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# A study of the confined hydrogen atom using the finite element method

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## Abstract

The hydrogen atom confined by an infinite spherical potential barrier is studied employing a variational procedure based on the p-version of the finite element method. In such a procedure, the spherical spatial confinement is imposed straightforwardly by removing a local basis function. The calculations have been performed for estimating the energy spectrum, the dipole polarizability and the effective pressure for various confinement radii. The effect of the spatial confinement on these quantities is analysed. The results obtained are compared with those previously published in the literature and the efficiency of the finite element method to treat confined quantum systems is discussed.

## 1. Introduction

The study of spatially confined quantum systems has increased considerably during the last few years (see [1] and references therein). Many physical phenomena occur in environments which could be considered cavities such as atoms and molecules under high pressure, and chemical reactions inside zeolite molecular sieves or fullerenes. Moreover, the arrival of modern experimental techniques has allowed the fabrication of semiconductors nanostructures, such as quantum wells and quantum dots, which has permitted us to explore the limits of dimension and confinement [2].

A simple but interesting example of a confined quantum system is the hydrogen atom limited by a spherical barrier of infinite potential. This model of a compressed atom was first proposed by Michels *et al* [3] to simulate the effect of pressure on an atom, while Sommerfeld and Welker [4] recognized the importance of the model for astrophysics. Furthermore, several articles have studied this system lately (see [5] and references therein) including its recent use in the understanding of the interiors of planets Jupiter and Saturn [6] and of atoms embedded in neutral media (e.g., neutral plasma or liquid helium; see [7, 8], for instance).

Several methods have been employed for the study of the confined hydrogen atom. For example, Goldman and Joslin [9] as well as De Groot and Ten Seldam [10] utilized the exact

solution of the problem, Aquino [11] applied a power series to solve the Schrödinger equation, while Laughlin *et al* [12, 13] employed algebraic methods and perturbation theory to derive the wavefunctions. However, methods based on variational principle are among the most employed in the literature such as, for example, the procedures that utilize trial wavefunction with nonlinear variational parameters [14–16] or that expand the wavefunction in a set of finite basis functions [17–19], that solve the Kohn–Sham equations [20, 21] and that use the configuration interaction model [22]. Particularly, we propose in the present paper a novel numerical variational methodology to solve the time-independent Schrödinger equation of confined quantum systems.

The procedure implemented for us is based on the variational formalism and the p-version of the finite element method (p-FEM) for expanding the wavefunction in a finite basis set. The finite element method (FEM) is a general nomenclature for a set of different procedures [23] which are based on the technique of space discretization into elements and on the use of local polynomial basis functions defined on these elements. The FEM has been utilized in molecular dynamics and electronic structure for bound states [24–26] and scattering problems [27, 28]. In particular, the p-version of the FEM employs linear interpolants and shape functions as basis functions and allows one to use different degrees of polynomials in different elements [25, 26, 28]. The present work is, to our knowledge, the first application of the p-FEM to treat confined quantum systems. In order to test the efficiency of our methodology we apply it to calculate the energy spectrum, dipole polarizability and effective pressure on the compressed hydrogen atom. This permits us to analyse the quality of the eigenvalues and eigenfunctions generated by using the p-FEM. The results are then compared with the ones previously published in the literature that use some approximative or exact methods.

This paper is organized as follows. In section 2 we apply the variational formalism and the one-dimensional p-FEM for solving the Schrödinger equation associated with the problem of the confined hydrogen atom. In section 3 we present the results for energy spectrum, dipole polarizability and effective pressure obtained by the p-FEM and other methods for various confinement radii. Finally, in section 4 we discuss the results and present our concluding remarks.

## 2. Methodology

### 2.1. Variational formalism

The centre of mass motion cannot be separated exactly from the relative one because of the spatial confinement. However, assuming an infinite mass for the nucleus and putting it on the centre of the hard sphere with radius  $r_c$ , the Hamiltonian of the confined system assumes the same form as the free one, except the potential energy, where it becomes (in atomic units)

$$V(r) = \begin{cases} -\frac{1}{r}, & r < r_c, \\ \infty, & r \geq r_c, \end{cases} \quad (1)$$

where an impenetrable spherical barrier at  $r = r_c$  is included.

From the variational principle, the problem of solving the non-relativistic time-independent Schrödinger equation is equivalent to finding stationary solutions of a functional of energy,

$$J[\Psi] = \int \Psi^*(r) \{H - E\} \Psi(r) dr, \quad (2)$$

with  $H$  being the Hamiltonian of the system.

Expanding the wavefunction in spherical harmonics,

$$\Psi(r) = \sum_l a_l \frac{\chi_l(r)}{r} Y_{lm}(\theta, \phi), \tag{3}$$

and using their orthonormalization relations, functional (2) can be written in terms of  $\chi_l(r)$  as follows:

$$J[\Psi] = \sum_l |a_l|^2 J_l[\chi_l],$$

where  $l$  is the total angular momentum, the functional  $J[\chi_l]$  is expressed as

$$J_l[\chi_l] = \int_0^{r_c} dr \left\{ \frac{\hbar^2}{2\mu} \frac{d\chi_l^*}{dr} \frac{d\chi_l}{dr} + \chi_l^* [V_l^{\text{ef}}(r) - E] \chi_l \right\} \tag{4}$$

and  $V_l^{\text{ef}}(r) = V(r) + [\hbar^2 l(l+1)/2\mu r^2]$ . Note that to obtain equation (4) we have utilized the Dirichlet's boundary conditions. The eigenstates and eigenvalues solutions of  $J_l[\chi_l]$  are found expanding the wavefunction in a finite basis set  $\{f_j^l\}$

$$\chi_l(r) = \sum_{j=1}^p c_j^l f_j^l(r), \tag{5}$$

with  $\{c_j^l\}$  being the coefficients of expansion, and imposing the stationarity condition on functional (4) under consideration. Thus, the variational solutions are obtained solving the generalized eigenvalue–eigenvector problem

$$\mathbf{H}^l \mathbf{c} = E \mathbf{O}^l \mathbf{c}, \tag{6}$$

where  $\mathbf{c}$  is the coefficient vector. In such an equation, the Hamiltonian and overlap matrix elements are given by

$$\{\mathbf{H}^l\}_{ij} = \int_0^{r_c} dr \left\{ \frac{\hbar^2}{2\mu} \frac{df_i^{l*}}{dr} \frac{df_j^l}{dr} + f_i^{l*} V_l^{\text{ef}}(r) f_j^l \right\} \tag{7}$$

and

$$\{\mathbf{O}^l\}_{ij} = \int_0^{r_c} dr f_i^{l*}(r) f_j^l(r). \tag{8}$$

The number of basis functions requires a computational effort to calculate the integrals (7) and (8) so as to solve equation (6). Therefore, the efficiency of the numerical calculation depends on the choice of the finite basis set utilized to expand the wavefunction  $\chi_l$ .

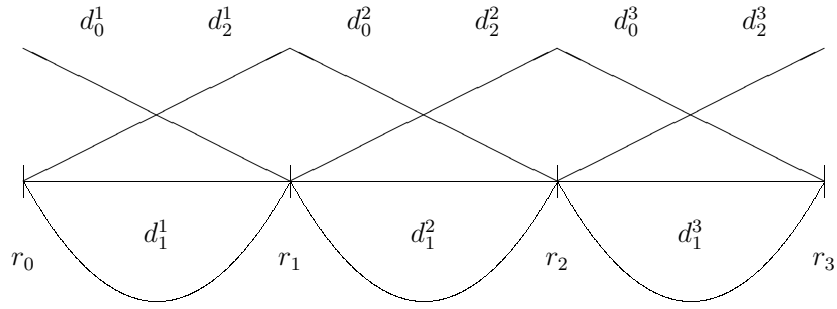
### 2.2. The p-version of the finite element method (p-FEM)

The one-dimensional p-FEM with an equidistant discretization is utilized for us to expand the wavefunction  $\chi_l(r)$  (see [25, 26, 28] and references therein). This method consists in dividing the integration interval  $[0, r_c]$  into  $N_e$  elements, where the  $i$ th element has the range of  $r_{i-1}$  to  $r_i$  with  $r_0 = 0$  and  $r_{N_e} = r_c$ , and expanding the wavefunction as follows:

$$\chi_l(r) = \sum_{i=1}^{N_e} \sum_{j=0}^{k_i} c_j^{l,i} d_j^i(r), \tag{9}$$

with  $k_i$  being the highest order of the basis functions associated with the  $i$ th element,  $d_j^i$  is the  $j$ th basis function of the same element and  $c_j^{l,i}$  is the related expansion coefficient. The basis functions  $\{d_j^i\}$  satisfy the following property:

$$\int_0^{r_c} dr d_j^{i*}(r) d_{j'}^i(r) = 0, \quad \forall i \neq i'. \tag{10}$$



**Figure 1.** Example of a p-FEM basis functions set with  $N_e = 3$  and  $k = 2$  used to expand the wavefunction.

The p-FEM utilizes as basis functions two linear interpolant functions defined by

$$d_0^i(r) = \frac{r_i - r}{r_i - r_{i-1}}, \quad d_{k_i}^i(r) = \frac{r - r_i}{r_i - r_{i-1}}, \quad r \in [r_{i-1}, r_i], \quad (11)$$

and  $k_i - 1$  shape functions defined by

$$d_j^i(r) = (4j + 2)^{-\frac{1}{2}} [P_{j+1}(y^i) - P_{j-1}(y^i)], \quad j = 1, \dots, k_i - 1, \quad (12)$$

where  $y^i = 2d_0^i(r) - 1$  and  $P_j$  are the Legendre polynomials<sup>1</sup>. The  $\{d_j^i(r)\}$  basis set satisfies the following relations:

$$\begin{aligned} d_0^i(r_{i-1}) &= 1 = d_{k_i}^i(r_i), \\ d_0^i(r_i) &= 0 = d_{k_i}^i(r_{i-1}), \\ d_j^i(r_{i-1}) &= 0 = d_j^i(r_i), \quad j = 1, \dots, k_i - 1. \end{aligned} \quad (13)$$

The imposition of the continuity of the wavefunction on the border of elements leads to the condition  $c_{k_i}^i = c_0^{i+1}$  and  $d_{k_i}^i(r) + d_0^{i+1}(r)$  being only one function actuating in two elements. Due to these properties, Hamiltonian and overlap matrices are symmetric and sparses, and they have a useful block structure.

As an example, we display pictorially in figure 1 the  $\{d_j^i(r)\}$  basis set for  $N_e = 3$  and  $k_i = 2$ . In such a case, the expansion of  $\chi_l(r)$  is given by

$$\chi_l(r) = \sum_{i=1}^3 \sum_{j=0}^2 c_j^{l,i} d_j^i(r). \quad (14)$$

However, if we consider the continuity condition on the  $\{c_j^{l,i}\}$  coefficients, the expansion (14) becomes

$$\begin{aligned} \chi_l(r) &= a_1 d_0^1(r) + a_2 d_1^1(r) + a_3 [d_2^1(r) + d_0^2(r)] + a_4 d_1^2(r) \\ &\quad + a_5 [d_2^2(r) + d_0^3(r)] + a_6 d_1^3(r) + a_7 d_2^3(r), \end{aligned} \quad (15)$$

where  $a_k = c_j^{l,i} \iff k = (i - 1)k_i + j + 1$  are new coefficients.

Observe that for the confined hydrogen atom we have to impose that  $\chi_l(r = 0) = 0$  and  $\chi_l(r = r_c) = 0$ . The first one is due to the continuity of the wavefunction (equation (3)) on the origin, while the second is due to the spherical spatial confinement. Both conditions are straightforwardly implemented with the p-FEM imposing  $c_0^{l,1} = c_{k_i}^{l,N_e} = 0$  in expansion (9) (or, for the previous example, imposing  $a_1 = a_7 = 0$  at expression (15)). Note that the **H** and **O** matrix dimensions in such a case will be  $(N_e \times k_i - 1) \times (N_e \times k_i - 1)$ .

<sup>1</sup> Note that equation (12) appears in [25, 26, 28] with a signal misprint.

### 3. Results

In this section results for eigenenergies, dipole polarizability and effective pressure of the confined hydrogen atom for various confinement radii have been calculated using a computational implementation (in FORTRAN 77) based on the p-FEM shown in section 2. In all calculations, atomic units were employed and the element mesh was built using equidistant discretization and polynomials of the same order for all elements ( $k_i = k, \forall i$ ).

#### 3.1. Energy spectrum

We compute the energies for 1s, 2s, 2p, 3s, 3p and 3d states of the confined hydrogen atom using different basis sets and for various confinement radii. Our results are compared, when possible, with the very accurate results obtained previously by Aquino [11] and Goldman and Joslin [9]. In particular, Aquino employed a numerical method, proposed initially by Palma and Campoy [29] to solve free quantum systems, that uses the Taylor series approximation of the wavefunction. On the other hand, Goldman and Joslin [9] utilized a general analytical solution of the radial part of the Schrödinger equation for a hydrogen atom (where it depends on the confluent hypergeometric function) and, for each  $l$  and  $r_c$  fixed, they searched numerically the zeros of such a function. The energy eigenvalues calculated by Aquino have a precision of 10–11 figures [11], while Goldman and Joslin found results that have at least an accuracy of 7 figures [9].

Initially, we analyse the convergence process of the p-FEM eigenenergies, when  $N_e$  and  $k$  are increased, by considering the following convergence factor:

$$\Delta E(N_e, k) = |E(N_e, k) - E(N_e, k - 1)|, \quad (16)$$

where  $E(N_e, k)$  is the p-FEM energy calculated using  $N_e$  elements and polynomials of order up to  $k$ . In tables 1 and 2, the energy eigenvalue and convergence factor results as a function of basis definition ( $N_e$  and  $k$ ) are presented for 1s, 2p and 3d states for  $r_c = 2.0a_0$  and  $r_c = 10.0a_0$ , respectively. The accurate energies obtained by Aquino [11] are also presented for comparison. We can note that the  $\Delta E(N_e, k)$  factor indicates the number of precision figures of the energy  $E(N_e, k)$  and, hence, we can observe how the p-FEM eigenvalue of a particular state reaches the convergence, i.e.,  $\Delta E(N_e, k) \leq 10^{-11}$ .

We point out that in tables 1 and 2 if  $N_e$  is fixed, the error decreases rapidly when  $k$  increases. On the other hand, if  $k$  is fixed, the error also decreases when  $N_e$  increases, but more slowly. For example, with  $r_c = 2.0a_0$  and  $N_e = 2$ , the p-FEM leads to a reasonable result (up to a precision of six figures) for  $k = 5$  (matrix dimension of  $9 \times 9$ ), while for  $k = 2$  (two linear interpolant and one shape functions) the p-FEM does not give an acceptable result. This suggests that the eigenfunctions for the confined hydrogen atom are more well approximated by high-order polynomials (for  $k = 6$ , the p-FEM provides reasonable values of energy for  $N_e \geq 3$ ). In this way, it should have a compromise between the number of elements and the polynomial order to reach a good convergence of the results. This justify the use of  $N_e = 5$  for all p-FEM calculations of this subsection while  $k$  is chosen to reach an accuracy of at least 11 figures for the energy. We point out that a similar analysis was done in [28] for scattering problems.

Next, in tables 3–5, the p-FEM energies for 1s, 2p and 3d states for various confinement radii are, respectively, presented and compared with the ones calculated by a variational method proposed by Marin and Cruz [14] and by a modification of the Marin–Cruz approach proposed by Varshni [15]. Moreover, in tables 3 and 4, the energies calculated by the other variational method utilizing the Gaussian basis set proposed by Zicovich-Wilson *et al* [17] (with basis set B1 and approach A3 presented in [17] which totalled 20 basis functions) and

**Table 1.** Energy eigenvalue and convergence factor ( $\Delta E(N_e, k) = |E(N_e, k) - E(N_e, k - 1)|$ ) results as a function of basis definition ( $N_e$  and  $k$ ) for  $r_c = 2.0a_0$ . The Aquino's values of energy [11] are presented for comparison; energies and convergence factors in Hartree.

State	$N_e$	$E$ and $\Delta$						Aquino	
		$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$		$k = 8$
1s	2	-0.1	-0.12	-0.125 00	-0.125 0000	-0.125 000 0000	-0.125 000 000 00		-0.125 000 000 00
		0.4	0.01	0.000 09	0.000 0003	0.000 000 0004	<1.0 (- 11)		
	3	-0.1	-0.125	-0.125 000	-0.125 000 00	-0.125 000 000 00			-0.125 000 000 00
		0.2	0.003	0.000 009	0.000 000 01	<1.0 (- 11)			
	5	-0.12	-0.1250	-0.125 0000	-0.125 000 0000	-0.125 000 000 00			-0.125 000 000 00
		0.09	0.0004	0.000 0004	0.000 000 0002	<1.0 (- 11)			
	7	-0.12	-0.1250	-0.125 000 00	-0.125 000 000 00				-0.125 000 000 00
		0.05	0.0001	0.000 000 06	0.000 000 000 01				
2p	2	1.7	1.6	1.5760	1.576 02	1.576 0188	1.576 018 786	1.576 018 785 61	1.576 018 785 60
		0.5	0.1	0.0008	0.000 03	0.000 0001	0.000 000 002	<1.0 (- 11)	
	3	1.6	1.58	1.576 02	1.576 019	1.576 018 786	1.576 018 785 61	1.576 018 785 61	1.576 018 785 60
		0.4	0.02	0.000 09	0.000 001	0.000 000 002	0.000 000 000 01	<1.0 (- 11)	
	5	1.6	1.576	1.576 019	1.576 018 79	1.576 018 785 61	1.576 018 785 61		1.576 018 785 60
		0.1	0.002	0.000 005	0.000 000 02	0.000 000 000 02	<1.0		
	7	1.58	1.5760	1.576 0188	1.576 018 786	1.576 018 785 61			1.576 018 785 60
		0.07	0.0005	0.000 0007	0.000 000 001	<1.0			
3d	2		3.346	3.33	3.327 52	3.327 50	3.327 509 16	3.327 509 156	
			0.007	0.02	0.000 03	0.000 01	0.000 000 02	0.000 000 001	
	3	3.3	3.33	3.328	3.327 509	3.327 5091	3.327 509 1565	3.327 509 156 50	
		0.6	0.02	0.001	0.000 008	0.000 0002	0.000 000 0004	<1.0 (- 11)	
	5	3.3	3.328	3.327 51	3.327 5092	3.327 509 1565	3.327 509 156 50		
		0.2	0.004	0.000 05	0.000 0002	0.000 000 0008	<1.0 (- 11)		
	7	3.33	3.328	3.327 509	3.327 509 16	3.327 509 156 50	3.327 509 156 50		
		0.08	0.001	0.000 006	0.000 000 01	0.000 000 000 03	<1.0 (- 11)		

**Table 2.** Energy eigenvalue and convergence factor ( $\Delta E(N_e, k) = |E(N_e, k) - E(N_e, k - 1)|$ ) results as a function of basis definition ( $N_e$  and  $k$ ) for  $r_c = 10.0a_0$ . The Aquino's values of energy [11] are presented for comparison; energies and convergence factors in Hartree.

State	$N_e$	$E$ and $\Delta$							Aquino
		$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$	$k = 8$	
1s	2	-0.3	-0.4	-0.49	-0.50	-0.500	-0.499 99	-0.499 999	-0.499 999 263 28
		0.1	0.1	0.05	0.01	0.001	0.000 09	0.000 004	
	3	-0.4	-0.48	-0.50	-0.500	-0.500 00	-0.499 999	-0.499 999 26	-0.499 999 263 28
		0.2	0.09	0.02	0.002	0.000 09	0.000 003	0.000 000 05	
	5	-0.5	-0.50	-0.500	0.500 00	-0.499 999	-0.499 999 26	-0.499 999 2633	-0.499 999 263 28
		0.1	0.04	0.003	0.000 09	0.000 001	0.000 000 01	0.000 000 0001	
	7	-0.5	-0.50	-0.5000	-0.499 999	-0.499 999 26	-0.499 999 2633	-0.499 999 263 28	-0.499 999 263 28
		0.1	0.02	0.0006	0.000 008	0.000 000 07	0.000 000 0004	<1.0 (- 11)	
2p	2	-0.103	-0.11	-0.118	-0.1188	-0.118 86	-0.118 8595	-0.118 859 545	-0.118 859 544 85
		0.006	0.01	0.004	0.0004	0.000 02	0.000 0004	0.000 000 007	
	3	-0.110	-0.118	-0.119	-0.118 86	-0.118 8595	-0.118 859 545	-0.118 859 544 85	-0.118 859 544 85
		0.004	0.007	0.001	0.000 04	0.000 0007	0.000 000 007	0.000 000 000 04	
	5	-0.116	-0.119	-0.118 86	-0.118 860	-0.118 859 545	-0.118 859 544 85	-0.118 859 544 85	-0.118 859 544 85
		0.009	0.002	0.000 09	0.000 001	0.000 000 006	0.000 000 000 02	<1.0 (- 11)	
	7	-0.118	-0.1188	-0.118 86	-0.118 859 54	-0.118 859 5449	-0.118 859 544 85	-0.118 859 544 85	-0.118 859 544 85
		0.007	0.0008	0.000 01	0.000 000 08	0.000 000 0002	<1.0 (- 11)		
3d	2	-0.002	-0.006	-0.0070	-0.007 09	-0.007 093	-0.007 092 78	-7.092 7840	-0.007 092 783 97
		0.051	0.004	0.0003	0.000 09	0.000 003	0.000 000 03	0.000 0001	
	3	-0.006	-0.0069	-0.0071	-0.007 093	-0.007 092 78	-7.092 7840	-0.007 092 783 97	-0.007 092 783 97
		0.028	0.0003	0.0001	0.000 007	0.000 000 07	0.000 0003	<1.0 (- 11)	
	5	-0.006	-0.0071	-0.007 09	-0.007 0928	-0.007 092 7840	-0.007 092 783 97	-0.007 092 783 97	-0.007 092 783 97
		0.007	0.0001	0.000 01	0.000 0001	0.000 000 0005	<1.0 (- 11)		
	7	-0.006	-0.007 09	-0.007 093	-0.007 092 78	-0.007 092 783 97	-0.007 092 783 970	-0.007 092 783 97	-0.007 092 783 97
		0.003	0.000 05	0.000 002	0.000 000 01	0.000 000 000 02	<1.0 (- 11)		



**Table 3.** Energy eigenvalue (in Hartree) for 1s state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

$r_c$	Marin and Cruz <sup>a</sup>	Varshni <sup>b</sup>	Zicovich-Wilson <i>et al</i> <sup>c</sup>	Saha <i>et al</i> <sup>d</sup>	Goldman and Joslin <sup>e</sup>	p-FEM <sup>f</sup>	Aquino <sup>g</sup>
0.1	474.902	469.427			468.9930	468.993 038 659	
0.5	14.897	14.758			14.747 97	14.747 970 0303	
0.81						4.391 641 570 91	4.391 641 570 90
1.0	2.3906	2.3749		2.381 87	2.373 991	2.373 990 866 10	
1.3	0.9218	0.9173				0.917 037 080 68	
1.6	0.272 33	0.271 35				0.271 312 312 64	
2.0	-0.125 00	-0.125 00		-0.122 10	-0.125 0000	-0.125 000 000 00	-0.125 000 000 00
3.0	-0.422 55	-0.422 55	-0.423 949			-0.423 967 287 73	
4.086 71						-0.485 330 855 11	-0.485 330 855 11
5.0		-0.4947 <sup>h</sup>	-0.496 275	-0.492 40		-0.496 417 006 59	
7.0		-0.4993 <sup>h</sup>	-0.499 794	-0.498 71		-0.499 862 577 55	-0.499 862 577 55
10.0			-0.499 981	-0.499 810	-0.499 9993	-0.499 999 263 28	-0.499 999 263 28
14.0						-0.499 999 999 50	0.499 999 999 49

<sup>a</sup> Reference [14].<sup>b</sup> Reference [15].<sup>c</sup> Reference [17].<sup>d</sup> Reference [8].<sup>e</sup> Reference [9].<sup>f</sup> Present results.<sup>g</sup> Reference [11].<sup>h</sup> From Dutt *et al* [16].**Table 4.** Energy eigenvalue (in Hartree) for 2p state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

$r_c$	Marin and Cruz <sup>a</sup>	Varshni <sup>b</sup>	Zicovich-Wilson <i>et al</i> <sup>c</sup>	Saha <i>et al</i> <sup>d</sup>	Goldman and Joslin <sup>e</sup>	p-FEM <sup>f</sup>	Aquino <sup>g</sup>
0.1					991.0076	991.007 589 441	
0.4		58.523 <sup>h</sup>				58.448 123 7200	
0.6	25.201	24.968				24.936 947 0365	
1.0	8.306	8.232		8.223 25	8.223 138	8.223 138 316 16	
1.4	3.8429	3.8107				3.806 884 767 19	
2.0	1.5896	1.5774		1.576 02	1.576 019	1.576 018 785 61	1.576 018 785 60
2.5		0.853 <sup>h</sup>				0.851 978 460 99	0.851 978 460 99
3.0	0.484 70	0.481 55	0.486 314			0.481 250 312 53	0.481 250 312 52
5.0	0.007 733	0.007 601	0.134 479	0.007 59		0.007 593 920 47	0.007 593 920 46
7.0	-0.087 41	-0.087 41	0.121 634	-0.087 49		-0.087 479 017 93	
8.0						-0.104 450 066 41	-0.104 450 066 40
10.0			0.121 471	-0.118 87	-0.118 8595	-0.118 859 544 85	-0.118 859 544 85
14.0						-0.124 540 597 99	-0.124 540 597 99
20.0						-0.124 994 606 65	-0.124 994 606 64

<sup>a</sup> Reference [14].<sup>b</sup> Reference [15].<sup>c</sup> Reference [17].<sup>d</sup> Reference [8].<sup>e</sup> Reference [9].<sup>f</sup> Present results.<sup>g</sup> Reference [11].<sup>h</sup> From Dutt *et al* [16].

**Table 5.** Energy eigenvalue (in Hartree) for 3d state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

$r_c$	Marin and Cruz <sup>a</sup>	Varshni <sup>b</sup>	Goldman and Joslin <sup>c</sup>	p-FEM <sup>d</sup>	Aquino <sup>e</sup>
0.1			1644.530	1644.529 922 40	
0.5			63.160 18	63.160 184 4674	
1.0	15.117	14.990	14.967 46	14.967 464 0862	
1.5	6.346	6.294		6.284 819 435 32	
2.0	3.3591	3.3320	3.327 509	3.327 509 156 50	
3.0	1.3044	1.2944		1.292 803 271 99	
4.0	0.6266	0.6220	0.651 3558	0.621 355 776 18	
5.0	0.331 74	0.329 43		0.329 117 142 97	
7.0	0.097 29	0.096 66		0.096 589 640 90	0.096 589 640 89
8.0				0.046 058 247 38	0.046 058 247 37
10.0	−0.007 04	−0.007 09	−0.007 092 784	−0.007 092 783 97	−0.007 092 783 97
14.0				−0.043 113 470 41	−0.043 113 470 41
20.0				−0.053 967 564 42	−0.053 967 564 42

<sup>a</sup> Reference [14].<sup>b</sup> Reference [15].<sup>c</sup> Reference [9].<sup>d</sup> Present results.<sup>e</sup> Reference [11].

the energies obtained by a time-dependent variation perturbation calculation performed by Saha *et al* [8] are shown for comparison, too.

We can note in these tables that the p-FEM results and the ones obtained by Aquino and by Goldman and Joslin agree in all figures evaluated for any energy state independently of the confinement radius. To obtain this precision, the value of highest order of polynomial basis functions associated with an element varied between  $k = 4$  and  $k = 9$  for small and large confinement radii, respectively. These values for  $k$  represent **H** and **O** matrices with dimensions between  $19 \times 19$  and  $44 \times 44$ . The total number of basis functions employed here is relatively smaller than the ones used in other variational procedures if we analyse the precision reached in the calculations. For example, Zicovich-Wilson *et al* employ a basis set with 20 functions and obtain a poor result for 2s and 2p states. We can also point out that the p-FEM basis are local functions and, consequently, the integration is not performed over all region of space. Moreover, when compared with the other results shown in tables 3–5, the p-FEM is the one that presents the best results.

For 2s, 3s and 3p states, the results obtained with the p-FEM are displayed in tables 6–8, respectively, and then are compared with the very precise ones calculated by Aquino [11] and Goldman and Joslin [9] for various values of  $r_c$ . Moreover, in table 6, the values tabulated by De Groot and Ten Seldan [10], Goodfriend [18] and Zicovich-Wilson *et al* [17] for larger confinement radii are also shown for comparison. Again the results obtained using the p-FEM within the 11 figures with those of Aquino and the 7 figures with those of Goldman and Joslin, demonstrate the excellent precision of the present method to obtain eigenenergies of confined hydrogen atom for ground and excited states for different values of  $l$ , even using a small number of basis sets.

An interesting effect to be shown is the splitting of the degeneracy observed in the free hydrogen atom for the levels  $nl$ , with  $0 \neq l \leq n - 1$ , due to isotropic compression. For this we plot in figure 2 the energy levels of 2s, 2p, 3s, 3p and 3d states as a function of the confinement radius,  $r_c$ . In this figure, we can easily note that the difference between the energy levels  $nl$

**Table 6.** Energy eigenvalue (in Hartree) for 2s state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

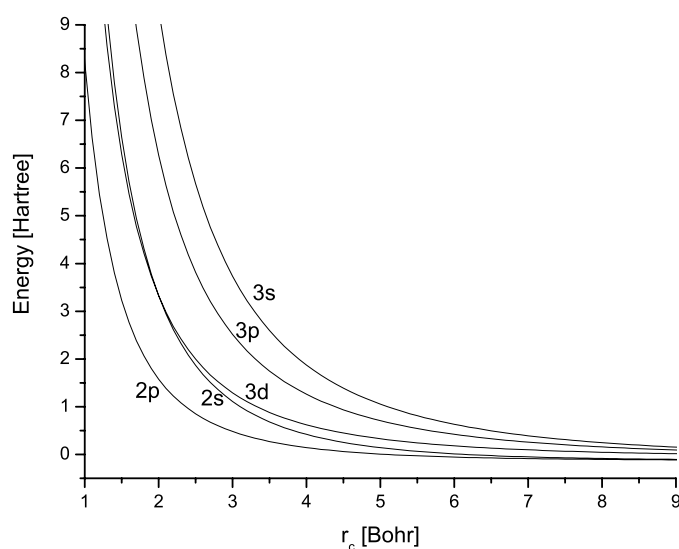
$r_c$	De Groot and Ten Seldam <sup>a</sup>	Goodfriend <sup>b</sup>	Zicovich-Wilson <i>et al</i> <sup>c</sup>	Goldman and Joslin <sup>d</sup>	p-FEM <sup>e</sup>	Aquino <sup>f</sup>
0.1				1942.720	1942.720 354 55	
0.5				72.672 04	72.672 039 1905	
1.0				16.570 26	16.570 256 0935	
2.0				3.327 509	3.327 509 156 50	3.327 509 156 49
4.0			0.420 525	0.420 235 6	0.420 235 631 71	
7.0	-0.0974	-0.0513	-0.021 059		-0.051 260 393 61	-0.051 260 393 61
8.0					-0.084 738 721 36	-0.084 738 721 35
10.0	-0.1162	-0.1120	-0.052 848	-0.112 806 2	-0.112 806 210 30	-0.112 806 210 29
14.0					-0.124 015 029 43	-0.124 015 029 43
17.0					-0.124 877 921 06	-0.124 877 921 05
20.0	-0.124 99	-0.125 00			-0.124 987 114 31	

<sup>a</sup> Reference [10].<sup>b</sup> Reference [18].<sup>c</sup> Reference [17].<sup>d</sup> Reference [9].<sup>e</sup> Present results.<sup>f</sup> Reference [11].**Table 7.** Energy eigenvalue (in Hartree) for 3s state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

$r_c$	Goldman and Joslin <sup>a</sup>	p-FEM <sup>b</sup>	Aquino <sup>c</sup>
0.5	170.5852	170.585 164 188	
1.0	40.863 12	40.863 124 6010	
2.0	9.314 150	9.314 150 435 40	9.314 150 435 51
4.0	1.872 702	1.872 702 065 62	
7.0		0.392 241 143 11	0.392 241 143 11
8.0		0.246 491 976 99	0.246 491 976 99
10.0	0.091 422 32	0.091 422 322 41	0.091 422 322 40
14.0		-0.016 065 576 45	-0.016 065 576 44
17.0		-0.040 456 745 64	-0.040 456 745 63
20.0		-0.049 918 047 60	

<sup>a</sup> Reference [9].<sup>b</sup> Present results.<sup>c</sup> Reference [11].

increases when  $r_c$  goes to zero. Another important aspect is that the confinement may cause accidental degeneracies between levels with different principal quantum number  $n$  and the inversion of the energy values. This can be observed with the 2s and 3d states when  $r_c = 2.0$  in both figure 2 and tables 5 and 6. The inversion of the electronic occurs because the influence of the confinement is more noticeable for states with a large number of nodes in the radial direction due their wavefunction extension. These phenomena can also be seen as a hidden symmetry which is described by the Lenz vector formalism [30]. Moreover, Connerade *et al* have shown that this inversion between the  $ns$  and  $nd$  energy levels is a general behaviour of many compressed multi-electron atoms, where the s-p competition disappears with increasing confinement pressure (see [31] for details).



**Figure 2.** Energy values (in Hartree) as a function of confinement radius (in Bohr) for 2s, 2p, 3s, 3p and 3d states of the compressed hydrogen atom. The p-FEM results are calculated with  $N_e = 5$  and  $k = 5$ .

**Table 8.** Energy eigenvalue (in Hartree) for 3p state for a compressed hydrogen atom as a function of confinement radius (in Bohr); the p-FEM results are calculated using  $N_e = 5$ .

$r_c$	Goldman and Joslin <sup>a</sup>	p-FEM <sup>b</sup>
0.5	114.6436	114.643 552 519
1.0	27.474 00	27.473 995 3025
2.0	6.269 003	6.269 002 791 99
4.0	1.261 521	1.261 521 214 88
7.0		0.257 800 616 93
8.0		0.157 368 197 44
10.0	0.049 190 76	0.049 190 760 59
14.0		-0.027 268 482 49
20.0		-0.051 611 419 76

<sup>a</sup> Reference [9].

<sup>b</sup> Present results.

### 3.2. Other properties

It is well known that not always a useful method for computing the energy spectrum is able to reproduce other electronic properties. In order to examine the efficiency of the p-FEM method for the calculation of such properties, we determine the dipole polarizability ( $\alpha$ ) and the effective pressure ( $P$ ) for the confined hydrogen atom in the 1s state. Dipole polarizability is an important quantity in the description of interatomic interactions and electron-atom scattering (see [16, 32] and references cited therein). To obtain accurate values of  $\alpha$ , it is necessary to know the behaviour of the wavefunction of excited states over the entire confined space. On the other hand, the evaluation of the effective pressure for a given confinement radius is important to understand the interior of planets such as Jupiter and Saturn [6]. In both cases,  $N_e = 6$  and  $k = 6$  have been utilized in the p-FEM calculation while for the

**Table 9.** Polarizability  $\alpha$  (in atomic units) for the 1s state as a function of confinement radius  $r_c$ . The p-FEM results are calculated using  $N_e = 6$  and  $k = 6$ .

$r_c$	Dutt <i>et al</i> <sup>a</sup>	Banerjee <i>et al</i> <sup>b</sup>	Saha <i>et al</i> <sup>c</sup>	Laughlin <sup>d</sup>	Laughlin <sup>e</sup>	p-FEM <sup>f</sup>
0.4	0.000 85					0.000 853 148 792
1.0	0.028 68	0.03	0.0291			0.028 792 0226
1.4	0.098 57					0.099 091 2992
2.0	0.340 16	0.35	0.3344	0.342 558	0.342 558	0.342 558 109
2.5	0.694 90					0.700 675 176
3.0	1.024 32	1.20				1.191 706 06
4.0	2.357 82	2.39		2.336 311 498	2.377 982 333	2.377 982 33
5.0	3.402 94	3.43	3.2176	3.402 946 464	3.422 454 224	3.422 454 22
7.0	3.512 98	4.35	3.8079	4.346 176 702	4.347 638 027	4.347 638 03
9.0		4.49		4.487 342 421	4.487 413 391	4.487 413 38
12.0				4.499 827 685	4.499 828 228	4.499 828 19

<sup>a</sup> Reference [16].

<sup>b</sup> Reference [21].

<sup>c</sup> Reference [8].

<sup>d</sup> Approximate values from [13].

<sup>e</sup> Precise numerical values from [13].

<sup>f</sup> Present results.

calculation of the effective pressure also  $N_e = 10$  and  $k = 10$  have been used to investigate the convergence of the results. These p-FEM basis definitions assure an excellent precision of our results.

The dipole polarizability describes the second-order response of a system to an external electric field. It can be calculated by using the perturbation method from its second-order term. The dipole polarizability of the 1s state assumes then the following expression [33]:

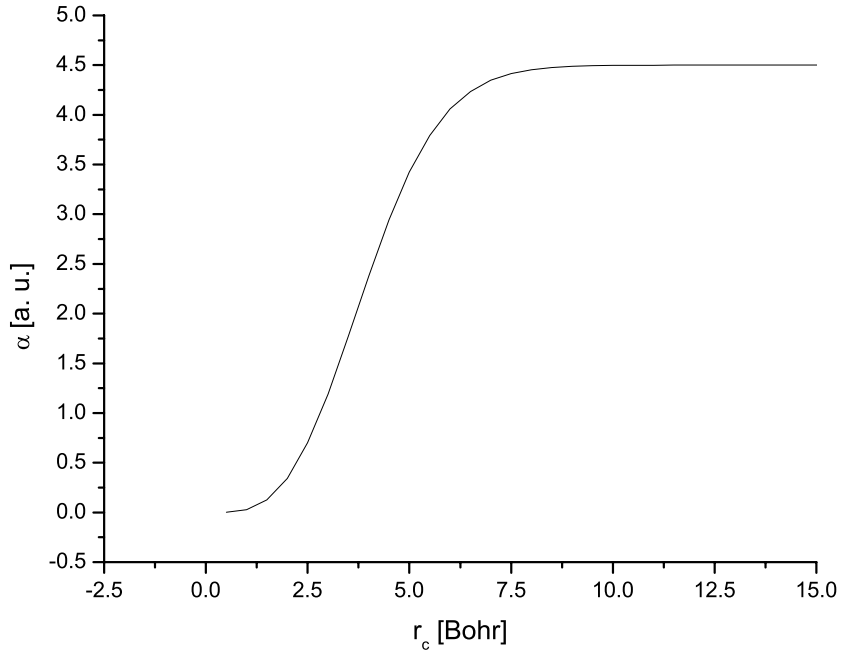
$$\alpha = 2 \sum_{n \geq 2} \frac{|\langle \Psi_{np}(\mathbf{r}) | r \cos \theta | \Psi_{1s}(\mathbf{r}) \rangle|^2}{(E_{np} - E_{1s})}, \quad (17)$$

where the summation is over all electronic states with  $l = 1$ .

In table 9 and figure 3, we show the p-FEM results of  $\alpha$  for various confinement radii. They are compared in table 9 with the values computed by Dutt *et al* [16], obtained from an approximate formula suggested by Buckingham [34] using a numerical exact calculation, with the values calculated by Banerjee *et al* [21] who utilized the variational perturbation procedure, with the values calculated by Saha *et al* [8] who also utilized variation perturbation calculations, with those from Laughlin [13] who utilized a method followed by Dalgarno and Lewis [35], and with the precise numerical values extracted from the same Laughlin's paper. Note that our results are identical to the precise numerical values of Laughlin, which indicates that the wavefunction obtained within the p-version of the finite element method is accurate enough.

We also calculated as the last test of the p-FEM, effective pressure ( $P$ ) for the 1s state of the confined hydrogen atom. The effective pressure is proportional to the variation of the energy as a function of the confinement radius, as can be seen in the following expression [3]:

$$P(r_c) = -\frac{1}{4\pi r_c^2} \frac{dE_{1s}}{dr_c}, \quad (18)$$



**Figure 3.** Polarization (in atomic units) of the 1s state of a compressed hydrogen atom as a function of confinement radius (in Bohr). The p-FEM results are calculated with  $N_e = 6$  and  $k = 6$ .

**Table 10.** Effective pressure  $P$  (in  $10^8$  atm) for the 1s state as a function of confinement radius (in Bohr).

$r_c$	Banerjee <i>et al</i> <sup>a</sup>	p-FEM <sup>b</sup> ( $h = 10^{-2}$ )	p-FEM <sup>b</sup> ( $h = 10^{-5}$ )	p-FEM <sup>c</sup> ( $h = 10^{-5}$ )
1.0	$5.926\,2368 \times 10^{-1}$	$5.927\,6127 \times 10^{-1}$	$5.926\,2356 \times 10^{-1}$	$5.926\,2358 \times 10^{-1}$
2.0	$1.278\,3740 \times 10^{-2}$	$1.278\,4664 \times 10^{-2}$	$1.278\,3740 \times 10^{-2}$	$1.278\,3740 \times 10^{-2}$
3.0	$1.025\,9727 \times 10^{-3}$	$1.026\,0178 \times 10^{-3}$	$1.025\,9727 \times 10^{-3}$	$1.025\,9728 \times 10^{-3}$
4.0	$1.263\,271 \times 10^{-4}$	$1.263\,318 \times 10^{-4}$	$1.263\,271 \times 10^{-4}$	$1.263\,2707 \times 10^{-4}$
5.0	$1.790\,01 \times 10^{-5}$	$1.790\,02 \times 10^{-5}$	$1.790\,01 \times 10^{-5}$	$1.790\,0090 \times 10^{-5}$
6.0	$2.6079 \times 10^{-6}$	$2.6072 \times 10^{-6}$	$2.6071 \times 10^{-6}$	$2.607\,0534 \times 10^{-6}$
7.0	$3.763 \times 10^{-7}$	$3.763 \times 10^{-7}$	$3.763 \times 10^{-7}$	$3.762\,9083 \times 10^{-7}$

<sup>a</sup> Reference [21].

<sup>b</sup> Present results with  $N_e = 6$  and  $k = 6$ .

<sup>c</sup> Present results with  $N_e = 10$  and  $k = 10$ .

where  $E_{1s}$  is the energy of the 1s state. Since we do not have an analytical expression for  $E_{1s}$ , it is necessary to evaluate equation (18) by using the following approximate formula:

$$P(r_c) \approx -\frac{1}{4\pi r_c^2} \frac{E_{1s}(r_c + h) - E_{1s}(r_c - h)}{2h}. \tag{19}$$

In table 10 are displayed three sets of the p-FEM results for  $P$ : first with  $N_e = 6$ ,  $k = 6$  and  $h = 10^{-2}$ ; second with  $N_e = 6$ ,  $k = 6$  and  $h = 10^{-5}$ ; and the last with  $N_e = 10$ ,  $k = 10$  and  $h = 10^{-5}$ . Moreover, the results obtained by Banerjee *et al* [21] are also shown for comparison. We can note that the p-FEM results with  $N_e = 6$  and  $k = 6$  are sensible when there is a change of  $h = 10^{-2}$  to  $h = 10^{-5}$ . The last ones are very close to the values obtained

by Banerjee *et al* for  $P$ , while the first ones differ a little, mainly for small values of  $r_c$ . Thus, it is our expectation that the p-FEM results with the basis  $N_e = 10$  and  $k = 10$  are the most accurate values for the effective pressure.

#### 4. Conclusion

In this paper we have proposed a novel numerical methodology to determine the energy spectrum and other properties of a hydrogen atom confined by an infinite spherical barrier. This procedure is based on the variational principle and utilized the p-version of the finite element method as a finite basis set to expand the radial wavefunction. We point out that the imposition of the confinement boundary conditions within the p-FEM is straightforward, being sufficient to remove a local basis function of the wavefunction expansion. Moreover, we observe that our results are in close agreement with the more precise ones previously published in the literature.

We point out some important aspects regarding the results of section 3: (i) we can see that the present methodology provides all energy states (within an infinite basis limit), while some of the usual methods are restricted to few states; for example, the methods proposed by Marin–Cruz [14] and Varshni [15] are restricted to the states with wavefunction holding no node between the origin and the confinement radius (viz 1s, 2p, 3d, etc); (ii) the variational p-FEM procedure is sufficiently accurate for the whole range of the confinement radius; for example, the method proposed by Laughlin [13] to obtain the polarizability is only satisfactory for large values of the confinement radius; and (iii) the number of basis functions necessary to converge the results is small; for example, with the basis set  $N_e = 5$  and  $k$  up to 9 (where it represents up to 44 basis functions), the results are close to those of Aquino [11] for all confinement radii and electronic states studied.

Another remark is that many methods use trial basis functions modelled to describe specific problems and such modelled functions would have to be modified if we study a different or more complex systems. On the other hand, the p-FEM can be applied to a variety of systems without the need of new trial basis functions. Moreover, the p-FEM can be employed to solve multi-dimensional problems [24, 27, 25].

Finally, we accentuate that although the computational effort was very little, the matrices generated by using the p-FEM are sparses and concentrated on the diagonal and we utilize optimized computational routine to calculate the integrals of Legendre polynomials. We can improve the computational time employing, for example, a non-uniformly discretized mesh to obtain more faster convergence [26]. The possibility of using non-uniform meshes, beyond the previous applications of the finite element method for multi-electronic systems, indicates that the FEM can be applied to systems with larger nuclear charges. Moreover, as our basis expansion is exact (in the sense of an infinite basis set), the finite element method can be used to fill the Coulomb cusp properly. Consequently, the present methodology can be a useful tool in the area of confined quantum systems. Works in these directions are in progress and will be published elsewhere. In particular, we are conducting a study of the two-electron confined systems with a three-dimensional anisotropic harmonic confinement potential [36] by using the present methodology.

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