

## A Simple Matrix Approach to Determination of the Helium Atom Energies

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### Abstract

Calculation of He atomic energy levels using the first order perturbation theory taught in the Basic Quantum Mechanics course has led to relatively large errors. To improve its accuracy, several methods have been developed but most of them are too complicated to be understood by undergraduate students. The purposes of this study are to apply a simple matrix method in calculating some of the lowest energy levels of He atom ( $1s^2$ , triplet  $1s2s$ , and singlet  $1s2s$  states) and to reduce errors obtained from calculations using the standard perturbation theory. The convergence of solutions as a function of the number of bases is also examined. The calculation is done analytically for 3 bases and computationally with the number of bases  $3 \leq n \leq 25$  using MATHEMATICA. First, the 2-electron wave function of the Helium atom is written as the multiplication of two  $He^+$  ion wave functions, which are then expanded into finite dimension bases. These bases are used to calculate the elements of the Hamiltonian matrix, which are then substituted back to the energy eigenvalue equation to determine the energy values of the system. Based on the calculation results, the error obtained for the He ground state energy using 3 bases is 2.51 %, smaller than the errors of the standard perturbation theory (5.28 %). Despite the fact that the error is still relatively large from the analytical calculations for singlet-triplet  $1s2s$  energy splitting of He atom, this error is successfully reduced significantly as more bases were used in the numerical calculations. In particular, for  $n = 25$ , the current calculation error for all states is much smaller than the errors obtained from calculations using standard perturbation theory. In conclusion, the analytical calculations for the energy eigenvalue equation for the 3 lowest states of the Helium atom using 3 bases have been carried out. It was also found in this study that increasing the number of bases in our numerical calculations has significantly reduced the errors obtained from the analytical calculations.

**Keywords:** Helium atom, matrix approach, ground state energy,  $1s2s$  singlet-triplet energy

### Pendekatan Matriks Sederhana untuk Penentuan Tingkat-Tingkat Energi Atom Helium

#### Abstrak

Perhitungan tingkat energi atom He menggunakan teori perturbasi orde 1 yang diajarkan di mata kuliah mekanika kuantum dasar menghasilkan eror yang cukup besar. Untuk meningkatkan akurasi, telah banyak metode yang dikembangkan namun kebanyakan dari metode ini menggunakan metode-metode tingkat lanjut yang terlalu rumit dipahami oleh mahasiswa strata 1. Tujuan penelitian ini adalah untuk menerapkan suatu metode matriks sederhana dalam menghitung beberapa tingkat energi terendah atom

*He (state  $1s^2$ ,  $1s2s$  triplet, dan  $1s2s$  singlet) dan untuk mengurangi error yang diperoleh dari perhitungan menggunakan teori perturbasi standar. Konvergensi solusi sebagai fungsi jumlah basis juga dikaji. Perhitungan dilakukan secara analitik untuk 3 basis dan secara komputasi dengan jumlah basis  $3 \leq n \leq 25$  menggunakan MATHEMATICA. Pertama, fungsi gelombang 2 elektron atom Helium ditulis sebagai perkalian 2 buah fungsi gelombang ion  $He^+$ , yang kemudian diekspansi menjadi basis-basis berdimensi berhingga. Basis-basis ini digunakan untuk menghitung elemen-elemen matrix Hamiltonian, yang selanjutnya disubstitusi kembali ke persamaan nilai eigen energi untuk menentukan nilai-nilai energi sistem. Berdasarkan hasil perhitungan, error yang diperoleh untuk energi keadaan dasar He dengan menggunakan 3 basis adalah 2,51 %, jauh lebih kecil dibanding error dari teori perturbasi standar (5,28 %). Walaupun error yang cukup besar masih diperoleh dari hasil perhitungan analitik kami untuk splitting energi singlet-triplet  $1s2s$  atom He, nilai error ini berhasil dikurangi secara signifikan ketika semakin banyak basis digunakan dalam perhitungan numerik kami. Khususnya, untuk  $n=25$ , error perhitungan kami untuk semua state jauh lebih kecil dari error yang diperoleh dari perhitungan menggunakan teori perturbasi standar. Sebagai kesimpulan, perhitungan analitik untuk persamaan nilai eigen energi untuk 3 state terendah atom Helium menggunakan 3 basis telah dilakukan. Dalam penelitian ini juga ditemukan bahwa penambahan jumlah basis dalam perhitungan numerik kami telah berhasil mengurangi secara signifikan error yang diperoleh dari perhitungan analitik.*

**Kata Kunci:** atom Helium, pendekatan matriks, energi keadaan dasar, energi singlet-triplet  $1s2s$

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## I. INTRODUCTION

As part of the Quantum Mechanics courses in undergraduate programs, students are often asked to calculate energies of the He atom using standard first order time-independent perturbation theory. This is a good exercise for the students as they are able to learn and apply quantum theory to solving real quantum problems. However, errors in the He atomic energies calculation obtained from the standard textbook perturbation theory calculations are relatively large, as it is estimated around 5.28 % for ground state  $1s^2$  energy and about 201.44 % for energy splitting of  $1s2s$  singlet-triplet state. This often makes many undergraduates think that to obtain much better results than the first order perturbation theory for the He energies, one

needs to apply more advanced methods which are inaccessible to them.

Many simple approaches have been developed to reduce errors obtained from standard perturbation theory calculations on the He atom. One study utilized the shooting method to calculate the singlet and triplet energy levels of the He atom [1]. The method used is familiar to undergraduate students since similar methods were used in treating the hydrogen atom in undergraduate Quantum Mechanics classes. Despite the simplicity of the method, their calculations on He energies agree well with the corresponding experimental values, with errors being 1.44 % for ground state energy, 0.05 % for  $1s2s$  triplet, and 0.33 % for  $1s2s$  singlet energy. In addition, detailed density functional theory (DFT)

calculations of ground state energy of the He atom was presented [2]. This method is believed to be accessible to undergraduates and give accurate results, with the error for the He ground state energy is estimated to be 1.44 %. Many other quantum calculations on the He atom have also been conducted recently using Hartree-Fock theory [3-4], variational methods [5-8], perturbative and variational methods [9], combination of Heisenberg's uncertainty principle and variational methods [10], Lagrange-mesh method [11], Hamilton-Jacobi equation [12], Bohr's theory-based methods [13-14], and analytic matrix calculation with logarithmic terms [15].

In addition, many high quality quantum calculations have now been performed massively and effectively due to the increasing computing capacity [16]. This allows the use of various computer-based method to perform more accurate calculations of energies of the He atom. Some of the methods are variational quantum Monte Carlo method [17-20], path integral Monte Carlo method [21], finite element method [22], finite volume discretization method [23], variational approach with free iterative - complement - interaction method [24], Hylleraas - Configuration interaction [25], fifth-order variational perturbation theory [26], extensive variational calculations [27], and numeric matrix method [28-30].

Most of the above mentioned methods are very accurate to calculate the energy, but they are considered too advanced for undergraduates. In 2015, Masse and Walker [31] developed a simple method using matrix mechanics introduced in Quantum Mechanics course for undergraduate program to numerically calculate energy of  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states using *MATHEMATICA*. With seven basis states, errors obtained from their calculations were 2.14 %, 0.19 %, and 0.43 % for the respective

states. In addition, error for singlet-triplet energy splitting was about 17 %, much lower than the error obtained from standard 1<sup>st</sup> order perturbation theory calculations (about 201.44 %).

However, in their article, Masse and Walker [31] did not provide an analytic calculation on the helium atom energies. Also, they only used 7 basis states in the expansion of the wave function. In this article, on the other hand, the analytic calculation on the helium atom energies is provided to highlight its simplicity as well as numeric calculation using various number of basis states to investigate the convergence of the solutions as a function of number of basis states.

The aim of this research is to apply a simple matrix approach to calculate energy eigenvalues of the low-lying states of the He atom ( $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states), both analytically and computationally using various number of basis states. Convergence of the solutions as a function of number of basis states will also be studied. Through the implementation of the simple matrix approach to the calculation, it is expected to significantly increase the accuracy of standard 1<sup>st</sup> order perturbation theory calculations on the energies of He atom. All calculations in this article are based on a matrix approach developed in [31]. It is expected that the approach presented in this study can be used as an alternative method along with other simple quantum calculation methods such as standard perturbation theory and variational approaches to perform simple but quite accurate calculations in Quantum Mechanics classes in undergraduate program.

In this article, the analytic calculation of the energies of the He atom is presented using  $n = 3$  basis states. After that, the convergence of the solutions is investigated as a function of number of basis states ( $n$ ). The basis states used in this article are formed using s orbitals.

## II. METHOD

Energies of the Helium atom are determined by solving the time independent of Schrödinger equation  $\hat{H}|\Psi\rangle = E|\Psi\rangle$ . In this article, the Schrödinger equation is solved by using a matrix approach, assuming that  $|\Psi\rangle$  is expanded in finite number of basis states. In this approach, therefore,  $|\Psi\rangle$  is an  $(n \times 1)$  column vector and  $\hat{H}$  is an  $(n \times n)$  matrix, with  $n$  being the number of basis states.

Overall, steps involved in the calculations of the He atom energies are as follows. First, Hamiltonian matrix is determined along with all its elements, using the usual equation  $H_{pq} = \langle \psi_p | H | \psi_q \rangle$ , where  $H$  is the Hamiltonian of the He atom. To calculate the matrix elements, the wave function  $|\psi_p\rangle$  has to be expanded first, depending on number of basis states one wants to use. Here, basis states used range from 3 to 25, therefore Hamiltonian is a matrix of  $(n \times n)$  dimension where  $3 \leq n \leq 25$ . For  $n = 3$ , both analytic and numeric calculations are presented while for  $n \geq 4$  only numeric calculations are performed. Once all elements of the matrix are found, the matrix is then diagonalized. The diagonalization of this  $n \times n$  matrix results in  $n$  energy eigenvalues, the lowest three of which are the energy eigenvalues of  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states. To simplify the calculations, Hartree atomic unit (a.u.) is used in this article.

## III. RESULTS AND DISCUSSION

### Elements of the He atom Hamiltonian Matrix

Hamiltonian operator can be represented in matrix form as follow

$$H = \sum_{p,q} H_{pq} |\psi_q\rangle \langle \psi_p| \quad (1)$$

Which can be represented as follows:

$$H = \begin{bmatrix} H_{11} & H_{12} & \dots & H_{1q} \\ H_{21} & H_{22} & \dots & H_{2q} \\ \dots & \dots & \dots & \dots \\ H_{p1} & H_{p2} & \dots & H_{pq} \end{bmatrix} \quad (2)$$

Where  $H_{pq}$  are elements of the Hamiltonian matrix obtained as follows:

$$H_{pq} = \langle \psi_p | H | \psi_q \rangle \quad (3)$$

Here,  $|\psi_p\rangle$  is the two-electron wave function, which can be written as a product of two  $\text{He}^+$  wave functions (orbital approximation). Using this approximation,  $|\psi_p\rangle$  can be written

$$|\psi_p\rangle = |\phi_1 \phi_2\rangle = |n_1 l_1 n_2 l_2\rangle \quad (4)$$

As usual, the spatial wave function of hydrogenic wave function contains the radial function and the standard spherical harmonics. The normalized hydrogenic radial wave function (in a.u.) can be written in terms of Laguerre Polynomial

$$R_{nl}(r) = \left\{ \left( \frac{2Z}{n} \right)^3 \frac{(n-l-1)!}{(n+l)!(2n)!} \right\}^{\frac{1}{2}} \left( \frac{2Zr}{n} \right)^l e^{-\frac{Zr}{n}} L_{n-l-1}^{2l+1} \left( \frac{2Zr}{n} \right) \quad (5)$$

The radial function for  $\text{He}^+$  ion ( $Z = 2$ ) is therefore

$$R_{nl}(r) = \left\{ \frac{2(n-l-1)!}{n^2(n+l)!} \right\}^{\frac{1}{2}} \left( \frac{4}{n} \right) \left( \frac{4r}{n} \right)^l e^{-\frac{2r}{n}} L_{n-l-1}^{2l+1} \left( \frac{4r}{n} \right) \quad (6)$$

Hamiltonian operator  $H$  in equation (3) is nothing but the Hamiltonian of the He atom,

consisting of the unperturbed Hamiltonian  $H_0$  and the interaction potential  $V$ . Where,

$$H_0 = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} \quad (7)$$

and

$$V = \frac{1}{r_{12}} = \sum_{lm} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} (-1)^m Y_l^{-m}(\Omega_1) Y_l^m(\Omega_2)$$

$$V = \begin{cases} \frac{1}{r_1}, & \text{if } r_2 < r_1 \\ \frac{1}{r_2}, & \text{if } r_1 < r_2 \end{cases} \quad (8)$$

Therefore, equation (3) can be rewritten as

$$H_{pq} = \langle \psi_p | H_0 | \psi_q \rangle + \langle \psi_p | V | \psi_q \rangle \quad (9)$$

Using orthonormality of the wave function, equation (9) becomes

$$H_{pq} = E_{n_1, n_2}^0 \delta_{pq} + \langle \psi_p | V | \psi_q \rangle \quad (10)$$

Where  $E_{n_1, n_2}^0$  is the unperturbed energy obtained by solving time-independent Schrödinger equation for hydrogenic ions, which is already solved in Quantum Mechanics classes in undergraduate program. As in the present case there are two electrons,  $E_{n_1, n_2}^0$  is the superposition of the unperturbed energy of each electron, written as

$$E_{n_1, n_2}^0 = -\frac{2}{n_1^2} - \frac{2}{n_2^2} \quad (11)$$

To evaluate equation (10), it can be written in its integral forms as

$$H_{pq} = E_{n_1, n_2}^0 \delta_{pq} + (Y_0^0)^4 \iint R_{n_1 0}(r_1) R_{n_2 0}(r_2) \frac{1}{r_{12}} R_{n_3 0}(r_1) R_{n_4 0}(r_2) d^3 r_1 d^3 r_2 \quad (12)$$

Where we have used that fact that only s orbitals are considered here, for which  $l=0$ . Since the angular integrals in the second term of equation (12) cancels  $(Y_0^0)^4$ , the 6-fold integrals in this equation reduce to 2-fold

integrals. Thus, equation (12) can be further simplified as follows

$$H_{pq} = E_{n_1, n_2}^0 \delta_{pq} + \iint r_1^2 R_{n_1 0}(r_1) R_{n_2 0}(r_2) \frac{1}{r_{12}} r_2^2 R_{n_3 0}(r_1) R_{n_4 0}(r_2) dr_1 dr_2 \quad (13)$$

For convenience in calculations, equation (13) is written as

$$H_{pq} = E_{n_1, n_2}^0 \delta_{pq} + \iint P_{n_1 0}(r_1) P_{n_2 0}(r_2) \frac{1}{r_{12}} P_{n_3 0}(r_1) P_{n_4 0}(r_2) dr_1 dr_2 \quad (14)$$

Where, our new radial function is now  $P_{nl}(r)$ , which is just the modified version of equation (6). Where

$$P_{nl}(r) = \left\{ \frac{2(n-l-1)!}{n^2(n+l)!} \right\}^{\frac{1}{2}} \left( \frac{4r}{n} \right)^{l+1} e^{-\frac{2r}{n}} L_{n-l-1}^{2l+1} \left( \frac{4r}{n} \right) \quad (15)$$

As basis states used here consist of only s orbitals, then

$$P_{n0}(r) = \left\{ \frac{2(n-1)!}{n^2(n)!} \right\}^{\frac{1}{2}} \left( \frac{4r}{n} \right) e^{-\frac{2r}{n}} L_{n-1}^1 \left( \frac{4r}{n} \right) \quad (16)$$

Equations (8), (10), (11), (14), and (16) are the equations used to calculate elements of the Hamiltonian matrix for the He atom in this study.

### Analytic Solutions to Energy Eigenvalue Equation using 3 Basis States ( $n=3$ )

Energy eigenvalue equation to be solved here is

$$H|\Psi\rangle = E|\Psi\rangle \quad (17)$$

Before solving equation (17) for  $E$ , Hamiltonian matrix elements  $H_{PQ}$  should be determined. In addition, since the wave function  $|\Psi\rangle$  has infinite dimension, it has to be expanded in terms of Eigen states with

finite dimension  $|\Psi\rangle = \sum_{i=1}^N c_i |\psi_i\rangle$ , where  $N$  has

to be finite. If its wave function is expanded in 3 basis states, then

$$|\Psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle + c_3|\psi_3\rangle \quad (18)$$

In this section, the three bases used in performing the analytic calculation are as

$$H = \begin{bmatrix} E_{1,1}^0 + \langle 1s1s|V|1s1s\rangle & \langle 1s1s|V|1s2s\rangle & \langle 1s1s|V|2s1s\rangle \\ \langle 1s2s|V|1s1s\rangle & E_{1,2}^0 + \langle 1s2s|V|1s2s\rangle & \langle 1s2s|V|2s1s\rangle \\ \langle 2s1s|V|1s1s\rangle & \langle 2s1s|V|1s2s\rangle & E_{2,1}^0 + \langle 2s1s|V|2s1s\rangle \end{bmatrix} \quad (20)$$

Elements of the Hamiltonian matrix are determined as shown below. In this case, only the first element of the matrix is calculated, i.e.  $H_{11}$ . The rest of the elements are calculated exactly in the same way. For  $H_{11}$ , one has

$$H_{11} = E_{1,1}^0 + \langle 1s1s|V|1s1s\rangle \quad (21)$$

which can be rewritten in integral forms as the following equation

$$H_{11} = E_{1,1}^0 + \iint P_{10}(r_1)P_{10}(r_2) \frac{1}{r_{12}} P_{10}(r_1)P_{10}(r_2) dr_1 dr_2 \quad (22)$$

Using equation (16) for  $P_{10}(r)$ , one obtains

$$H_{11} = E_{1,1}^0 + (32)^2 \iint r_1^2 e^{-4r_1} \frac{1}{r_{12}} r_2^2 e^{-4r_2} dr_1 dr_2 \quad (23)$$

To evaluate the integral in equation (23),  $r_1$  is assumed to be constant so that integral over  $r_2$  ( $I_2$ ) is evaluated first.

$$I_2 = \int_0^\infty \frac{1}{r_{12}} r_2^2 e^{-4r_2} dr_2 \quad (24)$$

so that equation (23) can be rewritten

$$H_{11} = E_{1,1}^0 + (32)^2 \int_0^\infty r_1^2 e^{-4r_1} dr_1 (I_2) \quad (25)$$

Then by using equation (8),  $I_2$  can be evaluated as follows

$$I_2 = \frac{1}{r_1} \int_0^{r_1} r_2^2 e^{-4r_2} dr_2 + \int_{r_1}^\infty r_2 e^{-4r_2} dr_2 \quad (26)$$

follows

$$|\psi_1\rangle = |1s1s\rangle; |\psi_2\rangle = |1s2s\rangle; |\psi_3\rangle = |2s1s\rangle \quad (19)$$

From equation (10) and (19), the  $3 \times 3$  Hamiltonian matrix for the He atom can be written

from which one obtains

$$I_2 = \frac{1}{32r_1} \{(-2r_1 - 1)e^{-4r_1} + 1\} \quad (27)$$

Equation (27) is substituted back into equation (25) to give

$$H_{11} = E_{1,1}^0 + 32 \int_0^\infty \{(-2r_1^2 - r_1)e^{-8r_1} + r_1 e^{-4r_1}\} dr_1 \quad (28)$$

Integral in equation (28) is simply evaluated using partial integral to give

$$\int_0^\infty \{(-2r_1^2 - r_1)e^{-8r_1} + r_1 e^{-4r_1}\} dr_1 = \frac{5}{128} \quad (29)$$

Equation (28) then becomes

$$H_{11} = E_{1,1}^0 + 32 \left( \frac{5}{128} \right) \quad (30)$$

Using equation (11) for  $E_{1,1}^0$ , the Hamiltonian matrix  $H_{11}$  in equation (30) is finally found to be (in a.u.)

$$H_{11} = -2.75 \quad (31)$$

All other Hamiltonian matrix elements ( $H_{12}$ ,  $H_{13}$ ,  $H_{21}$ ,  $H_{22}$ ,  $H_{23}$ ,  $H_{31}$ ,  $H_{32}$ , and  $H_{33}$ ) can be determined in the same way as  $H_{11}$ . All the results are summarized in the following  $3 \times 3$  Hamiltonian matrix

$$H = \begin{bmatrix} -2.7500 & 0.1787 & 0.1787 \\ 0.1787 & -2.0802 & 0.0439 \\ 0.1787 & 0.0439 & -2.0802 \end{bmatrix} \quad (32)$$

Equation (32) is substituted to equation (17), and the characteristic equation for the energy eigenvalue equation is then solved to obtain three energy eigenvalues as follows.

$$\det \begin{bmatrix} -2.7500-E & 0.1787 & 0.1787 \\ 0.1787 & -2.0802-E & 0.0439 \\ 0.1787 & 0.0439 & -2.0802-E \end{bmatrix} = 0 \quad (33)$$

From which one finally obtains (in a.u.)

$$\begin{aligned} E_1 &= -2.8304 \\ E_2 &= -2.1241 \\ E_3 &= -1.9559 \end{aligned} \quad (34)$$

where  $E_1$ ,  $E_2$ , and  $E_3$  correspond to energies of  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states respectively. These values agree with the numeric calculations for  $n = 3$  (see Table 1).

Comparisons of relative errors in energies using our analytic calculations in equation (34) with standard textbook perturbation theory calculation are presented below, where all errors are calculated using experimental energies [32]. For He ground state energy  $E_1$ , relative error from calculations in this study is 2.51 %, significantly smaller than errors of the standard textbook perturbation theory calculation of 5.28 % [33]. This indicates that with this simple analytic calculation using only 3 basis states, this study has proven significantly improvement in terms of accuracy than the standard textbook perturbation theory. It is believed in order to improve the current results, more basis states need to be included in the calculations. For the He  $1s2s$  excited state energies, on the other hand, errors resulted from the calculations are relatively large. Error for  $1s2s$  singlet-triplet energy splitting ( $E_3-E_2$ ) from the calculation in this study is higher than the calculation taken from the standard textbook perturbation theory calculation (474.95 % compared to 201.44 %). This is because in this calculation

we only use 3 basis states, which are combinations of  $1s$  and  $2s$  orbitals (equation 19) and omit contributions from higher states ( $3s$ ,  $4s$ , ..., etc). Because  $1s2s$  excited states are higher in energy than the  $1s^2$  ground state, the formers' wave function (to first order) should depend more heavily on higher states than the latter's. Therefore, with only 3 basis states, we expect to have more errors in excited state energies than in ground state energy. The errors, however, are significantly reduced as the number of basis states in the wave function is increased by including higher states in this numeric calculation.

### Numeric Solutions to Energy Eigenvalue Equation using $n$ Basis States ( $3 \leq n \leq 25$ )

For  $n > 3$ , analytic solutions would be very inefficient and difficult to obtain. Fortunately, this can be solved much faster and easier with the help of modern scientific software.

Masse and Walker [31] wrote a *MATHEMATICA* code to solve energy eigenvalue equation for the He atom using 7 basis states. Here, the code to calculate the He energies was modified using various basis states, ranging from 3 to 25. By doing this, the convergence of current solutions can be investigated as a function of number of basis states as well as reduce the errors resulting from our previous analytic calculations.

The three lowest energy eigenvalues from the diagonalization of the Hamiltonian matrix correspond to  $1s^2$  (ground state),  $1s2s$   $^3S_1$  (triplet state), and  $1s2s$   $^1S_0$  (singlet state), respectively. Results of the energy calculations with their errors are shown in Table 1. Experimental values of energy of  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states can be found in [32], where the energies being -2.90339 a.u., -2.17503 a.u., and -2.14577 a.u. for the respective states.

**Table 1. Energies of the Three Lowest States of the He Atom (in atomic unit) for Different Number of Basis States and Their % Errors**

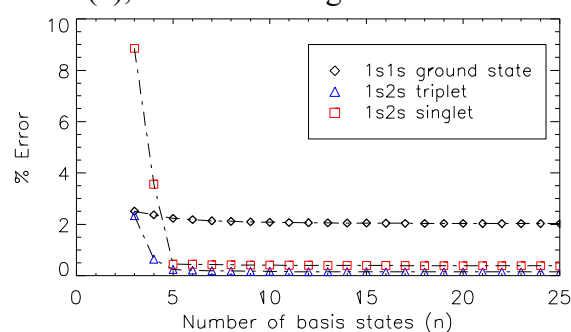
n	1s <sup>2</sup> (% error)	1s2s triplet (% error)	1s2s singlet (% error)
3	-2.83044 (2.51 %)	-2.12414 (2.34 %)	-1.95591 (8.85 %)
4	-2.83458 (2.37 %)	-2.16101 (0.65 %)	-2.06923 (3.57 %)
5	-2.83865 (2.23 %)	-2.16988 (0.24 %)	-2.13619 (0.45 %)
6	-2.84002 (2.18 %)	-2.17043 (0.21 %)	-2.13639 (0.44 %)
7	-2.84138 (2.14 %)	-2.17096 (0.19 %)	-2.13660 (0.43 %)
8	-2.84202 (2.11 %)	-2.17113 (0.18 %)	-2.13677 (0.42 %)
9	-2.84265 (2.09 %)	-2.17138 (0.17 %)	-2.13694 (0.41 %)
10	-2.84300 (2.08 %)	-2.17148 (0.16 %)	-2.13704 (0.41 %)
11	-2.84335 (2.07 %)	-2.17158 (0.16 %)	-2.13714 (0.40 %)
12	-2.84356 (2.06 %)	-2.17164 (0.16 %)	-2.13721 (0.40 %)
13	-2.84378 (2.05 %)	-2.17170 (0.15 %)	-2.13727 (0.40 %)
14	-2.84392 (2.05 %)	-2.17174 (0.15 %)	-2.13731 (0.39 %)
15	-2.84406 (2.04 %)	-2.17178 (0.15 %)	-2.13735 (0.39 %)
16	-2.84416 (2.04 %)	-2.17181 (0.15 %)	-2.13738 (0.39 %)
17	-2.84425 (2.04 %)	-2.17183 (0.15 %)	-2.13741 (0.39 %)
18	-2.84432 (2.03 %)	-2.17185 (0.15 %)	-2.13743 (0.39 %)
19	-2.84439 (2.03 %)	-2.17187 (0.15 %)	-2.13745 (0.39 %)
20	-2.84444 (2.03 %)	-2.17188 (0.14 %)	-2.13747 (0.39 %)
21	-2.84450 (2.03 %)	-2.17189 (0.14 %)	-2.13748 (0.39 %)
22	-2.84454 (2.03 %)	-2.17190 (0.14 %)	-2.13750 (0.39 %)
23	-2.84458 (2.03 %)	-2.17191 (0.14 %)	-2.13751 (0.38 %)
24	-2.84461 (2.02 %)	-2.17192 (0.14 %)	-2.13752 (0.38 %)
25	-2.84464 (2.02 %)	-2.17193 (0.14 %)	-2.13753 (0.38 %)

From Table 1, it is clear that for  $n > 7$ , the convergence is slow, with the maximum error reduction is 0.03 % for 1s<sup>2</sup> state, 0.01 % for 1s2s triplet, and 1s2s singlet states for each increase in the number of states. Despite being slow, the errors [31] for 7 basis states decrease as the number of states increases. As a comparison, for  $n = 25$ , errors for the respective states are 2.02 %, 0.14 %, and 0.38 %, compared to 2.14 %, 0.19 %, and 0.43 % [31]. This shows an error reduction of 0.12 % for energy of 1s<sup>2</sup> state, of 0.05 % for energies of 1s2s triplet, and 1s2s singlet states.

**Convergence of the Numeric Solutions**

To see the convergence of our solutions more clearly, the percentage errors in energies

for all states are plotted versus number of states ( $n$ ), as shown in Figure 1.



**Figure 1. Errors in Energies are Plotted Against Number of Basis States**

From Figure 1, it is obvious that errors in energies of all the 3 states are the highest for the smallest number of basis states ( $n = 3$ ) and they are reduced as the number of states increases. This means that as the number of



basis states increases, the theoretical energies get closer to the corresponding experimental values. This is expected as the more the number of basis states in the wave function, the more physical information contained and therefore, the wave function should represent more completely the quantum states of the system of interest. Thus, the results closest to the experimental values in this article are obtained for the largest number of basis states, i.e.  $n = 25$ .

In addition, errors for energies of all three states are reduced rapidly between  $n = 3$  to  $n = 5$ , with errors for 1s2s singlet state experiencing the most dramatic reduction and the  $1s^2$  ground state having the least significant one. For  $n \geq 5$ , the errors for all

the three states tend to be steady, indicating that adding more basis states would not significantly reduce the errors. This is due to the fact that higher  $l$  orbitals and continuum are neglected in our basis states [31].

### Comparisons with Experimental Data and other Theoretical Energies

Energy comparisons of the three lowest states of the He atom from our calculations and from other theoretical calculations as well as with the experimental data are shown in Table 2. Here, we only compare our calculations to 1<sup>st</sup> order perturbation theory calculations and some other methods that use simple undergraduate quantum mechanics approaches.

**Table 2. Comparisons of Energies from Our Calculations for  $n = 25$  with Experimental Data and other Theoretical Calculations, with All Energies in Atomic Unit**

States	Experimental data [32]	This study (% error)	Matrix method with 7 bases (% error) [31]	1 <sup>st</sup> order Perturbation theory (% error) [33]
$1s^2$	-2.90339	-2.84464 (2.02 %)	-2.84138(2.14 %)	-2.74995(5.28 %)
1s2s triplet	-2.17503	-2.17193 (0.14 %)	-2.17097 (0.19 %)	-
1s2s singlet	-2.14577	-2.13753 (0.38 %)	-2.13662 (0.43 %)	-
1s2s singlet-triplet splitting	0.02926	0.03440 (17.57 %)	0.03435 (17.39 %)	0.08820 (201.44 %)

It is clear from Table 2 that errors in this study are significantly lower than those from 1<sup>st</sup> order perturbation theory. This applies to all energies of the three states. For  $1s^2$  state, with only 3 basis states, the calculations in this study have more accuracy than the standard perturbation theory calculations (2.51 % compared to 5.28 % [33]). The error is significantly reduced to 2.02 % by utilizing 25 basis states. This error of 2.02 % is also smaller than that of 2.60 % [10] and that of 2.14 % [31], and comparable to others with errors of 1.44 % [1-2, 4]. Of course, results from the simple calculation method in this study are not to be compared with highly accurate calculations using advanced methods such as the ones found in other studies

[5-7, 15, 17-18, 20-26] with errors being less than 0.20 %. For 1s2s singlet-triplet energy splitting, the error from standard textbook perturbation theory is about 201.44 %. The error is significantly reduced to 17.57% in this research. Our 1s2s triplet and singlet state energies are also more accurate than Filippi et al [34], with errors being 0.14 % and 0.38 % from our calculations compared to about 0.23 % and 0.52 % [34], respectively.

All the results show that although the matrix approach applied here is very simple and straightforward, it can significantly reduce the errors obtained from standard 1<sup>st</sup> order perturbation theory calculation found in undergraduate quantum mechanics textbooks. To further improve the accuracy

using this matrix approach, one would need to use more basis states in the wave function by including higher  $l$ -orbitals.

#### IV. CONCLUSION

It is shown that the simple matrix approach has been successfully applied to calculate three lowest energies of the Helium atom, i.e.  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states. The time independent Schrodinger equation was analytically solved using three basis states and it was found that ground state  $1s^2$  energy of the He atom is much more accurate than that of the standard 1<sup>st</sup> order perturbation theory. Although the analytic calculations in this study for energy splitting of  $1s2s$  singlet-triplet still have relatively large errors, the errors are significantly reduced in the numeric calculations by adding the number of basis states in the wave function. In particular, when 25 basis states were used, the errors resulted from the calculations for  $1s^2$ ,  $1s2s$  triplet, and  $1s2s$  singlet states of the He atom were lower than those from the standard 1<sup>st</sup> order perturbation theory. To conclude, it has been proven that the matrix approach can be used to obtain accurate energies on the three lowest states of the He atom using the common Quantum Mechanics skills for undergraduates. Therefore, this method can be applied in undergraduate classes in addition to the 1<sup>st</sup> order perturbation theory to accurately calculate energies of quantum systems, especially the He atom.

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