Numerical study of the radial Schrödinger Equation for Hydrogen atom using Legendre wavelet

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ABSTRACT. This paper deals with the Legendre wavelet (LW) collocation method for the numerical solution of radial Schrödinger equation for hydrogen atom. Energy eigenvalues for the hydrogen bound system is derived $-13.6\,eV$. Numerical results of the ground state modes of wave function for the hydrogen atom $R(r)$, or the electron probability density function, has been presented. The numerical results have been compared to the other existing method and exact solution.

Keywords: Schrödinger equation, Hydrogen atom, Legendre wavelet, Collocation method.

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1. INTRODUCTION

One of the most important eigenvalue equations in physics is the Schrödinger's wave equation. For atomic mass m in the potential energy $V(r)$ is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r}) = E\psi(\mathbf{r}), \qquad (1.1)$$

in which $\psi(\mathbf{r})$ is the particle wave function and E is an energy eigenvalue [1]. For one-dimensional potential energy, equation (1.1) is as follow:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x) = E\psi(x). \qquad (1.2)$$

The Schrödinger's wave function, must be convergent as $x \to \infty$, because:

$$\int_{-\infty}^{+\infty} \psi(x)\psi^*(x)dx = 1, \qquad (1.3)$$

which means that the particle must be somewhere in the x axes [1]. The first derivative of the wave function also must be continuous as if, it's second derivative which is appearing in the equation (1.2), could be exist.

The numerical solution of the above equation is the subject of many research papers in the last two decades [2, 3, 4, 5, 6]. This equation has the analytical answers for few potential energies $V(r)$. For many potential energies, in physics and chemistry, it cannot be solved analytically. So, in quantum mechanics the numerical or approximate analytical solution of the Schrödinger wave equation is real need. The aim of this paper is to study and obtain the results of Legendre wavelet approach for solving the Schrödinger's wave equation (1.1). Comparison will be made whit the other well known numerical solution methods and exact solution.

2. Schrödinger equation for Hydrogen atom

In the Hydrogen atom, electron constraint to nucleus, in the Colombian force. The radial Schrödinger equation for the central potential V(r) is as follow:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right]R(r) + \frac{2\mu}{\hbar^2}\left[E + V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R(r) = 0, \qquad (2.1)$$

where μ is the reduced mass of electron-proton system, l is the orbital quantum number and $R(r)$ is the radial wave function. The Coulomb potential between electron and proton in the hydrogen atom is V(r) = e2/4πε0r, thus:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right]R(r) + \frac{2\mu}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R(r) = 0, \qquad (2.2)$$

where:

$$\mu = \frac{m_p m_e}{m_p + m_e}. \qquad (2.3)$$

For simplicity, we can rewrite Eq. (2.2) in dimensionless form as [1]:

$$\frac{d^2 R(\rho)}{d\rho^2} + \frac{2}{\rho}\frac{dR(\rho)}{d\rho} - \frac{l(l+1)}{\rho^2}R(\rho) + (\frac{\lambda}{\rho} - \frac{1}{4})R(\rho) = 0, \qquad (2.4)$$

where:

$$\rho = 2\sqrt{\frac{2\mu}{\hbar^2}}\sqrt{|E|}\,r, \qquad (2.5)$$

and

$$\lambda = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\sqrt{\frac{2\mu}{\hbar^2}}\frac{1}{\sqrt{|E|}}. \qquad (2.6)$$

We need to consider physical constant values and units. The amount of Planck's constant, in the SI unit is $h = 6.63 \times 10^{-34}$j.s , which is too small to perform computation, therefore we use Angstrom for the length and the energy is in term of the electron volt which is denoted as (eV):

$$\hbar^2 = 7.6199682\, m_e \text{ eV.A}^{\circ 2}. \qquad (2.7)$$

In Eq. (2.7), $m_e (= 0.51101 \times 10^6 \text{eV}/c^2)$ is the rest mass of atomic's electron. Another constant which is appeared in the Shrödinger equation for the Coulomb potential is:

$$\frac{e^2}{4\pi\varepsilon_0} = 14.39998\, \text{eV.A}^{\circ}, \qquad (2.8)$$

so the approximate values of the dimensionless parameters (2.5) and (2.6), could be written as:

$$\rho \simeq \frac{2\sqrt{2}}{\sqrt{7.6199682}}\sqrt{|E|}\,r, \qquad (2.9)$$

$$\lambda \simeq \frac{14.39998}{\sqrt{2 \times 7.6199682}}\frac{1}{\sqrt{|E|}}. \qquad (2.10)$$

From quantum mechanics it is known that $r^2|R(r)|^2$, represents the probability density of finding the electron in place of r from the center of the atom [1]. So in order to solve Eq. (2.4), we must consider the following facts:

a. Initial conditions: at the center of the atom, which is nucleus, the probability of electron presence must be zero, then we imposed the initial conditions in the vicinity of center, r $\simeq 10^{-4}$A$^{\circ}$, as follow [7]:

$$R(r)|_{r=10^{-4}} = 10^{-6}, \left.\frac{dR}{dr}\right|_{r=10^{-4}} = -1000. \qquad (2.11)$$

b. Energy eigenvalue E: From the statistics it is known that, the probability is finite, so the solution of Eq. (2.2), $R(r)$, must not diverge to infinity for any value of $r > 0$. For the ground state of the hydrogen, which is $l = 0$ (S wave), trying various amounts of the energy E, one

easily finds that, E must be $-13.6\,eV$. The wave function $R(r)$, for any greater or smaller values of $-13.6\,eV$, is divergent to $-\infty$ or $+\infty$ respectively. For example, Fig 1 shows the behaviour of the wave function $R(r)$ for two sample value $E = -13.0\,eV$ and $E = -14.0\,eV$.

c. Range of r: Outside the atom, the probability presence of the electron, and consequently the wave function, must be 0. So, we take the $0 < r \le 4\,\text{A}°$ for hydrogen atom. Notice that the first Bohr's atomic radius is about $0.5\,\text{A}°$.

3. Legendre Wavelet

Recently, wavelet basis have found their way into many different fields of science and engineering. Particularly, wavelets are very successfully used in signal analysis, time-frequency analysis and accurate representation of functions. Wavelets constitute a family of functions constructed from dilation and translation of a single function ψ called the mother wavelet. When the dilation parameter a and translation parameter b vary continuously, we have the following family of continuous wavelets

$$\psi_{a,b}(t) = a^{-\frac{1}{2}} \psi\left(\frac{t-b}{a}\right), \quad a,b \in \mathbb{R},\ a \neq 0. \tag{3.1}$$

The Legendre wavelets are defined on the interval $[0,1)$ as

$$\psi_{mn}(t) = \begin{cases} \sqrt{m + \frac{1}{2}} 2^{\frac{k+1}{2}} p_m\left(2^{k+1}t - (2n+1)\right) & \frac{n}{2^k} \le t < \frac{n+1}{2^k}, \\ 0 & otherwise, \end{cases} \tag{3.2}$$

where $n = 0, 1, ..., 2^k - 1$ and $m = 0, 1, \cdots, M - 1$ is the degree of the Legendre polynomials for a fixed positive integer M. Here $P_m(t)$ are the well-known Legendre polynomials of degree m [9, 8].

Any square integrable function $f(x)$ defined over $[0, 1)$ can be expanded in terms of the extended Legendre wavelets as

$$f(x) \simeq \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_{nm} \psi_{nm}(x) = C^T \Psi(x), \tag{3.3}$$

where $c_{mn} = (f(t), \psi_{mn}(t))$ and $(.,.)$ denotes the inner product on $L^2[0,1]$. If the infinite series in (3.3) is truncated, then it can be written as

$$f(x) \simeq \sum_{n=0}^{2^k-1} \sum_{m=0}^{M-1} c_{mn} \psi_{mn}(x) = C^T \Psi(x), \tag{3.4}$$

where C and $\Psi(x)$ are $\hat{m} = 2^k M$ column vectors given by

$$C = \left[c_{00}, \ldots, c_{0(M-1)} | c_{10}, \ldots, c_{1(M-1)} |, \ldots, | c_{(2^k-1)0}, \ldots, c_{(2^k-1)(M-1)}\right]^T, \tag{3.5}$$

$$\Psi(x) = [\psi_{00}(x), \ldots, \psi_{0(M-1)}(x)|\psi_{10}(x), \ldots, \psi_{1(M-1)}(x)|, \ldots,$$
$$|\psi_{(2^k-1)0}(x), \ldots, \psi_{(2^k-1)(M-1)}(x)]^T. \quad (3.6)$$

By changing indices in the vectors $\Psi(x)$ and C the series (3.4) can be rewritten as

$$f(x) \simeq \sum_{i=1}^{\hat{m}} c_i \psi_i(x) = C^T \Psi(x), \quad (3.7)$$

where

$$C = [c_1, c_2, ..., c_{\hat{m}}]^T, \quad \Psi(x) = [\psi_1(x), \psi_2(x), ..., \psi_{\hat{m}}(x)]^T, \quad (3.8)$$

and

$$c_i = c_{nm}, \quad \psi_i(x) = \psi_{nm}(x), \quad i = (n-1)M + m + 1. \quad (3.9)$$

Theorem 3.1. [13] *Let $\Psi(x)$ be the Legendre wavelet vector defined in (3.6). The derivative of the vector $\Psi(x)$ can be expressed by*

$$\frac{d\Psi(x)}{dx} = D\Psi(x) \quad (3.10)$$

where D is the $2^k(M+1)$ operational matrix of derivative defined as follows

$$D = \begin{pmatrix} F & 0 & \cdots & 0 \\ 0 & F & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & F \end{pmatrix} \quad (3.11)$$

in which F is $(M+1) \times (M+1)$ matrix and its (r,s)th element is defined as follow

$$F_{r,s} = \begin{cases} 2^{k+1}\sqrt{(2r-1)(2s-1)}, & r = 2, ..., (M+1), s = 1, ..., r-1, \ (r+s)odd \\ \\ 0, & otherwise. \end{cases}$$

4. Method of solution

Consider the the Schrödinger equation (2.4). First, we approximate $R(t)$ in terms of the LWs as follows

$$R(\rho) \simeq C^T \Psi(\rho) = \Psi^T(\rho)C, \quad (4.1)$$

where C is the LWs coefficient vector. By using the approximate $R(t) \simeq C^T \Psi(t)$ and operational matrix of derivative D, the residual function for the Schrödinger equation (2.2) can be written as

$$\mathbf{Res}(r) = C^T D^2 \Psi(\rho) + \frac{2}{\rho} C^T D\Psi(\rho) - \frac{l(l+1)}{\rho^2} C^T \Psi(\rho) + (\frac{\lambda}{\rho} - \frac{1}{4})C^T \Psi(\rho),$$

Hereafter, in order to approximate solution of the Schrödinger equation (2.2) with initial conditions (2.11), as in the typical collocation method [11], we generate $2^k(M+1) - 2$ equations by applying

$$\textbf{Res}(r_i) = 0, \ i = 1, 2..., 2^k(M+1) - 2. \tag{4.2}$$

Moreover, by using the initial condition (2.11) we have two algebraic equations as

$$C^T \Psi(10^{-4}) = 10^{-6}, \tag{4.3}$$

$$C^T D \Psi(10^{-4}) = -1000, \tag{4.4}$$

Eqs. (4.2) together with (4.3) and (4.4) generate a system of $2^k(M+1)$ algebraic equations for $2^k(M+1)$ unknown elements of the unknown vector C. This system can be solved for unknown coefficient vector C and unknown function $R(r)$ can be obtained by substituting the obtained vector C in Eq. (4.1).

With the above considerations, approximate analytical LW expansion of wave function, $R(r)$, with $M = 20, k = 0$ is obtained as follow:

$$R(r) \simeq \begin{cases} 0.0001000000000000000 & r < 0 \\ \\ \begin{aligned} &0.0004027790697680989r^{20} - 0.01672149121526701r^{19} \\ &+0.3222282172276126r^{18} - 3.825614370207146r^{17} \\ &+31.32110889156184r^{16} - 187.5518819507251r^{15} \\ &+850.1112364103842r^{14} - 2978.048798212946r^{13} \\ &+8161.299539338049r^{12} - 17600.16297554591r^{11} \\ &-39838.37945962377r^9 + 29893.05791979935r^{10} \\ &+41312.92593261955r^8 + 19705.76528547583r^6 \\ &-32889.32452321992r^7 + 2661.067074335042r^4 \\ &-8638.426438862927r^5 - 542.7959231374756r^3 \\ &+66.69939813083678r^2 - 4.053099656590226r \\ &+0.001710602629839316 \end{aligned} & 0 < r \le 4 \\ \\ 0.0001000000000000000 & 4 < r \end{cases}$$

Numerical results for the solution of the radial Schrödinger Eq. (2.2) in the case of $l = 0$, is shown in Table 1, for various methods. As the numerical results confirm, the LW collocation method is in a good agreement with the exact analytical calculation.

5. Conclusion

In this paper a Legendre wavelet (LW) approach is used to find an approximate analytic expansion for the radial Schrödinger equation for hydrogen atom. Numerical results obtained from LW expansion, are compared to the exact and other well known numerical methods. Runge
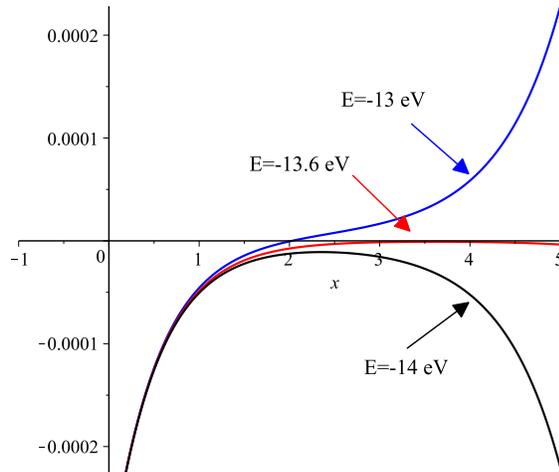
FIGURE 1. Solutions of the Schrödinger equation in the ground state $l = 0$, for three different values of E. As it is shown, $R(r)$ is convergent to 0 in the energy eigenvalue $E = -13.6\,eV$, and is divergent to $-\infty$ or $+\infty$ in $E = -14\,eV$ or $E = -13\,eV$, respectively.

TABLE 1. Comparison of the numerical solution for the radial Schrödinger equation in the ground state of the hydrogen atom $R(r)$ for $0 < r < 4\,\mathrm{A}^\circ$.

r	Exact solution	RKF45	RK4 $h = 10^{-4}$	HUEN $h = 10^{-4}$	LW expansion
0.1	-0.08282	-0.08282	-0.08283	-0.08291	-0.08289
0.5	-0.03896	-0.03896	-0.03897	-0.0391	-0.0354
0.9	-0.01831	-0.01831	-0.01832	-0.01841	-0.01686
1.3	-0.00861	-0.00861	-0.00862	-0.00868	-0.00852
1.7	-0.00405	-0.00405	-0.00406	-0.00412	-0.00388
2.1	-0.00192	-0.00192	-0.00192	-0.00199	-0.00148
2.5	-0.00092	-0.00092	-0.00093	-0.00101	-0.00099
2.9	-0.00046	-0.00046	-0.00047	-0.0006	-0.00057
3.3	-0.00026	-0.00026	-0.00028	-0.00048	-0.0001
3.7	-0.0002	-0.0002	-0.00023	-0.00055	-0.00016

Kutta Fehlberg method, Forth order Runge Kutta method with step size 10^{-4} and modified Euler method (Heun's method), with step size

10^{-4}, also are used in numerical solution of the radial Schrödinger equation. The numeical results show a good agreement with the exact and other numerical results for the presented LW method. It is worth noting that the presented LW method results a semi-analytical expanssion for solution of the the radial Schrödinger equation, while the other methods result discrete numerical solution. Since, approximate semi-analytical solution of wave function is useful in estimating physical quantities for some complex quantum systems, the LW method is more efficient and applicable in compare to other mentioned methods.

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