A Simple Numerical Matrix Method for Accurate Triplet-1s2s 3S1 Energy Levels of Some Light Helium-like Ions

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Abstract. Triplet-1s2s 3S1 energy levels of some light Helium-like ions (Li+ to Ne8+) were numerically calculated using a truncated-matrix method implemented in a simple Mathematica code. The two-electron wave functions were expanded in finite number of basis states consisting of hydrogenic s-orbitals. Here, the Hamiltonian matrix used was of size 15x15, 25x25 and 35x35. From the results, triplet-1s2s 3S1 energies of the ions were in good agreement with other advanced and highly accurate calculations in the literature. Comparisons with one of the most accurate calculations in the literature showed that our results were very accurate with the largest error in energy being only 0.135 % for Li+ ion and the smallest one being approximately 0.018 % for Ne8+ ion energy, when 35 basis states were used in our calculations. Errors from our calculations were also much lower than those from the geometrical model.

1. Introduction
Two-electron atoms or ions are essential not only because they can be used to study photoelectron and other atomic processes but also to test new theoretical methods [1]. Excited state energies are among the most important physical quantities studied for these systems. Therefore, a large number of theoretical investigations has been conducted to solve the Schrödinger equation of the He atom and He-like ions to obtain accurate excited state energies of the systems. One of the most accurate calculations was presented by Cox et al [2], who solved the Schrödinger equation within the fixed-nucleus approximation to obtain highly accurate ground state and lowest excited state energies of the systems. They then extended the calculations to include the motion of the nucleus [3]. Other theoretical calculations of energies of the systems were also conducted using various approaches such as the Hartree-Fock method [4,5], inner truncation of the Coulomb inter-electron repulsion [6], perturbation theory [7-10], quantum electrodynamical calculation [11], density functional theory [12], relativistic configuration-interaction method [13-15], the complex rotation method [16-18], the discretization method [19-20], a numerical matrix method based on the perimetric coordinates and specific properties of the Laguerre polynomials [21], the screening constant by unit nuclear charge method [22], non-orthogonal Laguerre-L2 method [23-24], the variational principle [25], and the configuration weight function method [26]. Some recent calculations include the implementation of an accurate spectral approach to calculate energy spectrum of the Li+ ion, especially for doubly excited 1P0 states [27], doubly excited 1S1 states [28], and triplet doubly excited states 3P0 [29].
In addition, Gomez [30] developed a simple geometrical method to calculate ground state energies and estimate first excited state energies of some Helium-like ions \((2 \leq Z \leq 9)\). Ground state energies of the ions from this model were quite accurate but errors from the first excited state energy calculations were still large. Furthermore, Masse et al [31] introduced a straightforward numerical matrix method to calculate three lowest energies of the Helium atom. Basis states used in the matrix method were formed using simple hydrogenic \(s\)-orbitals. Their calculations yielded accurate energies, where errors for ground state energy, 1s2s triplet and 1s2s singlet energy were found to be about 2.14 \%, 0.19 \% and 0.43\% respectively. Analytical calculations of the He atom energies based on the matrix method were presented in [32]. The matrix method was proved to be accurate for the Helium atom and therefore it is interesting to investigate the accuracy of the method in calculating energies of other two-electron quantum systems.

Hence, it is the purpose of the present work to apply the numerical matrix method to obtain accurate lowest triplet state energy \((1s2s \ ^3S_1)\) of light Helium-like ions \((3 \leq Z \leq 10)\). This simple calculation is expected to have higher accuracy than other simple approaches such as the geometrical model [30]. The number of basis states will also be varied to investigate the effects of the number of basis states on the accuracy of the calculated energies.

2. Method
Numerical calculations of excited triplet-1s2s \(^3S_1\) energies of helium-like ions in this article are extended from the matrix method developed by Masse et al. [31]. Using this method, the Schrödinger equation was projected into a subspace of finite dimension. The details of the calculations in this article are explained in this section. The Hartree atomic units are used throughout.

The projected Schrödinger equation for Helium-like ions to be solved here is

\[
\left(-\frac{\nabla^2_i}{2} - \frac{Z}{r_i} + \frac{1}{r_{i2}}\right)\psi_i = E\psi_i \tag{1}
\]

Where, \(i=1,2\) for electron 1 and electron 2 respectively, and the Hamiltonian is

\[
\hat{H} = -\frac{\nabla^2_i}{2} - \frac{Z}{r_i} + \frac{1}{r_{i2}} \tag{2}
\]

In this finite subspace, the wave function is expanded in finite number of Eigen functions as basis states, which can be written as

\[
\psi_i = \sum_{p=1}^{N} \psi_{ip} \tag{3}
\]

Where, \(N\) is a finite number representing the number of basis states. Here, each Eigen function \(\psi_{ip}\) was formed by assuming that the function was written as the product of two hydrogenic ion \(s\)-orbitals \(|nsn's\rangle\). Moreover, one of the electrons was assumed to be in the ground state \((n=1)\) and the other one in any energy level \(n'\) of the ions. Therefore, Equation (3) can also be written as

\[
\psi_i = \sum_{n'=2}^{(N+1)/2} |s1s\rangle + |1sn's\rangle + |n's1s\rangle \tag{4}
\]

where the number of basis states \(N\) was assumed to be an odd number greater than 1, depending on the number of basis states one wanted to use in the calculation. In this study, the values of \(N\) used were 15, 25 and 35. Each basis state can be written as the product of the hydrogenic radial functions and the spherical harmonics. Thus, Equation (4) was further written as
diagonalisation of the matrix results in diagonalisation of the matrix to obtain energy eigenvalues shown in Equation (11), elements of the Hamiltonian Equation (5) and As using the Schrödinger equation. Meanwhile, the interaction potential between the two electrons can be obtained using the addition theorem of the spherical harmonics [33] as follows

$$\psi_{i} = \sum_{m=0}^{\infty} \sum_{l=0}^{m} Y_{m}^{l}(\Omega) Y_{m}^{l}(\Omega_{i})$$

As only s-orbitals were used here, for which \(l=0\) and \(m=0\), Equation (9) became

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_{1}}, & \text{for } r_{2} < r_{1} \\ \frac{1}{r_{2}}, & \text{for } r_{1} < r_{2} \end{cases}$$

Equation (5) and Equation (10) were then substituted into Equation (8) to numerically calculate all elements of the Hamiltonian matrix. As a result, the Hamiltonian matrix was of the size \(N \times N\) as shown in Equation (11), where \(N\) was taken to be 15, 25 and 35 in this study.

$$H = \begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix}$$

After all the elements of the Hamiltonian matrix were obtained, the final step was to diagonalise the matrix to obtain energy eigenvalues. The calculations of the Hamiltonian matrix elements and the diagonalisation of the matrix were performed using a Mathematica code modified from [31]. The diagonalisation of the matrix results in \(N\) energy eigenvalues and the second lowest energy eigenvalue corresponds to the excited triplet-1s2s \(^3\)S, energy of the ions.
3. Results and Discussion

In this section, calculated energies for the triplet 1s2s \(^3S_1\) state of Li\(^+\) through Ne\(^8+\) ion are presented and discussed. Comparisons of the calculated energies with energies calculated using different methods are also given. Finally, effect of adding number of basis states on the accuracy of our calculations is investigated.

3.1. Numerical Results

The triplet-1s2s \(^3S_1\), energies of the ions obtained by diagonalising Equation (11) using 15, 25 and 35 basis states are presented in Table 1.

Table 1. Triplet-1s2s \(^3S_1\) energies of Li\(^+\) to Ne\(^8+\) calculated using matrix of size N = 15, 25 and 35. All results are in a.u. ‘Exact’ energies are taken from one of the most accurate calculations in [3].

| Z (ion) | N = 15 (% error) | N = 25 (% error) | N = 35 (% error) | ‘Exact’ [3] |
|---------|------------------|------------------|------------------|------------|
| 3 (Li\(^+\)) | -5.10345(0.135 %) | -5.10384(0.127 %) | -5.10395(0.125 %) | -5.11033 |
| 4 (Be\(^2+\)) | -9.28761(0.097 %) | -9.28813(0.091 %) | -9.28827(0.090 %) | -9.29660 |
| 5 (B\(^3+\)) | -14.72294(0.069 %) | -14.72353(0.065 %) | -14.72369(0.064 %) | -14.73316 |
| 6 (C\(^4+\)) | -21.40888(0.051 %) | -21.40950(0.048 %) | -21.40968(0.047 %) | -21.41977 |
| 7 (N\(^5+\)) | -29.34515(0.039 %) | -29.34579(0.037 %) | -29.34598(0.036 %) | -29.35653 |
| 8 (O\(^6+\)) | -38.53163(0.030 %) | -38.53229(0.029 %) | -38.53248(0.028 %) | -38.54332 |
| 9 (F\(^7+\)) | -48.96824(0.024 %) | -48.96892(0.023 %) | -48.96912(0.023 %) | -48.98022 |
| 10 (Ne\(^8+\)) | -60.65495(0.020 %) | -60.65564(0.019 %) | -60.65584(0.018 %) | -60.66698 |

From Table 1, it is clear that energies from our simple calculations are in very good agreement with those obtained from one of the most accurate theoretical calculations using much more advanced method in [3]. The largest error in our calculations was only about 0.135 % for calculation of 1s2s \(^3S_1\) energy of Li\(^+\) ion using 15 basis states. Meanwhile, calculation of Ne\(^8+\) 1s2s \(^3S_1\) energy using 35 basis states yielded the most accurate energy in this work, with error of approximately 0.018 %.

The hydrogenic orbital approach used in this work is expected to perform better as atomic number of the ions increases. This can be clearly seen in Table 1, where errors become smaller for energies of ions with larger atomic number. The reason for this is that the electron-electron interactions become less dominant compared to the nuclear-electron electrostatic interactions as Z increases.

3.2. Comparison with the Geometrical Model

Here, results from Table 1 with 35 basis states are compared with other simple calculations using the geometrical model as presented in [30]. Energies in [30] were presented in eV and therefore they were converted to Hartree atomic units in this article. The comparisons are shown in Table 2.

Table 2. Triplet-1s2s \(^3S_1\), energies of Li\(^+\) to Ne\(^8+\) ion calculated using matrix of size N = 35, compared with the corresponding energies obtained from the geometrical model [30] using two different types of calculations.

| Z (ion) | This study, N = 35 (% error) | 1\(^st\) calculation in [30] (% error) | 2\(^nd\) calculation in [30] (% error) | ‘Exact’ [3] |
|---------|-------------------------------|----------------------------------------|----------------------------------------|------------|
| 3 (Li\(^+\)) | -5.10395(0.125 %) | -5.04090(1.359 %) | -5.07141(0.762 %) | -5.11033 |
| 4 (Be\(^2+\)) | -9.28827(0.090 %) | -9.21563(0.871 %) | -9.24319(0.575 %) | -9.29660 |
| 5 (B\(^3+\)) | -14.72369(0.064 %) | -14.64019(0.631 %) | -14.66629(0.454 %) | -14.73316 |
| 6 (C\(^4+\)) | -21.40968(0.047 %) | -21.31497(0.489 %) | -21.33996(0.373 %) | -21.41977 |
| 7 (N\(^5+\)) | -29.34598(0.036 %) | -29.23960(0.398 %) | -29.26349(0.317 %) | -29.35653 |
| 8 (O\(^6+\)) | -38.53248(0.028 %) | -38.41407(0.335 %) | -38.43795(0.273 %) | -38.54332 |
| 9 (F\(^7+\)) | -48.96912(0.023 %) | -48.83838(0.290 %) | -48.86190(0.242 %) | -48.98022 |
| 10 (Ne\(^8+\)) | -60.65584(0.018 %) | - | - | -60.66698 |
It is obvious from Table 2 that our results have higher accuracy than those obtained from the geometrical model. For instance, percentage error from the geometrical model using the first calculation for Li$^+$ ion energy is approximately 11 times larger than ours, while that from the same model using the second calculation for Li$^+$ ion energy is about 6 times larger than ours. Figure 1 shows comparisons of the errors from our calculations with those from calculations using the geometrical model. As can be seen from Figure 1, errors from our calculations are much lower than those from the geometrical model for all Helium-like ions compared in this study ($3 \leq Z \leq 9$).

![Figure 1](image1.png)

**Figure 1.** Comparisons of % errors from our calculations with those from the Geometrical Model [30], plotted against the atomic number (Z) of the ions.

3.3. **Effect of increasing number of basis states on the accuracy of our calculation**

Increasing number of basis states in the wave function was expected to improve the accuracy of our calculations. Figure 2 shows the percentage errors obtained from 3 different calculations in this article using different number of basis states, i.e. 15, 25 and 35 basis states.

![Figure 2](image2.png)

**Figure 2.** Comparisons of % errors from our calculations using different number of basis states, plotted against the atomic number (Z) of the ions.
From Figure 2, it is apparent that the energies resulted from our calculation using 35 basis states yielded the smallest errors compared to those from 15-basis state and 25-basis state calculations. This is more obvious for ions with relatively small atomic number, such as Li$^+$ (Z=3), Be$^{2+}$ (Z=4) and B$^{3+}$ (Z=5). The differences, however, become less significant as atomic number becomes larger. This indicates that increasing number of basis states (N>35) would have a relatively small impact on the accuracy of our calculations. The accuracy of our model can be improved such as by including other higher $\ell$-orbitals in the expansion of the wave function.

4. Conclusion

Accurate triplet 1s2$^2$ 3S$_1$ energies of some Helium-like ions (Li$^+$ to Ne$^{4+}$) have been obtained using a simple numerical matrix calculation. The results were proved to be accurate, with small percentage errors ranging from 0.018 % to 0.135 %. Comparisons of our results with the geometrical model results clearly showed that the matrix method applied here is more accurate than the geometrical model. Moreover, it was found that increasing number of basis states in our calculations did not have a major effect on the accuracy of the calculations.

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