

# The confined hydrogen atom

Manuel Antonio Cánovas Montes and Advisor: José M. Fernández-Varea

**Abstract:** We consider the confined hydrogen atom (CHA) in position and momentum space. To this end, we calculate numerically the wavefunctions and energies for various confinement radii and quantum numbers. We show breaking of degeneracy in CHA for  $n$  states. In the limit of an infinite confinement radii the well-known results for the non-confined hydrogen atom are recovered. In addition, the static polarizability and pressure are obtained.

## I. INTRODUCTION

Since quantum physics was born, one of its biggest achievements was to understand and compute the spectrum of the hydrogen atom. Later in the mid-1930s Michels [1, 2] thought about how confinement due to extreme pressure would affect its wavefunction. However, this problem could not be solved analytically, and therefore computational methods are needed. In recent years, owing to technological advances, this topic has gained renewed interest in the context of semiconductor quantum dots [1], for example.

In this work we will study the wave functions and energies of the confined hydrogen atom (CHA) with an infinite barrier. To do so, we developed a program which solves numerically the radial Schrödinger equation of the CHA for an arbitrary confinement radii, and for different combinations of the quantum numbers  $n$  and  $\ell$ . We will compare our results with those reported in reference [2]. In addition, we will evaluate the wave functions in momentum space using a Fourier Transform program.

Some authors have addressed the CHA with a penetrable wall [3–5]. However, this more complex situation is beyond the scope of the present work.

We will use Hartree atomic units  $\hbar = e = m_e = 1$  unless indicated otherwise. The Bohr radius  $a_0 \approx 0.529 \text{ \AA}$  is the unit of length and  $p_0 = \hbar/a_0$  is the unit of linear momentum. The unit of energy is the hartree,  $E_h \approx 27.2 \text{ eV}$ .

## II. THEORY

In this section we will discuss some theoretical points which will provide us with analytical expressions to be used later on.

From the atomic physics course we know that for a central potential  $V(r)$  the wavefunction  $\psi_{n\ell m}$  in spherical coordinates is the product of the reduced ra-

dial wavefunction  $P_{n\ell}$  and a spherical harmonic  $Y_{\ell m}$ ,

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}) = \frac{P_{n\ell}(r)}{r} Y_{\ell m}(\hat{\mathbf{r}}), \quad (1)$$

where  $\hat{\mathbf{r}}$  means angular directions in position space. The radial Schrödinger equation for the potential  $V(r)$  is

$$-\frac{1}{2r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left( V(r) + \frac{\ell(\ell+1)}{2r^2} \right) R(r) = E R(r). \quad (2)$$

To obtain the wave function in momentum space we need to evaluate the Fourier Transform

$$\tilde{\psi}_{n\ell m}(\mathbf{p}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d^3\mathbf{r} \exp(-i\mathbf{p}\cdot\mathbf{r}) \psi_{n\ell m}(\mathbf{r}). \quad (3)$$

To compute it we replace the exponential by its expansion

$$\exp(i\mathbf{p}\cdot\mathbf{r}) = 4\pi \sum_{\lambda=0}^{\infty} i^\lambda j_\lambda(pr) \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}^*(\hat{\mathbf{p}}) Y_{\lambda\mu}(\hat{\mathbf{r}}), \quad (4)$$

where  $j_\lambda$  are spherical Bessel functions. Now using the orthonormality property of the  $Y_{\ell m}$  functions we compute in (3), using (1) and (4), we get

$$\tilde{\psi}_{n\ell m}(\mathbf{p}) = (-i)^\ell \tilde{P}_{n\ell}(p) Y_{\ell m}(\hat{\mathbf{p}}) \quad (5)$$

with

$$\tilde{P}_{n\ell}(p) = \sqrt{\frac{2}{\pi}} \int_0^\infty j_\ell(pr) P_{n\ell}(r) r dr. \quad (6)$$

The phase  $(-i)^\ell$  in equation (5) is irrelevant because it disappears in  $|\tilde{\psi}_{n\ell m}(\mathbf{p})|^2$ . So if we know the wavefunction in position space using equations (5) and (6) we know it in momentum space. An alternative way to obtain these results can be done solving directly the Schrödinger equation in momentum space [5], in the case of the ordinary hydrogen atom. Both solution methods involve Gegenbauer polynomials.

Finally, in this section, we are going to solve the Schrödinger equation for the CHA, whose potential for no penetrable walls is

$$V(r) = \begin{cases} -\frac{1}{r} & \text{if } r \leq r_0, \\ +\infty & \text{if } r > r_0, \end{cases} \quad (7)$$

where  $r_0$  is the confinement radius. In order to solve equation (2) with this potential we make the substitution

$$\beta = \frac{1}{\sqrt{-2E}}, \quad \rho = \frac{2r}{\beta}. \quad (8)$$

Now we make the *Ansatz*

$$R(\rho) = \rho^\ell e^{-\rho/2} F(\rho). \quad (9)$$

Inserting equations (7), (8) and (9) in equation (2) we get

$$\rho \frac{d^2 F}{d\rho^2} + (2\ell + 2 - \rho) \frac{dF}{d\rho} - (\ell + 1 - \beta) F = 0. \quad (10)$$

In order to have finite values of the wavefunction at the origin,  $F$  should be a confluent hypergeometric function,

$$F(\rho) = {}_1F_1(\ell + 1 - \beta; 2\ell + 2; \rho). \quad (11)$$

In the case of the CHA we demand another boundary condition. At  $r_0$  the wavefunction must vanish, so we impose the following condition

$${}_1F_1(\ell + 1 - \beta; 2\ell + 2; \rho_0) = 0, \quad (12)$$

where  $\rho_0 = 2r_0/\beta$ . If  $r_0$  is finite,  ${}_1F_1$  is not analytical so we have to use a computational method. We will solve numerically equation (12) in the next section. Moreover, as wavefunction in position space is not analytical neither in momentum space will be. Hence we will solve equation (6) numerically.

### III. COMPUTER PROGRAMS

In this section we will explain the two programs that were developed to obtain the wavefunction in CHA conditions: one to solve equation (12) and the other to solve (6), as both are not, in general, analytical.

In the first program we created the hypergeometric function using a recurrence relation. The definition of our function is

$${}_1F_1 = \sum_{k=0}^{\infty} \frac{(1 - \beta + \ell)_k}{(2\ell + 2)_k} \frac{(2r/\beta)^k}{k!} \equiv \sum_{k=0}^{\infty} A_k, \quad (13)$$

where  $(\alpha)_k \equiv \Gamma(\alpha + k)/\Gamma(\alpha)$  are Pochhammer symbols. From this equation we get the recurrence relation

$$\frac{A_{k+1}}{A_k} = \frac{(1 - \beta + \ell + k)(2r_0/\beta)}{(2\ell + 1 + k)(k + 1)}. \quad (14)$$

Making a loop using (14) we can compute hypergeometric functions starting from  $A_0 = 1$  with an error

of  $10^{-6}$ . Now we have to solve equation (12). We will use the Regula-Falsi method to find a  $\beta$  that solves equation (12). With  $\beta$  and 8 we get the Energy, and with 9 and 1 we obtain the wavefunction for CHA. Exploring different ranges on Regula-Falsi we find all states for a given  $\ell$ . The first root corresponds to the  $n = 1$  state and successive roots are the excited states [1]. Then, we compare these energies with [2], which has really high precision. They fit perfectly within our tolerance.

The second program is responsible for transforming the wavefunction from position space to momentum space. It reads  $P_{n\ell}(r)$  delivered by the first program. Then it uses linear interpolation to obtain more points. Finally it uses equation (6) to get  $P_{n\ell}(p)$ , taking care of the indeterminacy  $\sin(pr)/r$  when  $r \rightarrow 0$ . To do the integral we adopted Simpson's method with  $10^5$  points. In order to convince ourselves that our program worked correctly we checked with the analytical expressions of  $P_{n\ell}(r)$  for the non-confined hydrogen atom. Using equation (6) we obtain the reduced radial distribution function in momentum space of them. Then we checked if it fits with our program. Here are some examples that can be found in reference [5]

$$\tilde{P}_{10}(p) = \frac{2^{5/2}}{\sqrt{\pi}} \frac{1}{(p^2 + 1)^2}, \quad (15)$$

$$\tilde{P}_{20}(p) = \frac{32}{\sqrt{\pi}} \frac{4p^2 - 1}{(4p^2 + 1)^3}, \quad (16)$$

$$\tilde{P}_{21}(p) = \frac{128\sqrt{2}}{\sqrt{3\pi}} \frac{p}{(4p^2 + 1)^3}, \quad (17)$$

$$\tilde{P}_{30}(p) = \frac{108\sqrt{2}}{\sqrt{3\pi}} \frac{81p^4 - 30p^2 + 1}{(9p^2 + 1)^4}. \quad (18)$$

As we see in figure 1 we represented correctly  $P_{n\ell}$  in momentum space for some analytical functions. Which means that our program does accurately the Fourier Transform.

### IV. RESULTS AND DISCUSSION

In this section we show some numeric and graphic results calculated with our programs and [2] in CHA conditions as some interesting physical properties.

In table I we display some energies obtained with our program for different values of  $r_0$ . Our tolerance for the energy is  $10^{-6}$ .

As we can see in table I as our  $r_0$  decreases energies increases. In addition our results for negatives en-

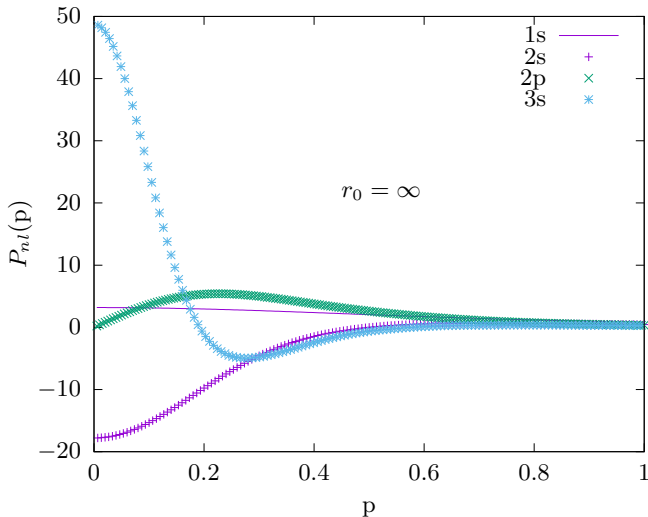


FIG. 1: Reduced radial wavefunctions in momentum space for the non-confined hydrogen atom for 1s, 2s, 3s and 2p obtained using our program. They fit perfectly equations 15 to 18.

TABLE I: Energies of low states for different values of  $r_0$ . Negative energies are computed using our program and positives are extracted from [2].

$r_0$	1s	2s	2p
2	-0.125 000	3.327 509	1.576 019
2.5	-0.334 910	1.865 480	0.851 978
3	-0.423 967	1.111 684	0.481 250
4	-0.483 265	0.420 236	0.143 527
5	-0.496 417	0.141 254	0.007 594
6	-0.499 277	0.012 725	-0.055 555
7	-0.499 863	-0.051 260	-0.087 479
8	-0.499 996	-0.084 739	-0.104 450
9	-0.499 999	-0.102 835	-0.113 727
10	-0.483 265	-0.112 806	-0.118 859
$\infty$	-0.500 000	-0.125 000	-0.125 000

energies matches perfectly with the values reported by [2]. Our program can not compute positive energies as  $\beta$  would be imaginary. These energies will be taken from [2]. Furthermore, energies become positive. In the non-confined hydrogen atom bound-state energies are all negative and between  $[-\frac{1}{2}, 0]$  as  $n$  increases because the potential is Coulombic for all  $r$ . But in the CHA as seen in equation (7) our potential has an infinite barrier. This allows the existence of bound states with positive energies.

As a consequence of equation (12) all wavefunctions in position space go to 0 at  $r = r_0$ . In addition as the wavefunctions does not extend to infinity we see

that in momentum space our wavefunction is smaller near  $p = 0$ . This can be understood easily from the properties of Fourier transform.

Let us show now some graphics of  $P_{n\ell}(r)$  and  $\tilde{P}_{n\ell}(p)$  comparing them for  $r_0$  with  $r_0 = \infty$ .

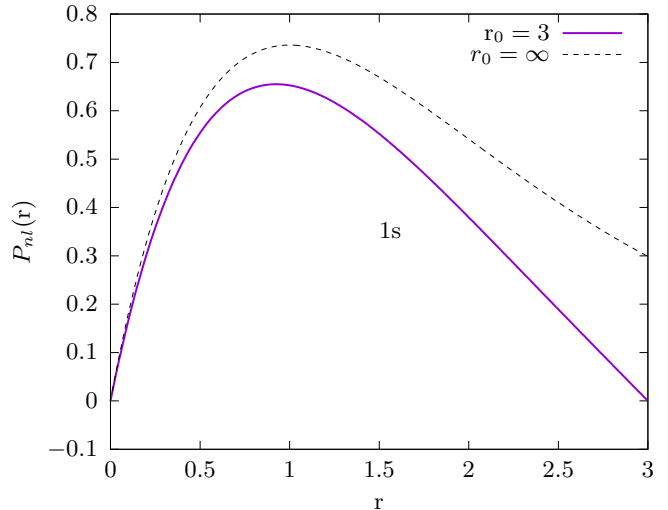


FIG. 2: Comparing of  $r_0 = 3$  with  $r_0 = \infty$  for 1s in position space.

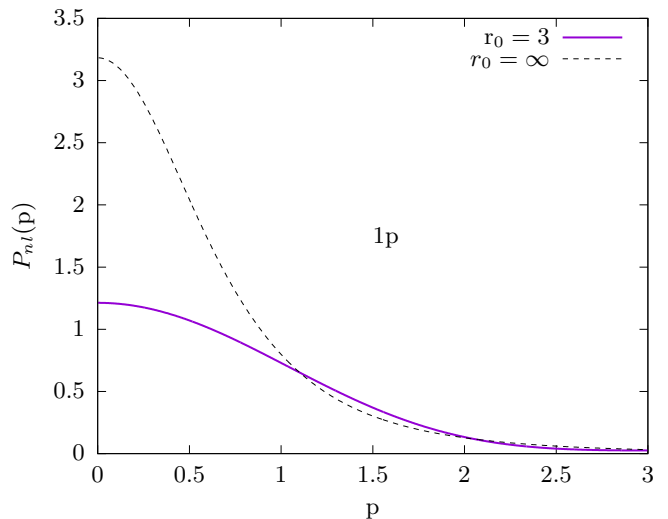
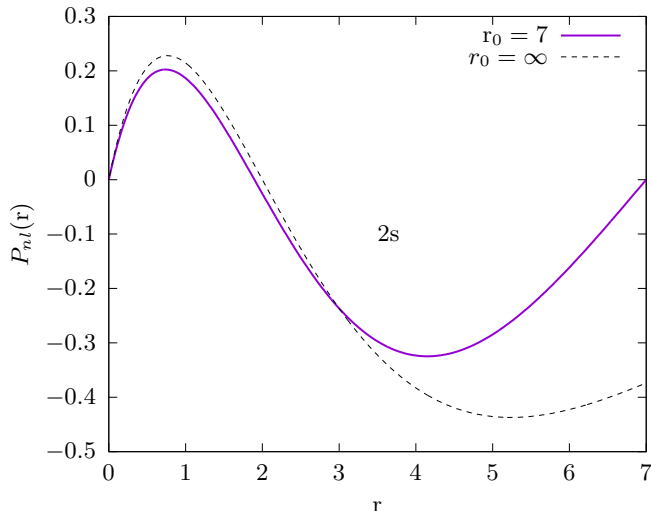
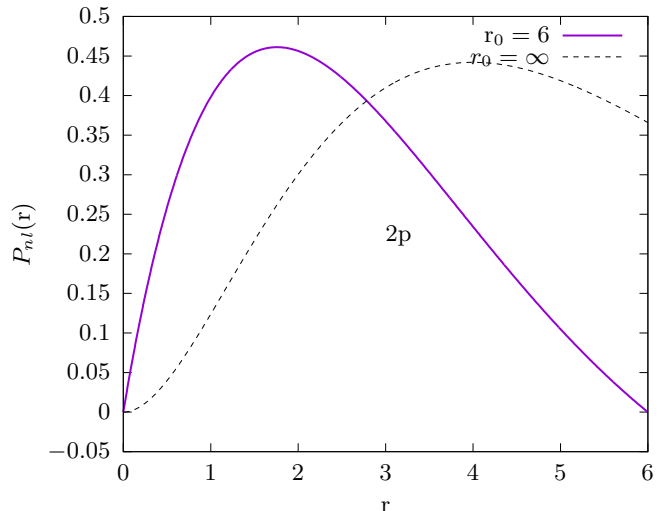
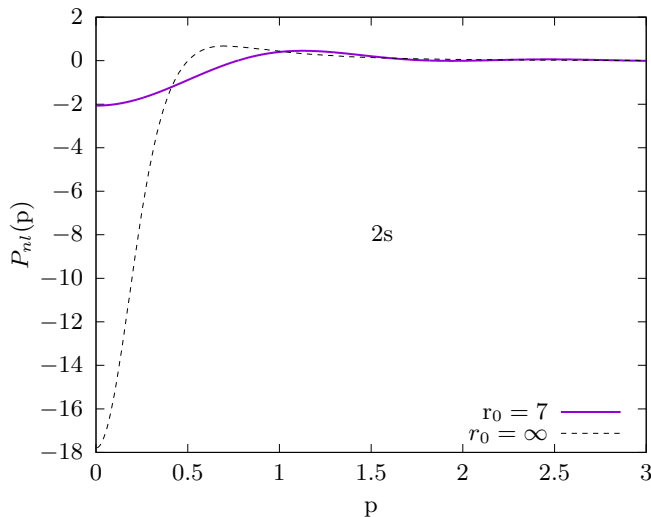
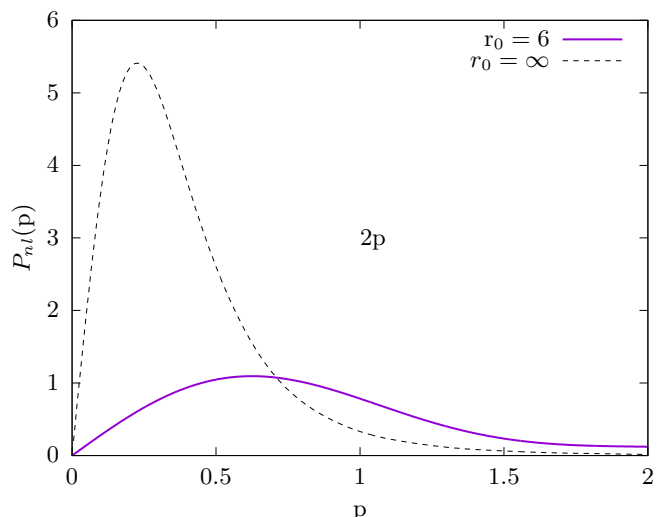


FIG. 3: Comparing of  $r_0 = 3$  with  $r_0 = \infty$  for 1s in momentum space.

Using computed negatives energies with our program and positives from [2], we will show energy evolution depending on  $r_0$  in figure 8.

From figure 8 we can extract interesting properties for CHA. As  $r_0$  grows, the energy approaches to ordinary hydrogen atom energies:  $E = -\frac{1}{2n^2}$ . In addition, states with the same  $n$  now have different ener-

FIG. 4: Comparing of  $r_0 = 7$  with  $r_0 = \infty$  for 2s.FIG. 6: Comparing of  $r_0 = 7$  with  $r_0 = \infty$  for 2p.FIG. 5: Comparison of  $r_0 = 7$  with  $r_0 = \infty$  for 2s in momentum space.FIG. 7: Comparison of  $r_0 = 7$  with  $r_0 = \infty$  for 2p in momentum space.

gies. We have broken the accidental degeneracy. Also  $E_{n,\ell+1} < E_{n,\ell}$  as expected owing to the centrifugal barrier.

Now we will compute the force per unit area required to confine the hydrogen atom to  $r_0$ . This is called electronic pressure [6] and is given by

$$P(r_0) = -\frac{1}{4\pi r_0^2} \frac{\partial E(r_0)}{\partial r_0} = \frac{1}{4\pi r_0^3} (2E - \langle V \rangle), \quad (19)$$

where we have used the Virial Theorem.

Next we are going to compute the static polarizability

$$\alpha = \frac{4}{9} \langle r^2 \rangle^2. \quad (20)$$

In table II we list  $P(r_0)$  and  $\alpha$  for different values of  $r_0$  for the 1s ground state, which results fit with [3–5]. As could be anticipated, we clearly see that as  $r_0$  is reduced we need more pressure to confine the atom. Moreover, the atom is harder to polarize as it becomes more confined. At  $r_0 = \infty$  we recover polarizability obtained in the atomic case and pressure, obviously, is 0.

Finally, we will mention that CHA can be treated using an approximation method which is linear in energy [1]. There ground-state energy correction can be computed numerically for  $r_0 \gg 1$ , see [1], as

$$\Delta E_0(r_0) \approx 8r_0(r_0 - 1)e^{-2r_0}. \quad (21)$$

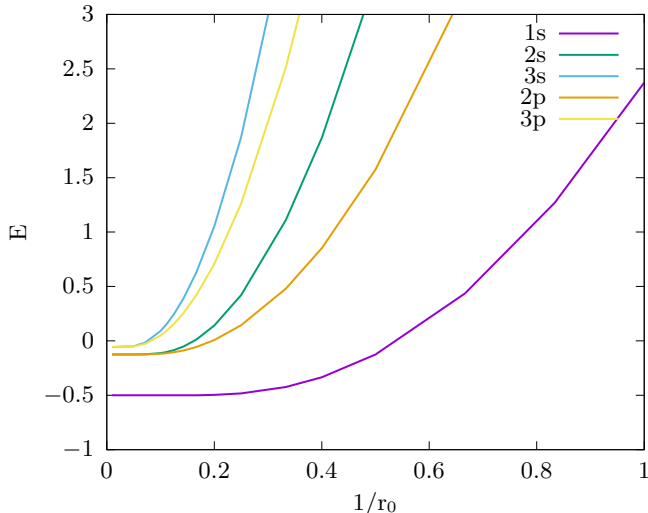


FIG. 8: Energies of the low states in CHA as a function of  $1/r_0$ .

TABLE II: Pressure and polarizability for some  $r_0$  at ground state 1s

$r_0$	$P$ ( $10^6$ atm)	$\alpha$ ( $10^{-24}$ cm <sup>3</sup> )
2	3.7115	0.05040
2.5	1.1104	0.10284
3	0.2724	0.17386
4	0.0368	0.33946
5	0.0052	0.47479
6	0.0010	0.54909
10	0.0000	0.59253
$\infty$	0.0000	0.59274

With this equation we can approximate the pressure when  $r_0 \gg 1$  as

$$P(r_0) \approx \frac{4e^{-2r_0}}{\pi} \left[ 1 - \frac{2}{r_0} + \frac{1}{r_0^2} \right] \quad (22)$$

## V. CONCLUSIONS

- We found a way to treat with CHA and compute negative energies fitting with [2] for different states changing  $r_0$ .
- We passed position wave function to momentum space and graphic both as shown in figures 2-7.
- We have seen that confinement breaks accidentally degeneracy and  $E_{n,l+1} < E_{n,l}$ .
- We obtained same results as [3–5] for pressure and polarizability.
- We demonstrate higher electronic pressure means more confinement but less polarizability.
- A possible continuation of this article would be study potential with penetrable walls [3–5] or state transitions [7].

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