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Research Article

Energy Eigenvalues, Dipole Polarizability, Electron Pressure and Effect of Dielectrics on the Confined Hydrogen Atom

Rupachandra Maibam and Ashish Sharma*

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India
Corresponding author: asashish10@gmail.com

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Abstract. In this work, we used an efficient computational technique to solve the Schrödinger equation for the confined hydrogen atom (CHA) which is confined inside a hard spherical cavity with impenetrable wall. The wavefunctions, energy eigenvalues, polarizability and pressure have been calculated for different confinement radius. The energy eigenvalues and expectation values obtained are in good agreement with those calculated values obtained by Aquino *et al*. [2]. The hydrogen atoms under high pressure are real physical systems which can be found inside astrophysical objects.

Keywords. Atomic properties, Polarizability, Dielectric constant, Finite difference method

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1. Introduction

Right from the birth of quantum mechanics, the hydrogen atom has been a topic of interest as its hamiltonian takes quite a simple form and the Schrödinger equation could be solved analytically. The solution of the hydrogen-like atoms (interaction via coulomb potential) was included in Schrödinger's first paper on wave-mechanics published in 1926. Since then, people have tried to make modifications to the hamiltonian and obtain physically valid solutions. The emergence of the problem of the confined hydrogen atom could be credited to the paper by Michels *et al*. [12] published in 1937. In that paper, they studied the effect of pressure on

the atomic systems and its relation with the change of Claussius-Mosotti expression at high densities. Due to the lack of theoretical and experimental information for the problem, the effect of pressure and density was calculated on a wave-mechanical basis in a simplified case. A year later, Sommerfeld and Welkel [21] published a paper in which the hydrogen atom is centrally confined in an impenetrable cavity.

In recent decades, more accurate solutions for the confined hydrogen problem have been obtained. One of the most accurate values of the energy eigenvalues were obtained by Aquino *et al*. [2] using two methods: hypergeometric function and series method. The values of energy eigenvalues obtained by the two methods differ by less than 10^{-100} hartrees. They also calculated the radial expectations values with very high accuracy. Patil and Varshni [16] worked on the properties of confined hydrogen and helium atoms where they considered different kinds of confinement potentials namely, spherical, harmonic oscillator and off-center potentials. They made use of the series solution and some model wavefunctions and calculated the energies and atomic polarizabilities at different confinements. Similar work by Sarsa and Sech [18] used variational Monte Carlo method with Dirichlet boundary conditions. Longo [11] studied the confined hydrogen atom under different geometries using Diffusion Monte-Carlo method. They considered geometries such as spherical and circular box, and square and cubical box. Patil [15] solved the problem of hydrogen atom confined in an ellipsoid analytically. He took a simplified model where the atom is fixed at one of the foci and so the Schrödinger equation is separable in elliptical coordinates. Kang *et al*. [9] generalized the work by Patil [15] by considering the nucleus to be at any position along the symmetry axis. The problem was solved using linear variational method since an exact solution was not possible.

Confined quantum systems find applications in many fields such as astrophysics [6, 7], nanoscience [23], condensed matter physics [3, 4, 20], etc. Guillot [6] studied the interior of Jupiter and found that it is mostly made up of hydrogen and helium which is in a very dense condition. The behaviour of dense hydrogen under extreme condition of density and pressure was also studied by Helled [7]. Quantum confinement effect is the main idea in the development of quantum dots. Yakar and Çakır [23] produced spherical quantum dots by using 3-dimensional confinement and studied their dipole and quadrupole polarizabilities. As an application to information theory, the calculation of the Shannon entropy of the confined quantum systems [1, 8, 13] has gained some attention. The work by Nascimento and Frederico [13]focused on the calculation of Shannon entropy of confined hydrogen-like atoms confined using hard impenetrable walls. Another work by Salazar *et al*. [17] modified the problem by adding a static electric field to the hamiltonian and the behaviour of the Shannon entropy sum in confined hydrogenic systems subject to the influence of electric field was studied. For the first time, the quantum mechanical effect for a hydrogen atom confined in a dielectric spherical microcavity was studied by Wang *et al*. [22].

In our present work the problem of the confined hydrogen atom is solved numerically using a rather simple yet effective technique. The energy eigenvalues are obtained using finite difference method and the wavefunctions for different atomic orbitals are obtained by Numerov's method. Using these wavefunctions, radial expectation values are also calculated for different orbitals which in turn is used to calculate the dipole polarizability and pressure. The effect of pressure

on the energy and electron distribution have been studied by changing the confinement radius. The main idea is to study the hydrogen atom under high pressure condition as we observed that the wall of the cavity exerts an extremely high pressure onto the electron at small confinement radius ($r_c < 5$ a.u.). In the region of strong confinement, the electron pressure becomes very high ($\sim 10^9$ atm) and some interesting features could be observed such as positive value of energy and breaking of accidental degeneracy. The polarizability of the atom in the ground state at different confinement radius have also been calculated using the Kirkwood approximation [10]. The results obtained in our study are matched with those obtained by N Aquino *et al*. [2]. A brief study of the effect of dielectrics on the energy eigenvalues of the CHA is also included in this article.

This article is structured as follows: the theoretical calculations including the numerical methods we have adopted are discussed in section 2, the results obtained are given in section 3 and finally the conclusions are given in section 4.

2. Theoretical Calculations

In this section, we will discuss how to write the Hamiltonian and and the corresponding Schrödinger equation of the CHA. We will also outline the numerical methods that we have used to solve the Schrödinger equation.

2.1 Setting up the Problem

In addition to the Coulomb potential, we have to introduced an additional confining potential in the Hamiltonian of the free-hydrogen atom. In our case, we have considerd a step-potential of the form

$$\widetilde{V}(r) = \begin{cases} 0, & \text{for } r < r_c, \\ \infty, & \text{for } r \geq r_c, \end{cases} \tag{2.1}$$

where r_c is the radius of the spherical cavity. The time independent Schrödinger equation for the confined hydrogen atom can be written as

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + \widetilde{V}(r) \right] \Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi). \tag{2.2}$$

We can see that the potential is still dependent only on the radial coordinate r and so, the new problem is also spherically symmetric as in the case of the free hydrogen atom. The wavefunction can be written as a product of a radial function and an angular function

$$\Psi(r,\theta,\phi) = \psi_r(r) Y_{lm}(\theta,\phi). \tag{2.3}$$

Here the set of functions Y_{lm} are the spherical harmonics. We have to find a new set of radial functions by solving the new radial equation

$$\left\{ -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} + \widetilde{V}(r) \right\} \psi_r(r) = E\psi_r(r). \tag{2.4}$$

By defining a new function

$$\phi_r(r) = r\psi_r(r), \tag{2.5}$$

we can write the radial equation as:

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}+\widetilde{V}(r)\right\}\phi_r(r)=E\phi_r(r). \tag{2.6}$$

Now we make use of atomic units to make the notation much simpler and compact. These units can be considered as the natural units for an atom as they are intrinsic to the atomic dimension. In this system of units we require that

$$m_e=\hbar=e=4\pi\epsilon_0=1. \tag{2.7}$$

The reduced mass of hydrogen atom can be taken as almost equal to the mass of an electron, so $\mu\approx m_e=1$. The simplified form of the radial equation (2.6) is

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}+2\widetilde{V}(r)+\frac{l(l+1)}{r^2}\right]\phi_r(r)=\varepsilon\phi_r(r) \tag{2.8}$$

where, $\varepsilon=2E$. With the introduction of an effective potential

$$V_{eff}(r)=-\frac{1}{r}+\widetilde{V}(r)+\frac{l(l+1)}{2r^2} \tag{2.9}$$

we can write

$$\left[-\frac{d^2}{dr^2}+2V_{eff}(r)\right]\phi_r(r)=\varepsilon\phi_r(r). \tag{2.10}$$

The effect of dielectrics is studied by using a linear dielectric material. The presence of a dielectric will affect the coulomb potential term. We recall from electrostatics that the potential inside a dielectric medium decreases by a factor of the κ (dielectric constant) as compared to its value in vacuum

$$V_k=\frac{V_0}{\kappa}. \tag{2.11}$$

So, the coulomb potential in the Hamiltonian in the presence of a dielectric medium will be given by

$$V(r)\rightarrow V_\kappa(r)=-\frac{1}{\kappa r}. \tag{2.12}$$

2.2 Numerical Methods

The energy eigenvalues have been obtained using the finite difference method. It is an effective numerical technique which can be used to solve eigenvalue equations. Our task is to solve the second order differential equation given in eq. (2.10) First we have to convert the wavefunction into a column vector and the Hamiltonian into a matrix.

$$\psi_r(r)\longrightarrow\{\psi_i\}\quad\text{and}\quad-\frac{d^2}{dr^2}+V_{eff}(r)\longrightarrow[H]. \tag{2.13}$$

In this way, the differential equation will become an eigenvalue equation

$$[H]\{\psi_i\}=E\{\psi_i\}. \tag{2.14}$$

The conversion of the wavefunction into a column vector is achieved by discretizing the variable r into a 1-D lattice. In other words, we have to divide the r axis into a number of discrete points separated by a fixed interval. We will get a unique value of ψ_r corresponding to each value of r_i which will give us the components of the eigenvector corresponding to an eigenvalue.

The next task is to write the Hamiltonian in its matrix representation. Using the central difference formula, the second derivative of ϕ_r with respect to r can be written as [19]

$$\left.\frac{d^2\phi_r}{dr^2}\right|_{r=r_i} \equiv \frac{\phi_{i+1}-2\phi_i+\phi_{i-1}}{h^2} \tag{2.15}$$

and the potential energy operator acting on ϕ_r is

$$V_{eff}(r)\phi_r(r) \equiv V_{eff}(r_i)\phi_r(r_i). \tag{2.16}$$

Using this representation, the elements of the Hamiltonian matrix in eq. (2.14) are

$$H_{ij} = [V_i + 2]\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1} \tag{2.17}$$

where, $V_{eff}(r_i)$ is written as V_i for a more compact notation. The eigenvalues of this Hamiltonian matrix will give the energy eigenvalues of the CHA and the corresponding eigenvector will give the required radial wavefunction. There are various methods which can be used to find the eigenvectors and eigenvalues of a matrix. . Since most of the methods require the matrix to be in tridiagonal form, our task is half done as the Hamiltonian matrix [H] is already in a tridiagonal form. Most of the programming languages have numerous subroutines and inbuilt functions for the spectral decomposition of a matrix. Here we use the inbuilt function **spec** command in scilab which generates the similar matrix for H along with the diagonal matrix made up of the eigenvalues of H. The columns of the similar matrix are the required eigenvectors. More details of this method can be found in [5].

Although the finite-difference method gives the correct value of the energy eigenvalues up to a reasonable accuracy, it is not effective for the calculation of the wavefunction. In order to get the desired accuracy for the wavefunction, the number of elements in the eigenvector must be increased along with the size of the Hamiltonian matrix and diagonalizing a larger matrix takes more computational time. So, we have adopted a different method for the calculation of the wavefunction namely, Numerov's method. The Numerov's method is a useful numerical technique which can be used to solve ordinary differential equations of the form

$$y''(x) + q(x)y(x) = f(x). \tag{2.18}$$

The algorithm is derived by using the three-point formula for the second and fourth order derivatives. The complete derivation and method of application can be found in the book on computational physics by Pang [14]. The range of the variable x in equation (2.18) must be discretized into n points $\{x_1, x_2, x_3, \ldots, x_n\}$ with equal step size h between each point. Now the solution to equation (2.18) given by Numerov's algorithm is

$$y(x_{i+1}) = \frac{a_i y(x_i) + b_i - a_{i-1}y(x_{i-1})}{a_{i+1}}, \tag{2.19}$$

where

$$a_i = 2 - \frac{5h^2}{6}q(x_i), \tag{2.20}$$

$$a_{i+1} = 1 + \frac{h^2}{12}q(x_{i+1}), \tag{2.21}$$

$$a_{i-1} = 1 + \frac{h^2}{12}q(x_{i-1}), \tag{2.22}$$

$$b_i = \frac{h^2}{12}[f(x_{i+1}) + 10f(x_i) + f(x_{i-1})]. \tag{2.23}$$

The value of the function at x_i is coupled with its values at x_{i+1} and x_{i-1}. So, we need to know the values of the function at least at two points before we apply this algorithm and this makes it suitable for application to boundary value problems. In our case, we have imposed the boundary condition that the wavefunction must vanish at the origin as well as the wall of the spherical cavity. The Schrödinger equation given in equation (2.10) can be written as

$$\phi_r''(r) + 2[E - V_{eff}(r)]\phi_r(r) = 0. \tag{2.24}$$

This is in the form of equation (2.18) with

$$y(x) = \phi_r, \tag{2.25}$$

$$q(x) = 2[E - V], \tag{2.26}$$

$$f(x) = 0. \tag{2.27}$$

The value of E is found using the finite difference method and the wavefunctions could be calculated by solving eq. (2.24) for different values of E.

3. Results and Discussion

3.1 Radial Electron Probability Density

The radial electron probability densities ($|\phi_r|^2$) have been plotted as a function of radial distance for various orbitals. As expected, the probability densities at large confinement radii ($r_c = 50$ a.u.) resemble that of a free atom which is shown in Figure 1 for $1s$, $2s$, $3s$, $2p$ and $3p$ orbitals. The number of nodes is equal to $(n - l - 1)$, where n is the principal quantum number and l is the azimuthal quantum number.

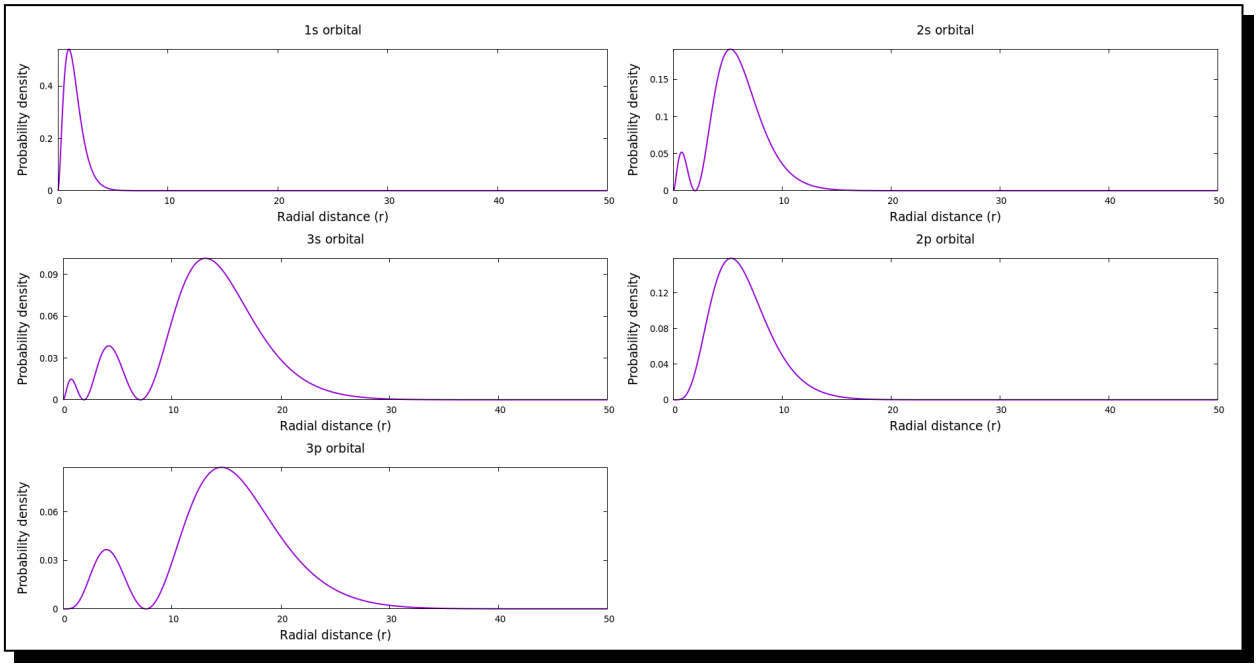


Figure 1. The radial probability densities of electron at large confinement radius ($r_c = 50$) for different orbitals

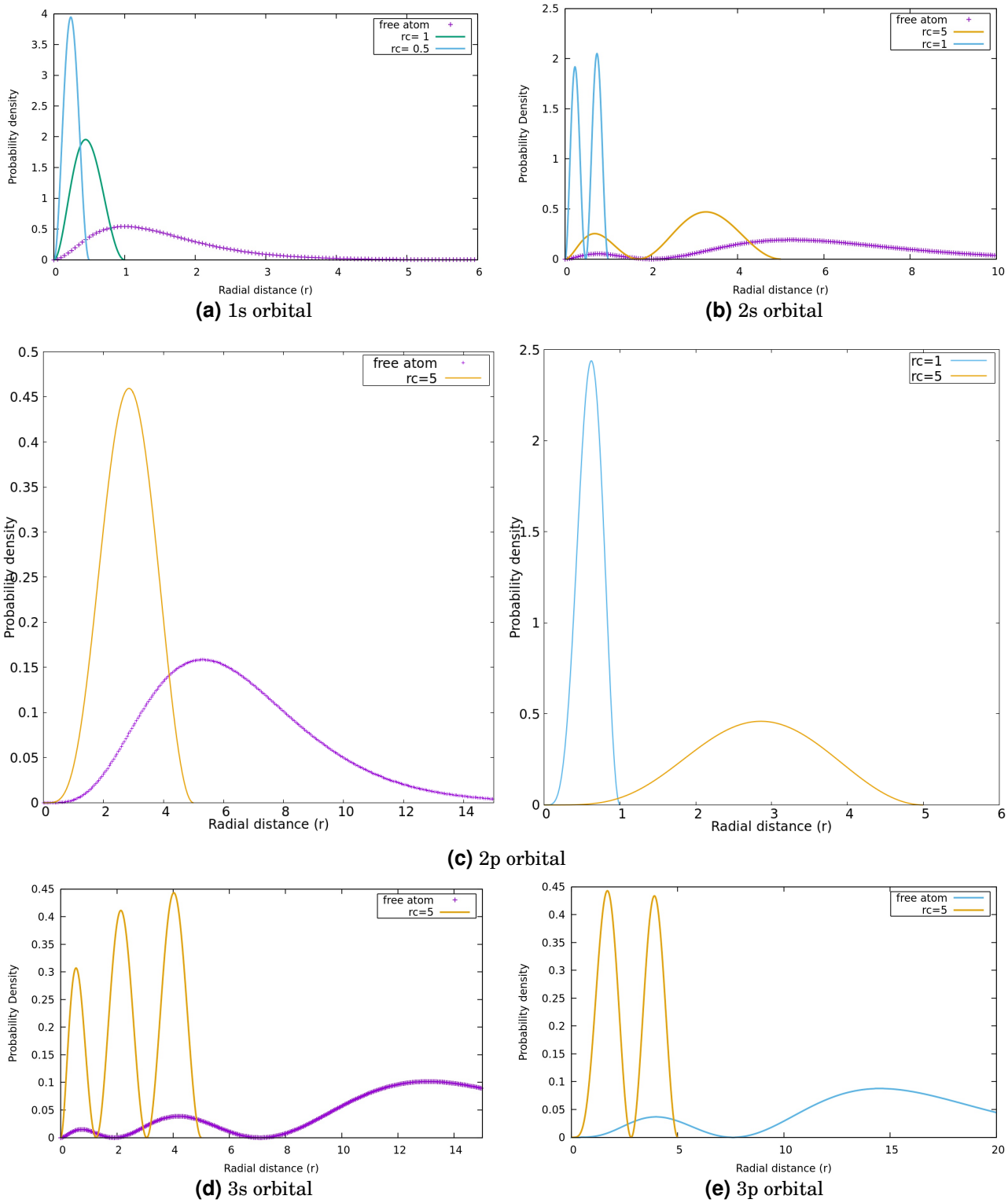


Figure 2. The radial probability density for different orbitals ($1s$, $2s$, $2p$, $3s$ and $3p$) at small confinement radii

The probability densities for smaller confinement radii are shown in Figure 2. They are plotted along with that of the free atom for comparison. When the confinement radius is decreased the curves start to shifts towards the origin. The effect of the confinement on the

electron density is to push the electron density towards the origin while the number of nodes remain the same. The peaks become narrower with the decrease in r_c which indicates that the uncertainty in the position of the electron is reduced and that the electron is more localized. We observe that the probability density vanishes at $r = r_c$ for all the orbitals which is consistent with the Dirichlet boundary condition, $\psi_r(r_c) = 0$.

3.2 Energy Eigenvalues

The energy eigenvalues for different orbitals ($1s$, $2s$, $2p$, $3s$ and $3p$) at various confinement radii are shown in Table 1. Our calculated values (represented by A in Table 1) are in good agreement with the values obtained by Aquino *et al*. [2] (represented by B in the Table 1). It is observed that the energies increase with the decrease in the confinement radius. The energy eigenvalues become positive after some value of the confinement radius. This value of critical confinement radius are different for different orbitals: 1 a.u. for $1s$ orbital, 6 a.u. for $2s$ orbital, 5 a.u. for $2p$ orbital, 10 a.u. for $3s$ and $3p$ orbitals. We must recall that the energy of the free hydrogen atom is always negative because the Coulomb potential allows bound states only for negative values of energies but when the atom is confined by an infinite potential, there is a possibility of bound states for positive values of energy. As the confinement increases (r_c decreases), the electron density is pushed towards the nucleus and the potential energy becomes very large and negative. In order to maintain a finite energy value, the kinetic energy also increases. The kinetic energy is always positive and it dominates over the potential energy since, for a central potential, the virial theorem give

$$\frac{T}{V} = -2\,. \tag{3.1}$$

Thus, the total energy becomes positive for strong confinement.

Another striking feature can be seen from the graphs given in Figure 3. This is the breaking of accidental degeneracy. The energy of the free hydrogen atom goes as $\frac{1}{n^2}$ and is independent of l. So, the orbitals with the same value of n have the same energy and they are said to be degenerate. Perturbations to the hamiltonian often lead to splitting of these degenerate energy levels. The spherical cavity is also a sort of perturbation to the hamiltonian and as we decrease the confinement radius, the degenerate energy levels start to split and they no longer remain degenerate. All the atomic orbitals now have different energies since they have different sets of quantum numbers n and l. For a fixed value of n and at a particular radius, the orbital with the larger value of l has smaller value of energy ($E_{n,l+1} < E_{n,l}$). Further, we can see that the amount of splitting depends on the confinement where there is little spilling at larger values of r_c and increase as we decrease r_c. This can serve as a useful information in atomic spectroscopy for studying such confined systems.

3.3 Expectation Values, Dipole Polarizability and Electron Pressure

The radial expectation values for various orbitals at different confinement radii are given in Table 2. The values obtained with our method are not far off from the values obtained by [2]. These values can be used to calculate the dipole polarizability and the electron pressure for the ground state.

Table 1. The energy values calculated at confinement radius for various orbitals

r_c		Energy				
		1s orbital	2s orbital	3s orbital	2p orbital	3p orbital
∞	**Theoretical**	**−0.500000**	**−0.125000**	**−0.055555**	**−0.125000**	**−0.055555**
20	A	−0.499799	−0.124975	−0.049989	−0.124995	−0.051639
	B	−0.500000	−0.124987	−0.049918	−0.124995	−0.051611
15	A	−0.499887	−0.124502	−0.027146	−0.124774	−0.035143
	B	−0.500000	−0.124015	−0.016066	−0.124541	−0.027268
10	A	−0.499986	−0.112878	0.090916	−0.118897	0.048833
	B	−0.499999	−0.112806	0.091422	−0.118860	0.049191
9	A	−0.499955	−0.103068	0.151931	−0.113788	0.092099
	B	−0.499996	−0.102835	0.153282	−0.113727	0.092572
8	A	−0.499967	−0.084930	0.245572	−0.104548	0.156731
	B	−0.499975	−0.084739	0.246492	−0.104450	0.157368
7	A	−0.499841	−0.051888	0.389668	−0.087638	0.256918
	B	−0.499863	−0.051260	0.392241	−0.087479	0.257801
6	A	−0.499273	0.011673	0.628009	0.017727	0.534424
	B	−0.499277	0.012725	0.631737	−0.055556	0.421509
5	A	−0.496441	0.140345	1.050384	0.007149	0.705798
	B	−0.496417	0.141254	1.053221	0.007594	0.707718
4	A	−0.483364	0.418583	1.868032	0.142722	1.258374
	B	−0.483265	0.420236	1.872702	0.143527	1.261521
3	A	−0.424313	1.108358	3.726246	0.479620	2.510353
	B	−0.423967	1.111685	3.734958	0.481250	2.516209
2	A	−0.126283	3.319201	9.293646	1.571894	6.255239
	B	−0.125000	3.327509	9.314150	1.576019	6.269003
1	A	2.366547	16.533861	40.777555	8.204797	27.416588
	B	2.373991	16.570256	40.863125	8.223138	27.473995
0.9	A	3.252704	20.808748	50.784004	10.362760	34.141205
	B	3.262190	20.854067	50.890081	10.385635	34.212368
0.8	A	4.531000	26.836477	64.831163	13.410030	43.581002
	B	4.543380	26.894322	64.965968	13.439265	43.671435
0.7	A	6.453264	35.703288	85.404577	17.899070	57.406090
	B	6.469926	35.779476	85.581365	17.937632	57.524687
0.6	A	9.504357	49.480155	117.233120	24.883946	78.793904
	B	9.527708	49.584719	117.474716	24.936947	78.955981
0.5	A	14.713378	72.520227	170.235870	36.581814	114.409220
	B	14.747970	72.672039	170.585164	36.658876	114.643553

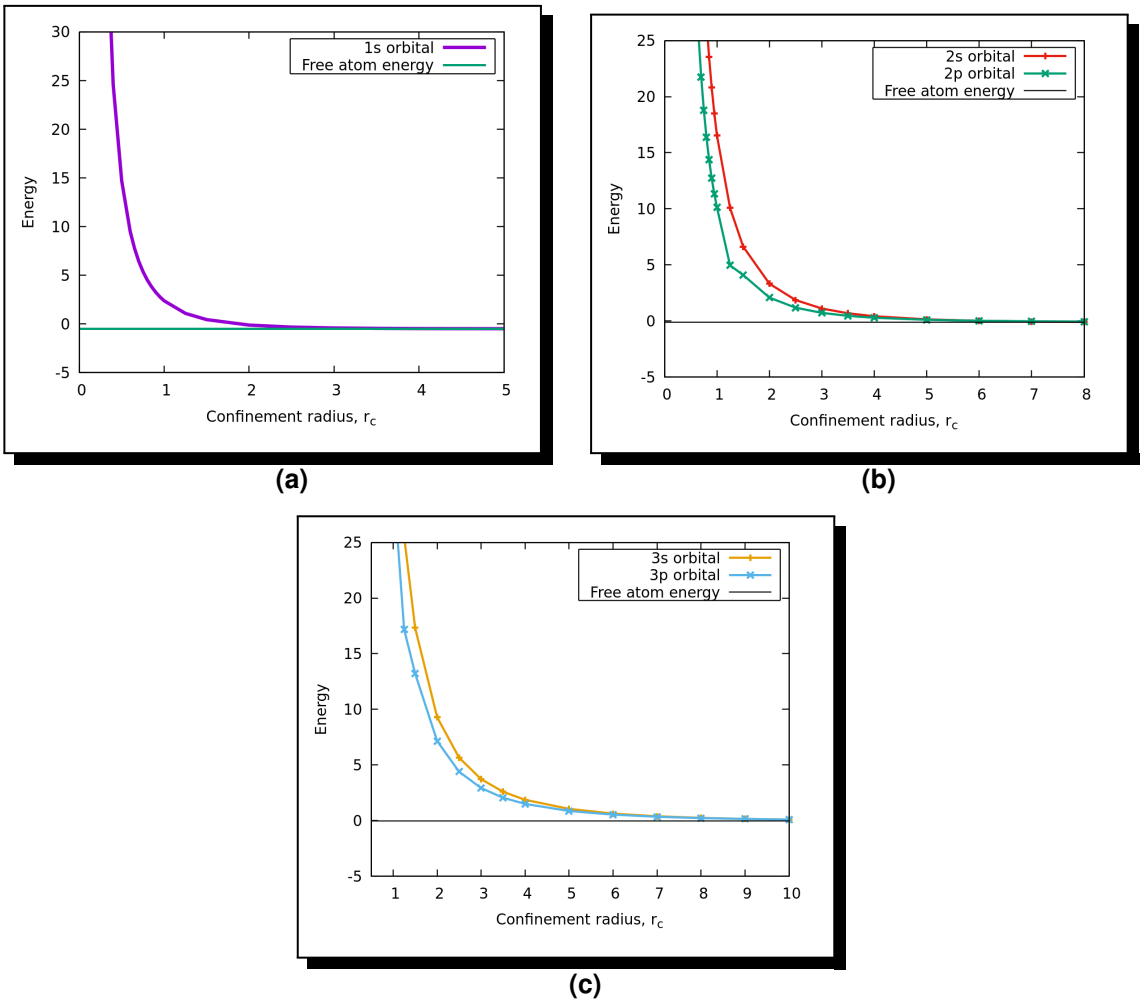


Figure 3. The energy at different values of confinement radius, r_c. (a) $n = 1$, (b) $n = 2$, (c) $n = 3$

Without applying any electric field we can calculate the dipole polarizability of the confined hydrogen atom using its radial expectation values. We have used Kirkwood approximation [10] in this work. The approximated value of the dipole polarizability is given by

$$\alpha = \frac{4}{9a_0}\langle r^2\rangle^2. \tag{3.2}$$

The values of the dipole polarizability at different confinement radius are given in Table 3.

The change in polarizability as a function of the confinement radius is shown in Figure 4. It is observed that at larger confinement radius ($r_c > 10$ a.u.), the value of polarizability is large and remains almost constant. So, the electron cloud could be distorted easily and up to the same extent for confinement radius above 10 a.u. When the confinement radius is decreased below 10 a.u., the effect of the confinement starts to show and it becomes more difficult to distort the electron cloud since the electron is confined inside a small region.

We have calculated the pressure exerted by the walls of the spherical cavity on the electron density by using [22]

$$P(r_c) = -\frac{1}{4\pi r_c^2}\frac{dE(r_c)}{dr_c}. \tag{3.3}$$

Table 2. The radial expectation values for the 1s and 2s orbitals. ($*$ values obtained in [2])

r_c	$\langle r\rangle^*$	$\langle r\rangle$	$\langle r^2\rangle^*$	$\langle r^2\rangle$	$\langle r^{-1}\rangle^*$	$\langle r^{-1}\rangle$
			1s orbital			
∞	1.5	1.500626	3	3.002505	1.000000	0.998749
20	1.499999	1.5001	2.999999	3.000401	1.000000	0.999799
10	1.499936	1.499962	2.999459	2.999567	1.000011	0.999961
9	1.499703	1.499727	2.997671	2.997781	1.00006	1.000018
8	1.498697	1.498728	2.990632	2.990796	1.000294	1.000258
7		1.494795		2.965894		1.001308
6		1.481059		2.888222		1.005566
5	1.440026	1.440348	2.684971	2.686466	1.020951	1.020808
4	1.341709	1.342266	2.270311	2.27247	1.068128	1.067818
3		1.153929		1.626964		1.195438
2.5		1.020128		1.251494		1.322762
2	0.859353	0.860044	0.874825	0.876283	1.535161	1.534062
1.5	0.674841	0.675429	0.532129	0.533078	1.912411	1.910866
1	0.468317	0.468751	0.253127	0.253602	2.699145	2.696753
0.9		0.425006		0.207999		2.962538
0.6		0.289348		0.095777		4.301773
0.5	0.128629	0.242725	0.067128	0.0672591	5.114044	5.109193
			2s orbital			
0.5	0.250584	0.250836	0.080655	0.080817	6.339617	6.333400
1	0.503321	0.503830	0.325322	0.325980	3.220106	3.216973
1.5	0.759865	0.760642	0.739814	0.741322	2.174779	2.172671
2	1.021979	1.023042	1.332090	1.334831	1.646270	1.644665
3		1.570375		3.092335		1.100678
4	2.146227	2.148582	5.631603	5.643345	0.811450	0.810542
5	2.736824	2.739755	8.905503	8.923408	0.626762	0.626008
8	4.294623	4.298063	20.884945	20.917486	0.362517	0.362147
9	4.692357	4.695643	24.850755	24.885383	0.324542	0.324260
10	5.025765	5.028787	28.524320	28.559260	0.298837	0.298624
20	5.992662	5.992855	41.849321	41.852723	0.250173	0.250158

Table 3. The electron pressure and dipole polarizability for the ground state at different confinement radius. ($*$ reference values) [2]

r_c	P (a.u)	P^* (10^6 atm)	P (10^6 atm)	$\alpha^*(10^{-24}$ cm)	α (10^{-24} cm)
∞	-3.98×10^{-10}	0	0	0.592739	0.593132
20	-9.96×10^{-10}	0	0	0.592739	0.592301
10	9.63×10^{-10}	0	0	0.592525	0.591972
9	5.20×10^{-9}	0.000002	0.000002	0.591818	0.591268
8	5.04×10^{-8}	0.000015	0.000015	0.589043	0.588515
7	0.0000004		0.000118		0.578756
5	0.0000178	0.005197	0.005237	0.474788	0.47484
4	0.0001257	0.03668	0.036983	0.339462	0.339766
3	0.0010222		0.300751	0.17386	0.174156
2.5	0.0033188	1.1104	0.976455	0.10284	0.103048
2	0.0127473	3.7115	3.7505	0.0504	0.050521
1.5	0.0655326	19.07962	19.280946	0.018649	0.018696
1	0.5912486	172.07584	173.956662	0.004219	0.004231
0.9	1.033519		304.081084		0.002846
0.8	1.9207531		565.12235		0.00182

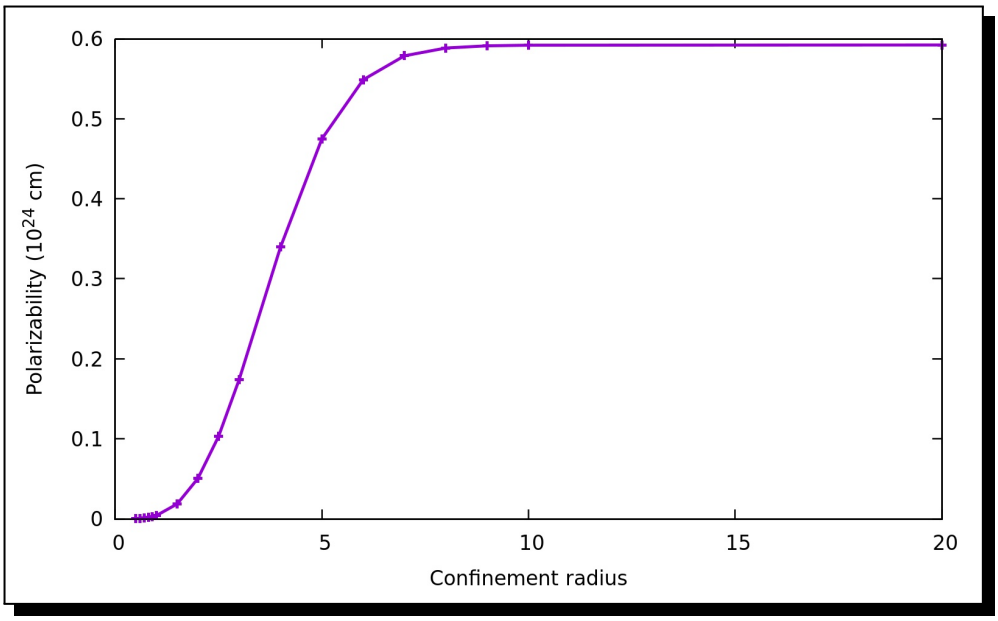


Figure 4. The polarizability of CHA as a function of the confinement radius

Using a linear approximation and the virial relation, we can write

$$P(r_c) = \frac{1}{4\pi r_c^3}[2E(r_c) - \langle V(r)\rangle]. \tag{3.4}$$

The electron pressure becomes larger as we decrease the confinement radius which is illustrated in Figure 5. This is because the electron pressure depends on $\frac{dE}{dr_c}$ which is the change in energy with respect to the change in confinement radius. Referring to Figure 3, we observe that the energy changes more rapidly when the confinement radius is smaller and thus, the pressure increases with decreasing r_c. Moreover, the values of the electron pressure given in Table 3 could go beyond 10^8 atm. This is a tremendous amount of pressure which is not achievable in laboratories. So, this model could be used to study the hydrogen atom under very high pressure condition. For instance, the interior of the Sun is so dense that hydrogen and helium atoms are confined in a very small volume with pressure rising up to 10^{10} atm.

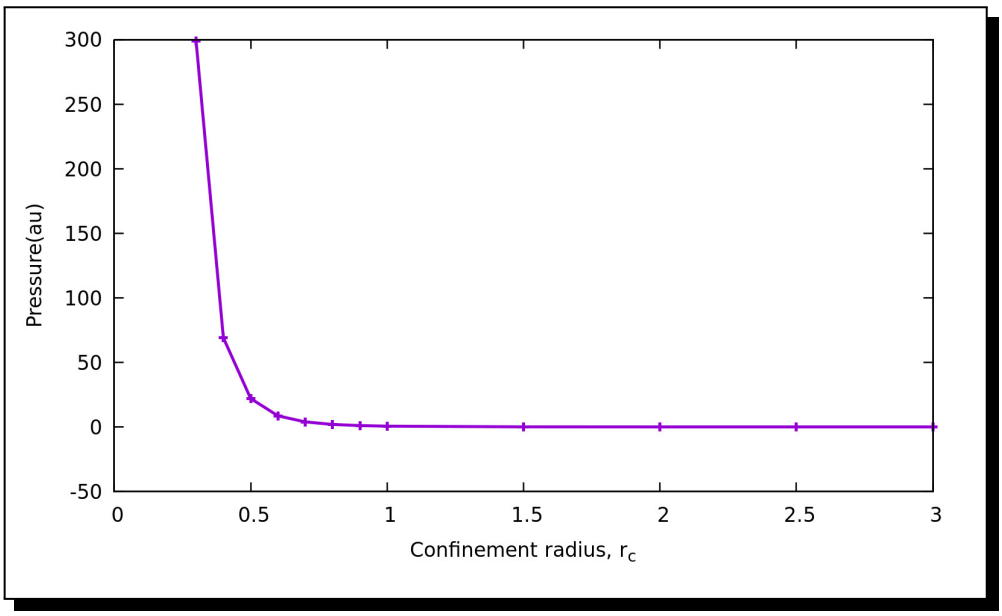
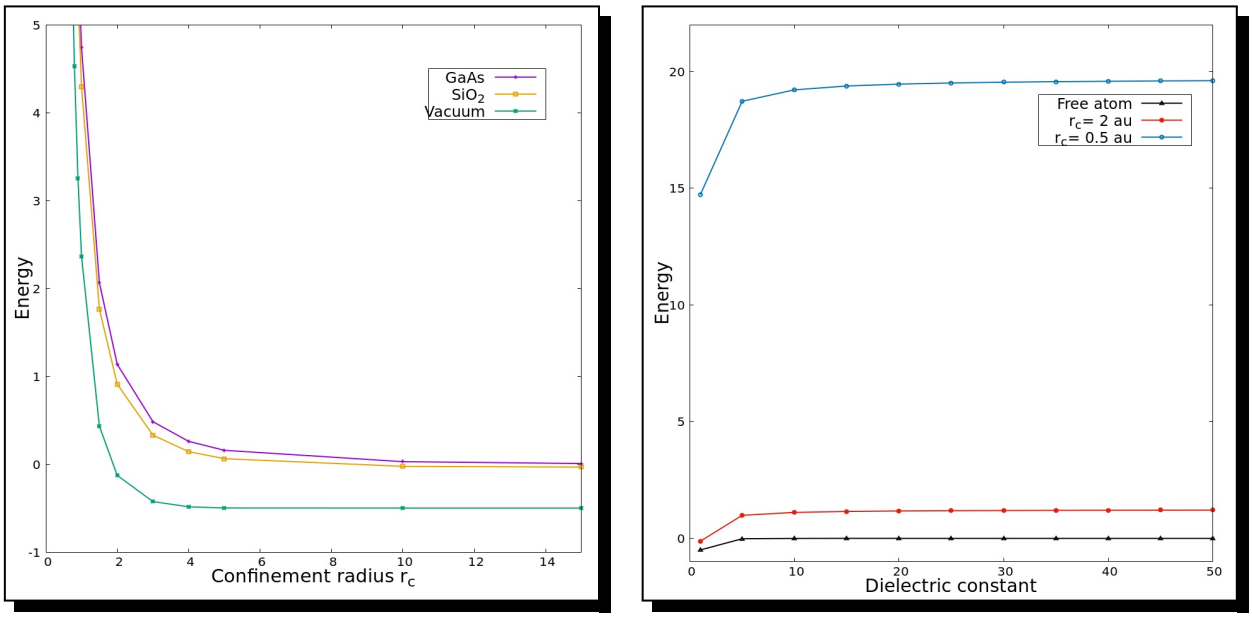


Figure 5. The pressure exerted by the wall of the cavity on the electron as a function of the confinement radius

3.4 Effect of Dielectrics

We have studied the effect of dielectrics on the energy eigenvalues of the CHA. The change in energy of the ground state as a function of confinement radius is shown in Figure 6a. Here, the ground state energy vs the confinement radius have been plotted for GaAs (κ = 13.13), SiO_2 (κ = 3.7) and vacuum (κ = 1). The change in the ground state energy with the confinement radius in the presence of dielectric is similar to the case in vacuum; it increases and becomes positive as the confinement radius decreases. However, due to the presence of the dielectric medium, the ground state energy is higher than that in the case of vacuum. This effect can be explained by the fact that the dielectric medium somewhat produces a shielding effect and the effective nuclear charge experienced by the electron is decreased. As a consequence the electron can move more freely which leads to an increase in the kinetic energy. The energy is higher for higher value of κ due to more shielding. The energy difference between different values of κ

decreases as the confinement radius decreases which shows that the effect of confinement is stronger than that of the dielectric at small confinement radius.



(a) (b)

Figure 6. The effect of dielectric on the ground state energy. (a) The energy is plotted against confinement radius for different values of κ. (b) The plot of ground state energy as a function of κ for different confinement radius

The variation of the energy with the the dielectric constant for different confinement radius are also shown in Figure 6b. At large confinement radius, the change in the energy with κ is small. However at small confinement radius, 0.5 a.u. for instance, the change in energy is more profound. As the dielectric constant keeps increasing, the energy values changes slowly and becomes almost constant. So, the effect of the dielectric is not very profound at larger values of dielectric constant ($\kappa > 20$). We could say the effect saturates at larger values of dielectric constant.

4. Conclusion

We have calculated the energy eigenvalues, the wavefunctions, dipole polarizability and pressure of the hydrogen atom confined in a hard spherical cavity. The calculated values of energy and pressure are in good agreement with those calculated by other authors using different methods and so, the numerical method adopted in this work is quite efficient in handling the above model of the CHA. This model is not limited only to the hydrogen atom but could be extended to other hydrogen-like atoms. Confined atoms find applications in many areas of physics like astrophysics, nanotechnology, condensed matter physics, etc. The results obtained in section 3.4 is also quite compelling. It shows that atomic energy levels could be manipulated by confining the atom inside a dielectric medium without the use of any external field.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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