

Confined Ground State of Beryllium Atom and Its Isoelectronic Ions

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In the framework of the variational Monte Carlo and the Hartree–Fock methods, the four-electron system is investigated to calculate several properties of the beryllium atom. For the beryllium atom and its isoelectronic ions, we calculated the ground-state energy eigenvalues and the energy of the compressed ground state beryllium atom in an impenetrable spherical box at different radii of the spherical box. Furthermore, the correlation energies are calculated as well. Moreover, the pressure and the kinetic energy of the confined beryllium atom are also calculated at certain radii of the spherical box. A good agreement between the calculated values and the corresponding available previous results is shown. The results obtained using the variational Monte Carlo method are slightly better than those obtained using the Hartree–Fock method.

topics: variational Monte Carlo method, Hartree–Fock method, confined beryllium atom

1. Introduction

The equations of correlated many-body quantum systems, such as the Coulombic system, which are described mainly by the Schrödinger equation, are not possible to solve analytically. The problem arises with the integrals in the calculation of the expectation values of energy, namely that the integrals generally are multi-dimensional and can seldom be calculated analytically. For this reason, one must use an appropriate approximation method to solve the Schrödinger equation. For the four-electron system, A.G.H. Barbosa and M.A.C. Nascimento [1] used a proper independent particle model at the generalized valence bond and generalized multi-structural levels (GMS) for the ground state of the beryllium atom. The used wave functions showed that the correlation energy of the valence shell is small. Also, it was found that by including the $1s^2 2p^2$ configuration, the stabilization happened neither due to non-dynamic nor dynamic correlation effects. Feng Wu and Lijuan Meng [2] used the double-parameter double-fold perturbation scheme by considering the spin–spin interaction of electrons to calculate the ground state energy of the beryllium atom. It was found that the effective nuclear charge seen by the outer shell electrons is optimized by the repulsion of the inner shell electrons.

Also, A.D. Sañu-Ginarte et al. [3] studied the effect of pressure on the ground and the low-lying excited states of the beryllium atom inside a box with spherical symmetry and impenetrable walls using the variational method. They used a trial wave function based on Slater’s determinant using spin-orbital hydrogen functions for the $1s$ and the $2s$ orbitals multiplied by a cut-off factor to achieve the Dirichlet boundary conditions using different variational parameters for each hydrogenic wave function.

When using appropriate methods for such systems, the quantum Monte Carlo (QMC) techniques are used to solve the Schrödinger equation of many-body quantum systems. The QMC techniques are classified as variational Monte Carlo (VMC) [4–6], diffusion Monte Carlo [7], and Green’s function Monte Carlo methods [8].

The VMC is based on a combination of two ideas, namely the variational principle and the Monte Carlo evaluation of integrals using importance sampling based on the Metropolis algorithm [9]. Using the VMC method, the lithium atom and its isoelectronic ions up to $Z = 10$ in a strong magnetic field are studied by S.B. Doma et al. [10]. The calculations of the ground and some excited states of the lithium atom under the presence of magnetic field strengths up to 100 a.u. have been provided in that

study. Moreover, the VMC method was used by S.B. Doma et al. [11] to evaluate the ground state of the beryllium atom, the mean distance of the electrons from the nucleus, and the mean distance between the electrons, where two different kinds of orbital functions and correlated functions were used in the calculations.

The self-consistent field approximation (Hartree–Fock) [12] is known to be an accurate description of many of the properties of multi-electron atoms and ions. In this approximation, each electron is described by a separate single-particle wave function (as distinct from the many-electron wave function) that solves a Schrödinger-like equation. The potential appearing in this equation is that generated by the average motion of the other electrons, so it depends on their single-particle wave functions. The rest is a set of non-linear eigenvalue equations, which can be solved by the methods of solving the eigenvalue problems, such as the shooting method. The calculated total energies can be compared directly with experimental values.

Accordingly, the aim of this work is to apply the VMC method using trial wave functions including the correlation term, and the Hartree–Fock (HF) method to evaluate the ground state of the

beryllium atom and its isoelectronic ions, and to study the ground state of beryllium atom as a confined system in an impenetrable spherical box with varying radii.

2. The ground state of the beryllium atom and its isoelectronic ions

The Schrödinger equation for the beryllium atom and its isoelectronic ions is written as

$$H \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = E \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4). \quad (1)$$

The Hamiltonian operator in (1) using the Born–Oppenheimer approximation, where the nucleus has an infinite mass, in atomic units [a.u.] ($e = \hbar = m = 4\pi\epsilon_0 = 1$), is given by

$$H = -\frac{1}{2} \sum_{i=1}^4 \left(\nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}, \quad (2)$$

where Z is the nuclear charge (here, $Z = 4, 5$, and 6 for Be, B^+ , and C^{++} , respectively), \mathbf{r}_i is the distance between the i -th electron and the nucleus, and r_{ij} are the inter-electron distances. In the present work, the Hamiltonian was introduced using the Hylleraas coordinates [13] as

$$\begin{aligned} H = & -\frac{1}{2} \left[\sum_{i=1}^4 \frac{\partial^2}{\partial r_i^2} + \sum_{i=1}^4 \frac{2}{r_i} \frac{\partial}{\partial r_i} + \sum_{i<j}^4 2 \frac{\partial^2}{\partial r_{ij}^2} + \sum_{i<j}^4 \frac{4}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i \neq j}^4 \frac{r_i^2 + r_{ij}^2 - r_j^2}{r_i r_{ij}} \frac{\partial^2}{\partial r_i \partial r_{ij}} \right. \\ & + \sum_{i \neq j}^4 \sum_{k>j}^4 \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} + \sum_{i=1}^4 \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} + \sum_{i=1}^4 \frac{1}{r_i^2 \sin^2(\theta_i)} \frac{\partial^2}{\partial \varphi_i^2} + \sum_{i=1}^4 \frac{\cot(\theta_i)}{r_i^2} \frac{\partial}{\partial \theta_i} \\ & + \sum_{i \neq j}^4 \left(2 \frac{r_j \cos(\theta_j)}{r_i r_{ij} \sin(\theta_i)} + \cot(\theta_i) \frac{r_{ij}^2 - r_i^2 - r_j^2}{r_i^2 r_{ij}} \right) \frac{\partial^2}{\partial \theta_i \partial r_{ij}} + \sum_{i \neq j}^4 2 \frac{r_j \sin(\theta_j)}{r_i r_{ij} \sin(\theta_i)} \sin(\varphi_i - \varphi_j) \frac{\partial^2}{\partial \varphi_i \partial r_{ij}} \left. \right] \\ & + \sum_{i=1}^4 \frac{(-Z)}{r_i} + \sum_{i<j}^4 \frac{1}{r_{ij}}. \end{aligned} \quad (3)$$

The ground state energy of the lithium atom was calculated using the following spatial wave function [14]

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & \frac{(z')^3 (z'')^{3/2}}{2\pi\sqrt{2\pi}} \left(1 - \frac{z'' r_3}{2} \right) \\ & \times \exp \left(-z' (r_1 + r_2) - \frac{z'' r_3}{2} \right). \end{aligned} \quad (4)$$

In our calculations of the ground state energy of the beryllium atom and its isoelectronic ions by using the VMC method, we used a modified trial wave function with the spin part and correlation factor, constructed from the function (4) as follows

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) =$$

$$A \left[\varphi(r_1, r_2, r_3, r_4) \chi(1, 2, 3, 4) \prod_{i<j} f(r_{ij}) \right], \quad (5)$$

where A is the antisymmetrization operator [15] which takes the form

$$\begin{aligned} A = & \hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{14} - \hat{P}_{23} - \hat{P}_{24} - \hat{P}_{34} \\ & + \hat{P}_{123} + \hat{P}_{132} + \hat{P}_{124} + \hat{P}_{142} + \hat{P}_{134} + \hat{P}_{143} \\ & + \hat{P}_{234} + \hat{P}_{243} - \hat{P}_{1234} - \hat{P}_{1243} - \hat{P}_{1324} - \hat{P}_{1342} \\ & - \hat{P}_{1423} - \hat{P}_{1432} + \hat{P}_{12} \hat{P}_{34} + \hat{P}_{13} \hat{P}_{24} + \hat{P}_{14} \hat{P}_{23}. \end{aligned} \quad (6)$$

Here, \hat{e} is the identity permutation, while \hat{P}_{ij} is the permutation of the i -th and j -th particles. Analogously, the operators \hat{P}_{ijk} and \hat{P}_{ijkl} are the permutations of three particles i, j, k and four particles i, j, k, l , respectively. The spin part ($\chi(1, 2, 3, 4)$) of the wave function is given by

$$\chi(1, 2, 3, 4) =$$

$$\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}} \frac{\alpha(3)\beta(4)-\alpha(4)\beta(3)}{\sqrt{2}}, \quad (7)$$

where α, β are the spinor indices. The spatial part of the trial wave function is introduced as

$$\varphi(r_1, r_2, r_3, r_4) = \frac{(z'z'')^3}{8\pi^2} \left(1 - \frac{z'r_3}{2}\right) \left(1 - \frac{z''r_4}{2}\right) \times \exp\left(-z'(r_1+r_2) - z''\left(\frac{r_3}{2} + \frac{r_4}{2}\right)\right) \quad (8)$$

and $f(r_{ij})$ is the Jastrow correlation function [16] given by

$$f(r_{ij}) = \exp\left(\frac{r_{ij}}{n(1 + \mu r_{ij})}\right). \quad (9)$$

Here, z' and z'' are the variational parameters of the orbital part, while μ is the variational parameter of the correlation part. In (9), one has $n = 2$ for unlike spins and $n = 4$ for like spins, which makes the function $f(r_{ij})$ satisfy the cusp conditions [17]. The three variational parameters $z', z'',$ and μ are varied in order to obtain the best fit to the energy eigenvalues of the beryllium atom and its isoelectronic ions by using the VMC method.

3. The confined ground state of the beryllium atom

The VMC method was applied here to study the compressed beryllium atom placed at the center of an impenetrable spherical box (hard walls), which is a repulsive cavity to avoid the eccentricity of the atom to be an orbit within the cavity. The Schrödinger equation of this confined system is given by

$$H_C \psi_C = E_C \psi_C. \quad (10)$$

Here, $H_C = H + V_C(r_1, r_2, r_3, r_4)$, and $V_C(r_1, r_2, r_3, r_4)$ is the confined potential due to the box of radius r_C , which is given by

$$V_C(r_1, r_2, r_3, r_4) = \begin{cases} 0, & r_1, r_2, r_3, r_4 < r_C, \\ \infty, & r_1, r_2, r_3, r_4 \geq r_C. \end{cases} \quad (11)$$

The trial wave function ψ_C is taken in the form

$$\psi_C = \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \prod_i \left(1 - \frac{r_i}{r_C}\right). \quad (12)$$

In the above equation, the cut-off factor $\prod_i (1 - \frac{r_i}{r_C})$ satisfies the Dirichlet boundary conditions for which $\psi_C = 0$ at $r_i = r_C$.

In addition, the pressure exerted on an atom by the system boundaries was evaluated at different values of the box radius [18] from the equation

$$p(r_C) = -\frac{1}{4\pi r_C^2} \frac{dE}{dr_C} = \frac{1}{4\pi r_C^3} (2E - \langle V \rangle). \quad (13)$$

Here, E is the ground state total energy of the atom, and $\langle V \rangle$ is the expectation value of the potential at various radii of the spherical box. Besides this, the kinetic energy K [19] of the system, as a function of the box radius, was calculated from the following equation

$$K(r_C) = 4\pi r_C^3 p(r_C) - E(r_C). \quad (14)$$

4. Results and discussions

4.1. The ground state energy of the beryllium atom and its isoelectronic ions

To calculate the ground state energy eigenvalues of the beryllium atom and its isoelectronic ions B^+ and C^{++} , we applied the VMC method with a number of points equal to 10^7 , using the trial wave function of (5). This trial wave function contains three variational parameters, namely $z', z'',$ and μ . Our computational program enables us to vary the parameters successively in loops until the minimum energy eigenvalue is obtained. The values of the parameters, which produced the best energy eigenvalues of Be, are given in Table I.

TABLE I

The values of the best parameters of the trial wave function (5).

z'	z''	μ
3.9925	3.984	0.459

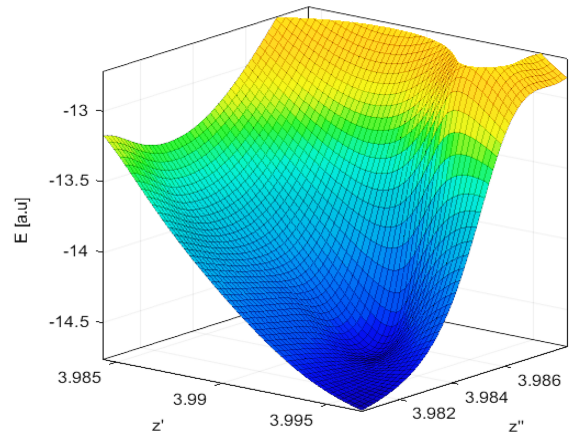


Fig. 1. The variation of the ground state energy of the beryllium atom with respect to the variational parameters z' and z'' for $\mu = 0.459$.

Ground-state energies, standard deviations (S.D.), and relative errors of Be, B⁺, and C⁺⁺ in [a.u.] TABLE II

	VMC	S.D.	HF	Exact	Relative error
Be	-14.667219	5.3×10^{-6}	-14.57302316	-14.6674 [21]	1.36×10^{-5}
B ⁺	-24.349122	1.78×10^{-5}	-24.23757517	-24.3490 [23]	4.11×10^{-6}
C ⁺⁺	-36.950641	2.73×10^{-5}	-36.40849530	-36.9505 [21, 22]	2.71×10^{-6}

TABLE III

Energies of confined ground beryllium atom calculated using VMC and HF methods compared with results in [3].

R_c	E_{VMC}	E_{HF}	$-E_{\text{corr.}}$	Ref. [3]
∞	-14.667219312200	-14.573023168447	0.094196143753	-14.55884
10	-14.667202032720	-14.572919271699	0.094282761021	-14.55671
9	-14.667123885053	-14.572603371025	0.094520514028	-14.55567
8	-14.666035778980	-14.571454779928	0.094580999052	-14.55355
7	-14.663462917823	-14.567504006202	0.095958911621	-14.54850
6	-14.654573702594	-14.554479994549	0.100093708045	-14.53455
5	-14.622133356984	-14.512476257762	0.109657099222	-14.49181
4	-14.498217115563	-14.374585118755	0.123631996808	-14.35212
3	-14.016365925571	-13.876096336455	0.140269589116	-13.84680
2	-11.702299344427	-11.541080322427	0.161219022000	-11.48950
1.5	-7.189354841901	-7.007112665778	0.182242176123	-6.92237

In Table II, we have reported the HF total energy values using the numerical HF code [20] with 8-decimal accuracy. Also, the obtained results of the energy eigenvalues and the standard deviations, together with the relative errors and the exact values, are given. It is to be noticed that the energies of B⁺ and C⁺⁺ were calculated by considering their exact non-relativistic ground state energies [21] in addition to the ionization energies [22]. It is seen in Table II that our results showed good agreement with the exact results [21–23]. The variations of the ground state energy of the beryllium atom with respect to the variational parameters z' and z'' are given in Fig. 1 for $\mu = 0.459$.

4.2. The confined ground state of the beryllium atom

In this section, we present the obtained results of the confined ground state of the beryllium atom at different radii of the spherical box. In Table II, we present the results of calculating the energy of the confined beryllium atom placed at the center of an impenetrable spherical box (hard walls) using the VMC method with 10^7 Monte Carlo integration points and the Hartree–Fock method. Also, the results from [3] are given, which used six parameters in the trial wave function to improve the results of the confined system. It is seen in Table III that our results are more accurate than those in [3] for all different radii of the spherical box. Furthermore, the correlation energies of the system, $E_{\text{corr.}} = E_{\text{VMC}} - E_{\text{HF}}$ are also given.

TABLE IV

The pressure (P) and kinetic energy (K) of the confined beryllium atom (R_c given in [a.u.]).

R_c	P	K
1.63	0.0246	18.38173
1.68	0.0223	17.82091
2.7	0.0041	16.59168
3.45	0.0014	15.97331
3.51	0.0013	15.75598
3.58	0.0012	15.60422
4.08	0.0006	15.49422

Table IV shows the results of calculating the pressure exerted on the beryllium atom and the kinetic energy using (13) and (14) at certain radii of the box. These radii are related to the energy values of some excited states of the beryllium atom and its ions [21, 22, 24, 25], which are shown in Table V.

In the last column of Table V, we present the results of calculating the energies of the states, which are compared with the other works. Furthermore, the correlation energy was plotted against the different radii of the spherical box, as shown in Fig. 2. It is also seen, in Table III, that by decreasing the radius of the box, the atom is more compressed, and hence the energy of the system increases where the kinetic energy becomes predominant perturbed by the attractive Coulomb potential, and the absolute value of the correlation energy increases at small values of radii.

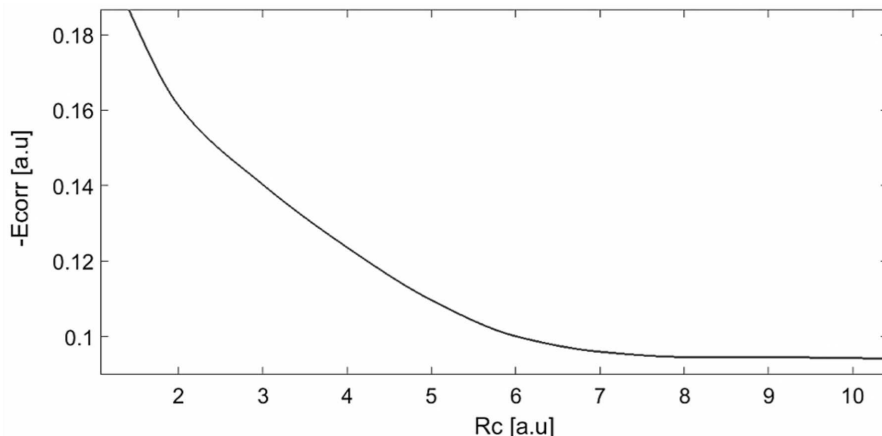


Fig. 2. The energy of the beryllium atom as function of the box radius (R_c).

TABLE V
Energies of the confined states of the beryllium atom (in [a.u.]) as functions of the box radius R_c .

R_c	Unconfined state of similar energy	Energy of the state	VMC
1.63	$1s2s3s^2$	-8.6210 [24]	-8.6211(1)
1.68	$1s2s^23s$	-9.1753 [24]	-9.1743(1)
2.7	$1s^2$ (Be^{++})	-13.6603 [21, 22]	-13.6607(3)
3.45	$1s^22s$ (Be^+)	-14.3182 [21, 22]	-14.3272(6)
3.51	$1s^22s3p$	-14.3501 [25]	-14.3400(7)
3.58	$1s^22s3s$	-14.3773 [24]	-14.3774(7)
4.08	$1s^22s2p$	-14.5161 [25]	-14.5112(3)

5. Conclusions

In the present paper, we applied the VMC method and the HF method to study the ground-state energy of the beryllium atom and its isoelectronic ions by incorporating suitable trial wave functions, which consider the correlation part, due to the interactions between the electrons and the cusp conditions. In addition, the confined beryllium atom in an impenetrable spherical box was investigated successfully at different radii. Also, good results for the pressure and the kinetic energy of the confined beryllium atom at specific values of radii have been obtained using the VMC method.

Moreover, the results obtained in the present paper proved that the VMC and HF techniques provide a simple, robust, and efficient way to solve the ground state energy of a quantum many-particle system. Also, they have been proven to be very powerful tools for studying quantum mechanical systems in the field of physics particularly atomic and molecular structures. Since the VMC method is relatively insensitive to the size of the system, it can be applied to large systems where some other methods are computationally not feasible.

Finally, the major advantage of the applied methods is the possibility to freely choose the analytical form of the trial wave function, which may contain highly sophisticated terms, in such a way that electron correlation is explicitly considered. This is an important feature, valid for these methods, which are therefore extremely useful for studying physical cases where the electron correlation plays a crucial role.

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