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Spherically confined hydrogen atom: variational cut-off factor

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The hydrogen atom confined within an impenetrable spherical cavity of radius R under the influence of a uniform constant magnetic field B is considered. For the ground state, using the variational method, we employ a physically meaningful trial wavefunction characterized by three variational parameters, including a novel cut-off factor that acts as an additional degree of freedom in the optimization process. This approach allows us to systematically analyze the interplay between quantum confinement and the external magnetic field, providing insights into their combined effects on the energy spectrum and wavefunction behavior. Our results reveal how the ground state energy E and eigenfunction evolve as functions of the cavity radius $R \in [1, 5]$ a.u. and magnetic field strength $B \in [0, 1]$ a.u., offering a deeper understanding of quantum confinement in atomic systems subjected to external fields. These findings have potential implications for confined quantum systems in astrophysical and nanotechnological applications.

Keywords: Confined hydrogen atom; spherical cavity; ground state; magnetic field; variational method; cut-off factor.

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1. Introduction

Spatial confinement plays a crucial role in determining various observable physical properties, such as the energy spectrum, transition frequencies, optical characteristics, and polarizability. To investigate the evolution of pressure and polarizability under compression, Michels *et al.* [1] proposed a model in which a hydrogen atom is confined at the center of an impenetrable spherical cavity. Since then, the study of atomic and molecular systems under spatial confinement has expanded significantly, encompassing cavities of different geometries and sizes [2]. These investigations have broad applications in physics, chemistry, and materials science, including energy storage, the development of novel materials, and advancements in nanotechnology.

The study of a hydrogen atom within a spherical cavity is particularly relevant to various confined systems, such as quantum dots, fullerene traps, and nanofluidic channels. For instance, an inverted Gaussian penetrable barrier was used in Ref. [3] to model the hydrogen atom confined by C_{36} and C_{60} fullerenes. It also extends to confined Rydberg atoms and excitons in two-dimensional materials like MoS_2 and graphene [4-7]. Furthermore, these models can be generalized to explore systems subjected to an external magnetic field B, offering insights into emergent quantum phenomena. Prior research has examined cases such as a two-dimensional hydrogen atom confined within a circular region under a perpendicular magnetic field, with the proton fixed at the center [8], as well as hydrogenic impurities in quantum dots in the presence of a magnetic field [9].

In this study, we analyze the behavior of a three-dimensional hydrogen atom confined within an impenetrable spherical cavity of radius R, subjected to a uniform magnetic field B along the z-axis. Using a variational approach, we focus on the role of the cut-off factor in energy calculations. The Born-Oppenheimer approximation is adopted, assuming that the proton remains fixed at the cavity's geometric center.

Several studies have employed trial functions incorporating a cut-off factor of the form $f(r, R) = 1 - (r/R)^\nu$, with $\nu = 1, 2, 3, 4$ [10], where these values have been arbitrarily chosen in the literature, see also [11]. This cut-off factor ensures that the wavefunction satisfies the Dirichlet boundary condition. In contrast, this work proposes a modified cut-off factor that incorporates a variational term [12], treating it with the same level of importance as other terms in the wavefunction.

Specifically, for the ground state, we employ the variational method using a simple, compact, and physically meaningful trial function based on three parameters to obtain the energy $E = E(B, R)$. The goal of this study is not to establish reference values but to provide reasonably accurate energy estimates within the non-relativistic regime. It goes without saying that the development of physically relevant trial functions in atomic and molecular physics remains an active and highly researched field, see [13-17] and references therein.

2. Theory

In the Bohr-Oppenheimer approximation, the Hamiltonian of the hydrogen atom confined by an impenetrable spherical cavity of radius R in the presence of a constant magnetic field B is of the form[i]

$$\hat{H} = -\frac{1}{2}\left(\mathbf{p} + \mathbf{A}\right)^2 - \frac{1}{r} + V_c \,, \tag{1}$$

where the proton is placed at the geometric center of the spherical cavity (the origin of the reference system) and the confinement potential V_c reads

$$V_c \; = \; \begin{cases} 0 & \text{if } r < R\,, \\ \infty & \text{if } r \geq R\,. \end{cases} \tag{2}$$

In the symmetrical gauge, with the vector potential $\mathbf{A}$ as $\mathbf{A} = (1/2)\mathbf{B} \times \mathbf{r}$ and choosing the magnetic field in the z-direction, the expression for the Hamiltonian in spherical coordinates (r, θ, ϕ) turns out to be

$$\hat{H} = -\frac{1}{2}\Delta^{(3)} - \frac{1}{r} + \frac{m\,B}{2} + \frac{B^2}{8}\,r^2 \sin^2\theta + V_c\,, \tag{3}$$

where $\Delta^{(3)}$ is the 3-dimensional Laplacian operator and $m = 0, \pm1, \pm2, \ldots$ is the magnetic quantum number. The presence of the impenetrable spherical cavity requires that the wave function $\psi(r, \theta, \phi)$ satisfies the boundary condition $\psi(r = R, \theta, \phi) = 0$.

Since this system does not have an exact analytical solution, the variational method is employed to approximate the solution of the Schrödinger equation $\hat{H}\psi = E\,\psi$ associated with the Hamiltonian (3). To estimate the variational energy of the ground state, a simple trial function is chosen, explicitly given by

$$\psi(r, \theta, \phi) \; = \; f(r)\, e^{-\alpha\, r - \beta\, \frac{B}{4}\, r^2 \sin^2\theta}\,. \tag{4}$$

The structure of this variational function, which has been implemented previously [12], consists of three physically motivated building blocks:

- i) the hydrogen-like function $e^{-\alpha\, r}$ describing the Coulomb interaction between the electron and the proton,
- ii) the Landau orbital $e^{-\beta\,(B/4)\, r^2 \sin^2\theta}$ which takes into account the interaction of the electron with the magnetic field, and
- iii) the cut-off function $f(r)$ given as

$$f(r) = 1 - \left(\frac{r}{R}\right)^{\nu}\,, \tag{5}$$

introduced to satisfy the confining boundary condition $\psi(R, \theta, \phi) = 0$.

Traditionally, the value of ν is treated as a fixed parameter, limiting the flexibility of the trial function ψ (4). In this work, however, ν is introduced as a variational parameter, resulting in a total of three variational parameters: α, β, ν. It will be demonstrated that this strategy is essential for enhancing the accuracy of variational results.

The binding energy E_b

$$E_b = E_0 - E\,, \tag{6}$$

is the ground-state energy of the system without the proton, E_0, minus the ground-state energy of the system with the proton, E. Finally, it is important to emphasize the physical significance of the cusp condition,

$$1 = -\frac{1}{2n(r)}\frac{dn(r)}{dr}\bigg|_{r\to 0}\,, \tag{7}$$

which dictates the correct short-range behavior of the electron density $n(r) = |\psi|^2$ near the origin due to the singular nature of the Coulomb potential. This condition ensures that the trial wave function properly captures the electron-nucleus cusp, a key physical feature in atomic systems. By evaluating the right-hand side of (7) using the trial function defined in (4), we find that it is identically equal to α. Therefore, the cusp condition is exactly fulfilled when $\alpha = 1$, highlighting the fact that a physically accurate trial function must satisfy $\alpha \approx 1$. Deviations from this value would result in an incorrect representation of the electron density near the nucleus, thereby reducing the physical reliability of the variational approximation.

3. Results

The variational energy E of a hydrogen atom confined within an impenetrable spherical cavity of radius R in the presence of a constant magnetic field B is presented below.

We first consider the case where the magnetic field is absent ($B = 0.0$ a.u.). Under this condition, the trial wave function depends on two variational parameters, $\{\alpha, \nu\}$ only. The corresponding variational energy values are shown in Table I. As expected, the total energy E increases monotonically as the cavity radius R decreases, as illustrated in Table I and Fig. 1.

TABLE I. Total energy E of the ground state of the hydrogen atom confined by an impenetrable spherical cavity of radius R without magnetic field $B = 0$. For comparative purposes, the third and fourth columns present the results obtained using the Lagrange mesh method and those reported in Ref. [18], respectively (both results rounded).

R [a.u.]	E [Hartree]	Mesh	Ref [18]
1.0	2.3783	2.373990866	2.373990866
1.5	0.4371	0.437018065	0.437018065
2.0	-0.1249	-0.125000000	-0.125000000
2.5	-0.3347	-0.334910185	-0.334910185
3.0	-0.4238	-0.423967288	-0.423967288
3.5	-0.4642	-0.464357128	
4.0	-0.4832	-0.483265302	-0.483265302
4.5	-0.4921	-0.492205428	
5.0	-0.4964	-0.496417007	-0.496417007
20.0	-0.5000	-0.500000000	-0.500000000

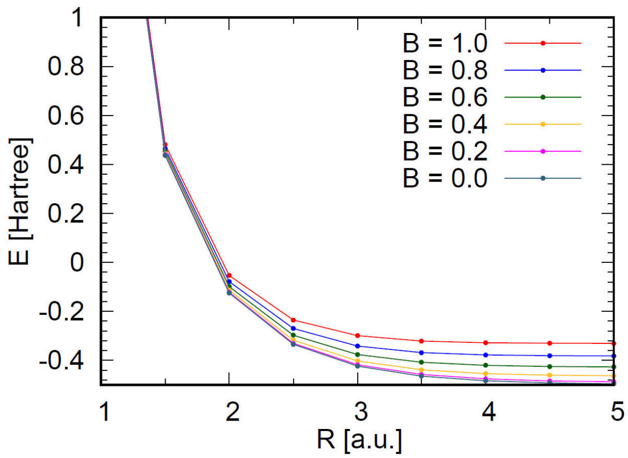

FIGURE 1. Total energy of a confined hydrogen atom as a function of the impenetrable spherical cavity radius R for different values of the magnetic field B.

A comparison of our results with the values obtained by implementing the Lagrange mesh method (see for instance [19]) and those reported in Ref. [18] reveals that the absolute energy difference is approximately 10^{-3} a.u. for $R \sim 2$, improving to 10^{-4} a.u. for larger values of R. The flexibility of the trial function allows for an accurate recovery of the free hydrogen atom energy in the limit of large cavity radii ($R \sim 10$ a.u.).

When a magnetic field B is present, the energy E of the confined hydrogen atom increases compared to the case where $B = 0.0$ a.u., for any given cavity radius R. Table II presents the energy values E as a function of the spherical cavity radius R for three magnetic field strengths: $B = 0.2$, 0.4, and 1.0 a.u. Similar to the case of $B = 0.0$ a.u., the energy E decreases as the cavity radius R increases (see also Fig. 1). Moreover, the variational parameters $\{\alpha, \beta, \gamma\}$ exhibit reasonably smooth behavior as functions of the cavity radius R for the different magnetic field values considered, as shown in Table II.

It is worth mentioning that the accuracy of the computed results is governed by the two fundamental parameters characterizing the system: the cavity radius R and the magnetic field strength B. In general, for systems subject solely to spatial confinement, the accuracy tends to deteriorate as the cavity size decreases. Conversely, when only a magnetic field is present, increasing its strength typically reduces numerical precision. In our case, both a spherical confinement and a magnetic field are simultaneously present. Consequently, to ensure that the last digit reported in the energy values of Table II is reliable, one would need to employ either a more sophisticated trial function or a refined computational methodology capable of achieving higher precision. Such enhancements, however, lie beyond the scope of the present study.

3.1. Optimal variational parameter ν versus cusp condition

In Fig. 3, we present the optimal variational parameter ν as a function of the confinement radius R for different values of the magnetic field B. Notably, ν exhibits significant variation within the range $R \in [1, 5]$, in one order of magnitude approximately.

To illustrate the importance of treating ν as a variational parameter, let us consider the specific case of $B = 1$ a.u. and $R = 1.5$ a.u. We analyze in detail how the ground-state energy depends on ν. By evaluating the energy at fixed values of $\nu = 1, 2, 3, 4$, we obtain the results summarized in Table III. These results demonstrate that allowing ν to vary enhances both the energy minimization and the fulfillment of the cusp conditions.

In particular, when fixing $\nu = 1$, the deviation from the exact cusp condition exceeds 50%. At $\nu = 4$, this error is reduced to approximately 33%. This underscores the significance of treating ν as a variational parameter to improve the accuracy of the model.

TABLE II. Variational energy and optimal parameters $\{\alpha, \beta, \nu\}$ for the ground state of the confined hydrogen atom as a function of the radius R of the spherical cavity for magnetic fields $B = 0.2, 0.4$ and 1.0 a.u. The last value represents the unconfined hydrogen atom case, with results rounded for clarity [20].

	$B = 0.2$ a.u.				$B = 0.4$ a.u.				$B = 1.0$ a.u.			
R [a.u.]	E [a.u.]	α	β	ν	E [a.u.]	α	β	ν	E [a.u.]	α	β	ν
1.0	2.3783	1.047	1.529	1.936	2.3808	1.046	0.774	1.935	2.3984	1.046	0.337	1.934
1.5	0.4388	1.008	0.083	2.225	0.4441	1.008	0.064	2.226	0.4811	1.013	0.089	2.240
2.0	-0.1220	1.071	-0.011	3.022	-0.1133	1.073	0.036	3.030	-0.0533	1.082	0.130	3.081
2.5	-0.3306	1.064	0.032	3.723	-0.3182	1.066	0.079	3.736	-0.2349	1.076	0.204	3.795
3.0	-0.4184	1.047	0.076	4.409	-0.4024	1.049	0.125	4.420	-0.2992	1.058	0.277	4.364
3.5	-0.4577	1.032	0.109	5.112	-0.4385	1.034	0.165	5.093	-0.3210	1.041	0.333	4.570
4.0	-0.4757	1.020	0.131	5.834	-0.4540	1.023	0.197	5.714	-0.3279	1.027	0.365	4.146
4.5	-0.4839	1.012	0.144	6.561	-0.4605	1.015	0.221	6.188	-0.3300	1.012	0.377	3.316
5.0	-0.4876	1.007	0.152	7.259	-0.4630	1.011	0.237	6.335	-0.3306	0.995	0.384	2.601
∞ [20]	-0.4904				-0.4646				-0.3312			

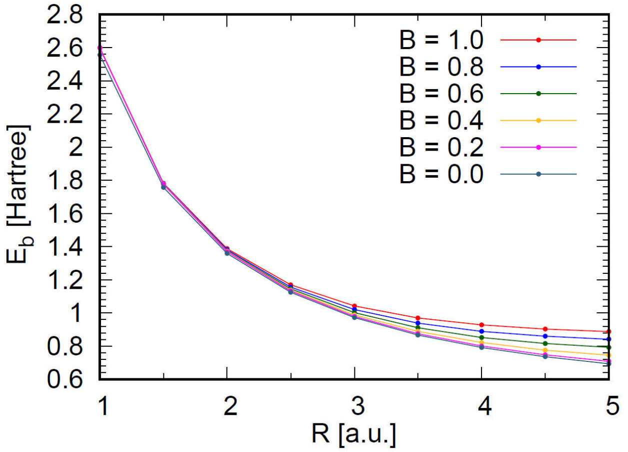

FIGURE 2. Binding energy of the confined hydrogen atom as a function of the impenetrable spherical cavity of radius R for different values of the magnetic field B.

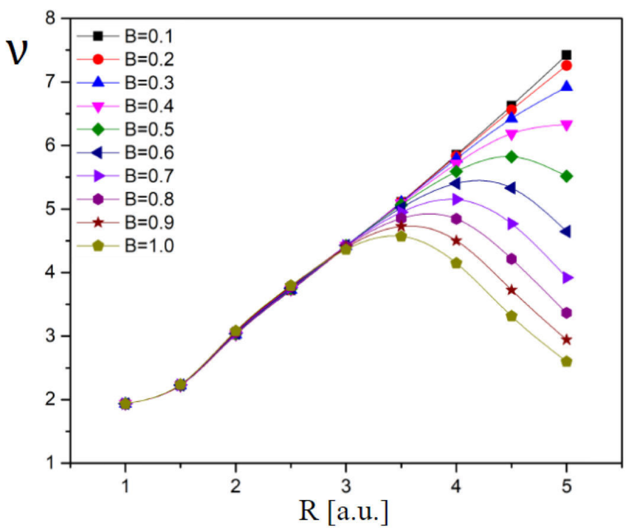

FIGURE 3. Optimal variational parameter ν, appearing in the cut-off factor $f(r) = 1 - (r/R)^\nu$, as a function of the radius R for different values of the magnetic field B.

TABLE III. Confined hydrogen atom. Ground state energy E, with $B = 1.0$ a.u. and $R = 1.5$ a.u., at fixed values of $\nu = 1, 2, 3, 4$.

ν	α	β	E [a.u.]
1	0.43626	0.215081	0.4823
2	0.93537	0.073197	0.4811
3	1.19349	0.194991	0.4821
4	1.33324	0.383351	0.4881

The binding energy E_b (6), depicted in Fig. 2, is a monotonically increasing function as the cavity radius R decreases.

Analysis of limiting cases

To validate the accuracy and physical relevance of our variational approach, we analyze several limiting cases of the confined hydrogen atom system:

- **Free atom limit ($R \to \infty$):** As the cavity radius becomes large, the influence of spatial confinement vanishes. In this limit, the system approaches the behavior of a free hydrogen atom, with a ground-state energy of $E = -0.5$ a.u. Our variational results correctly reproduce this asymptotic value, as evidenced by the energy at $R = 20$ a.u., which matches the known result to within 10^{-4} a.u.

- **Zero magnetic field ($B \to 0$):** When the magnetic field is absent, the problem reduces to that of a hydrogen atom confined in a spherical cavity. Our calculations in this regime closely agree with established results in the literature, confirming the validity of our trial function in the absence of external fields.

- **Strong confinement / high field limit ($R \to 1$ or $B \gg 1$):** In the regime of small cavity radii or large magnetic field strengths, the electron experiences strong confinement, leading to a significant increase in energy. The trial function adapts through the optimization of variational parameters, particularly the cut-off exponent ν, which increases to enforce the boundary condition $\psi(R) = 0$ more effectively. These extreme cases are physically relevant in applications such as quantum dots and high-field astrophysical environments.

These limiting behaviors support the consistency and robustness of the proposed variational model across a broad range of physical conditions.

4. Conclusions

We have investigated the ground-state energy of a hydrogen atom confined within an impenetrable spherical cavity of radius R under the influence of a uniform magnetic field B. Using a variational approach with a trial wave function incorporating three variational parameters, including a novel cut-off factor, we obtained energy estimates as a function of R and B.

Our results confirm that the total energy E increases monotonically as R decreases due to quantum confinement effects. When $B = 0$, the variational energy closely matches previous results [18], with absolute differences of 10^{-3} a.u. for $R \sim 2$, improving to 10^{-4} a.u. for larger cavity radii. The trial function successfully recovers the free hydrogen atom energy limit for $R \sim 10$ a.u. .

For nonzero magnetic fields, the energy increases with B for fixed R, reflecting the additional confinement imposed by the Lorentz force. The optimized variational parameters α, β, ν exhibit smooth behavior as functions of R, ensuring stability in the optimization process. Even without explicitly imposing the cusp condition on the trial function, the resulting expression yields a remarkably accurate value compared to the exact result, thereby highlighting the physical significance of the parameter α.

The introduction of a novel variational cut-off factor and its role in improving the accuracy of variational results–both for the ground-state energy and the fulfillment of the cusp condition–was quantitatively demonstrated.

These findings provide insights into the interplay between spatial confinement and external magnetic fields, with potential applications in nanostructured materials, quantum dots, and astrophysical systems. Future work may extend this approach to excited states and relativistic effects.

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i. Atomic units are adopted, $\hbar = 1$, $m_e = 1$, $e = -1$.

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