Improved variational method that solves the energy eigenvalue problem of the hydrogen atom

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Abstract. In most quantum mechanics textbooks for graduate studies, the hydrogen atom is studied in an approximate way by means of the variational method. The type of trial functions commonly used are the Gaussian and the Lorenzian. In this paper we consider a natural generalization of the Mei method to improve the trial wave functions [1] applied to hydrogen atom. We propose a sequence of functions as trial wave functions to calculate the eigen-energies of the hydrogen atom. These trial wavefunctions are given in terms of three variational parameters, one of them is fixed by means of the normalization condition and the other two are adjustable parameters. One of these parameters can be chosen as being an integer number, then this parameters will define the sequence of functions. We will show that when the integer parameter approaches to infinity, the ground state, first excited state and second excited state converge to the exact results.

1. Introduction

The hydrogen atom is the simplest atom which consists of a bound state of a proton and an electron. This simpler quantum mechanical system has been used as test-bed for new theories and researches. For instance, transitions in hydrogen are being used to examine in a more accurate way the fine structure constant over a cosmological time scale [2], and more recently, using the variational approach to the determination of the spectral of the hydrogen atom [3], the celebrated Wallis product formula for \(\pi\) has been calculated.

Although the conceptual simplicity of the hydrogen atom to analytically calculate its energy eigenvalues, we need mathematical tools such as partial differential equations in spherical coordinates, the theory of angular momentum, and the introduction of some special functions as the associated Laguerre polynomials. Let us remark that the hydrogen atom is actually one of few quantum mechanical systems whose energy levels can be obtained exactly.

Generally, and not only in quantum mechanics, most of the problems cannot be solved analytically, and hence need to be dealt with numerical or other alternative approximation. In quantum mechanics, the most used methods to approximate solutions are perturbation theory and the variational method. Perturbation theory is useful when there is a small dimensionless parameter in the problem, and the system is exactly solvable when this parameter approaches zero. On the other hand, the variational method allow us to calculate approximations to the lowest energy eigenstate or ground state in a quantum system.
The variational method consists of choosing a trial wave function that depends on one or more parameters and finding the values of these parameters such that the expectation value of the Hamiltonian operator which defines the energy as the lowest possible [5]. By finding a suitable trial wave function orthogonal to the ground state, an upper bound state on the first excited state can be calculated, then, by computing a set of orthogonal trial wave functions, it is also possible to determine approximately the excited states.

Regarding to the variational method applied to the case of the hydrogen atom, as far as we know, the proposed trial wave functions provide results that have an error close to 10% when compared to the exact answer. For instance, the most popular types of trial wave functions are the gaussians and the lorentziants, which lead to error about of 15%, and 10% respectively for the ground state energy [4, 5, 6].

One way to improve the errors is by adding more parameters to the trial wave functions, such as the Hylleras method for the He atom [7]. In using this approach, calculations soon become very lengthy and tedious. Another and more effective way to improve the trial functions was performed by Mei [1] for the harmonic oscillator problem. He concludes that introducing an integer parameter that determines the asymptotic behavior of the trial function, he is able to show that the energy of the ground state and the first excited state converge to the exact results.

Motivated by the work of Mei, in this article we propose a general trial wave functions for the hydrogen atom that can be indexed by a integer number. This index can be identified as being one of the variational parameters. We are going to show that when this positive integer parameter approaches to infinity, the analytical solutions of the energy eigenvalue problem are recovered.

The paper is organized as follows. In Section 2 we define our trial wave function and the variational parameters. In Section 3 and 4, we apply the variational method to calculate the ground state energy and the ground state wave function respectively. In Section 5 we calculate the energy eigenvalue and wave function for the first exited state. In Section 6 we calculate higher level energies. We end with some concluding remarks summarizing the main results.

2. The ground state trial wave function

Since the energy of the hydrogen atom does not depend on the angular momentum quantum number \( l \), it is possible to use trial wave functions that only depend on the radial coordinate, namely, states with \( l = 0 \). Furthermore, to take into account the asymptotic behavior of the trial wave function, we are going to choose the following trial wave function for the ground state:

\[
\Psi_1 = \frac{C_1}{(A + r)^n},
\]

where \( C_1 > 0, A > 0 \) are real parameters and \( n \) is an integer number \( n > 0 \). From the normalization condition for the wave function, we obtain

\[
4\pi C_1^2 \int_0^\infty \frac{r^2}{(A + r)^{2n}} \, dr = 1.
\]

To perform the radial integral, we are going to employ the following very useful integral identity:

\[
\int_0^\infty \frac{r^M}{(A + r)^N} \, dr = \frac{M!(N - M - 2)!A^{M-N+1}}{(N-1)!},
\]

where in order to the integral be a convergent one, we must have \( -1 < M < N - 1 \).

Using equation (3) and equation (2), we have

\[
8\pi C_1^2 A^{3-2n} \frac{(2n-4)!}{(2n-1)!} = 1.
\]
so that we get
\[ C_1^2 = \frac{A^{2n-3}(2n-1)(2n-2)(2n-3)}{8\pi}. \] (5)

This result shows that the parameter \( C_1 \) depends on the parameter \( A \). Thus, our trial function will depend only on parameters \( A \) and \( n \). We will take \( A \) as a variational parameter and \( n \) as an index that defines the sequence of functions.

3. The ground state energy by means of a variational calculation

The next step is to calculate the expected value of the Hamiltonian. Using spherical coordinates, the Hamiltonian of the hydrogen atom can be written as [5]
\[ H = H_r - \frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right], \] (6)
where \( \mu \) is the reduced mass and \( H_r \) is the radial part of the Hamiltonian given by
\[ H_r \equiv -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{e^2}{4\pi \epsilon_0 r}. \] (7)

Using the trial wave function given by equation (1) and the expression for \( C_1 \) in equation (5), we can compute the energy associated to this state \( \Psi_1 \)
\[ E_1(A) \equiv \langle H \rangle_{\Psi_1} = 4\pi C_1^2 \int_0^\infty \frac{r^2}{(A + r)^n} H_r \left( \frac{1}{(A + r)^n} \right) dr. \] (8)
Performing the integration, we find
\[ E_1(A) = 4\pi C_1^2 \left[ -\frac{\hbar^2}{2\mu(2n+1)(2n-1)} + \frac{\hbar^2 A^{-2n+1}}{2\mu(2n-1)} - \frac{e^2 A^{-2n+2}}{8\pi \epsilon_0 (2n-1)(n-1)} \right]. \] (9)
Replacing the expression of the parameter \( C_1 \) which is given in equation (5) into this equation (9), we obtain
\[ E_1(A) = \frac{\hbar^2 n(n-1)(2n-3)}{2\mu(2n+1) A^2} - \frac{e^2 (2n-3)}{8\pi \epsilon_0 A}. \] (10)

We now compute the derivative respect to the parameter \( A \) to find the minimum value of \( E_1(A) \):
\[ \frac{dE_1}{dA} = -\frac{\hbar^2 n(n-1)(2n-3)}{\mu(2n+1) A^3} + \frac{e^2 (2n-3)}{8\pi \epsilon_0 A^2} = 0. \] (11)
The solution to this equation (11) is given by
\[ A_{\text{min}} = \frac{8\pi \epsilon_0 \hbar^2 n(n-1)}{e^2 \mu(2n+1)}. \] (12)
Therefore, using equation (10), the energy evaluated at this point \( A_{\text{min}} \) is given by
\[ E_1(A_{\text{min}}) = -\frac{e^4 \mu (2n-3)(2n+1)}{128\pi^2 \hbar^2 \epsilon_0^2 n(n-1)}. \] (13)
Note that taking the limit to $n \to \infty$, the energy of the ground state tends to the exact answer:

\[
\lim_{n \to \infty} E_1(A_{\text{min}}) = \lim_{n \to \infty} \left[ -\frac{e^4 \mu (2n - 3)(2n + 1)}{128 \pi^2 \hbar^2 c_0^2 n(n - 1)} \right] = -\frac{e^4 \mu}{32 \pi^2 \hbar^2 c_0^2} = -\frac{e^4 \mu}{2(4\pi e_0)^2 \hbar^2}.
\]

(14)

Just as a matter of comparison, let us write the exact analytical expression for the energy of the hydrogen atom obtained by solving explicitly the differential equation [5]

\[
E_N = -\frac{e^4 \mu}{2(4\pi e_0)^2 \hbar^2 N^2}, \quad N = 1, 2, 3, \ldots .
\]

(15)

So in fact, the result (14) corresponds to the energy for the ground state $N = 1$.

### 4. The ground state wave function

To simplify the expressions, let us write the quantities in terms of the Bohr radius $a = \frac{4\pi e_0 \hbar^2}{mc^2}$. For instance, the expression for the $A_{\text{min}}$ given in equation (12) in terms of the Bohr radius reduces to

\[
A_{\text{min}} = \frac{2a(n - 1)n}{2n + 1}.
\]

(16)

Now using equation (5), we can obtain the expression for the parameter $C_1$ evaluated at the minimum value

\[
C_{1,\text{min}} = \frac{A_{\text{min}}^{(2n-3)/2} \sqrt{(2n-1)(2n-2)(2n-3)}}{2\sqrt{2\pi}}.
\]

(17)

Therefore, the trial wave function (1) evaluated at this minimum value is given by

\[
\Psi_{1,\text{min}}(r) = \frac{C_{1,\text{min}}}{(A_{\text{min}} + r)^n} = \sqrt{\frac{(n - 1)(2n - 3)(2n - 1)}{4\pi a^3 n^3}} \left( \frac{2n - 2}{2n + 1} \right)^{n-\frac{3}{2}} \left( \frac{2n - 2}{an} + \frac{r}{2n + 1} \right)^{-n}.
\]

(18)

In order to compare the wave function obtained with the well known analytical expression for the ground state wave function of the hydrogen atom ($\Psi_{100}(r) = \frac{r^2}{\sqrt{a}} e^{-r/\sqrt{a}}$) we define the function $\Psi_{1,n}(r) \equiv \frac{r^2}{\sqrt{a}} \Psi_{1,\text{min}}(r)$.

Figure 1 shows the behavior of $\frac{r^2}{\sqrt{a}} \Psi_{100}$ and $\Psi_{1,n}$ as a function of $r/a$. We observed that the function $\Psi_{1,n}(r)$ is approaching to the analytical solution $\frac{r^2}{\sqrt{a}} \Psi_{100}$ (solid line) when we increase the value of $n$. Remarkably, in the limiting case of $n \to \infty$ both functions are identical.

For completeness, we also have calculated the limit of (18) as $n \to \infty$ analytically:

\[
\lim_{n \to \infty} \Psi_{1,\text{min}}(r) = \lim_{n \to \infty} \sqrt{\frac{(n - 1)(2n - 3)(2n - 1)}{4\pi a^3 n^3}} \left( \frac{2n - 2}{2n + 1} \right)^{n-\frac{3}{2}} \left( \frac{2n - 2}{an} + \frac{r}{2n + 1} \right)^{-n} = \frac{1}{a^{7/2} \sqrt{\pi}} e^{-\frac{r}{\sqrt{a}}}.
\]

(19)

Where we have used the well know limit

\[
\lim_{n \to \infty} \left( 1 + \frac{z}{n} \right)^n = e^z.
\]

In that way, the solution converges to the analytical expression for the ground state.

Our next task will be the derivation of the energy for the first excited state, namely with $N = 2$ by means of the variational method and using a clever trial function just like the one we have done in the case of the ground state.
5. The case of the first excited state

In this section we are going to calculate the energy eigenvalue and wave function of the first excited state and compare the result with the analytic value of the energy (15) for the case \( N = 2 \).

From the variational method we know that the trial function of the first excited state must be orthogonal to the trial function ground state \( \Psi_1 \) (1). Thus we are looking for a \( \Psi_2 \) such that

\[
\langle \Psi_1, \Psi_2 \rangle = \int \Psi_1^* \Psi_2 r^2 \sin \theta dr d\theta d\phi = 0. \tag{20}
\]

This \( \Psi_2 \) which is in agreement with the condition (20) is given by

\[
\Psi_2 = C_2 (1 + \frac{8 - 3n}{6A} r) \frac{1}{(A + r)^{n/2}}. \tag{21}
\]

In order for the radial part of the integral (20) to be a convergent one, the value of the integer \( n \) must be such that \( n > 2 \).

By using the normalization condition for \( \Psi_2 \), we are going to determine the coefficient \( C_2 > 0 \) in terms of the parameter \( A \). Then, from

\[
\int |\Psi_2|^2 r^2 \sin \theta dr d\theta d\phi = 1, \tag{22}
\]

we get

\[
C_2^2 = \frac{3(n - 5)(n - 4)(n - 3)(n - 2)(n - 1)A^{n - 3}}{8\pi(3n - 2)n + 4}. \tag{23}
\]
Next, we compute the expectation value of the Hamiltonian (6) using the trial wave function (21). Since the function (21) only depends on the radial coordinate, we have

\[
\langle H \rangle_{\Psi_2} = \int (\Psi_2^* H \Psi_2) r^2 \sin \theta d\theta d\phi = 4\pi \int_0^\infty r^2 \Psi_2^* H r \Psi_2 dr.
\]

Replacing the trial wave function (21) into equation (24), and performing computations similar to the ones given in the case of the ground state trial function (1) and using the result of the integral (3), we can show that

\[
E_2(A) \equiv \langle H \rangle_{\Psi_2} = \frac{C_2^2 A^{1-n} \left(3 A e^2 \mu (-3 n^2 + n + 4) + 2 \pi h^2 (n-4)(3 n(3n-8)-8) \epsilon_0 \right)}{18 \mu (n-4)(n-3)(n-1)(n+1) \epsilon_0}.
\]

Now, replacing equation (23) into equation (25), we get

\[
E_2(A) = \frac{\hbar^2 (n-5)(n-4)(n-2)(3 n(3n-8)-8)}{24 A^2 \mu (n+1)(3n-2)n+4} - \frac{\epsilon^2 (n-5)(n-2)(3n-4)}{16 \pi A (3 n^2 - 6n + 4) \epsilon_0}.
\]

Thus computing the minimum value by means of the following equation

\[
\frac{dE_2}{dA} \bigg|_{A=A_{min}} = 0,
\]

we obtain

\[
A_{min} = \frac{4 \pi h^2 (n-4)(3 n(3n-8)-8) \epsilon_0}{3 e^2 \mu (n+1)(3n-4)}.
\]

Evaluating the energy (26) at the minimum value (28), we arrive to

\[
E_2(A_{min}) = -\frac{3 e^4 \mu (4-3n)^2(n-5)(n-2)(n+1)}{128 \pi^2 h^2 (n-4)(n-2)n+4)(3 n(3n-8)-8) \epsilon_0^2}.
\]

Taking the limit \(n \to \infty\), we obtain

\[
\lim_{n \to \infty} E_2(A_{min}) = -\frac{e^4 \mu}{128 \pi^2 h^2 \epsilon_0^2} = -\frac{e^4 \mu}{2(4 \pi \epsilon_0)^2 h^2 2^2}.
\]

Therefore, as in the case of the ground state, surprisingly, when we take the limit \(n \to \infty\), we arrive to the correct analytical result (15) which corresponds to the value of the first exited state.

Now let us analyze the wave function. Using equations (23) and (28) into equation (21), we have

\[
\Psi_{2, min}(r) = C_{2, min} \left(1 + \frac{8-3n}{h A_{min}} r \right) \frac{1}{(A_{min} + r)^{n+2}}
\]

\[
= \frac{9}{2} \sqrt{\frac{(n-5)(n-3)(n-2)(n-1)(n+1)^3(3 n(3n-8)-8)^3}{e^4 (n-4)^2 (3 n(3n-8)-8)^4}} \left(1 + \frac{8-3n}{h A_{min}} r \right) \frac{1}{2 \sqrt{2 \pi}}
\]

Performing the limit \(n \to \infty\), we can show that

\[
\lim_{n \to \infty} \Psi_{2, min}(r) = \frac{1}{2a^{3/2} \sqrt{2 \pi}} (1 - \frac{r}{2a}) e^{-\frac{r^2}{a}}.
\]
Figure 2. Plot of $a^{3/2}\Psi_{200}(r)$ and $\Psi_{2,n}(r) \equiv a^{3/2}\Psi_{2,\text{min}}(r)$ for values of $n = 6, 12, 60$. The continuous curve represents the analytical function $a^{3/2}\Psi_{200}(r)$, while $\Psi_{2,6}(r)$, $\Psi_{2,12}(r)$ and $\Psi_{2,60}(r)$ are given by the dotted, dashed and dotted-dashed curves respectively.

In standard textbooks, we can find the analytical expression for the wave function corresponding to the first excited state (with $l = 0$)

$$\Psi_{200}(r) = \frac{1}{2a^{3/2}\sqrt{2\pi}}(1 - \frac{r}{2a})e^{-\frac{r}{2a}}.$$  \hspace{1cm} (33)

Thus, as we can see, the limit $n \to \infty$ converges to the right answer.

In figure 2 we plot the functions $a^{3/2}\Psi_{200}(r)$ and $\Psi_{n,2}(r) \equiv a^{3/2}\Psi_{2,\text{min}}(r)$ for values of $n = 6, 12, 60$. We can see, as in the case of the ground state, when we increment the value of $n$ the function $\Psi_{n,2}(r)$ is approaching to the analytical solution (continuous curve).

6. Results for higher level energies
Since using the variational method, the computations for higher level energies are almost the same as for the ground state and the first excited state, here we are only going to show the results.

For the second excited state, we have used the trial wave function

$$\Psi_3 = C_3(1 + \frac{q_1}{A}r + \frac{q_2}{A^2}r^2)\frac{1}{(A + r)^{n/3}},$$ \hspace{1cm} (34)

where

$$q_1 = \frac{1440 - 2n(135n - 814) + 1152)}{9(5n(9n - 14) + 48)}, \hspace{1cm} q_2 = \frac{(4n - 15)(5n - 36)(n(9n - 16) + 12)}{54(5n(9n - 14) + 48)}.$$ \hspace{1cm} (35)
We would like to point out that, the three trial wave functions (1), (21) and (34) are mutually orthogonal, namely
\[
\langle \Psi_1, \Psi_2 \rangle = \langle \Psi_1, \Psi_3 \rangle = \langle \Psi_2, \Psi_3 \rangle = 0. \tag{36}
\]

The computation of the energy by means of the variational method associated to the trial wave function (34) provides the result
\[
E_3 = \frac{-e^4(-21 + 2n)(3 + 2n)}{((-9 + n)(-15 + 2n)(2n^2 + 3n(-7 + 4q_1) + 9(6 + q_1(-8 + 3q_1)) + 54(-9 + n)(-15 + 2n + 12q_1)q_2 + 2430q_2^2 \mu^2)} / (128\hbar^2(-9 + n)(-6 + n)\pi^2)
\]
\[
((-3 + n)(-15 + 2n)(2n^2 + 9q_1(-3 + 2q_1) + n(-9 + 6q_1) + 162(-15 + 2n)(-1 + q_1)q_2 + 1458q_2^2)((-9 + n)(-21 + 2n)(2n^2 + 9n(-3 + 2q_1) + 9(10 + 3q_1(-5 + 2q_1)) + 54(-21 + 2n)(-18 + 2n + 15q_1)q_2 + 7290q_2^2 \epsilon_0^2) + 54(-21 + 2n)(-18 + 2n + 15q_1)q_2 + 7290q_2^2 \epsilon_0^2). \tag{37}
\]

Using the expressions of \( q_1 \) and \( q_2 \) given in equation (35), we can compute the limit of (37) when \( n \to \infty \), and we obtain
\[
\lim_{n \to \infty} E_3 = -\frac{e^4 \mu}{288\pi^2 \hbar^2 \epsilon_0^2} = -\frac{e^4 \mu}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{32}. \tag{38}
\]

Therefore, as in the case of the first exited state, when we take the limit \( n \to \infty \), we arrive to the correct analytical result (15) which corresponds to the value of the second excited state.

7. Summary and discussion

We have proposed a general trial function in the form of a sequence of functions to calculate the eigen-energies of the hydrogen atom. The most important advantage in comparison with previous trial functions [5, 6] is the inclusion of one integer variational parameter that defines the sequence of functions. The inclusion of this parameter has allowed us to show that when this parameter approaches to infinity we are able to reproduce the exact analytical solution of the hydrogen atom without the need to solve the differential equation and work with complicated special functions.

This type of trial functions are not only useful to find the energies of the ground state, these can also be employed to derive the energies and wave functions of excited states.

The relevance of this method lies in the possibility of including the analysis of multi-electronic atoms as well as systems like molecules. Therefore, the natural next step will be to apply this technique to more complex quantum mechanical systems.

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