Research Article

# On the Hydrogen Atom in a Spherical Box

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**We derive some properties of the hydrogen atom inside a box with an impenetrable wall that have not been discussed before. Suitable scaling of the Hamiltonian operator proves to be useful for the derivation of some general properties of the eigenvalues. The radial part of the Schrödinger equation is conditionally solvable, and the exact polynomial solutions provide useful information. There are accidental degeneracies that take place at particular values of the box radius, some of which can be determined from the conditionally-solvable condition. Some of the roots stemming from the conditionally-solvable condition appear to converge towards the critical values of the model parameter. This analysis is facilitated by the Rayleigh-Ritz method, which provides accurate eigenvalues.**

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## 1. Introduction

Quantum mechanical models of particles confined within boxes of different shapes have received considerable attention for many years[1][2][3][4]. In such reviews, one can find all kinds of atomic and molecular systems enclosed inside surfaces that are impenetrable or penetrable. In a recent paper, Amore and Fernández[5] came across a most interesting accidental degeneracy that had not been discussed before. The purpose of this paper is the analysis of possible accidental degeneracies in the case of the hydrogen atom in a spherical box with the nucleus clamped at the origin.

In section 2, we discuss the model and some of its mathematical properties. In section 3, we investigate exact polynomial solutions to the radial part of the Schrödinger equation. In section 4, we obtain accurate eigenvalues by means of the Rayleigh-Ritz method (RRM)[6][7]. Finally, in section 5, we summarize the main results of the paper and draw conclusions.

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## 2. The model

In this section, we present the model and discuss some of the properties of the time-independent Schrödinger equation. We are interested in the eigenvalue equation $H\psi = E\psi$ for the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m_e\nabla^2} - \frac{K}{r}, \tag{1}$$

where $m_e$ is the electron mass and $K > 0$ is the strength of the Coulomb potential (with units of energy $\times$length). For simplicity, we assume that the nucleus is clamped at the origin. The solutions $\psi(r,\theta,\phi)$ in spherical coordinates $x = r\sin\theta\cos\phi,\ y = r\sin\theta\sin\phi,\ z = r\cos\theta,\ 0 < \theta < \pi,\ 0 \leq \phi < 2\pi,$ satisfy the boundary condition $\psi(r_0,\theta,\phi) = 0$ because of the impenetrable wall of a spherical box of radius $r_0$. Therefore, $0 < r \leq r_0$.

In order to discuss some useful analytical properties of the solutions to the eigenvalue equation, it is convenient to carry out the scaling transformation $(x,y,z) \to (L\tilde{x}, L\tilde{y}, L\tilde{z}),\ r \to L\tilde{r},\ \nabla^2 \to L^{-2}\tilde{\nabla}^2,$ where $L$ is a real positive constant with units of length. In this way, we derive a useful dimensionless eigenvalue equation $\tilde{H}\tilde{\psi} = \tilde{E}\tilde{\psi}$, where[8]

$$\tilde{H} = \frac{m_e L^2}{\hbar^2} H = -\frac{1}{2}\tilde{\nabla}^2 - \frac{m_e L K}{\hbar^2 \tilde{r}}. \tag{2}$$

The boundary condition becomes $\tilde{\psi}\left(\tilde{r}_0,\theta,\phi\right) = 0$, where $\tilde{r}_0 = r_0/L$, and the unit of energy is $\hbar^2/\left(m_e L^2\right)$. If $E(r_0,K)$ denotes an eigenvalue, then equation (2) tells us that

$$E(r_0,K) = \frac{\hbar^2}{m_e L^2} E\left(\frac{r_0}{L}, \frac{m_e L K}{\hbar^2}\right). \tag{3}$$

The scaling transformation of the Hamiltonian operator proves useful for the derivation of many properties of quantum-mechanical systems as discussed elsewhere[8]. In what follows, we add another example.

If we choose $L = r_0$ then

$$\tilde{H} = -\frac{1}{2}\tilde{\nabla}^2 - \frac{m_e r_0 K}{\hbar^2 \tilde{r}}, \tag{4}$$

and $\tilde{\psi}(1,\theta,\phi) = 0$. Therefore,

$$\lim_{r_0 \to 0} \tilde{H} = -\frac{1}{2}\tilde{\nabla}^2, \tag{5}$$


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and the problem reduces to a particle within a spherical box of radius $\tilde{r}_0 = 1$. In this case, the unit of energy is $\hbar^2/\left(m_e r_0^2\right)$.

Alternatively, we may also choose $L = \hbar^2/(m_e K)$ that leads to

$$\tilde{H} = -\frac{1}{2}\tilde{\nabla}^2 - \frac{1}{\tilde{r}}, \tag{6}$$

and the unit of energy $\hbar^2/(m_e L^2) = m_e K^2/\hbar^2$.

Throughout this paper, we will omit the tilde over the dimensionless quantities and will write, for example, the Hamiltonian operator (4) as

$$H = -\frac{1}{2}\nabla^2 - \frac{\beta}{r}, \beta = \frac{m_e r_0 K}{\hbar^2}. \tag{7}$$

Before proceeding with our discussion of the model (7), we want to point out that expressions like "we choose units such that $\hbar = m = 1$" are meaningless if we do not clearly indicate the units of length and energy actually used. Note that the two dimensionless Hamiltonians $\tilde{H}$ shown in equations (4) and (6) formally correspond to setting $\hbar = m = 1$ though the units of length and energy in one case are different from those in the other.

If we substitute the two values of $L$ shown above into equation (3) and equate the results, we can easily derive the relationships

$$\begin{aligned}\tilde{E}(1,\beta) &= \beta^2\tilde{E}(\beta,1), \\ \tilde{E}\left(1,\tilde{r}_0\right) &= \tilde{r}_0^2\tilde{E}\left(\tilde{r}_0,1\right),\end{aligned} \tag{8}$$

that clearly show the connection between $\beta$ and $r_0$ in the two alternative approaches to the problem.

The Schrödinger equation for any of the Hamiltonian operators shown above is separable in spherical coordinates as $\psi(r,\theta,\phi) = R(r)Y_l^m$, where $l = 0, 1, \ldots$ and $m = 0, \pm 1, \pm 2, \ldots, \pm l$ are the angular and magnetic quantum numbers, respectively, and $Y_l^m$ are the well-known spherical harmonics. The energy eigenvalues depend only on the radial quantum number $n = 0, 1, \ldots$ and on $l$ so that we write them as $E_{nl}$ from now on. For convenience, we do not resort to the principal quantum number $n_p = n + l + 1 = 1, 2, \ldots$ that is mostly useful in the case of the free hydrogen atom. It follows from the Hamiltonian operator (6) that

$$\lim_{r_0 \to \infty} E_{nl} = E_{nl}^H = -\frac{1}{2(n+l+1)^2}, \tag{9}$$

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from which we conclude that $E_{nl}^{H} > E_{n'l'}^{H}$ if $n+l > n'+l'$. This obvious inequality will be useful later on.

Since $E(1,0)$ is positive and $\lim_{\beta\to\infty} \beta^{-2}E(1,\beta)$ is negative, then for each eigenvalue $E_{nl}$ there is a value $\beta = \beta_{nl}^{c}$ such that $E_{nl}\left(\beta_{nl}^{c}\right) = 0$. We will discuss these critical values of $\beta$ in section 4.

## 3. Exact polynomial solutions

The radial part of the Schrödinger equation for the Hamiltonian operator (7) is

$$-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)R(r)+\left[\frac{l(l+1)}{2r^2}-\frac{\beta}{r}\right]R(r)=ER(r), \tag{10}$$

with the boundary condition $R(1)=0$. This eigenvalue equation admits some exact polynomial solutions because it is conditionally solvable (see, for example, [9][10] and references therein). In order to derive them, we propose a solution of the form

$$R(r)=r^{l}(1-r)e^{-\alpha r}\sum_{j=0} c_j r^j. \tag{11}$$

It is not difficult to verify that the expansion coefficients $c_j$ satisfy the three-term recurrence relation

$$\begin{aligned} c_{j+2} &= A_j c_{j+1} + B_j c_j, j=0,1,\ldots \\ A_j &= \frac{2\alpha\left(j+l+2\right)-2\beta+j^2+j\left(2l+5\right)+2\left(2l+3\right)}{\left(j+2\right)\left(j+2l+3\right)}, \\ B_j &= 2\frac{\beta-\alpha\left(j+l+2\right)}{\left(j+2\right)\left(j+2l+3\right)}, \end{aligned} \tag{12}$$

where we have set $E=-\alpha^2/2$ in order to remove one of the terms.

In order to obtain exact polynomial solutions, we require that $c_\nu \neq 0$ and $c_{\nu+1}=c_{\nu+2}=0$, $\nu=0,1,\ldots$. These conditions are satisfied if $B_\nu = 0$ from which we obtain

$$\alpha=\frac{\beta}{l+\nu+2}, E=-\frac{\beta^2}{2(l+\nu+2)^2}. \tag{13}$$

Therefore

$$\begin{aligned} A_j &= \frac{2\beta\left(j-\nu\right)+\left(j^2+j\left(2l+5\right)+2\left(2l+3\right)\right)\left(l+\nu+2\right)}{\left(j+2\right)\left(j+2l+3\right)\left(l+\nu+2\right)}, \\ B_j &= \frac{2\beta\left(\nu-j\right)}{\left(j+2\right)\left(j+2l+3\right)\left(l+\nu+2\right)}. \end{aligned} \tag{14}$$

The expression for $E$ in equation (13) does not give us the spectrum of the problem. Note that $E=0$ when $\beta=0$ while the Hamiltonian (7) tells us that we should obtain the spectrum of the particle

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in a box of radius $r_0 = 1$ when $\beta = 0$. Besides, the polynomial solutions only provide negative eigenvalues while all the eigenvalues are positive for sufficiently small values of $\beta$ as argued in section 2. Any smart reader may think that it is not necessary to stress such an obvious fact, but unfortunately, many researchers have misinterpreted the polynomial solutions of several conditionally-solvable models as discussed elsewhere[11][12].

Since $B_\nu = 0$ the only remaining condition is $c_{\nu+1} = 0$ from which we obtain $\nu + 1$ roots $\beta_l^{(\nu,i)}$, $i = 0, 1, , \ldots, \nu$, that we arbitrarily arrange so that $\beta_l^{(\nu,i+1)} > \beta_l^{(\nu,i)}$. Thus, the energies of the polynomial solutions should be more properly written as

$$E_l^{(\nu,i)} = -\frac{\left[\beta_l^{(\nu,i)}\right]^2}{2(l+\nu+2)^2}. \tag{15}$$

In the expressions above $\nu$ is the degree of the polynomial factor in the exact solution, and $i$ is the number of real zeros of the polynomial in the interval $0 < r < 1$. For this reason, $i$ (and not $\nu$) is related to the radial quantum number $n$. This fact was overlooked by many researchers as discussed in the papers just mentioned[11][12]. Of particular interest are the roots

$$\beta_l = \beta_l^{(0,1)} = (l+1)(l+2), E_1^{(0,1)} = -\frac{(l+1)^2}{2}, \tag{16}$$

as shown below.

## 4. Accurate numerical results

One can obtain accurate numerical results in several ways, as shown in suitable reviews on the subject[1][2][3][4]. Here, we resort to the RRM[6][7] that provides increasingly accurate upper bounds to the exact eigenvalues[13][14].

For simplicity, we resort to the non-orthogonal basis set

$$f_{il}(r) = r^{i+l}(1-r), i = 0, 1, \ldots. \tag{17}$$

The RRM secular equations are well-known[6][7][14][15] and will not be discussed here.

Table 1 shows some eigenvalues for the case $\beta = 0$. We appreciate that there are several cases in which $E_{nl}^{PB} > E_{n'l'}^{PB}$ with $n + l < n' + l'$. Consequently, we expect that such eigenvalues $E_{nl}$ and $E_{n'l'}$ should cross at some nonzero value of $\beta$ because $E_{n'l'}^{H} > E_{nl}^{H}$ as argued in section 2.


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Figure 1 shows the lowest eigenvalues with $l = 0, 1, 2, 3$. We appreciate the crossings at $\beta = \beta_0 = 2$ between $E_{10}$ and $E_{02}$ and also between $E_{20}$ and $E_{12}$. This fact suggests that the values $\beta_l$ of the model parameter given by the exact polynomial solutions are special. It is worth noting that the former accidental degeneracy appeared in an earlier paper[16] (see also Table 4 on page 140 in reference[2]) but nobody paid attention to it as far as we know. The blue points in Figure 1 are values of exact energies given by equation (15) when $i = 0$. Since the polynomial factors of such solutions do not exhibit nodes, they correspond to the ground state, as the figure already shows.

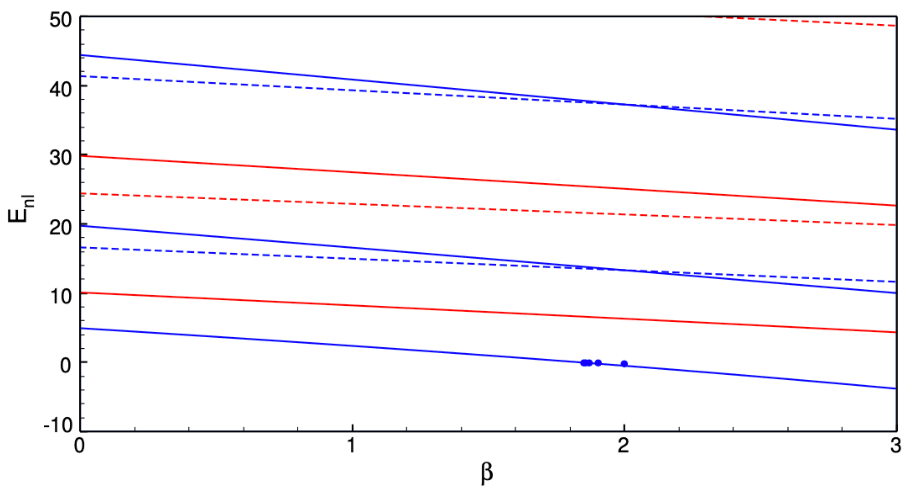


**Figure 1.** Lowest eigenvalues with $l = 0$ (blue solid lines), $l = 1$ (red solid lines), $l = 2$ (blue dashed lines), $l = 3$ (red dashed lines)

Table 2 shows several RRM eigenvalues calculated at $\beta = \beta_l$, $l = 0, 1, 2$. It is worth noting that the RRM yields the exact eigenvalue $E_{0l}$ at $\beta = \beta_l$. From these results, we draw the following

**Conjecture 1.** *Pairs of eigenvalues* $(E_{n+1l}, E_{nl+2})$, $n = 0, 1, \ldots, l = 0, 1, \ldots$ *cross at* $\beta = \beta_l$

At present, we are unable to prove this conjecture, but all our numerical results confirm it.

The RRM enables us to obtain the critical values of $\beta$ introduced in section 2. We simply set $E = 0$ in the secular equation[6][7][14][15] and solve for $\beta$. Table 3 shows some critical values of $\beta$ for $l = 0, 1, 2, 3$. The roots $\beta_l^{(\nu,i)}$ decrease as $\nu$ increases and appear to approach $\beta_{nl}^c$ when $n = i$. This fact, which is shown in Figure 2, suggests the following

**Conjecture 2.** $\lim\limits_{\nu \to \infty} \beta_l^{(\nu,n)} = \beta_{nl}^c$

At present, we are unable to prove this conjecture that our numerical results confirm.

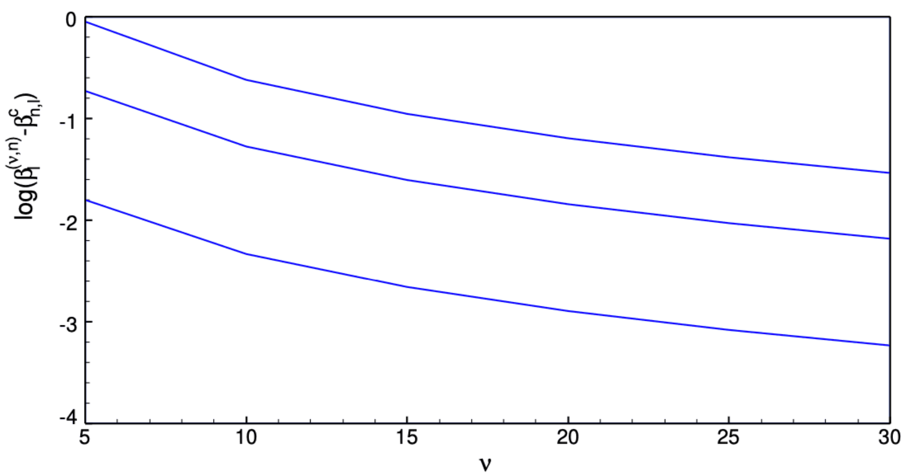


**Figure 2.** $\log\left(\beta_l^{(\nu,n)} - \beta_{nl}^c\right)$

## 5. Conclusions

In this paper, we have shown several aspects of the well-known hydrogen atom inside a box with an impenetrable spherical wall that have passed unnoticed, as far as we know. In the first place, a suitable scaling of the Hamiltonian operator is extremely useful for the derivation of several general properties of the eigenvalues. In the second place, the radial part of the Schrödinger equation is conditionally solvable. In the third place, there are most interesting seemingly accidental degeneracies that take place at particular values of the box radius, some of which can be determined from the conditionally-solvable condition. In the fourth place, some of the roots stemming from the conditionally-solvable condition appear to converge towards the critical values of the model parameter. At present, we cannot prove the two latter results rigorously and have, therefore, presented them as conjectures. In this analysis, the RRM proved to be most useful.

## Tables

| $(n,l)$ | $E_{nl}^{PB}$ |
|---|---|
| (0,0) | 4.934802200 |
| (0,1) | 10.09536427 |
| (1,0) | 19.73920880 |
| (0,2) | 16.60873095 |
| (1,1) | 29.83975797 |
| (2,0) | 44.41321980 |
| (0,3) | 24.41559682 |
| (1,2) | 41.35961555 |
| (2,1) | 59.44993458 |
| (3,0) | 78.95683520 |
| (0,4) | 33.47715596 |
| (1,3) | 54.25817941 |
| (2,2) | 75.92743708 |
| (3,1) | 98.92890559 |
| (4,0) | 123.3700550 |
| (0,5) | 43.76561012 |
| (1,4) | 68.50242574 |
| (2,3) | 93.81791915 |
| (3,2) | 120.3514532 |
| (4,1) | 148.2772060 |
| (5,0) | 177.6528792 |
| (0,6) | 55.25985415 |
| (1,5) | 84.06545236 |

| $(n, l)$ | $E_{nl}^{PB}$ |
|---|---|
| **(2,4)** | 113.0957572 |
| **(3,3)** | 143.2044787 |
| **(4,2)** | 174.6400399 |
| **(5,1)** | 207.4949921 |

**Table 1.** Some eigenvalues for $\beta = 0$

| l | $n = 0$ | $n = 1$ | $n = 2$ | $n = 3$ |
|---|---|---|---|---|
| $\beta_0 = 2$ | | | | |
| 0 | $-0.5$ | 13.31003662 | 37.25660174 | 71.26437398 |
| 2 | 13.31003662 | 37.25660174 | 71.26437398 | 115.2540228 |
| $\beta_1 = 6$ | | | | |
| 1 | $-2$ | 15.17434035 | 42.95936431 | 81.04494034 |
| 3 | 15.17434035 | 42.95936431 | 81.04494034 | 129.2643219 |
| $\beta_2 = 12$ | | | | |
| 2 | $-4.5$ | 15.84159512 | 47.2388141 | 89.18513747 |
| 4 | 15.84159512 | 47.2388141 | 89.18513747 | 141.4317571 |

**Table 2.** Some level crossings at $\beta_l$


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| l | $\beta^c_{0,l}$ | $\beta^c_{1,l}$ | $\beta^c_{2,l}$ | $\beta^c_{3,l}$ |
|---|---|---|---|---|
| **0** | 1.835246330 | 6.152307040 | 12.93743173 | 22.19009585 |
| **1** | 5.088308227 | 11.90969656 | 21.17443122 | 32.90010678 |
| **2** | 9.617366041 | 19.03014419 | 30.81193326 | 45.03068523 |
| **3** | 15.36345002 | 27.45875083 | 41.80446073 | 58.54453721 |

**Table 3.** Some critical values of $\beta$

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## Declarations


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