

The hydrogen atom with an origin centred singularity

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We study the problem of a hydrogen atom with an infinitely repulsive singularity at the origin, in two cases: in the first, the electron is free to move throughout space, while in the other, the system is confined in a spherical box of impenetrable walls centred at the nucleus. We show that spherically symmetric s states cannot exist in these systems.

Keywords: Confined hydrogen atom; energy eigenvalues; eigenfunctions.

Estudiamos el problema del átomo de hidrógeno con una singularidad infinitamente repulsiva en el origen, en dos casos: en el primero, el electrón se mueve libremente en todo el espacio, mientras que en el otro, el sistema se confina dentro de una caja esférica de paredes impenetrables centrada en el núcleo. Mostramos que no existen estados esféricamente simétricos en este problema.

Descriptores: Átomo de hidrógeno confinado; energías propias; funciones propias.

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1. Introduction

There has recently been an increased interest in the study of quantum confined systems. Some examples refer to the so-called artificial atoms or quantum dots, which consist of electrons moving inside quantum wells [1-3]. Atoms or molecules trapped inside cavities as fullerenes or zeolite cages [4,5] also fall into this category.

Another system recently analyzed corresponds to the so-called shell-confined hydrogen atom [6-8], which refers to a hydrogen atom with the nucleus placed at the centre of two concentric impenetrable spheres, where the electron is subject to the following potential

$$V(r) = \begin{cases} +\infty & \text{if } 0 \leq r \leq a \\ -\frac{1}{r} & \text{if } a < r < b \\ +\infty & \text{if } r \geq b \end{cases} \quad (1)$$

Studies based on this model have been devoted to the analysis of variations in the static dipole polarizability and Shannon entropy as functions of the wall positions.

In this report we analyze the energy spectrum of the system in two cases: in the first we take $a = 0$ and $b \rightarrow \infty$, while in the second we choose $a = 0$ and $b = r_0$ (finite). We show that these systems possess no spherically symmetric solutions (s states). It should be pointed out that this property has not been discussed in previous works.

In Sec. 2 we obtain the energy spectrum of the hydrogen atom with an impenetrable wall at the origin, while in Sec. 3 we identify the eigensolutions for confinement at $r = b$. Finally, in Sec. 4 we give some conclusions.

2. The hydrogen atom with a singularity at the origin

The system under consideration is a hydrogen atom with a singularity at the origin. The radial Schrödinger equation of the system in atomic units ($\hbar = m = e = 1$) is given by

$$-\frac{1}{2}\nabla^2\psi + V_c(r)\psi = E\psi, \quad (2)$$

where $V_c(r)$ is the potential

$$V_c(r) = \begin{cases} \infty, & \text{if } r = 0 \\ -\frac{1}{r}, & \text{if } r > 0 \end{cases} \quad (3)$$

As usual, the wave function can be separated as

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi). \quad (4)$$

By substituting Eq. (4) into Eq. (2), the radial Schrödinger equation reads

$$-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{l(l+1)}{2r^2} + V_c(r)\right)R = ER. \quad (5)$$

The radial wave function must fulfil the boundary conditions,

$$R(r = 0) = 0, \quad (6)$$

$$\lim_{r \rightarrow \infty} R(r) = 0. \quad (7)$$

The singularity at the origin implied by Eq. (6) prevents the electron from being found at that point, while Eq. (7) ensures the square integrability character of the wave function.

In order to find solutions to the radial Schrödinger equation, we first consider the region spanned by $r > 0$. Accordingly, Eq. (5) is transformed into the common radial Schrödinger equation of the hydrogen atom

$$-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{l(l+1)}{2r^2} - \frac{1}{r}\right)R = ER. \quad (8)$$

By making the substitutions

$$n = 1/\sqrt{-2E}, \quad \rho = 2r/n, \tag{9}$$

Eq. (8) is transformed into

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \left(\frac{1}{4} - \frac{n}{\rho} + \frac{l(l+1)}{\rho^2} \right) R = 0. \tag{10}$$

By using the ansatz

$$R = e^{-\rho/2} \rho^l F(\rho), \tag{11}$$

Eq. (10) becomes

$$\rho \frac{d^2 F}{d\rho^2} + (2l+2-\rho) \frac{dF}{d\rho} + (n-l-1)F = 0. \tag{12}$$

This is the well known Kummer differential equation, whose general solution is given by [9,10]

$$F(\rho) = AM(-n+l+1, 2l+2; \rho) + BU(-n+l+1, 2l+2; \rho), \tag{13}$$

where A and B are constants and M and U are the Kummer functions. The first Kummer function, or the confluent hypergeometric function $M(a, b, z)$, is regular at the origin, while the second Kummer function $U(a, b, z)$ is singular at the origin. The radial wavefunction (Eq. 11) becomes,

$$R(\rho) = e^{-\rho/2} \{ A\rho^l M(-n+l+1, 2l+2; \rho) + B\rho^l U(-n+l+1, 2l+2; \rho) \}. \tag{14}$$

Since the second parameter $2l+2$ of the Kummer function U is an integer, its appropriate representation is given by [9]

$$U(a, n+1, z) = \frac{(-1)^{n+1}}{n! \Gamma(a-n)} \left[\frac{M(a, n+1, z) \ln z}{1} + \sum_{r=0}^{\infty} \frac{(\alpha)_r z^r}{(n+1)_r r!} \{ \psi(a+r) - \psi(1+r) - \psi(1+n+r) \} \right] + \frac{(n-1)!}{\Gamma(a)} z^{-n} M(a-n, 1-n, z)_n \tag{15}$$

for $n = 0, 1, 2, 3, \dots$, where $\psi(x) = \Gamma'(x)/\Gamma(x)$, and the last factor is the sum of n terms with value zero for $n = 0$.

Since the radial wave function must vanish at the origin (see Eq. 6), then $B = 0$, and $l > 0$, *i.e.*, there are no s states. Therefore

$$R(\rho) = Ae^{-\rho/2} \rho^l M(-n+l+1, 2l+2; \rho). \tag{16}$$

In order for the wave function to be well-behaved as $r \rightarrow \infty$, the hypergeometric function must be truncated. This requirement will be met provided there exists some non-negative integer n_r such that

$$-n_r = -n+l+1, \quad \text{with } l > 0. \tag{17}$$

By substituting n from equation (9) we get

$$E_n = -\frac{1}{2n^2}, \quad n = n_r + l + 1, \quad l > 0. \tag{18}$$

3. The confined hydrogen atom with a singularity at the origin

When the hydrogen atom is enclosed in an impenetrable sphere of radius r_0 , the potential energy (Eq. 3) becomes

$$V_c(r) = \begin{cases} +\infty, & \text{if } r = 0 \\ -\frac{1}{r}, & \text{if } 0 < r < r_0 \\ +\infty, & \text{if } r_0 < r \end{cases} . \tag{19}$$

The solutions of the corresponding Schrödinger equation are of the form given by Eq. (4). In the region $0 < r < r_0$ the radial Schrödinger equation is given by Eq. (10), where the radial wave function must satisfy the following boundary conditions:

$$R(r=0) = 0, \tag{20}$$

$$R(r_0) = 0. \tag{21}$$

The first of the above equations relates to a repulsive infinite wall at the origin, while the second (Dirichlet's boundary condition) is imposed by the impenetrable spherical wall. The general solution of the radial equation in this region is also given by Eq. (14). Applying the boundary condition at the origin we found that $B = 0$, and the integer $l > 0$. Equation (20) yields the energy eigenvalues

$$R(\rho_0) = Ae^{-\rho_0/2} \rho_0^l M(-n+l+1, 2l+2; \rho_0) = 0, \tag{22}$$

where $\rho = 2r/n$. It is enough to find the roots of the confluent hypergeometric function for a given angular momentum l and a box radius ρ_0 . This procedure was successfully applied by Aquino *et al* [11], where they found very accurate energy eigenvalues for a wide range of states of the confined hydrogen atom.

4. Conclusions

In this work we have shown that the problem of a hydrogen atom with a singularity at the origin yields no solutions for $l = 0$, *i.e.*, s states are excluded. This problem is a limiting case of the so-called *shell-confined hydrogen atom* (shell-CHA). The potential energy in Eq. (3) is obtained from Eq. (1) as $a \rightarrow 0$ and $b \rightarrow \infty$. On the other hand, the poten-

tial energy in Eq. (19) is obtained when $a \rightarrow 0$ and $b \rightarrow r_0$. It is worth pointing out that solutions for $l = 0$ states had not been discussed previously and so far had remained an open question.

The eigenfunctions and eigen-energies of the hydrogen atom with a singularity at the origin were found. For the CHA problem with a singularity at the origin, the eigen-energies are numerically obtained, as shown by Aquino *et al* [11].

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