Confined beryllium atom electronic structure and physicochemical properties

A D Sañu-Ginarte, L. Ferrer-Galindo, R A Rosas, A Corella-Madueño, Ri Betancourt-Riera, L A Ferrer-Moreno and R Riera

1 Universidad de Sonora, Departamento de Física, Apartado Postal 1626, 83000 Hermosillo, Sonora, México
2 Universidad de Sonora, Departamento de Investigación en Física, Apartado Postal 5-088, 83190 Hermosillo, Sonora, México
3 Instituto Tecnológico de Hermosillo, Avenida Tecnológico S/N, Colonia Sahuaro, C.P.83170, Hermosillo, Sonora, México
4 Tecnológico de Monterrey Campus Sonora Norte, Departamento de Ciencias Básicas, Blvd. Enrique Mazón López 965, 83000 Hermosillo, Sonora, México

E-mail: alejandro.sanu1985@gmail.com

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

\[ \hat{H} \Psi = E \Psi, \]

where \( E \) is the atom electron energy, \( \Psi \) 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:

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

where \( V_c \) is the ansatz potential, limited by spherically symmetrical cavity and is defined by:

\[ V_c(r_1, r_2, r_3, r_4, r_0) = \begin{cases} 0, & r_1, r_2, r_3, r_4 < r_0, \\ \infty, & r_1, r_2, r_3, r_4 \geq r_0, \end{cases} \]

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

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

\[ \Psi(r_1, r_2, r_3, r_4) = \frac{1}{\sqrt{24}} \begin{vmatrix} \psi_1(\xi)(\eta) & \psi_2(\xi)(\eta) & \psi_3(\xi)(\eta) & \psi_4(\xi)(\eta) \\ \psi_1(\tau)(\xi) & \psi_2(\tau)(\xi) & \psi_3(\tau)(\xi) & \psi_4(\tau)(\xi) \\ \psi_1(\tau)(\rho)(\xi) & \psi_2(\tau)(\rho)(\xi) & \psi_3(\tau)(\rho)(\xi) & \psi_4(\tau)(\rho)(\xi) \\ \psi_1(\tau)(\rho)(\sigma)(\xi) & \psi_2(\tau)(\rho)(\sigma)(\xi) & \psi_3(\tau)(\rho)(\sigma)(\xi) & \psi_4(\tau)(\rho)(\sigma)(\xi) \end{vmatrix}, \]

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

\[ \varphi_1(r) = n e^{-\alpha r} f_1, \]

\[ \varphi_2(r) = n e^{-\beta r} f_1, \]

\[ \varphi_3(r) = n_3(2 - \gamma r) e^{-\gamma r} f_1, \]

\[ \varphi_4(r) = n_4(2 - \delta r) e^{-\delta r} f_1, \]
where \( f_c = \left( 1 - \frac{r}{r_0} \right) \) is the cutoff function; \( \alpha, \beta, \gamma, \delta \) are variational parameters and \( n_i \) are normalization constants, which are determined by the following condition:

\[
1 = \langle \Psi | \Psi \rangle = \int_0^{r_0} |\Psi|^2 \, dr.
\]

Making direct variational method use

\[
E(\alpha, \beta, \gamma, \delta) = \frac{\langle \Psi^* | \hat{H} | \Psi \rangle}{\langle \Psi^* | \Psi \rangle} \geq E_0,
\]

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

Using \( \Psi(n_1, r_2, r_3, r_4) \) spatial part and spin functions orthonormality conditions, it is possible to obtain the energy functional:

\[
E(\alpha, \beta, \gamma, \delta) = \frac{1}{\left(S_{11}S_{33}(S_{22}S_{44} - S_{24}^2) + S_{13}^2(S_{24}^2 - S_{22}S_{44}) \right)}
\times \left((S_{22}S_{44} - S_{24}^2)(S_{33}H_{11} + S_{13}H_{13} - 2S_{13}H_{33})
+ (S_{13}S_{33} - S_{13}^2)(S_{24}H_{13} + 2S_{23}H_{44} - 2S_{24}H_{34} + 2S_{34}H_{24} + S_{34}S_{44}H_{12} + 2S_{44}S_{44}H_{34} + S_{44}S_{44}H_{24} + S_{44}S_{44}H_{34} + 4S_{44}S_{44}H_{12} - 2S_{13}S_{33}H_{12} - S_{13}S_{33}H_{24} - S_{13}S_{33}H_{34} - S_{13}S_{33}H_{44}) \right)
+ \left(S_{22}S_{44} - S_{24}^2\right) + \left(S_{13}S_{33} - S_{13}^2\right) + \left(S_{23}S_{34} + S_{24}S_{33} + S_{34}S_{23} + S_{34}S_{24} + S_{34}S_{44} + 4S_{44}S_{44}H_{12} - 2S_{13}S_{33}H_{12} - S_{13}S_{33}H_{24} - S_{13}S_{33}H_{34} - S_{13}S_{33}H_{44}) \right)
- \left(2S_{13}S_{33}H_{12} - S_{13}S_{33}H_{24} - S_{13}S_{33}H_{34} - S_{13}S_{33}H_{44} \right)
- \left(2S_{13}S_{33}H_{12} - S_{13}S_{33}H_{24} - S_{13}S_{33}H_{34} - S_{13}S_{33}H_{44} \right)
- \left(2S_{13}S_{33}H_{12} - S_{13}S_{33}H_{24} - S_{13}S_{33}H_{34} - S_{13}S_{33}H_{44} \right),
\]

where:

\[
S_{ij} = \langle \varphi_i(r) | \varphi_j(r) \rangle \text{ are overlapped integrals.}
\]

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

\[
K_{ij} = \left( \langle \varphi_i(r_1) | \varphi_j(r_2) \rangle \right) \frac{1}{r_{12}} \left| \varphi_i(r_2) \varphi_j(r_1) \right\rangle \text{ are exchange integrals.}
\]

\[
H_{ij} = -\left( \langle \varphi_i(r) \right| \frac{1}{2} \nabla^2 \left| \varphi_j(r) \right\rangle \right) - \left( \langle \varphi_i(r) \right| \frac{\hbar^2}{2m} \left| \varphi_j(r) \right\rangle \right) \text{ kinetic and potential energy contains terms and}
\]

\[
M_{1234} = \left\{ \varphi_i(r_1) \varphi_2(r_2) \right\} \frac{1}{r_{12}} \left\{ \varphi_3(r_3) \varphi_4(r_4) \right\}, \quad M_{1214} = \left\{ \varphi_1(r_1) \varphi_2(r_2) \right\} \frac{1}{r_{12}} \left\{ \varphi_3(r_3) \varphi_4(r_4) \right\},
\]

\[
M_{3243} = \left\{ \varphi_2(r_1) \varphi_3(r_2) \right\} \frac{1}{r_{12}} \left\{ \varphi_4(r_3) \varphi_4(r_4) \right\}, \quad M_{2332} = \left\{ \varphi_1(r_1) \varphi_2(r_2) \right\} \frac{1}{r_{12}} \left\{ \varphi_3(r_3) \varphi_4(r_4) \right\},
\]

\[
M_{4343} = \left\{ \varphi_1(r_1) \varphi_2(r_2) \right\} \frac{1}{r_{12}} \left\{ \varphi_3(r_3) \varphi_4(r_4) \right\}.
\]

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:

\[
\frac{\partial E(\omega_j, r_0)}{\partial \omega_j} = 0,
\]

where \( \omega_j \) are variational parameters.

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

\[
\varphi_1(r) = n_1(2 - \lambda r)e^{-\frac{1}{2}r^2f_c},
\]

\[
\varphi_2(r) = n_2(2 - \mu r)e^{-\frac{1}{2}r^2f_c}.
\]

Once hydrogenic functions have been modified, 2s 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 \( 2p_x, 2p_y, 2p_z \), in this work, the projections in \( z \)-direction and \( x \)-direction will be the one considered, the hydrogenic functions for that state are:

\[
\varphi_3(r) = n_3 r e^{-\frac{1}{2}r^2} \cos \theta f_c,
\]

\[
\varphi_4(r) = n_4 r e^{-\frac{1}{2}r^2} \sin \theta f_c.
\]
\[ \varphi_{4}(r) = n_{4}r^{3/2}e^{-r/2} \sin \theta \cos \phi f_{r}. \] (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 \[ P(t_0) = -\frac{dE}{dV} = -\frac{1}{4\pi r_0^2} \frac{dE}{dV}, \] (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:

\[ K(t_0) = 4\pi r_0^3P(t_0) - E(t_0). \] (18)

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

\[ \alpha = \frac{4}{9a_0} \sum_{i} \langle \mathbf{r}_i^2 \rangle, \] (19)

where \( a_0 \) is Bohr radius, and \( \alpha \) 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\(^2\)2s\(^2\) 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 \( E_{\text{HF}} \) in Hartrees.

The 1s orbital electrons experience higher nuclear charge than those in the 2s 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 2s 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 \( E_{\text{HF} - 4p} \), six parameters \( E_{\text{HF} - 6p} \) and those obtained by Ludeña [3] \( E_{\text{SCF} - 1s3p} \), 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 \( r_0 \to \infty \). 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...
where a 1.318% difference was obtained for four variational parameters, and 0.690% for six when the 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 $-14.669$ Hartrees, where a 1.318% difference was obtained for four variational parameters, and 0.690% for six when $r_0 \to \infty$. 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 nuclear movement with its finite mass (mass polarization), relativistic and radiative corrections and possibly nuclear charge distribution effect.
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.

### Table 3. Pressure and kinetic energy using (a) four variational parameters and (b) six variational parameters.

| $r_0$ | $P(r_0)[H/\text{a.u.}]$ | $K(r_0)[\text{a.u.}]$ | $P(r_0)[H/\text{a.u.}]$ | $K(r_0)[\text{a.u.}]$ |
|-------|----------------|------------------|----------------|----------------|
| $\infty$ | $3.87824 \times 10^{-11}$ | $14.46828$ | $2.07942 \times 10^{-13}$ | $14.55885$ |
| 10    | $5.48230 \times 10^{-6}$ | $14.49574$ | $6.01417 \times 10^{-7}$ | $14.56427$ |
| 9     | $9.53052 \times 10^{-6}$ | $14.50598$ | $1.39510 \times 10^{-6}$ | $14.56845$ |
| 8     | 0.00001 | $14.52291$ | $3.84096 \times 10^{-6}$ | $14.57826$ |
| 7     | 0.00003 | $14.55548$ | 0.00001 | $14.60362$ |
| 6     | 0.00009 | $14.61517$ | 0.00005 | $14.67197$ |
| 5     | 0.00029 | $14.75729$ | 0.00023 | $14.84282$ |
| 4     | 0.00124 | $15.13523$ | 0.00124 | $15.32314$ |
| 3     | 0.00789 | $16.32450$ | 0.00789 | $16.65899$ |
| 2.5   | 0.02473 | $17.83150$ | 0.02473 | $18.27167$ |
| 2     | 0.09811 | $21.25170$ | 0.10137 | $21.68010$ |
| 1.75  | 0.21669 | $24.49450$ | 0.22326 | $24.86038$ |
| 1.5   | 0.54035 | $29.82420$ | 0.54536 | $30.05207$ |
| 1.4   | 0.80493 | $32.91950$ | 0.80846 | $33.04492$ |
| 1.3   | 1.22982 | $36.83680$ | 1.22982 | $36.81801$ |
| 1.275 | 1.37328 | $37.97500$ | 1.37090 | $37.91392$ |
| 1.250 | 1.53636 | $39.18710$ | 1.53185 | $39.07924$ |
| 1.225 | 1.72237 | $40.48360$ | 1.71517 | $40.32309$ |
| 1.2   | 1.93473 | $41.86540$ | 1.92403 | $41.64299$ |
| 1.1   | 3.14842 | $48.41040$ | 3.11669 | $47.92139$ |
| 1     | 5.33531 | $57.11615$ | 5.28627 | $56.59411$ |

3.2. $1s^22p^2s$ and $1s^22p^5$ 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 $1s^22p^2s$, as well as values obtained in different papers, are shown in Table 4. It is evident from variational parameters that for the electron in $2p$ 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.
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 1s2p2s2s 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 1s 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 1s2p2s2s. In figure 2, we show that the change in the beryllium atom’s configuration confinement to the ground state 1s2p2s2s takes place in the region 0 < r0 < 2.3 Bohr radius, now being 1s2p2s2s the configuration for the ground state. Consequently, for r0 < 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 r0 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

| α | β | γ | δ | λ | r0 | Ei | Hibbert | Weiss | Chao Chen |
|---|---|---|---|---|----|----|---------|-------|-----------|
| 3.66621 | 3.69575 | 1.54089 | 2.14054 | 7.44362 | ∞ | −14.42385 | −14.51844 | −14.56637 |
| 3.56873 | 3.59772 | 1.28844 | 1.84806 | 9.05442 | 10 | −14.41912 |
| 3.55651 | 3.58531 | 1.26244 | 1.78962 | 9.85974 | 9 | −14.41684 |
| 3.53049 | 3.56955 | 1.23904 | 1.70699 | 11.45126 | 8 | −14.41255 |
| 3.52045 | 3.54901 | 1.22197 | 1.59290 | 14.92492 | 7 | −14.40369 |
| 3.49198 | 3.52200 | 1.21260 | 1.45418 | 21.43889 | 6 | −14.38325 |
| 3.44972 | 3.48538 | 1.21372 | 1.32709 | 20.88832 | 5 | −14.33050 |
| 3.38062 | 3.43278 | 1.24211 | 1.26174 | 11.48636 | 4 | −14.18025 |
| 3.24923 | 3.35057 | 1.33765 | 1.31523 | 6.72654 | 3 | −13.69599 |
| 3.12893 | 3.29159 | 1.43479 | 1.43317 | 5.51901 | 2.5 | −13.06771 |
| 3.09680 | 3.27800 | 1.46035 | 1.47063 | 5.32168 | 2.4 | −12.87439 |
| 3.06101 | 3.26379 | 1.48844 | 1.51475 | 5.33316 | 2.3 | −12.64714 |

Table 4. Comparison between energy values for confined beryllium atom’s electronic configuration 1s2p2s2s and values obtained by Hibbert [20], Weiss [21], Chao Chen [35].
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 5. Direct variational calculation for confined beryllium atom’s electronic configuration 1s\(^2\)2p\(^2\).

| \( \alpha \) | \( \beta \) | \( \gamma \) | \( \delta \) | \( r_0 \) | \( E_H \) |
|---|---|---|---|---|---|
| 3.199 | 4.000 | 1.054 | 2.817 | \( \infty \) | -14.35598 |
| 3.201 | 3.913 | 0.698 | 2.585 | 10 | -14.35446 |
| 3.087 | 3.901 | 0.648 | 2.562 | 9 | -14.35223 |
| 3.068 | 3.888 | 0.594 | 2.541 | 8 | -14.34611 |
| 3.043 | 3.870 | 0.541 | 2.521 | 7 | -14.33145 |
| 3.006 | 3.847 | 0.491 | 2.506 | 6 | -14.29814 |
| 2.949 | 3.814 | 0.452 | 2.495 | 5 | -14.22260 |
| 2.855 | 3.764 | 0.440 | 2.495 | 4 | -14.04265 |
| 2.764 | 3.673 | 0.498 | 2.530 | 3 | -13.55894 |
| 2.510 | 3.592 | 0.585 | 2.584 | 2.5 | -13.00227 |
| 2.467 | 3.570 | 0.610 | 2.600 | 2.4 | -12.83898 |
| 2.419 | 3.546 | 0.638 | 2.640 | 2.3 | -12.64032 |
| 2.366 | 3.519 | 0.670 | 2.640 | 2.2 | -12.43110 |
| 2.242 | 3.454 | 0.744 | 2.691 | 2 | -11.87248 |
| 2.050 | 3.348 | 0.865 | 2.773 | 1.75 | -10.83430 |
| 1.816 | 3.205 | 1.019 | 2.879 | 1.5 | -9.11970 |
| 1.713 | 3.136 | 1.094 | 2.930 | 1.4 | -8.10897 |
| 1.607 | 3.064 | 1.180 | 2.987 | 1.3 | -6.80714 |
| 1.580 | 3.041 | 1.203 | 3.003 | 1.275 | -6.42352 |
| 1.553 | 3.021 | 1.227 | 3.019 | 1.250 | -6.01229 |
| 1.526 | 3.001 | 1.251 | 3.036 | 1.225 | -5.57087 |
| 1.499 | 2.980 | 1.277 | 3.053 | 1.2 | -5.09636 |
| 1.391 | 2.894 | 1.390 | 3.131 | 1.1 | -2.79675 |
| 1.283 | 2.807 | 1.522 | 3.224 | 1 | 0.37481 |

---

**Figure 2.** Change in the orbitals configuration.
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 \( r_0 \to \infty \), 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 \( r_0 \geq 2.3 \) Bohr radius refers to the ground state, while \( r_0 < 2.3 \) Bohr radius refer to the second excited state. The energy values shown in table 5 for the region \( r_0 \geq 2.3 \) Bohr radius refers 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.

| \( r_0 \) | \( \alpha_{K,6} \) | State | Reference |
|----------|----------------|-------|-----------|
| \( \infty \) | 34.861 | \( ^1S \) | 37.733 [36] |
| \( \infty \) | 34.861 | \( ^1S_0 \) | 37.80 [37] |
| \( \infty \) | 34.861 | \( ^1S_\infty \) | 37.71 [38] |
| 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 | 0.995 | | |

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

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

ORCID iDs

A D Sañu-Ginarte @ https://orcid.org/0000-0002-5344-4006
L Ferrer-Galindo © https://orcid.org/0000-0001-9686-5233
R A Rosas © https://orcid.org/0000-0003-1597-3326
A Corella-Madueño © https://orcid.org/0000-0001-8743-647X
L A Ferrer-Moreno © https://orcid.org/0000-0003-1804-8734
R Riera © https://orcid.org/0000-0003-3164-2009

References

[1] Michels A, De Boer J and Bijl A 1937 Remarks concerning molecular interaction and their influence on the polarisability *Physica* 4 981–94
[2] Aquino N 2009 The hydrogen and helium atoms confined in spherical boxes *Adv. Quantum Chem.* 57 123–71
[3] Ludeña E 1978 SCE Hartree–Fock calculations of ground state wavefunctions of compressed atoms *J. Chem. Phys.* 69 1770–75
[4] Ludeña E V and Gregori M 1979 Configuration interaction calculations for two-electron atoms in a spherical box *J. Chem. Phys.* 71 2235
[5] Gorecki J et al 1988 Padded-box model for the effect of pressure on helium *J. Phys. B: At. Mol. Opt. Phys.* 21 403–10
[6] Ley-Koo E and Flores-Flores A 1998 Helium atom inside boxes with paraboloidal walls *Int. J. Quantum Chem.* 66 123–30
[7] Corella-Madueño A, Rosas R A, Marín J L and Riera R 2000 Two-electron atomic systems confined within spherical boxes *Int. J. Quantum Chem.* 77 509–15
[8] Hernández-Rojas J, Bretón J and Gomez Llorente J M 1996 Rotational spectra for off-center endohedral atoms at C60 fullerene *J. Chem. Phys.* 104 1179
[9] Garza J, Vargas R and Vela A 1998 Numerical self-consistent-field method to solve the Kohn–Sham equations in confined many-electron atoms *Phys. Rev. E* 58 3949–54
[10] Boeyens J C A 1984 Fine and hyperstructure of the metastable $^1S$ state of the beryllium atom by many-electron calculations *J. Phys. B: At. Mol. Opt. Phys.* 17 4497–502
[11] Garza J, Vargas R, Aquino N and Sen K D 2005 DFT reactivity indices in confined many-electron atoms *J. Chem. Sci.* 117 379–86
[12] Chattaraj P K and Sarkar U 2003 Effect of spherical confinement on chemical reactivity *J. Phys. Chem.* A 107 (24) 4877–82
[13] Corella-Ríos J and Byers Brown W 1988 On the ground state of the hydrogen molecule–ion $^1H+^2$ confined in hard and soft spherical boxes *J. Chem. Phys.* 89 2138
[14] Francisco Adrián Duarte A 2013 Estudio de sistemas cuánticos confinados de tres electrones usando el método variacional directo y DFT Master's Thesis DIFUS, Univ. Son. Son. México
[15] Kryachko E S and Ludeña E V 2014 Density functional theory: foundations reviewed *Phys. Rep.* 544 123–239
[16] Corella-Madueño A 2000 Tesis Doctoral, Un Estudio de sistemas cuánticos confinados de uno y dos electrones mediante el método variacional PhD Thesis DIFUS, Univ. Son. Son. México
[17] Zhu J L and Chen X 1994 Spectrum and binding of an off-center donor in a spherical quantum dot *Phys. Rev. B* 50 4497–502
[18] Marin J L et al 1992 Use of the direct variational method for the study of one- and two-electron atomic systems confined by spherical penetrable boxes *J. Phys. B: At. Mol. Opt. Phys.* 25 4365–71
[19] Marin J L et al 1991 Enclosed quantum systems: use of the direct variational method *J. Phys. B: At. Mol. Opt. Phys.* 24 2899–907
[20] Hibbert A 1976 Oscillator strengths of transitions involving 2s3l3L states in the beryllium sequence *J. Phys. B: At. Mol. Opt. Phys.* 9 2805–13
[21] Weiss A W 1972 Calculations of the 2ns S1 and 2p3p P3,1 levels of Be I *Phys. Rev.* A 6 1261–6
[22] Laughlin C, Constantiñides E R and Victor G A 1978 Two-valence-electron-model potential-studies of the Be I isoelectronic sequence *Ark. Fys.* 11 2243–56
[23] Ray S N, Lee T and Das T P 1973 Many-body theory of the magnetic hyperfine interaction in the excited state (1s2s2p P3) of the beryllium atom *Phys. Rev.* A 7 1469–79
[24] Ray S N, Lee T and Das T P 1973 Study of the nuclear quadrupole interaction in the excited (2p3) state of the beryllium atom by many-body perturbation theory *Phys. Rev.* A 8 1746–52
[25] Beck D R and Nicolaides C A 1984 Fine and hyperfine structure of the two lowest bound states of Be? and their first two ionization thresholds *Int. J. Quantum Chem.* 26 667–81
[26] Sundholm D and Olsen J 1991 Large MCHF calculations on the hyperfine structure of Be(3P0): the nuclear quadrupole moment of 9Be *Chem. Phys. Lett.* 177 91–7
[27] Jönsson P and Fischer C F 1993 Large-scale multiconfiguration Hartree–Fock calculations of hyperfine–interaction constants for low-lying states in beryllium, boron, and carbon *Phys. Rev.* A 48 4113–23
[28] Blanchman A G and Lurio A 1967 Hyperfine structure of the metastable (1s2s2p P3) states of Be94 and the nuclear electric quadrupole moment *Phys. Rev.* 153 164–76
[29] Gorecki J et al 1989 Variational boundary perturbation theory for enclosed quantum systems *J. Phys. B: At. Mol. Opt. Phys.* 22 2659–68
[30] Fernández E M and Castro E A 1981 Hyperpolarizability analysis of confined quantum mechanical systems: I. von Neumann boundary conditions and periodic potentials *Int. J. Quantum Chem.* 19 533–43
[31] Ley-Koo E and Cruz S A 1981 The hydrogen atom and the $^1H+^2$ and HeH+++ molecular ions inside prolate spheroidal boxes *J. Chem. Phys.* 74 4603
[32] Ley-Koo E and Rubinstein S 1979 The hydrogen atom within spherical boxes with penetrable walls *J. Chem. Phys.* 71 351
[33] Levine I N 2000 Quantum Chemistry (Upper Saddle River, NJ: Prentice Hall) (https://doi.org/10.1007/s13598-014-0173-7.2)
[34] Lindroth E 1992 Corrections to the beryllium ground-state energy *Phys. Rev.* A 45 1493–6
[35] Chen C 2012 Energies, fine structures, and hyperfine structures of the 1s22snp 3P (n = 2–4) states for the beryllium atom J. At. Mol. Opt. Phys. 2012 1–6
[36] Komasa J 2001 Dipole and quadrupole polarizabilities and shielding factors of beryllium from exponentially correlated Gaussian functions Phys. Rev. A 65 125061
[37] Sahoo B K and Das B P 2008 Relativistic coupled-cluster studies of dipole polarizabilities in closed-shell atoms Phys. Rev. A 77 62516
[38] Porsev S G and Derevianko A 2006 High-accuracy calculations of dipole, quadrupole, and octupole electric dynamic polarizabilities and van der Waals coefficients C6, C8, and C10 for alkaline–earth dimers J. Exp. Theor. Phys. 102 195–205
[39] Montgomery H E Jr and Sen K D 2012 Dipole polarizabilities for a hydrogen atom confined in a penetrable sphere Phys. Lett. A 376 1992–6
[40] Goldman S and Joslin C 1992 Spectroscopic properties of an isotropically compressed hydrogen atom J. Phys. Chem. 96 6021–7
[41] Rodriguez-Bautista M et al 2015 Roothaan’s approach to solve the Hartree–Fock equations for atoms confined by soft walls: basis set with correct asymptotic behavior J. Chem. Phys. 143 034103
[42] Garza J et al 2005 DFT reactivity indices in confined many-electron atoms J. Chem. Sci. 117 379–86
[43] Aquino N, Flores-Riveros A and Rivas-Silva J F 2013 Shannon and Fisher entropies for a hydrogen atom under soft spherical confinement Phys. Lett. A 377 2062
[44] Dolmatov V K, Baltenkov A S, Connerade J P and Manson S T 2004 Structure and photoionization of confined atoms Radiat. Phys. Chem. 70 417–33