Study of a confined Hydrogen-like atom by the Asymptotic Iteration Method

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Abstract. The asymptotic iteration method (AIM) is used to obtain both special exact solutions and general approximate solutions for a Hydrogen-like atom confined in a spherical box of arbitrary radius $R$. Critical box radii, at which states are no longer bound, are also calculated. The results are compared with those in the literature.

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1. Introduction

Recently, there has been great interest in studying the properties of confined quantum systems. There are many reasons for this. The recent developments in nanotechnology have generated intensive research activity in modeling spatially confined quantum systems \[1\]-\[2\]. When an atom or a molecule is trapped inside any kind of microscopic cavity, or is placed in a high pressure environment, it experiences spatial confinement that affects its physical and chemical properties \[3\]-\[4\]. The concept of a confined quantum system goes back to the early work of Michels et al \[1\] who studied the properties of an atomic system under very high pressures. They suggested to replace the interaction of the atoms with surrounding atoms by a uniform pressure on a sphere within which the atom is considered to be enclosed. This led them to consider the problem of hydrogen with modified external boundary conditions \[2\]. Since then, the confined hydrogen atom attracted widespread attention \[2\]-\[33\]. The approach to this confined problem is the same as that used to study a hydrogenic donor located at the center of a spherical \(Ga\)\(^{As} - (Ga, Al)As\) quantum dot, a semiconductor device that confines electrons \[13\]-\[17\]. Considerable interest in calculating the properties of donor states in a quantum dot has been renewed recently and a number of calculations on the bound states of a hydrogenic donor in a quantum dot have been reported (\[17\], and the references therein). Many researchers have carried out accurate calculations of eigenvalues of the confined hydrogen atom using various techniques. Some of these are variational methods \[18\]-\[27\], finite element methods \[28\], and algebraic methods \[29\]. In the present work, we have calculated the energy eigenstates of the confined hydrogen atom for different quantum levels using the Asymptotic Iteration Method (AIM) \[34\]. In addition to calculating the energy eigenvalues, we also used AIM to compute the critical cage radius at which a state is no longer bound. Sommerfeld and Welker \[5\] gave a detailed investigation on the variation of the binding energy of \(1s\) state of hydrogen atom with respect to the sphere radius. They showed that there is critical value of the sphere radius \(r_c\) at which the binding energy is zero. This radius is now known as the ‘critical cage radius’ \[30\]. It has been found that, for \(r < r_c\), the energy of the system is positive, i.e. the electron exerts pressure on the walls of the sphere \[30\]. Later some workers calculated this critical cage radius for various atoms and different quantum levels. For example, Boeyens \[32\] has calculated the \(r_c\) values for the ground state of many atoms by the Hartree-Fock-Slater method.

The organization of the paper is as follows. In the next section, we give a brief outline of the confined Hydrogen-like atom problem. In section 3, we summarize the asymptotic iteration method (AIM) used in this work. In section 4, we apply AIM to the confined Hydrogen-like atom problem and derive certain exact solutions for special parameter values. In section 5, we present the results of our general calculations for any box radius \(R\), and we compare them with the most accurate results available in the literature. We present our calculated critical cage radii in section 6.
2. Formulation of the Problem

In atomic units, the radial Schrödinger equation of a Hydrogen-like atom located in the center of a spherical box of radius \( R \) can be written as

\[
-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{A}{r}\psi(r) = E\psi(r), \quad \psi(0) = \psi(R) = 0
\]  

where \( A > 0 \) is real parameter, \( E \) is the atom's energy and the boundary condition for the exact eigenfunction \( \Psi(r) \) is \( \Psi(0) = \Psi(R) = 0 \) (i.e. it satisfies the Dirichlet boundary condition). Here, \( \mathbf{r} \) is the electron position vector with respect to the nucleus and \( r = ||\mathbf{r}|| \) is the length of this vector. Of course, the presence of the Dirichlet boundary condition changes the structure of the atomic energy spectrum drastically as compared with that of the free, non-confined, hydrogen atom corresponding to the limit \( R \to \infty \). The interesting hidden symmetry that manifests itself in extra degeneracy of energy levels at specific values of \( R \) has been studied [9]-[12] in number of articles.

It is interesting to note that when \( r \) tends to zero, the wavefunction \( \Psi(r) \) behaves as \( r^{l+1} \), and when \( r \) approaches \( R \), \( \Psi \) must approach zero. Under these assumptions, we may represent the unnormalized wavefunction in the form

\[
\psi(r) = \begin{cases} 
  r^{l+1}(R-r) \exp(-ar)f(r), & \text{if } r < R \\
  0, & \text{if } r \geq R
\end{cases}
\]  

where \( f(r) \) is to be determined, and \( a \) is a parameter that will be used to obtain the energy and to control the convergence of the iterative method used by AIM. As we shall show, this simple form of wave function (2) gives good results for the confined hydrogen atom. Substituting (2) in the Schrödinger equation (1), we find that the radial function \( f(r) \) must satisfy the differential equation

\[
f''(r) = 2 \left( a + \frac{1}{R-r} - \frac{l+1}{r} \right)f'(r) + \left( \frac{(2l+2)a - A}{r} + \frac{2l+2}{r(R-r)} - \frac{2a}{R-r} \right)f(r)
\]

where we denote

\[ E = -a^2. \]  

The problem is then reduced to solving this second-order homogeneous differential equation for \( f(r) \). The asymptotic iteration method (AIM) was developed with the idea of using minimal algebraic computations to solve such differential equations. In the next section, we give a brief introduction to the asymptotic iteration method. Detailed proofs and applications to unconfined systems can be found in [34] and [35].

3. Brief Introduction to the Asymptotic Iteration Method

Given \( \lambda_0(x) \) and \( s_0(x) \) sufficiently differentiable functions, the asymptotic iteration method tells us that the second-order differential equation

\[
y'' = \lambda_0(x)y' + s_0(x)
\]

is reduced to solving the first-order equations

\[
y' = \lambda_0(x), \quad y(0) = 0 \\
y'' = s_0(x)
\]
has a general solution
\[ y(x) = \exp\left(-\int x \alpha \, dt\right) \left(C_2 + C_1 \int x \exp \left(\int \left(\lambda_0(\tau) + 2\alpha(\tau)\right) d\tau\right) d\right) \] (6)
if for some \( n > 0, \)
\[ \frac{s_n}{\lambda_n} = \frac{s_{n-1}}{\lambda_{n-1}} \equiv \alpha \] (7)
where
\[
\begin{cases}
\lambda_n = \lambda'_{n-1} + s_{n-1} + \lambda_0 \lambda_{n-1}, \\
s_n = s'_{n-1} + s_0 \lambda_{n-1}.
\end{cases}
\] (8)

In general, the (asymptotic) termination condition Eq.(7) can be written equivalently as follows
\[ \delta_n(r) = \lambda_n s_{n-1} - s_n \lambda_{n-1} = 0, \quad n = 1, 2, \ldots \] (9)

Note that, we can start the computation of the recurrence relation (9) from \( n = 0 \) with the initial conditions \( \lambda_{-1} = 1 \) and \( s_{-1} = 0 \). It follows that if \( \delta_n(r) = 0 \), then \( \delta_{n+1}(r) = 0 \) for all \( n \). The termination condition (9) has a crucial role for the computation of the eigenenergies (4). Indeed, using (3), we obtain, by means of
\[
\begin{cases}
\lambda_0 = 2\left(a + \frac{1}{2} - \frac{l+1}{r}\right), \\
s_0 = \left(\frac{2l+2}{r}A - \frac{2l+2}{r(R-r)} - \frac{2a}{R-r}\right),
\end{cases}
\] (10)
the recursive relations for \( s_n \) and \( \lambda_n \), \( n = 1, 2, \ldots \) given by (8). These quantities are, in general, functions of the parameter \( a \) and the variable \( r \). If, for a suitable choice of \( a \), the termination condition Eq.(9) is satisfied at every \( r < R \), then the problem is called ‘exactly solvable’. If the differential equation is not exactly solvable, the function \( \delta(r) \), in general, will depends on both \( a \) and \( r \). In this case, we obtain \( a \) by iterating Eq.(9) with a suitable initial value of \( r = r_0 < R \).

4. Exact analytical solutions

In this section, we first present the exact analytical solutions for a Hydrogen-like atom confined in a spherical box of radius \( R \). The application of AIM which we employ here shows that for certain values of the parameter \( a \), we obtain exact solution provided the confinement radius \( R \) assumes corresponding definite values; that is to say, Eq.(3) is then exactly solvable. We first note that the integer \( n \) here is not to be identified for the hydrogenic problem with the radial quantum number, but rather by \( n = 1+\)number of radial nodes. Thus, with this notation, in the limit as \( R \to \infty \), the eigenvalues of Eq.(1) become exactly \( E = -A^2/(4(n+\ell)^2) \). Using (9) and (10) we find the following results.

- For \( n = 1 \) and \( a = \frac{A}{2(l+2)} \), we have \( \delta_1 = 0 \) if
  \[ AR - 2(l+1)(l+2) = 0. \]
For \( n = 2 \) and \( a = \frac{A}{2(l+3)} \), we have \( \delta_2 = 0 \) if
\[ A^2 R^2 - 2(2l+3)(l+3)AR + 2(l+3)^2(2l+3)(l+1) = 0. \]

For \( n = 3 \) and \( a = \frac{A}{2(l+4)} \), we have \( \delta_3 = 0 \) if
\[ A^3 R^3 - 6(l+2)(l+4)A^2 R^2 + 6(l+4)^2(l+2)(2l+3)AR - 4(l+4)^3(l+2)(l+1)(2l+3) = 0. \]

and so on. In general, we have for \( a = \frac{A}{2(n+l+1)} \), \( l = 0, 1, 2, \ldots \)
\[ \delta_n = 0, \quad n = 1, 2, \ldots \text{ if} \]
\[ \sum_{k=0}^{n} \frac{(-1)^k(l+n+1)^{n-k} \Gamma(2l+n+2) \Gamma(n+1)}{\Gamma(2l+k+2) \Gamma(n+1-k) \Gamma(k+1)} (AR)^k = 0. \]  

It is interesting to note that the polynomial conditions on \( R \) given by (12) can be written in terms of the confluent hypergeometric functions as
\[ \, _1F_1 \left(-n; 2l+2; \frac{AR}{l+n+1}\right) = 0, \quad n = 1, 2, \ldots. \]  

This means that, in order to obtain the energy spectrum as given by (4), we must find the roots of the confluent hypergeometric function (13). In this case, for given \( A \), the eigenvalues (4) are given by
\[ E_{nl} = -\frac{A^2}{4(n+l+1)^2}, \quad n = 1, 2, \ldots, \quad l = 0, 1, 2, \ldots \]
where \( R \) has values which are the roots of (13). The corresponding analytic wave functions can be computed by using Eq.(6) for \( A \) and \( R \), related by means of (13) for given \( n \) and \( l \). Straightforward computations then show that
\[ f_{0l}^m(r) = 1, \quad f_{nl}^m(r) = \prod_{i=0}^{n-1} \left(1 - \frac{r}{R_i}\right), \quad i \neq m \]  

where \( m = 0, 1, 2, \ldots n - 1 \) and \( R_i \) are the roots of (13). In Table 1, we report some eigenenergies of the enclosed hydrogen atom as a function of the radius \( R \) along with the corresponding wave functions \( f(r) \) computed by using (15). We can obtain the complete wavefunction from Eq.(2). For given \( n, l, m \) quantum numbers, the corresponding (un-normalized) wave functions are given by
\[ \Psi_{nl}^m = N_{nl}^m r^{l+1} \exp \left( -\frac{A}{2(n+l+1)} r \right) \prod_{i=0}^{n-1} \left(1 - \frac{r}{R_i}\right), \quad r \in (0, R_m) \]  

where \( R_{i(m)} \) are given as the roots of the confluent hypergeometric function Eq.(13). We have first obtained these exact solutions of the confined hydrogen-like problem, valid for special values of the parameters, since they can be very useful for verifying the correctness of general approximations. In the next section, we will give more general results for the problem by applying AIM to Eq.(3) for arbitrary given \( R \).
5. Energy eigenvalues of a Hydrogenic Donor

The Hamiltonian of an on-center impurity in a spherical quantum dot can be written in the effective-mass approximation as

\[ H = -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\epsilon r} \] \hspace{1cm} (17)

where \( m^* \) is the effective mass and \( \epsilon \) is the dielectric constant of the material of the quantum dot. The donor is assumed to be at the center of the quantum dot of radius \( R \) with an infinite barrier height. This means that the wave function vanishes at \( r = R \).

In atomic units, the radial Hamiltonian equation for the Coulomb Potential is given by

\[ \left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2}{r}\right] \psi(r) = E\psi(r), \quad \psi(0) = \psi(R) = 0. \] \hspace{1cm} (18)

In this section, we use AIM in order to obtain the energy states of the confined atom. We note first that, Eq. (3) now reads

\[ f''(r) = 2 \left(a + \frac{1}{R-r} - \frac{l+1}{r}\right) f'(r) \]

\[ + \left( \frac{(2l+2)a - 2}{r} + \frac{2l+2}{r(R-r)} - \frac{2a}{R-r} \right) f(r) \] \hspace{1cm} (19)
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Now, for a given $R$ value, we have calculated the energy values $a$ using (9) and the recursive relations (8) initiated with
\[
\begin{align*}
\lambda_0 &= 2(a + \frac{1}{R} - \frac{1}{r}), \\
\delta_0 &= \frac{(2l+2a-2)}{r} + \frac{2l+2}{r(R-r)}.
\end{align*}
\]
(20)

Since the system is not exactly solvable, and since $\delta_n(r) \equiv \delta_n(a; r) = 0$, we must choose a suitable value for $r_0 < R$ in order to initiate AIM. For our numerical results, we have fixed $r = r_0$ as $\frac{R}{2}$ for $R \leq 1$ and 1 for $R \geq 1$. The corresponding results are shown in Tables 2 and 3. Comparison is made with results from [17], which are based on a variational method.

Table 2. Exact energy eigenvalues for the 1st state (in Rydbergs) found with AIM, for different values of $R$. Comparison is made with the results of Ref. [17].

| $R$ | $a$         | $E_{AIM}$          | $E_{exact}$ [17] |
|-----|-------------|--------------------|------------------|
| 0.1 | 30.626 558 365 553 640 428 52i | 937.986 077 318 663 675 020 | 937.986 |
| 0.2 | 14.904 352 306 411 647 880 03i | 222.139 717 673 638 207 696 | 222.14(0) |
| 0.3 | 9.653 226 131 767 727 449 50i | 93.184 774 751 043 322 516 | 93.185(0) |
| 0.4 | 7.019 089 585 470 665 068 48i | 49.267 618 608 862 752 786 | 49.268(0) |
| 0.5 | 5.431 016 485 033 032 864 57i | 29.495 940 060 700 559 289 | 29.496(0) |
| 0.6 | 4.365 250 922 031 022 986 22i | 19.055 415 612 292 696 322 | 19.055(0) |
| 0.7 | 3.597 200 613 602 544 685 31i | 12.939 852 254 502 523 992 | 12.940(0) |
| 0.8 | 3.014 425 378 412 749 608 39i | 9.086 760 362 018 848 673 | 9.086(0) |
| 0.9 | 2.554 286 411 599 184 224 80i | 6.524 379 072 480 237 168 | 6.524(0) |
| 1.0 | 2.178 986 400 188 704 127 38i | 4.747 981 732 207 327 454 | 4.748(0) |
| 1.2 | 1.593 307 889 331 964 142 70i | 2.538 630 030 207 478 496 | 2.538(0) |
| 1.4 | 1.137 633 609 176 779 056 96i | 1.294 210 228 728 584 474 | 1.294(0) |
| 1.6 | 0.736 630 589 422 075 466 49i | 0.542 624 625 272 314 320 | 0.54262 |
| 1.8 | 0.255 171 521 889 990 724 15i | 0.065 112 505 583 654 015 | 0.06511 |
| 2.0 | 0.5 | -0.25* | -0.25 |
| 2.2 | 0.681 224 443 905 427 229 15 | -0.466 066 742 974 258 570 | -0.46407 |
| 2.4 | 0.782 812 885 873 172 513 99 | -0.612 796 014 289 084 615 | -0.61280 |
| 2.6 | 0.847 323 189 868 271 355 52 | -0.717 956 588 088 542 630 | -0.71796 |
| 2.8 | 0.890 692 535 878 441 133 67 | -0.793 333 193 469 568 146 | -0.79333 |
| 3.0 | 0.920 833 630 721 047 974 35 | -0.847 934 575 466 907 348 | -0.84793 |
| 3.2 | 0.942 234 555 027 191 412 81 | -0.887 805 956 687 289 402 | -0.88781 |
| 3.4 | 0.957 650 893 749 316 017 63 | -0.917 095 234 298 863 756 | -0.91710 |
| 3.6 | 0.968 866 519 413 519 397 41 | -0.938 702 332 440 467 559 | -0.93870 |
| 3.8 | 0.977 080 758 210 929 418 85 | -0.954 686 808 066 044 717 | -0.95469 |
| 4.0 | 0.983 122 883 548 157 499 83 | -0.966 530 604 156 044 052 | -0.96653 |

* Exact, see Table 1
Table 3. Exact eigenenergies (in Rydbergs) obtained with AIM for different values of $R$ for the $2p$ state ($\ell = 1$). Comparison is made with results of Ref. [17], see also Ref. [27].

| $R$  | $a$       | $E_{\text{AIM}}$ | $E_{\text{exact}}$ [17] |
|------|-----------|------------------|--------------------------|
| 0.4  | 10.811 856 798 907 243 508 22i | 116.896 247 440 076 786 588 403 | 116.896 |
| 1    | 4.055 400 921 280 376 683 83i  | 16.446 276 632 321 727 964 741   | 16.446  |
| 2    | 1.775 397 862 793 768 780 65i  | 3.152 037 571 212 681 836 807      | 3.1520  |
| 4    | 0.535 774 362 421 267 801 33i  | 0.287 054 167 427 916 019 155      | 0.28705 |
| 8    | 0.457 055 940 572 194 782 44   | −0.208 900 132 812 333 836 630     | −0.2089 |

6. Critical cage radii

In this section we report the results of our calculations for the critical cage radius, at which the total energy is zero, i.e., when the kinetic and potential energy contributions cancel one another. Such cage radii were first noted by Sommerfeld and Welker [5] in their detailed study on the variation of the binding energy of the $1s$ state of the hydrogen atom, as a function of the sphere radius, $R$. Assuming that the surface of the spherical box is impenetrable, they showed that, as $R$ decreases, the binding energy diminishes, and there is a critical value of the sphere radius at which the binding energy becomes zero. More systematic studies were later carried by Varshni [30] where the critical cage radius was first recorded; see also [31]. In this section we shall use AIM to calculate the cage radius at which the eigenvalues are zero. With $E = 0$, we find, by using (14), that $a = 0$; and then Eq. (19) reduces to

$$f''(r) = 2 \left( \frac{1}{R-r} - \frac{\ell + 1}{r} \right) f'(r) + \left( - \frac{2}{r} + \frac{2\ell + 2}{r(R-r)} \right) f(r) \quad (21)$$

We now apply AIM with $\lambda_0$ and $s_0$ extracted from (21). The termination condition $\delta_n(r) = 0$, is then dependent (see (9)) on both the variable $r$ and the parameter $R \equiv r_c$. Starting with $r \approx R/2$, the iteration process converges quickly to the cage radius $R \approx r_c$. For example, if $\ell = 0$ and $n = 5$, AIM takes 26 iterations to yield $r_c = 48.09774$ initiated with starting value of $r = 24$. The calculated values of $r_c$ found by using AIM are shown in Table 4 for different values of $\ell$ and $n$. Similar tables can be easily constructed for arbitrary values of $n$ and $\ell$. The numerical computation of eigenvalues and the critical cage radii in tables 2-4 were performed by using Maple version 10 running on an IBM architecture personal computer (Dell Dimension 4400). In many cases, we have removed some of the apparent divergence [37] experienced by AIM by increasing the number of significant digits that Maple uses in numerical computation; for the present results we have used $\text{Digits}=50$. In order to accelerate the computation we have written our code for the root-finding algorithm, instead of using the default procedure of Maple. All the numerical results reported using AIM in tables 2-4 are exact in sense that the numerical integration of the corresponding Schrödinger (confined) equation yields the same values.
Table 4. Exact values of the critical cage radius calculated by the use of AIM $r_c(AIM)$. Radii are in units of the Bohr radius. Comparison with [30] are also reported $r_c$.

| $\ell$ | $n$ | $r_c(AIM)$     | $r_c$ | $\ell$ | $n$ | $r_c(AIM)$     | $r_c$ |
|--------|-----|----------------|-------|--------|-----|----------------|-------|
| 0      | 1   | 1.835 246 330 265 5 | 1.8352| 1      | 1   | 5.088 308 227 275 0 | 5.0883|
| 2      | 2   | 6.152 307 040 211 8 | 6.1523| 2      | 2   | 11.909 696 568 004 6 | 11.910|
| 3      | 3   | 12.937 431 736 892 1 | 12.937| 3      | 3   | 21.174 431 228 262 4 | 21.174|
| 4      | 4   | 22.190 095 851 725 6 | 22.190| 4      | 4   | 32.900 106 781 876 0 | 32.900|
| 5      | 5   | 33.910 206 784 109 2 | 33.910| 5      | 5   | 47.090 674 929 020 9 | 47.091|
| 6      | 6   | 48.097 738 137 838 7 | 48.098| 6      | 6   | 63.747 459 484 409 4 | 63.747|

7. Conclusion

In this work, we have applied AIM to obtain the energy eigenstates of a confined hydrogen atom. The problem is similar to the confinement of electrons in a quantum dot. For certain cases, the eigenvalues under confinement are given by the roots of the Kummer (confluent) hypergeometric functions whose analytic and numerical properties are well known [36]. The method can be easily adapted to the study of more highly excited states, without necessitating extensive further algebraic manipulation or numerical work [33]. We have also calculated the critical cage radii $r_c$ at which various states become unbound. The numerical results are compared with the most accurate results in the literature. It is worth pointing that AIM provides a simple technique to obtain very accurate eigenenergies for a confined hydrogen atom, as well as the critical-cage radii, to any desired degree of precision. The method is easily realized by the use of any contemporary mathematical software. This makes the study of confined potentials more accessible.
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