

## ***Approximate Analytical Solution of the Ground State Problem of He and He-like Ions using Symmetrized-Hydrogenic States***

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### ***Abstract***

*The matrix method using three symmetrized-hydrogenic basis states has been applied to analytically obtain an approximate solution to the Schrödinger equation of the Helium atom and some He-like ions ( $2 < Z < 10$ ). This study aims at obtaining more accurate ground state energies of the systems compared to our previous calculation using un-symmetrized basis states and some other simple calculations in the literature. The contribution of the symmetrized basis states on the ground state energies of the systems is also investigated. The time-independent Schrödinger equation involving a  $3 \times 3$  Hamiltonian matrix, formed by hydrogenic  $s$ -states, was analytically solved to obtain three energy eigenvalues of the systems as well as their corresponding eigenvectors. Results showed that the  $1s^2$  energies of the systems were more accurate than our previous unsymmetrized basis calculations, with significant error reduction observed for He and  $Li^+$ . With the same matrix size, the ground state energies of He and He-like ions obtained from three symmetrized basis states in this study were found to be closer to the exact and experimental energies than those obtained from unsymmetrized basis states. It was also demonstrated that the  $|100;100\rangle$  state made the largest contribution to the ground state energies of the systems, i.e. about 90.9% for He and around 99.9% for  $Ne^{8+}$ , and consequently the smallest contribution came from the other two symmetrized states (less than 1%). To conclude, the calculated ground state energies were more accurate than some other simple calculations reported in the literature.*

*Keywords: Analytic solution, He-like ions, Matrix method, Schrödinger equation, Symmetrized-basis states.*

### **1. Background**

Two-electron atoms have gained lots of interest in theoretical physics since the failure of Bohr-Sommerfeld quantization for helium in the mid-1920s and remain active research to the present day. This can be seen from a large number of approximate methods proposed to solve the Schrödinger equation for the systems. The increasing interest is mainly because highly accurate experimental data is available for the atoms and therefore can be used to test the accuracy of theoretical approximations proposed. In addition, the atoms can be used as a prototype for a few electron atoms strongly affected by electron-electron correlations [1].

A large number of numerical methods have been developed to solve the Schrödinger equation for the two-electron atoms such as helium and helium-like ions to determine their low-lying state energies. The methods include the iteration method [2], the Hartree-Fock method [3], the variational method [4,5], the

Laguerre polynomials and perimetric coordinates [6], the shooting method [7], the spectral approach [8,9], and the numerical matrix method based on hydrogenic basis states [10,11].

Many analytical methods have also been reported. For example, a simple analytical calculation using the uncertainty principle was successfully applied to estimate the ground state energy of helium and helium-like atoms [12]. Some other methods include the geometrical model [13], the matrix method with logarithmic terms [14], the variational principle [15], and the matrix method with hydrogenic basis states [16,17].

Among various methods proposed, accuracy and simplicity are two main qualities that might be searched. However, the two are often not found simultaneously [18]. Simple analytical methods are often useful since they can introduce and discuss physics more straightforwardly and clearly. However, many



simple methods often lead to relatively large errors.

In our previous studies [16-17], it was proven that with simple analytical matrix calculation involving a  $3 \times 3$  matrix, low-lying state energies of helium and helium-like ions were obtained with good accuracy. In the studies, unsymmetrized hydrogenic basis states were used in the wavefunction expansion. However, the accuracy of the results may be further improved such as by using symmetrized basis states instead of the un-symmetrized ones. The use of this matrix method has also been successfully applied to study various quantum systems including the anharmonic oscillators [19,20] and the Morse oscillator [21].

Therefore, it is the purpose of the present study to apply the symmetrized-hydrogenic basis states in a  $3 \times 3$  matrix calculation to obtain accurate ground state energies of the He atom and some light he-like ions and to improve the accuracy of our previous calculations, where unsymmetrized basis states were used. Therefore, the main difference between the present study and our previous work [16] is the use of different basis states although the Hamiltonian matrix in the two studies is of the same size. Our previous calculation only used 3 un-symmetrized basis states namely  $|100;100\rangle$ ,  $|100;200\rangle$ , and  $|200;100\rangle$  while in the present work, more basis states are used in their symmetric forms:  $|100;100\rangle$ ,  $|100;200\rangle$ ,  $|200;100\rangle$ ,  $|300;100\rangle$ , and  $|100;300\rangle$ . As a result, it is expected that the accuracy of the calculation should improve with the use of a larger number of basis states. Here, the symmetrized basis states are the combination of hydrogenic spatial orbitals such that the spatial part of the wave function is symmetric with respect to the exchange of electrons. In addition, the spectral decomposition of the systems in terms of the hydrogenic-symmetrized basis states used in this research is also presented. The ground state energies are also expected to be more accurate than those obtained using some other simple approaches reported in the literature.

## 2. Theoretical Model

### 2.1 Matrix method for he and he-like ions with hydrogenic basis states

The Schrödinger equation can be written as usual:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (1)$$

To solve Equation (1) using truncated matrix methods implies that the wave function  $|\Psi\rangle$  should be written as a linear combination of some finite number of basis states  $n$  as follows

$$|\Psi\rangle = \sum_{i=1}^n c_i |\psi_i\rangle \quad (2)$$

where  $c_i$ 's are unknown coefficients. Substituting Equation (2) into Equation (1) and operating it with  $\langle \Psi|$ , Equation (1) becomes

$$\sum_{j=1}^n H_{ij} c_j = E c_i \quad (3)$$

where now the time-independent Schrödinger equation has become an energy eigenvalue equation involving an  $n \times n$  Hamiltonian matrix operating on an  $n \times 1$  column vector. The equation can be written explicitly as

$$\begin{bmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \dots \\ c_n \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ \dots \\ c_n \end{bmatrix} \quad (4)$$

The elements of the Hamiltonian matrix can be determined using

$$H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle \quad (5)$$

where the non-relativistic Hamiltonian of helium and helium-like ions can be written

$$\hat{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (6)$$

In the Hartree atomic unit, which will be used throughout this article, Equation (6) is written as

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - Z \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \quad (7)$$



Inserting equation (7) into equation (5) yields

$$H_{ij} = \langle \psi_i | -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} | \psi_j \rangle \quad (8)$$

To evaluate equation (8), one needs to determine the basis states used. Here, the basis states were formed from the product of two  $s$ -hydrogenic orbitals. It should be noted that in the ground state of the helium atom, only the singlet spin state is allowed as the spatial wave function is symmetric. In this state, the overall spin of the system is zero.

In the matrix method, after  $H_{ij}$  in equation (8) was obtained, the energy eigenvalue equation as shown in Equation (4) was solved for the energy eigenvalues  $E$  and the unknown coefficients  $c_i$ 's. In this article, the evaluation of equation (4) and equation (8) was all done analytically.

## 2.2 The use of symmetrized basis states in the matrix method.

The analytical matrix method reported in [16,17] utilized un-symmetrized hydrogenic basis states in forming  $|\Psi\rangle$ . Here, on the other hand,  $|\Psi\rangle$  was formed using three symmetrized-hydrogenic basis states  $|\Psi_i\rangle = |n_1 l_1 m_1; n_2 l_2 m_2\rangle$  as follows

$$|\psi_1\rangle = |100;100\rangle \quad (9)$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|100;200\rangle + |200;100\rangle)$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}(|100;300\rangle + |300;100\rangle)$$

The use of equation (9) is expected to improve the accuracy of our previous analytical calculations [16,17], which only used basis states consisting of combinations of  $|100; 100\rangle$ ,  $|100; 200\rangle$  and  $|200; 100\rangle$ . In addition, the use of symmetrized states in this article is conceptually more appropriate than our previous work [16] since it is well known that the ground state energy of He is a spin singlet state, meaning that the spatial part of the wave function should be symmetric with respect to exchange of electrons. Therefore, this study provides the first analytical solution of the ground state energy of He and He-like ions using the

symmetrized hydrogenic basis states in solving the eigenvalue equation involving a 3x3 Hamiltonian matrix. It is worth noting that for more accurate results, higher bound state orbitals ( $n>3$ ) including  $p, d, f, \dots$  orbitals, as well as unbound states, should be considered.

To obtain the ground state energy of the He atom and he-like ions using this method, equation (9) was used to calculate the elements of the Hamiltonian matrix as shown in Equation (8). After that, equation (4) was solved analytically.

## 3. Results and Discussion

### 3.1 Analytical matrix elements of the Hamiltonian.

Inserting Equation (9) into Equation (8) yields

$$H_{ij} = \left( -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \right) \delta_{ij} + \langle \psi_i | \frac{1}{r_{12}} | \psi_j \rangle \quad (10)$$

where the hydrogenic solutions to the Schrödinger equation had been used in obtaining the first two terms in Equation (10),  $\delta_{ij}$  is the delta Kronecker,  $n_1$  and  $n_2$  are the principal quantum numbers of electron 1 and electron 2 respectively, and  $i, j$  values are 1, 2, and 3. Since 3 basis states were used in the calculation, the Hamiltonian matrix was of size 3x3, whose nine elements were determined as follows.

The determination of  $H_{11}$  is as follows. As  $|\Psi\rangle$  used in this article was the same as that in [17],  $H_{11}$  took the same form as in the previous study, i.e.

$$H_{11} = -Z^2 + 4Z^3 \int_0^\infty \left\{ (-Zr_1^2 - r_1) e^{-4Zr_1} + r_1 e^{-2Zr_1} \right\} dr_1 \quad (11)$$

which was previously found to be

$$H_{11} = -Z \left( Z - \frac{5}{8} \right) \text{a.u.} \quad (12)$$

Steps involved in the determination of other elements of the Hamiltonian matrix are described below. From equation (9) and equation (10), one has the following forms for the matrix elements:



$$H_{12} = H_{21} = \sqrt{2} \langle 100;100 | \frac{1}{r_{12}} | 100;200 \rangle \quad (13)$$

$$H_{13} = H_{31} = \sqrt{2} \langle 100;100 | \frac{1}{r_{12}} | 100;300 \rangle \quad (14)$$

$$H_{22} = -\frac{5}{8} Z^2 + \langle 100;200 | \frac{1}{r_{12}} | 100;200 \rangle + \langle 100;200 | \frac{1}{r_{12}} | 200;100 \rangle \quad (15)$$

$$H_{23} = H_{32} = \langle 200;100 | \frac{1}{r_{12}} | 300;100 \rangle + \langle 100;200 | \frac{1}{r_{12}} | 300;100 \rangle \quad (16)$$

$$H_{33} = -\frac{5}{9} Z^2 + \langle 300;100 | \frac{1}{r_{12}} | 300;100 \rangle + \langle 100;300 | \frac{1}{r_{12}} | 300;100 \rangle \quad (17)$$

Each orbital  $|nlm_l\rangle$  can be written as the product of the radial wave function  $R_{nl}(r)$  and the spherical harmonics  $Y_l^m(\theta, \varphi)$ . In particular, since only  $s$  orbitals are used in this article (for which  $l=0$  and  $m=0$ ), the orbitals can then be written as the product of  $R_{n0}(r)$  and  $Y_0^0(\theta, \varphi)$ .

Furthermore, as  $Y_0^0(\theta, \varphi)$  cancels the angular parts of the integration for all matrix elements, the elements shown in Equation (13) to Equation (17) can be written in their integral forms respectively as shown in equation (19a) to equation (23a).

$$H_{12} = H_{21} = \sqrt{2} \iint r_1^2 R_{10}(r_1) R_{10}(r_2) \frac{1}{r_{12}} r_2^2 R_{10}(r_1) R_{20}(r_2) dr_1 dr_2 \quad (19a)$$

$$H_{12} = H_{21} = 2^3 Z^6 \int_0^\infty \left( \frac{4r_1^2}{3^3 Z^2} + \frac{2r_1^3}{3^2 Z} \right) e^{-7Zr_1/2} dr_1 \quad (19b)$$

$$H_{13} = H_{31} = \sqrt{2} \iint r_1^2 R_{10}(r_1) R_{10}(r_2) \frac{1}{r_{12}} r_2^2 R_{10}(r_1) R_{30}(r_2) dr_1 dr_2 \quad (20a)$$

$$H_{13} = H_{31} = \left( \frac{2^9}{3^5} \right)^{1/2} Z^6 \int_0^\infty \left( -\frac{r_1^4}{8} + \frac{9r_1^3}{16Z} + \frac{27r_1^2}{64Z^2} \right) e^{-10Zr_1/3} dr_1 \quad (20b)$$

$$H_{22} = -\frac{5}{8} Z^2 + \iint r_1^2 R_{10}(r_1) R_{20}(r_2) \frac{1}{r_{12}} r_2^2 R_{10}(r_1) R_{20}(r_2) dr_1 dr_2 + \iint r_1^2 R_{10}(r_1) R_{20}(r_2) \frac{1}{r_{12}} r_2^2 R_{20}(r_1) R_{10}(r_2) dr_1 dr_2 \quad (21a)$$

Here,  $R_{nl}(r)$  is the hydrogenic radial function, which in terms of associated Laguerre Polynomial can be written as

$$R_{n0}(r_i) = \left\{ \frac{Z(n-1)!}{n^2(n)!} \right\}^{1/2} \left( \frac{2Z}{n} \right) e^{-\frac{Zr_i}{n}} L_{n-1}^1 \left( \frac{2Zr_i}{n} \right) \quad (18)$$

Integrals from equation (19a) to (23a) were evaluated using the same procedure as presented in [17], i.e. evaluated over  $r_2$  first to obtain integral over  $r_1$  only. The results of integral over  $r_2$  are presented in equation (19b) to (23b):



$$H_{22} = -\frac{5}{8}Z^2 + \frac{Z^3}{2} \int_0^\infty \left\{ \left( -\frac{Z^3}{4}r_1^4 + \frac{3Z^2}{4}r_1^3 - r_1 \right) e^{-3Zr_1} + \left( \frac{Z^2}{4}r_1^3 - Zr_1^2 + r_1 \right) e^{-Zr_1} \right\} dr_1 + 2Z^6 \int_0^\infty \left( \frac{4r_1^2}{3^3Z^2} + \frac{2r_1^3}{3^2Z} - \frac{2r_1^3}{3^3Z} - \frac{r_1^4}{3^2} \right) e^{-3Zr_1} dr_1 \quad (21b)$$

$$H_{23} = H_{32} = \iint r_1^2 R_{20}(r_1) R_{10}(r_2) \frac{1}{r_{12}} r_2^2 R_{30}(r_1) R_{10}(r_2) dr_1 dr_2 + \iint r_1^2 R_{10}(r_1) R_{20}(r_2) \frac{1}{r_{12}} r_2^2 R_{30}(r_1) R_{10}(r_2) dr_1 dr_2 \quad (22a)$$

$$H_{23} = H_{32} = \left( \frac{2}{3} \right)^{5/2} Z^6 \int_0^\infty \left\{ \left( \frac{Z}{36}r_1^5 - \frac{5}{18}r_1^4 + \frac{41}{72Z}r_1^3 + \frac{r_1^2}{8Z^2} - \frac{3r_1}{4Z^3} \right) e^{-17Zr_1/6} + \left( -\frac{r_1^4}{36} + \frac{11}{36Z}r_1^3 - \frac{7}{8Z^2}r_1^2 + \frac{3r_1}{4Z^3} \right) e^{-5Zr_1/6} \right\} dr_1 + \quad (22b)$$

$$\left( \frac{2}{3} \right)^{5/2} Z^6 \int_0^\infty \left( \frac{4Zr_1^5}{3^4} - \frac{100r_1^4}{3^5} + \frac{10r_1^3}{3^3Z} + \frac{4r_1^2}{3^2Z^2} \right) e^{-17Zr_1/6} dr_1$$

$$H_{33} = -\frac{5}{9}Z^2 + \iint r_1^2 R_{30}(r_1) R_{10}(r_2) \frac{1}{r_{12}} r_2^2 R_{30}(r_1) R_{10}(r_2) dr_1 dr_2 + \iint r_1^2 R_{10}(r_1) R_{30}(r_2) \frac{1}{r_{12}} r_2^2 R_{30}(r_1) R_{10}(r_2) dr_1 dr_2 \quad (23a)$$

$$H_{33} = -\frac{5}{9}Z^2 + \frac{2^4}{3^5} Z^6 \int_0^\infty \left( \frac{4Z^4}{81}r_1^6 - \frac{8Z^3}{9}r_1^5 + \frac{16Z^2}{3}r_1^4 - 12Zr_1^3 + 9r_1^2 \right) e^{-2Zr_1/3} \left\{ \left( -\frac{1}{(2Z)^2} - \frac{2}{(2Z)^3}r_1 \right) e^{-2Zr_1} + \frac{2}{(2Z)^3}r_1 \right\} dr_1 + \frac{2^4}{3^5} Z^6 \int_0^\infty \left( -\frac{Z^2}{36}r_1^6 + \frac{3Z}{8}r_1^5 - \frac{45}{32}r_1^4 + \frac{27}{32Z}r_1^3 + \frac{81}{64Z^2}r_1^2 \right) e^{-8Zr_1/3} dr_1 \quad (23b)$$

The evaluations of the integrals above, for which the factorial function  $\int_0^\infty x^n e^{-ax} dx = n!/(a)^{n+1}$  can be used, resulting in the following simple forms of the Hamiltonian matrix elements:

$$H_{12} = H_{21} = \frac{8192}{64827} Z \quad (24)$$

$$H_{13} = H_{31} = \frac{1269}{5 \times 10^4} \sqrt{6} Z \quad (25)$$

$$H_{22} = \left( -\frac{5}{8} Z + \frac{507}{2187} \right) Z \quad (26)$$

$$H_{23} = H_{32} = \frac{1901518848}{17^6 5^5} \sqrt{6} Z \quad (27)$$

$$H_{33} = \left( -\frac{5}{9} Z + \frac{3449}{32768} \right) Z \quad (28)$$

Integrals from Equation (19a) to (23a) were evaluated using the same procedure as presented in [17], i.e. evaluated over  $r_2$  first to obtain integral over  $r_1$  only. The results of integral over  $r_2$  are presented in Equation (19b) to (23b):

### 3.2 Analytical ground state energies of helium and he-like ions.

In this section, the projected Schrödinger equation was solved analytically to obtain the ground state energies of the He atom and some light He-like ions. From matrix elements obtained in the previous section, the Schrödinger equation can then be written as shown in Equation (29), where atomic units were used. To the best of our knowledge, the simple expression for the ground state energy of two-electron systems as shown in equation (29), which is simply dependent on the atomic number  $Z$ , is the first time reported in the literature for these systems. Reasonably accurate ground state energy of any two electron atoms can be obtained just by inserting their atomic number



$$\begin{bmatrix} -Z\left(Z - \frac{5}{8}\right) & \frac{8192}{64827}Z & \frac{1269}{5 \times 10^4}\sqrt{6}Z \\ \frac{8192}{64827}Z & \left(-\frac{5}{8}Z + \frac{507}{2187}\right)Z & \frac{1901518848}{17^6 5^5}\sqrt{6}Z \\ \frac{1269}{5 \times 10^4}\sqrt{6}Z & \frac{1901518848}{17^6 5^5}\sqrt{6}Z & \left(-\frac{5}{9}Z + \frac{3449}{32768}\right)Z \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} \quad (29)$$

into equation (29). Of course, there are many advanced approaches reported in the literature with more accurate results. However, one of the purposes of this work is to show that with a straightforward quantum mechanics approach, reasonably accurate ground state energies of two-electron systems can be obtained.

The secular equation  $\det(H - EI_3) = 0$  was then solved to obtain 3 energy eigenvalues, with the lowest value being the ground state energy. The ground state energies of the He atom and He-like ions are shown in Table 1. Errors and % errors are calculated for He based on the experimental ground state energy [22]<sup>a</sup> and based on the exact energies for He-like ions [2]<sup>b</sup>. Comparison with the results of our previous calculation [16]<sup>c</sup> and [17]<sup>d</sup> is also presented in Table 1.

It is clear from Table 1 that the ground state energies are in very good agreement with the experimental and exact ground state energies. The accuracy of our calculation improves as the atomic number increases. The largest error is 2.23% for the He atom ground state energy and the smallest one is about 0.11% for the ground state energy of

the Ne<sup>8+</sup> ion. Additionally, a comparison with our previous calculation indicates that there is a significant reduction in the percentage error of our previous calculation, about 0.28% for He and 0.12% for Li<sup>+</sup> ion. This reduction becomes less significant for relatively high-Z ions, with percentage error ranging from 0.01% for Ne<sup>8+</sup> ion to 0.07% for Be<sup>2+</sup> ion. This shows that the accuracy of our calculation in this article is better than our previous calculations [16,17] for all atoms and ions considered. Further comparisons of these errors with those from our previous work and other simple methods are presented in the next section.

Better accuracy for higher Z ions can be explained by the fact that the higher Z, the more the electron-nuclei interaction, and hence the less the electron-electron repulsion. This is because electrons are more localized in higher Z ions compared to the lower ones [23]. In their study, Rahman et al., [23] observed that as nuclear charges of the he-like ions increase, the nuclei-electron interaction becomes much more dominant compared to the electron-electron interactions.

Table 1. Ground state 1s<sup>2</sup> energies of the He atom and some He-like ions

Atom or ions (Z)	Present work (error; % error)	Our previous work <sup>c,d</sup> (error; % error)	Experimental/Exact groundstate energies <sup>a,b</sup>
He (2)	-2.8386 (0.065; 2.23%)	-2.8304 (0.073; 2.51%) <sup>c</sup>	-2.9034 <sup>a</sup>
Li <sup>+</sup> (3)	-7.1980 (0.082; 1.13%)	-7.1886 (0.091; 1.25%) <sup>d</sup>	-7.2799 <sup>b</sup>
Be <sup>2+</sup> (4)	-13.5665 (0.089; 0.65%)	-13.5570 (0.099; 0.72%) <sup>d</sup>	-13.6556 <sup>b</sup>
B <sup>3+</sup> (5)	-21.9379 (0.093; 0.42%)	-21.9285 (0.103; 0.47%) <sup>d</sup>	-22.0310 <sup>b</sup>
C <sup>4+</sup> (6)	-32.3107 (0.096; 0.29%)	-32.3014 (0.105; 0.32%) <sup>d</sup>	-32.4062 <sup>b</sup>
N <sup>5+</sup> (7)	-44.6842 (0.097; 0.22%)	-44.6749 (0.107; 0.24%) <sup>d</sup>	-44.7814 <sup>b</sup>
O <sup>6+</sup> (8)	-59.0581 (0.098; 0.17%)	-59.0489 (0.108; 0.18%) <sup>d</sup>	-59.1566 <sup>b</sup>
F <sup>7+</sup> (9)	-75.4323 (0.099; 0.13%)	-75.4231 (0.109; 0.14%) <sup>d</sup>	-75.5317 <sup>b</sup>
Ne <sup>8+</sup> (10)	-93.8066 (0.100; 0.11%)	-93.7975 (0.109; 0.12%) <sup>d</sup>	-93.9068 <sup>b</sup>



### 3.3 Comparison with results from other simple methods in the literature.

A comparison of errors in the present study to those from other simple methods is shown in Figure 1. From Figure 1 it is clear that our approach is more accurate than the results of some other simple calculations in the literature.

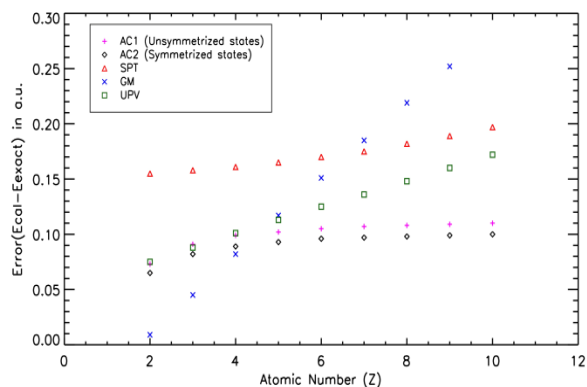


Figure 1. Comparisons of errors in ground state energies with other simple calculations.

Ground state energies presented in Figure 1 are obtained using the standard perturbation theory (SPT) [24], geometrical model (GM) [13], uncertainty principle variational approach (UPV) [12], and analytic calculation using unsymmetrized basis states (AC1) [16,17]. Meanwhile, energies from our present work using symmetrized states are labeled AC2.

Improved accuracy is obvious when comparing our analytical results for all atoms and ions using 3 symmetrized bases in the present study with 3 unsymmetrized bases in our previous work for He [16] and he-like ions [17]. All errors in energies here are smaller than those in our previous studies since although the Hamiltonian matrix involved in these studies are of the same size, the hydrogenic states  $|100, n00\rangle$  and  $|n00; 100\rangle$  used in the calculations are different. As can be seen from Equation (9), basis states used in the present work comprised of a combination of 5 states namely  $|100; 100\rangle$ ,  $|100; 200\rangle$ ,  $|200; 100\rangle$ ,  $|100; 300\rangle$ , and  $|300; 100\rangle$  compared to only  $|100; 100\rangle$ ,  $|100; 200\rangle$ , and  $|200; 100\rangle$  states used in the previous studies.

In addition, the ground state energies of our calculations for all ions are also more accurate than standard perturbation theory (SPT) calculations [24] and the uncertainty principle combined with the variational approach (UPV)

results [12]. Meanwhile, our results are less accurate than the geometrical model (GM) calculations [13] for He, Li<sup>+</sup>, and Be<sup>2+</sup>. This clearly showed that for relatively low atomic numbers (Z=2, 3, and 4) the Geometrical Model was more powerful than our method. However, as can be seen in Figure 1, the geometrical model becomes less accurate as the atomic number increases. In particular, our calculations are more accurate for ions with Z between 5 and 10.

Observations explained above strongly indicate that although the approximation used here was very simple, it could yield relatively good results and therefore can be used as an alternative method to demonstrate how accurate energies of real quantum systems are calculated using simple quantum approaches.

### 3.4 Spectral decomposition of the ground state energies of the systems.

Once the secular equation  $\det(H-EI)$  was solved to obtain the eigenvalue energies, especially the ground state energies as shown in Table 1, one can determine the corresponding eigenvectors for each energy eigenvalue obtained. Table 2 presents the eigenvectors of ground state energies for he and he-like ions, together with the probability amplitudes.

It is clear from Table 2 that about 90.9% of the contribution to the ground state energy comes from the  $|100; 100\rangle$  state. This agrees with the calculations reported in [25], which also used hydrogenic bound states in the calculations. They then improved their calculations to include continuum states and found that more than 92% contribution to the ground state energy of He came from  $|100; 100\rangle$  state.

The results presented here and in [17,24] showed that the largest contribution to the ground state energy of the helium atom comes from the singlet  $|100; 100\rangle$  hydrogenic orbital. The inclusion of hydrogenic basis states in the wavefunction of two-electron systems is also highlighted in [26,27], where reasonably good accurate energies of the systems were obtained. A comparison of errors in the present study to those from other simple methods is shown in Figure 1. From Figure 1 it is clear that our approach is more accurate than the results of some other simple calculations in the literature.



Table 2. Probability amplitudes corresponding to the ground state energies of he and he-like ions

Atom or ions (Z)	State		State		State	
	$ \psi_1\rangle =  100;100\rangle$		$ \psi_2\rangle = \frac{1}{\sqrt{2}}( 100;200\rangle +  200;100\rangle)$		$ \psi_3\rangle = \frac{1}{\sqrt{2}}( 100;300\rangle +  300;100\rangle)$	
	$c_1$	$ c_1 ^2$	$c_2$	$ c_2 ^2$	$c_3$	$ c_3 ^2$
He (2)	-0.95327856	0.909	0.28477864	0.081	0.10080233	0.0102
Li <sup>+</sup> (3)	-0.98526741	0.971	0.15964404	0.025	0.06133447	0.0038
Be <sup>2+</sup> (4)	-0.99306880	0.986	0.10933183	0.012	0.043138239	0.0019
B <sup>3+</sup> (5)	-0.99601113	0.992	0.082854355	0.007	0.033120692	0.0011
C <sup>4+</sup> (6)	-0.99741709	0,995	0.06662427	0.004	0.02683937	0.0007
N <sup>5+</sup> (7)	-0.99819386	0,996	0.05568355	0.003	0.02254669	0.0005
O <sup>6+</sup> (8)	-0.99866706	0,997	0.04781741	0.002	0.01943185	0.0004
F <sup>7+</sup> (9)	-0.99897627	0,998	0.04189286	0.002	0.01707029	0.0003
Ne <sup>8+</sup> (10)	-0.99918928	0,999	0.03727151	0.001	0.01521900	0.0002

Table 2 also shows that the significant contribution for the ground state energy of the he-like ions also comes from the  $|100;100\rangle$  state. For Li<sup>+</sup> ions, about 97% of the ground state energy comes from the  $|100;100\rangle$  state, while for the other ions, the contributions reach 99%. This indicates that the higher the atomic number Z, the more contributions come from the  $|100;100\rangle$  state. Consequently, the contributions from other states including  $|100;n00\rangle$  with n are not equal to one and become smaller as the atomic number increases. Two recent studies [28,29] also reported a similar trend and hence supported our present results.

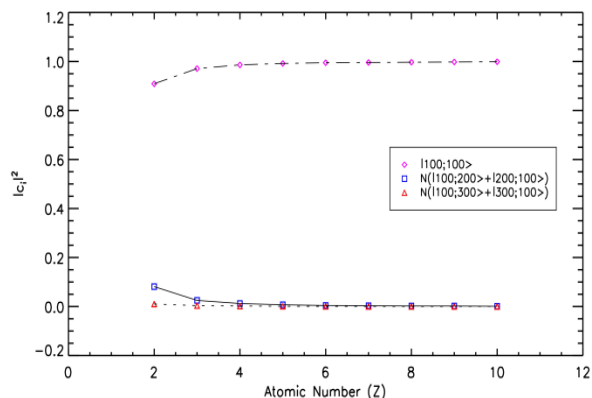


Figure 2.  $|c_i|^2$  values for all basis states used in the calculations for He and some He-like ions (Z between 2 and 10). N is the normalization constant.

To see the contribution of the basis states on the ground state energies more clearly, the probability amplitudes for each state used in this article are plotted as a function of atomic number Z in Figure 2. It is apparent from Figure 2 that  $|100;100\rangle$  made the largest contribution to the ground state energies of the atom and ions. The probability amplitude increased gradually approaching unity as the atomic number increased. The reverse was true for the other two states, which experienced a gradual decrease in the probability amplitude, approaching zero. This is also in good agreement with [17].

As shown in the previous section, the configuration of the two electrons in the form of  $|100;n00\rangle$  used in this study can result in reasonably accurate ground state energies. In this configuration, one electron is kept at the 1s state while the other one can be in any state of the systems. The same configuration was also applied in other studies including [7, 30-32]. To improve the accuracy of our approach, the inclusion of higher bound states and unbound states in the wavefunction of the systems is necessary.

#### 4. Conclusion

A new matrix method, which is based on symmetrized hydrogenic basis states, to calculate the energy of two-electron atoms and ions has been proposed in the present work. Approximate analytical values for the He atom and some He-like ions ground state energies using 3 symmetrized





hydrogenic basis states were successfully obtained and proved to be more accurate than our previous calculations using 3 unsymmetrized basis states. With three symmetric combinations of more basis states including  $|100;100\rangle$ ,  $|100;200\rangle$ ,  $|200;100\rangle$ ,  $|100;300\rangle$ , and  $|300;100\rangle$  in this study, compared to only three unsymmetrized basis states namely  $|100;100\rangle$ ,  $|100;200\rangle$ , and  $|200;100\rangle$  in the previous work, the ground state energies found here were more accurate. The results were also more accurate than some other results obtained from some simple methods in the literature including the standard perturbation theory approach and the uncertainty principle combined with the variational approach. Finally, the spectral decomposition analysis also indicated that the state  $|100;100\rangle$  makes the largest contributions to the ground state energies of the two electron systems considered. For the He atom, the contribution is about 90.9% and it increases as the atomic number becomes larger, reaching 99.9% for  $\text{Ne}^{8+}$  ion. These results strongly suggest that the matrix method can be used as an alternative way to obtain reasonably accurate energies of simple quantum systems.

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