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To cite this article: A D Sañu-Ginarte et al 2018 J. Phys. Commun. 2 015001

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Journal of Physics Communications

PAPER

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OPEN ACCESS

RECEIVED 26 June 2017

REVISED 13 November 2017

ACCEPTED FOR PUBLICATION 22 November 2017

PUBLISHED

9 January 2018

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Confined beryllium atom electronic structure and physicochemical properties

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Keywords: confined beryllium atom, ground state, first excited state, direct variational method, second excited state

Abstract

Confined beryllium atom ground and first excited states electronic structures are calculated by the direct variational method, taking into account the system asymmetric nature of the trial wave function, adding a cutoff function to ensure confinement boundary conditions. The trial wave function is built up from hydrogenic functions, which constitute an adequate basis for energies calculation. Physicochemical properties such as kinetic energy, pressure, and polarizability are also calculated from energy results previously obtained to different confined radii. Using different variational parameters in each hydrogenic function, the energy approximation obtained is improved. Electronic configuration changes as we move toward the strong confinement region (small cavity radii) in function of its atomic number using impenetrable walls, this region was obtained for Z = 4. This is a conclusion of this work. Another important result is that this method is computationally simpler and gives values inside the experimental precision. Aforementioned results are compared with other theoretical publications.

1. Introduction

Nowadays, it is of great interest to control and manipulate different systems properties, one way to achieve this is reducing space. When atom's electrons move is influenced by a potential barrier presence in at least one direction, it is said that the atom is confined. Confined quantum systems study began gaining importance around the 1930s, through a model proposal to study confined Hydrogen atom, located at a spherical box center with impenetrable walls; in order to determine its polarizability [1] variation as a pressure function.

It is well known that some system properties change when they are under spatial constraints effects, which may be either due to their size or to their particular environment; it is also possible that the system experiences restricted motion due to an external magnetic field presence. In many cases, system properties under such conditions may differ drastically with respect to those found in idealized or isolated systems. The reason why these changes occur can be found considering how most of the physical properties are implicitly related to the wave function and the energy, and this, in turn, is modified when the available space is restricted. So, to study this system type, it is generally necessary to find a solution for Schrödinger's equation using a Hamiltonian that includes space restrictions features.

The confinement model for atoms has also been used to study the electronic structure subjected to high pressures, as it has been for Helium atom [2–7] case; in effects of atoms and molecules trapped in nanostructures as fullerenes [8]; in multielectron systems such as atoms or molecules [9–15], as well as in quantum dots and quantum wires [16, 17] study. There are other applications of this model in physics areas such as acoustics, solid state physics, nuclear physics, and biological studies in nanotechnology [18, 19]. These systems physical

properties characterization allows design and constructs devices such as ultra-small lasers, quantum light generators, specific wavelengths optical and electrical filters, among others; which are useful in modern electronics and optoelectronics. Energy studies, beryllium atom [20–28] lower excited states fine, and hyperfine structure play an important role in multielectron atoms excited states theory development, and better correlation effects understanding between electrons.

In this work, we present a theoretical characterization of a confined beryllium atom in a spherical box with impenetrable walls. The intent is to determine the effects due to confinement such physicochemical properties and electronic configuration. It was confirmed that electronic configuration of the ground state of confined beryllium atom, is different from that of the free beryllium atom depending on the confinement region. We proposed the direct variational method to do this calculation, which is computationally much simpler in comparison with FDT or Hartree–Fock, due to it requires fewer operations and it does not need a specialized software, pointing that we use a four-element basis; giving energy values inside the experimental precision. Using different effective atomic numbers for each hydrogen function, it is improved considerably the energy values precision due to electron screening effect consideration.

2. Variational study of the ground state and the first excited states of the beryllium atom into a spherical potential

This section is dedicated to studying confined beryllium atom inside a box with spherical symmetry and impenetrable walls. Energies values will be obtained solving the time-independent Schrödinger equation using the direct variational method, based on the model proposed by Gorecki and Byers-Brown [29]. Hydrogenic functions will be used instead free-system functions, as well as introducing a cutoff function to ensure that the trial function is zero at the boundaries [5–13, 16–18, 30–32]. Considering a four-electron atomic system, the time-independent Schrödinger equation is given by the following eigenvalues equation

$$\hat{H}\Psi = E\Psi,\tag{1}$$

where *E*, is the atom electron energy, Ψ is the wave function, and \hat{H} is the Hamiltonian operator that depends on electrons coordinates.

Hamiltonian operator for a four-electron atom in atomic units, using Born–Oppenheimer approximation and dismissing spin-orbit interaction, is given by:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{4} \nabla_i^2 - Z \sum_{i=1}^{4} \frac{1}{r_i} + \sum_{i=1}^{4} \sum_{j>i}^{4} \frac{1}{r_{ij}} + V_c(r), \qquad (2)$$

where V_{c} is the ansatz potential, limited by spherically symmetrical cavity and is defined by:

$$V_c(r_1, r_2, r_3, r_4, r_0) = \begin{cases} 0, r_1, r_2, r_3, r_4 < r_0, \\ \infty, r_1, r_2, r_3, r_4 \ge r_0, \end{cases}$$
(3)

where r_0 , is confinement radius, and r_i are electrons position vectors in the system, with i = 1, ..., 4.

A trial wave function will be used, in Slater's determinant form, using spin–orbital hydrogen functions for 1s and 2s orbitals

$$\Psi(r_{1}, r_{2}, r_{3}, r_{4}) = \frac{1}{\sqrt{24}} \begin{pmatrix} \varphi_{1}(r_{1})\xi(r_{1}) & \varphi_{2}(r_{1})\chi(r_{1}) & \varphi_{3}(r_{1})\xi(r_{1}) & \varphi_{4}(r_{1})\chi(r_{1}) \\ \varphi_{1}(r_{2})\xi(r_{2}) & \varphi_{2}(r_{2})\chi(r_{2}) & \varphi_{3}(r_{2})\xi(r_{2}) & \varphi_{4}(r_{2})\chi(r_{2}) \\ \varphi_{1}(r_{3})\xi(r_{3}) & \varphi_{2}(r_{3})\chi(r_{3}) & \varphi_{3}(r_{3})\xi(r_{3}) & \varphi_{4}(r_{3})\chi(r_{3}) \\ \varphi_{1}(r_{4})\xi(r_{4}) & \varphi_{2}(r_{4})\chi(r_{4}) & \varphi_{3}(r_{4})\xi(r_{4}) & \varphi_{4}(r_{4})\chi(r_{4}) \end{pmatrix},$$
(4)

where functions $\xi(r_i)$ and $\chi(r_i)$, represent spin functions, $\varphi_1(r)$ and $\varphi_2(r)$ are hydrogenic functions for orbital 1*s*, while $\varphi_3(r)$ and $\varphi_4(r)$ are orbital 2*s* hydrogen functions.

From previously performed variational approaches [14], we know that a better energy values approximation is obtained using different effective atomic numbers for different each orbital so that electron screening effect is taken into account. Therefore, we will use different variational parameters for each hydrogenic function

$$\varphi_1(r) = n_1 \mathrm{e}^{-\alpha r*} f_c, \tag{5}$$

$$\varphi_2(r) = n_2 \mathrm{e}^{-\beta r*} f_c, \tag{6}$$

$$\varphi_3(r) = n_3(2 - \gamma r) \mathrm{e}^{-\frac{1}{2}\gamma r *} f_c, \tag{7}$$

$$p_4(r) = n_4(2 - \delta r) e^{-\frac{1}{2}\delta r * f_c},$$
(8)

4

where $f_c = \left(1 - \frac{r}{r_0}\right)$ is the cutoff function; α , β , γ , δ are variational parameters and n_i are normalization constants, which are determined by the following condition:

$$1 = \langle \Psi | \Psi \rangle = \int_0^{r_0} |\Psi|^2 \mathrm{d}\nu.$$
(9)

Making direct variational method use

$$E(\alpha, \beta, \gamma, \delta) = \frac{\langle \Psi^* | \hat{H} | \Psi \rangle}{\langle \Psi^* | \Psi \rangle} \ge E_0, \tag{10}$$

where E_0 is the lowest energy eigenvalue of \hat{H}

Using $\Psi(r_1, r_2, r_3, r_4)$ spatial part and spin functions orthonormality conditions, it is possible to obtain the energy functional:

$$E(\alpha, \beta, \gamma, \delta) = \left[\frac{1}{S_{11}S_{33}(S_{22}S_{44} - S_{24}^2) + S_{13}^2(S_{24}^2 - S_{22}S_{44})}\right] \\ \times \left[(S_{22}S_{44} - S_{24}^2)(S_{33}H_{11} + S_{11}H_{33} - 2S_{13}H_{13}) + (S_{11}S_{33} - S_{13}^2)(S_{44}H_{22} + S_{22}H_{44} - 2S_{24}H_{24}) + S_{33}S_{44}J_{12} \\ + (S_{22}S_{44} - S_{24}^2)J_{13} + S_{22}S_{33}J_{14} + S_{11}S_{44}J_{23} + (S_{11}S_{33}S_{13}^2)J_{24} + S_{11}S_{22}J_{34} \\ + (S_{24}^2 - S_{22}S_{44})K_{13} + (S_{13}^2 - S_{11}S_{33})K_{24} + 4S_{13}S_{24}M_{1234} - 2S_{33}S_{24}M_{1214} \\ - 2S_{11}S_{24}M_{2343} - 2S_{13}S_{44}M_{1232} - 2S_{22}S_{13}M_{1434}],$$
(11)

where:

 $S_{ij} = \langle \varphi_i(r) | \varphi_i(r) \rangle$ are overlapped integrals.

$$J_{ij} = \left\langle \varphi_i(r_1)\varphi_j(r_2) \middle| \frac{1}{r_{12}} \middle| \varphi_i(r_1)\varphi_j(r_2) \right\rangle \text{are electronic repulsion integrals}$$
$$K_{ij} = \left\langle \varphi_i(r_1)\varphi_j(r_2) \middle| \frac{1}{r_{12}} \middle| \varphi_i(r_2)\varphi_j(r_1) \right\rangle \text{are exchange integrals.}$$

 $H_{ij} = -\left\langle \varphi_i(r) \left| \frac{1}{2} \nabla^2 \right| \varphi_j(r) \right\rangle - \left\langle \varphi_i(r) \left| \frac{z}{r} \right| \varphi_j(r) \right\rangle$ kinetic and potential energy contains terms and integrals of the form:

$$\begin{split} M_{1234} &= \left\langle \varphi_1(r_i)\varphi_2(r_j) \left| \begin{array}{c} \frac{1}{r_{12}} \right| \varphi_3(r_k)\varphi_4(r_l) \right\rangle, \qquad M_{1214} = \left\langle \varphi_1(r_i)\varphi_2(r_j) \left| \begin{array}{c} \frac{1}{r_{12}} \right| \varphi_1(r_k)\varphi_4(r_l) \right\rangle, \\ M_{2343} &= \left\langle \varphi_2(r_i)\varphi_3(r_j) \left| \begin{array}{c} \frac{1}{r_{12}} \right| \varphi_4(r_k)\varphi_3(r_l) \right\rangle, \qquad M_{1232} = \left\langle \varphi_1(r_i)\varphi_2(r_j) \left| \begin{array}{c} \frac{1}{r_{12}} \right| \varphi_3(r_k)\varphi_2(r_l) \right\rangle, \\ M_{1434} &= \left\langle \varphi_1(r_i)\varphi_4(r_j) \left| \begin{array}{c} \frac{1}{r_{12}} \right| \varphi_3(r_k)\varphi_4(r_l) \right\rangle. \end{split}$$

After integrals calculation and plugged them into equation (11), it follows a numerical minimization process for each variational parameter (provided nuclear charge Z value and confinement radius r_0), namely:

$$\frac{\partial E(\omega_i, r_0)}{\partial \omega_i} = 0, \tag{12}$$

where ω_i are variational parameters.

In order to improve confined atom energy approximate calculation, a slight modification was considered for the 2*s* functions, adding a different variational parameter to each of them, to give them more flexibility, being as follows:

$$\varphi_3(r) = n_3(2 - \lambda r)e^{-\frac{1}{2}\gamma r*f_c},$$
(13)

$$\varphi_4(r) = n_4(2 - \mu r) e^{-\frac{1}{2}\delta r *} f_c.$$
(14)

Once hydrogenic functions have been modified, 2*s* functions nodes are properly adjusted to reduce energy value. This change only affects integrals values, the energy functional form remains unchanged.

It is worth to remember that the variational method can be used to estimate excited states energy value, as long as it is ensured that the trial wave function is normalized and orthogonal to lowest states [33] wave function. Since 2p orbital has three projections $2p_Z$, $2p_Y$, $2p_X$; in this work, the projections in *z*-direction and *x*-direction will be the one considered, the hydrogenic functions for that state are:

$$\varphi_3(r) = n_3 r e^{-\frac{1}{2}\gamma r} \cos \theta^* f_c, \tag{15}$$

$$\varphi_4(r) = n_4 r \mathrm{e}^{-\frac{1}{2}\delta r} \sin \theta \cos \phi^* f_c. \tag{16}$$

In our case the trial wave function is orthogonal to the ground state function; this is due to hydrogenic functions angular part being orthogonal. The energy functional form remains unchanged, due to the change residing solely in the 2p orbital function, only modifying the integrals values. There is no angular dependence in the wave function ground state because orbitals only depend on the radial coordinate. Because of this, the Laplacian operator, which acts on the function, depends exclusively on the radial coordinate. Once $2p_Z$ orbital with radial and angular dependence has been obtained, it is important to be very careful when calculating terms for kinetic energy so as not to make mistakes.

The so-obtained variational energy and the trial wave function, make it possible to calculate some confined beryllium atom properties. Average pressure exerted by system boundaries is given by the expression [16, 18]

$$P(r_0) = -\frac{dE}{dV} = -\frac{1}{4\pi r_0^2} \frac{dE}{dr_0},$$
(17)

where $V = \frac{4}{3}\pi r_0^3$, is the sphere volume and *E* is the atom ground state total energy.

To calculate kinetic energy, Ludeña [3] proposes the following equation, which relates kinetic energy K and pressure P with r_0 , as given by the virial theorem:

$$K(r_0) = 4\pi r_0^{3} P(r_0) - E(r_0).$$
⁽¹⁸⁾

An important physical quantity to calculate is polarizability, Kirkwood's [18] approximation was used:

$$\alpha = \frac{4}{9a_0} \sum_{i} (\overline{r_i^2})^2,$$
(19)

where a_0 , is Bohr radius, and α is polarizability.

3. Results and discussion

This section presents results associated with the variational method, as well as few confined beryllium atom physical properties, to describe pressure effect in the system electronic structure. Wolfram's mathematica software was used to optimize energy value for beryllium atom, using different confinement radii r_0 , provided the value for nuclear charge Z = 4.

3.1. $1s^2 2s^2$ energy

Using four and six variational parameters, energy values and their respective variational parameters for beryllium atom's electronic configuration $1s^22s^2$ are shown in tables 1 and 2, using the direct variational method and an antisymmetric wave function, where confinement radius r_0 is measured in Bohr and energy E_H in Hartrees.

The 1*s* orbital electrons experience higher nuclear charge than those in the 2*s* orbital. This is reflected in variational parameters values. As confinement radius decreases, system energy increases as expected, and the difference between values in variational parameters becomes smaller. A significant correction is observed in the energy using six variational parameters with respect to those obtained with four parameters. This is due to new parameters included in 2*s* hydrogenic functions, which allow for greater flexibility when energy value minimization is looked for.

Energy values comparison is shown in figure 1 using four parameters E_{H-4p} , six parameters E_{H-6p} and those obtained by Ludeña [3] E_{SCF-HF} , using a self-consistent field calculation.

Four and six variational parameters were used in this work. Compared to Ludeña's work [3], which used SCF approximation to the Hartree–Fock method, there was a 0.729% and 0.097% difference when $r_0 \rightarrow \infty$. For remaining r_0 difference fluctuates between 1.122% and 2.854% using four parameters. Using six variational parameters, they fluctuate between 0.114% and 2.672%, reaching the largest difference in $r_0 = 1.25$. Bohr for both cases. This difference has to do with the use of SCF approximation to the Hartree–Fock method, where the use of a sufficient number of basis functions is needed in order to calculate the analytical wave function precisely and, at the same time, to optimize orbital exponents, making calculations more complex and increasing computing time and effort. In contrast, in this work, we obtained sufficient energies to study a confined atom behavior with only six parameters. The use of such small base, composed of only four hydrogen-like functions, dramatically reduces calculation difficulty and execution time when minimizing energy values.

Compared to Rodriguez-Bautista's work [41], which used Roothaan's approach to solve the Hartree–Fock equations, there was a 0.097% difference when $r_0 = 10$. They used a new basis set for Hartree–Fock calculations related to many-electron atoms confined by soft walls, and reported that orbital energies present one behavior totally different to that observed for confinements imposed by hard walls. Inner orbital energies do not necessarily go up when the confinement is applied, contrary to the increments observed when the atom is

Table 1. Direct variational calculation for confined berylliu	m atom's electronic
configuration $1s^2 2s^2$ using four variational parameters.	

α	β	γ	δ	r_0	E_H
3.664 20	3.664 20	2.704 78	2.704 78	∞	-14.466 64
3.554 60	3.554 60	2.617 60	2.617 60	10	-14.42685
3.540 59	3.540 59	2.608 07	2.608 07	9	-14.41867
3.522 77	3.522 77	2.596 96	2.596 96	8	-14.40679
3.499 43	3.499 43	2.584 44	2.584 44	7	$-14.388\ 25$
3.467 69	3.467 69	2.571 91	2.571 91	6	-14.35622
3.422 64	3.422 64	2.564 15	2.564 15	5	$-14.292\ 32$
3.355 48	3.355 48	2.573 07	2.573 07	4	-14.136 92
3.249 82	3.249 82	2.619 05	2.619 05	3	$-13.645\ 84$
3.174 52	3.174 52	2.663 15	2.663 15	2.5	-12.97474
3.082 83	3.082 83	2.725 60	2.725 60	2	-11.387 90
3.035 53	3.035 53	2.766 49	2.766 49	1.75	-9.766 18
2.996 99	2.996 98	2.819 08	2.819 08	1.5	-6.906 96
2.987 79	2.987 77	2.845 71	2.845 70	1.4	-5.16346
2.984 92	2.984 94	2.877 42	2.877 44	1.3	$-2.883\ 48$
2.985 47	2.985 46	2.886 38	2.886 37	1.275	-2.20657
2.986 66	2.986 66	2.895 81	2.895 81	1.250	$-1.479\ 14$
2.988 50	2.988 48	2.905 79	2.905 77	1.225	-0.69643
2.991 12	2.991 15	2.916 34	2.916 36	1.2	0.146 62
3.010 24	3.010 24	2.965 58	2.965 58	1.1	4.249 65
3.047 74	3.047 74	3.029 80	3.029 80	1	9.929 39

Table 2. Direct variational calculation for confined beryllium atom's electronic configuration $1s^22s^2$ using six parameters.

α	β	γ	δ	λ	μ	r_0	E_H
3.684 72	3.684 72	2.008 10	2.008 10	9.391 09	9.391 09	∞	-14.558 84
3.586 80	3.586 80	1.721 90	1.721 90	12.472 61	12.472 61	10	-14.55671
3.574 54	3.574 54	1.671 70	1.671 70	13.884 31	13.884 31	9	-14.55567
3.559 07	3.559 07	1.605 26	1.605 26	16.466 04	16.466 04	8	-14.553555
3.539 03	3.539 03	1.519 21	1.519 21	21.297 10	21.297 10	7	-14.54850
3.512 31	3.512 31	1.418 07	1.418 07	27.000 43	27.000 43	6	-14.53455
3.475 20	3.475 20	1.324 28	1.324 28	21.410 33	21.410 33	5	-14.491 81
3.420 05	3.420 05	1.277 39	1.277 39	11.396 40	11.396 40	4	$-14.352\ 12$
3.329 72	3.329 72	1.337 63	1.337 63	6.694 86	6.694 86	3	$-13.846\ 80$
3.261 07	3.261 07	1.456 75	1.456 75	5.462 36	5.462 36	2.5	$-13.141 \ 34$
3.244 70	3.244 70	1.494 43	1.494 43	5.257 51	5.257 51	2.4	-12.91775
3.227 31	3.227 31	1.538 79	1.538 79	5.060 73	5.060 73	2.3	-12.651 98
3.208 85	3.208 85	1.591 19	1.591 19	4.869 50	4.869 50	2.2	-12.33429
3.168 49	3.168 49	1.727 20	1.727 20	4.492 97	4.492 97	2	-11.48950
3.110 94	3.110 94	1.982 79	1.982 79	4.001 63	4.001 63	1.75	-9.82401
3.043 81	3.043 81	2.395 41	2.395 40	3.425 38	3.425 38	1.5	-6.922 37
3.013 38	3.013 38	2.628 25	2.628 24	3.147 60	3.147 61	1.4	-5.167 37
2.979 95	2.979 97	2.916 95	2.917 01	2.823 86	2.823 81	1.3	$-2.883\ 61$
2.971 22	2.971 20	2.997 66	2.997 60	2.736 27	2.736 31	1.275	-2.20755
2.961 97	2.961 97	3.085 16	3.085 16	2.641 52	2.641 52	1.250	-1.48192
2.952 95	2.952 88	3.174 16	3.173 95	2.546 64	2.546 78	1.225	$-0.702\ 00$
2.941 81	2.941 95	3.279 52	3.279 95	2.432 10	2.431 85	1.2	0.136 81
2.896 08	2.896 41	3.737 52	3.738 49	1.941 94	1.945 24	1.1	4.207 79
2.993 48	2.993 48	3.876 95	3.876 95	2.000 00	2.000 00	1	9.835 15

confined by walls of infinite potential. This is because for atoms with large polarizability, like beryllium and Potassium, external orbitals are delocalized when confinement is imposed. Consequently, internal orbitals behave as if they were in ionized atom.

Considering four ionization energies for beryllium atom, ground state energy is -14.6693324 Hartrees, where a 1.318% difference was obtained for four variational parameters, and 0.690% for six when $r_0 \rightarrow \infty$. Nevertheless, before being able to compare a non-relativistic theoretically obtained value with experimental result, some additional effects have to be taken into account, such as nucleus movement with its finite mass (mass polarization), relativistic and radiative corrections and possibly nuclear charge distribution effect



	(a)		(b)	
r_0	$P(r_0)[H/a_0^{3}]$	<i>K</i> (<i>r</i> ₀)(a.u.)	$P(r_0)[H/a_0^{3}]$	K(r0)(a.u.)
∞	$3.878~24 imes 10^{-11}$	14.468 28	$2.079~42~ imes~10^{-13}$	14.558 85
10	$5.482\;30\times10^{-6}$	14.495 74	$6.014~17~ imes~10^{-7}$	14.564 27
9	$9.530\;52\times10^{-6}$	14.505 98	$1.395~10~ imes~10^{-6}$	14.568 45
8	0.000 01	14.522 91	$3.840~96~ imes~10^{-6}$	14.578 26
7	0.000 03	14.553 48	0.000 01	14.603 62
6	0.000 09	14.615 17	0.000 05	14.671 97
5	0.000 29	14.757 29	0.000 23	14.842 82
4	0.001 24	15.135 23	0.001 24	15.323 14
3	0.007 89	16.324 50	0.008 29	16.658 99
2.5	0.024 73	17.831 50	0.026 13	18.271 67
2	0.098 11	21.251 70	0.101 37	21.680 10
1.75	0.218 69	24.494 50	0.223 26	24.860 38
1.5	0.540 35	29.824 20	0.545 36	30.052 07
1.4	0.804 93	32.919 50	0.808 46	33.044 92
1.3	1.229 82	36.836 80	1.229 14	36.818 01
1.275	1.373 28	37.9750	1.370 90	37.913 92
1.250	1.536 36	39.187 10	1.531 85	39.079 24
1.225	1.722 37	40.483 60	1.715 17	40.323 09
1.2	1.934 73	41.865 40	1.924 03	41.642 99
1.1	3.148 42	48.410 40	3.116 69	47.921 39
1	5.335 31	57.116 15	5.286 27	56.5941

Table 3. Pressure and kinetic energy using (a) four variational parameters and (b) si	x
variational parameters.	

described by Lindroth, Persson [34], where the total energy for a beryllium atom, with all of these considerations, was -14.66953 Hartree.

As expected, as confinement radius r_0 decreases, kinetic energy system increases due to the system pressure effect. This can be seen in table 3.

3.2. $1s^2 2p_Z 2s$ and $1s^2 2p^2$ energies

First excited state experimental value for beryllium atom is unknown, therefore data obtained in this work will be compared to approximate results. The energy results obtained for different radius of confinement for the confined beryllium atom's electronic configuration $1s^2 2p_Z 2s$, as well as values obtained in different papers, are shown in table 4. It is evident from variational parameters that for the electron in 2_p orbital, the core is more shielded compared to other electrons. Its energy also rises when confinement radius decreases, same as ground state case. It is the largest, as well.

Table 4. Comparison between energy values for confined beryllium atom's electronic configuration $1s^2 2p_Z 2s$ and values obtained by Hibbert [20], Weiss [21], Chao Chen [35].

α	β	γ	δ	λ	r_0	E_H	Hibbert	Weiss	Chao Chen
3.666 21	3.695 75	1.540 89	2.140 54	7.443 62	∞	-14.423 85	-14.5184	-14.51844	-14.56637
3.568 73	3.597 72	1.288 44	1.848 06	9.054 42	10	$-14.419\ 12$			
3.556 51	3.585 31	1.262 44	1.789 62	9.859 74	9	-14.41684			
3.540 97	3.569 55	1.239 04	1.706 99	11.451 26	8	-14.41255			
3.520 45	3.549 01	1.221 97	1.592 90	14.924 92	7	-14.40369			
3.491 98	3.522 00	1.212 60	1.454 18	21.438 89	6	$-14.383\ 25$			
3.449 72	3.485 38	1.213 72	1.327 09	20.888 32	5	$-14.330\ 50$			
3.380 62	3.432 78	1.242 11	1.261 74	11.486 36	4	$-14.180\ 25$			
3.249 23	3.350 57	1.337 65	1.315 25	6.726 54	3	-13.695 99			
3.128 93	3.291 59	1.434 79	1.433 17	5.519 01	2.5	-13.06771			
3.096 80	3.278 00	1.460 35	1.470 63	5.321 68	2.4	-12.87439			
3.061 01	3.263 79	1.488 44	1.514 75	5.133 16	2.3	$-12.647\ 14$			
3.021 00	3.248 94	1.519 33	1.566 85	4.950 91	2.2	$-12.378\ 49$			
2.925 60	3.217 29	1.590 69	1.701 95	4.594 58	2	-11.67607			
2.769 35	3.173 79	1.701 85	1.955 28	4.132 66	1.75	$-10.324\ 20$			
2.560 73	3.124 04	1.845 26	2.363 47	3.590 70	1.5	-8.02263			
2.461 71	3.101 11	1.914 50	2.593 83	3.328 00	1.4	-6.64702			
2.355 14	3.075 27	1.992 50	2.878 32	3.022 07	1.3	$-4.865\ 98$			
2.243 26	3.045 20	2.081 31	3.232 23	2.654 57	1.2	$-2.518\ 13$			
2.129 14	3.009 00	2.183 99	3.676 40	2.198 11	1.1	0.641 72			
2.016 14	2.963 94	2.305 02	4.239 82	1.611 00	1	4.998 01			

Lower energy values obtained in this work have a 0.65% difference compared to those obtained by Hibbert [20], 0.64% compared to Weiss [21], and 0.92% compared to Chao Chen [35]. Hibbert and Weiss reported a set of large-scale configuration interaction (CI) calculations for the $1s^2 2snp(n = 2, 3)$ ³*P* states, which can give an accurate approximation for each state, but it may tend to obscure the global picture of the spectrum which is so transparent in the other approach. On the other hand, energies and wave functions for the beryllium atom are calculated with the full-core plus correlation wave functions by Chao Chen [35], obtaining a better approximation because of the use of many relevant angular and spin couplings which greatly contribute to the final energy values. Besides, Hibbert and Weiss did not include any intra-shell correlation in the 1*s* shell, because their calculations were those of transitions in outer subshells. The purposes of these works were to obtain the energy values in a precise way though in our case we tried to find acceptable energy values to calculate atomic properties which were energy-dependent, plus, we consider the case of the non-free confined atom as Chao Chen [35], Hibbert [20] Weiss [21] did. All of which adds an additional potential due to confinement, which in turn influences on the difference among the values with respect to those ones already mentioned.

These methods are more expensive in terms of computation compared to the direct variational method because the CI basis sets expansion grows factorially and hundreds (sometimes thousands) of terms are needed in order to obtain the precision desired.

Montgomery [39], Dolmatov [44] and Saul Goldman [40] report that for a strong confinement regime the behavior of the orbitals is different from that in which the confinement is weak. For small confinement radii in the hydrogen atom, the energies of 2p orbitals are lower than those of 2s orbitals; energies different to the ones in the free atom. The crossing (intersection) of orbital energy for confined atoms was also reported by Garza *et al* [42], in particular for the Kr atom. It is well known that confinement overestimates the energies of the systems. Aquino *et al* [43] reported that a more physical way to simulate spherical compression would be accomplished by using soft, penetrable walls. Table 5 shows the energy results obtained for different radius of confinement for the beryllium atom with configuration $1s^22p^2$. In figure 2, we show that the change in the beryllium atom's configuration confined to the ground state $1s^22s^2$ takes place in the region $0 < r_0 < 2.3$ Bohr radius, now being $1s^22p^2$ the configuration for the ground state. Consequently, for $r_0 < 2.3$ Bohr radius the energy values in tables 1 and 2 refer to the second excited state. The change in the electronic configuration of the beryllium atom, when r_0 decreases below 2.3, is one of the principal effects of spatial confinement [42], and can produce important changes in the physical properties such as electronegativity, softness, and hardness.

When an atom is confined, the energy of its ground state rises, as was showed above in figure 2. The same is true for the first and the second excited state, but the rise is much smaller. As a result, there is always a crossing point for cavities smaller than a critical size: the ground state of the atom lies higher in energy than the first confined states of the atom. Evidently, the ground state of the atom is no longer stable when it lies higher in

Table 5. Direct variational calculation for confined beryllium atom's electronic	С
configuration $1s^2 2p^2$.	

α	β	γ	δ	r_0	E_H
3.199 10	4.000 00	1.054 57	2.817 76	∞	-14.355 98
3.101 20	3.913 32	0.698 07	2.585 15	10	-14.35446
3.087 40	3.901 96	0.648 08	2.562 95	9	$-14.352\ 23$
3.068 87	3.888 03	0.594 86	2.541 39	8	-14.346 11
3.043 15	3.870 45	0.541 39	2.521 97	7	-14.33145
3.006 04	3.847 33	0.491 67	2.506 09	6	$-14.298\ 14$
2.949 47	3.814 85	0.452 61	2.495 40	5	$-14.222\ 60$
2.855 40	3.764 76	0.440 45	2.495 32	4	-14.04265
2.674 68	3.673 99	0.498 76	2.530 38	3	-13.55894
2.510 33	3.592 32	0.585 79	2.584 74	2.5	$-13.002\ 27$
2.467 00	3.570 53	0.610 70	2.600 97	2.4	-12.83898
2.419 11	3.546 26	0.638 72	2.619 50	2.3	$-12.640\ 32$
2.366 12	3.519 10	0.670 15	2.640 55	2.2	$-12.431\ 10$
2.242 56	3.454 30	0.744 61	2.691 27	2	-11.87248
2.050 45	3.348 00	0.863 52	2.773 26	1.75	$-10.834\ 30$
1.816 34	3.205 23	1.019 10	2.879 64	1.5	-9.119~70
1.713 51	3.136 62	1.094 65	2.930 60	1.4	$-8.108\ 97$
1.607 49	3.061 43	1.180 02	2.987 94	1.3	$-6.807\ 14$
1.580 66	3.041 68	1.203 14	3.003 49	1.275	$-6.423\ 52$
1.553 75	3.021 58	1.227 06	3.019 60	1.250	-6.012 29
1.526 78	3.001 15	1.251 82	3.036 32	1.225	$-5.570\ 87$
1.499 76	2.980 41	1.277 47	3.053 70	1.2	-5.09636
1.391 60	2.894 95	1.390 21	3.131 06	1.1	-2.79675
1.283 95	2.807 15	1.522 73	3.224 80	1	0.374 81



energy than the other states. When this occurs, the ground states transform into autoionizing states in the confined atom.

4. Beryllium atom polarizability

To calculate polarizability, Kirkwood's approximation [18] is used (equations (13) and (14)). Values obtained for free beryllium atom using different confinement radii r_0 and other reported results given by Komasa [36], Sahoo and Das [37] and Porsev and Derevianko [38], are shown in table 6. Polarizability is measured in units of a_0 ³, and as polarizability exact value is not reported for beryllium atom, we had to compare it to approximate data. For free atom case, we obtained a difference of 7.665%. Polarizability depends only on the box radius and varies monotonously with its radius as well. For a precise polarizability description, electronic correlation to a very

Table 6. Polarizability results obtained in this
work and the ones reported by Komasa <i>et al</i>
[36], Sahoo–Das [37] and Porsev and
Derevianko [38].

<i>r</i> ₀	$\alpha_{\mathrm{K},6p}$	State	Reference
∞	34.861	¹ S	37.755 [36]
		${}^{1}S_{0}$	37.80 [37]
		${}^{1}S_{0}$	37.71 [<mark>38</mark>]
10	33.218		
9	32.523		
8	31.324		
7	29.159		
6	25.328		
5	19.462		
4	12.512		
3	6.400		
2.5	4.122		
2	2.410		
1	0.095		

high level must be taken into account. Plus, a good outer region description is essential, thus electron density distribution becomes less important. Komasa *et al* [36], Sahoo–Das [37] and Porsev and Derevianko [38] calculated polarizability values with these aspects in mind. These requisites are met by very flexible wave functions that are explicitly correlated. In our case, we used a test function that is not the system's wave function.

5. Conclusions

The direct variational method, regardless of its complexity, turned out to be a simple and suitable approach from physicochemical and computational points of view. It is a method that allows saving computing time. Using six variational parameters we obtained better results than using four parameters, where the difference in energy values compared with Ludeña [3] results is 0.097% in case that the atom is not under any confinement potential ($r_0 \rightarrow \infty$), and between 0.114% and 2.672% in remaining cases. This difference is due to the Hartree–Fock, to accomplish major precision, needs enough basis functions, making more complex the calculation and increasing computing time. Whereas in our work, with only one basis formed by four elements we obtained a difference below 3.0%, which reduce computing time considerably.

In comparison with the beryllium atom experimental energy value, we obtained a 0.69% difference. And for this method simplicity used, this calculation can be implemented in personal computers, no requiring special conditions and computing time is less than an hour, which is a more efficient process than having a cluster.

There are only reported, by other authors, excited beryllium atom energy values in the ground state. We report here energy values to different confinement radii. The difference between reported energy values by cited author and ours for free atom, or non-confined, is 0.64% and 0.92%. No polarizability values have been reported for confined beryllium atom. In this work are reported values for this property with different confinement radii, where the difference between reported values for free atom and ours is 7.665%. In this work, we confirmed, as it was expected, that decreasing the confinement radii, energy, kinetic energy, pressure, and polarizability increased.

The energy functional expression presented in this work needed to calculate the energy values can be applied in further calculations regarding both free and confined beryllium and beryllium-like atoms with a base different from the hydrogenic one used in this paper.

Below $r_0 = 2.3$ Bohr radius, there is a change in the behavior of beryllium atom, where $1s^22p^2$, $1s^22p2s$, and $1s^22s^2$ are configurations for the beryllium atom ground state, first excited state and second excited state respectively. The energy values shown in tables 1 and 2 for the region $r_0 \ge 2.3$ Bohr radius refers to the ground state, while $r_0 < 2.3$ Bohr radius refers to the second excited state. The energy values shown in table 5 for the region $r_0 \ge 2.3$ Bohr radius refers to the second excited state, while $r_0 < 2.3$ Bohr radius refers to the second excited state, while $r_0 < 2.3$ Bohr radius refer to the second excited state, while $r_0 < 2.3$ Bohr radius refer to the ground state. Thus, it is possible to conclude that given a confinement Bohr radius of 2.3 for the beryllium atom, a change take place in the order the orbital energies in function of its atomic number.

Acknowledgments

This work was supported in part by CONACYT (Mexico) under contract 564944/297798.

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