have our interval, we should discretize it to N separate numbers. The distance between a number and it's nearest neighbors will be

$$h = \frac{b-a}{N} \qquad [19]$$

Instead of continuous t variables, now we have an array of t_ns. Each t_n will be defined as

$$T_n = a + n \cdot h \quad , \quad i = 0,1,2,3, \ldots \qquad [20]$$

RK-4 Method

We calculate every y values in every t_n by using this iteration

$$y_n = y_{n-1} + h\left(\frac{k_{1y} + 2k_{2y} + 2k_{3y} + k_{4y}}{6}\right) \quad [21]$$

$$x_n = x_{n-1} + h\left(\frac{k_{1x} + 2k_{2x} + 2k_{3x} + k_{4x}}{6}\right) \quad [22]$$

- k_1 is the slope at the beginning of the interval.
- k_2 and k_3 are the slopes at the midpoints of the interval.
- k_4 is the slope at the end of the interval.

Each round, we calculate the k_is for both x and y.

RK-4 Method

This is how we calculate slopes

$$\begin{cases} k_{1y} = f_1(x_{n-1} , y_{n-1} , t_{n-1}) \\ k_{1x} = f_2(x_{n-1} , y_{n-1} , t_{n-1}) \end{cases} \quad [23]$$

$$\begin{cases} k_{2y} = f_1\left(x_{n-1} + k_{1y} \cdot \frac{h}{2} , y_{n-1} + k_{1y} \cdot \frac{h}{2} , t_{n-1} + \frac{h}{2}\right) \\ k_{2x} = f_2\left(x_{n-1} + k_{1x} \cdot \frac{h}{2} , y_{n-1} + k_{1x} \cdot \frac{h}{2} , t_{n-1} + \frac{h}{2}\right) \end{cases} \quad [24]$$

$$\begin{cases} k_{3y} = f_1\left(x_{n-1} + k_{2y} \cdot \frac{h}{2} , y_{n-1} + k_{2y} \cdot \frac{h}{2} , t_{n-1} + \frac{h}{2}\right) \\ k_{3x} = f_2\left(x_{n-1} + k_{2x} \cdot \frac{h}{2} , y_{n-1} + k_{2x} \cdot \frac{h}{2} , t_{n-1} + \frac{h}{2}\right) \end{cases} \quad [25]$$

$$\begin{cases} k_{4y} = f_1(x_{n-1} + k_{3y} \cdot h , y_{n-1} + k_{3y} \cdot h , t_{n-1} + h) \\ k_{4x} = f_2(x_{n-1} + k_{3x} \cdot h , y_{n-1} + k_{3x} \cdot h , t_{n-1} + h) \end{cases} \quad [26]$$

Results

Now that there are 3 second order ODEs with separated variables and a method to solve them, the next step is to write Equations 6, 10 and 11 in a proper form

$$\begin{cases} \dfrac{dQ}{d\varphi} = x \\ Q = y \\ \varphi = t \end{cases} \Rightarrow \begin{cases} \dfrac{dx}{dt} = -m^2 y = f_2(x, y, t) \\ \dfrac{dy}{dt} = x = f_1(x, y, t) \end{cases} \quad [27]$$

$$\begin{cases} \dfrac{dP}{d\theta} = x \\ P = y \\ \theta = t \end{cases} \Rightarrow \begin{cases} \dfrac{dx}{dt} = y\left(\dfrac{m^2}{sin^2\,\theta} - k\right) - \dfrac{x}{tan\,\theta} = f_2(x, y, t) \\ \dfrac{dy}{dt} = x = f_1(x, y, t) \end{cases} \quad [28]$$

Results

$$\begin{cases} \dfrac{du}{dr} = x \\ u = y \\ r = t \end{cases} \Rightarrow \begin{cases} \dfrac{dx}{dt} = y\left(\dfrac{1}{n^2 a_\circ^2} - \dfrac{2}{t a_\circ} + \dfrac{k}{t^2}\right) = f_2(x, y, t) \\ \dfrac{dy}{dt} = x = f_1(x, y, t) \end{cases} \quad [25]$$

Now we have the equations and RK-4 algorithm. So we can explain them in a programming environment so that computer could do this massive calculations. In this project we used the Python language for solving and then plotting the equations. The reader could reach the scripts and plots by having full access to the **GitHub repository** of the project.

Results

After finding proper initial conditions for each equation, we run the scripts for different values of m and k and we get the following plots

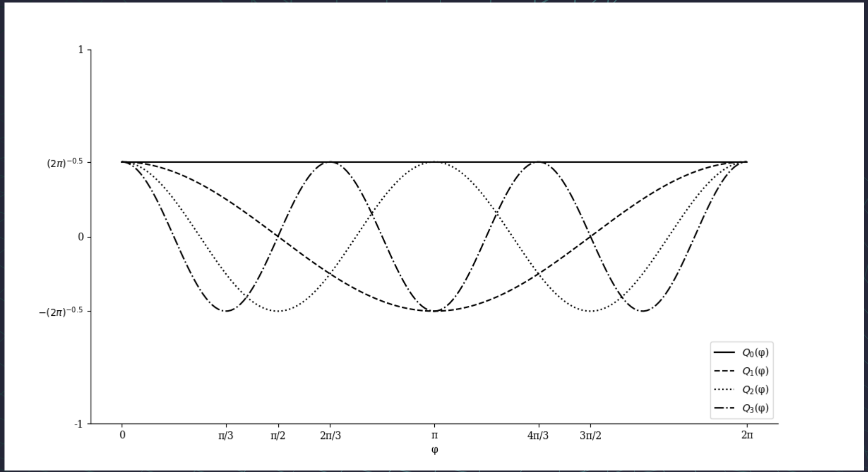

Table 1: Initial conditions of the $Q(\varphi)$

Plot	m	$x_\circ = Q'(\varphi = \circ)$	$y_\circ = Q(\varphi = 0)$	$[a, b]$
___	0	0	$\frac{1}{\sqrt{2\pi}}$	
-----	1	0	$\frac{1}{\sqrt{2\pi}}$	$[\circ\, , 2\pi]$
....	2	0	$\frac{1}{\sqrt{2\pi}}$	
.-.-.-.	3	0	$\frac{1}{\sqrt{2\pi}}$	

Results

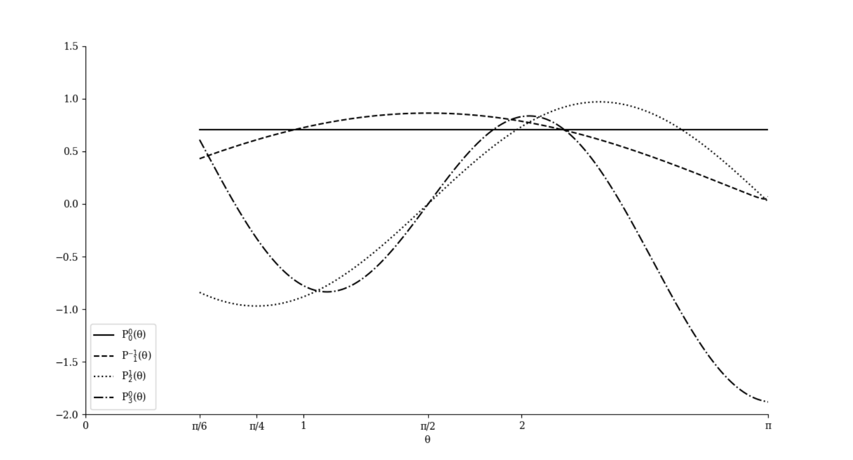

Table 1: Initial conditions of the $P(\theta)$

Plot	m	k	$x_\circ = P'\left(\theta = \frac{\pi}{6}\right)$	$y_\circ = P\left(\theta = \frac{\pi}{6}\right)$	$[a, b]$
___	0	0	0	$\frac{1}{\sqrt{2}}$	$\left[\frac{\pi}{6}, \pi\right]$
-----	-1	2	0.75	0.43	
....	1	6	-0.97	-0.84	
.-.-.-.	0	12	-3.85	0.61	

Results

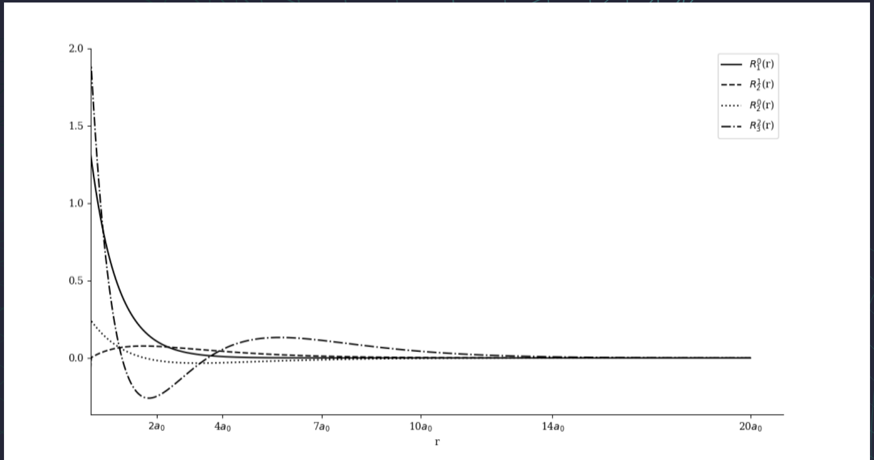

Table 1: Initial conditions of the R(r)

Plot	n	k	$x_\circ = R'(r=20)$	$y_\circ = R(r=20)$	$[a,b]$
___	1	0	-4×10^{-9}	4×10^{-9}	$[20,0]$
-----	2	2	-1×10^{-3}	2×10^{-3}	
…….	2	0	13×10^{-5}	-3×10^{-3}	
.-.-.-.	3	0	-17×10^{-4}	85×10^{-4}	

Results

According to the results we've shown in past slides, we can come to a conclusion. A conclusion that says the numerical methods are as efficient and qualified as analytical methods. In the real world that we live there are not much phenomena that could be solved and explained by analytical tools. Weather we like it or not, the nature most of the times acts in very complicated ways. Using computers and numerical treatments might help us in the way of better understanding our world.

References

- Nouredine Zettili, "*Quantum Mechanics: Concepts and Applications*" 2nd Edition, John Wiley and Sons, 2009.
- Griffiths, David J. , "*Introduction to Quantum Mechanics*", Prenticehall, 1955.
- Wolfgang Demtröder, *" Atoms, Molecules and Photons: An Introduction to Atomic-, Molecularand Quantum Physics"*, Third Edition, Springer, 2006