Parameter-free Separable Non-relativistic Hamiltonian for Helium Atom

Eric Ouma Jobunga

Department of Mathematics and Physics, Technical University of Mombasa, P. O. Box 90420-80100, Mombasa, Kenya

Electron-electron correlation forms the basis of difficulties encountered in many-body physics. Accurate treatment of the correlation problem is likely to unravel some nice physical properties of matter embedded in this correlation. In an effort to tackle this many-body problem, a symmetry-dependent partition function for the correlation energy between two interacting states of helium atom is suggested in this study. Using this partition function, a simple parameter-free pseudopotential for a two-electron system is derived. The groundstate, singly and doubly excited state non-relativistic energies generated by the potential are in good comparison with literature values.

I. INTRODUCTION

Helium atom and helium-like ions are the simplest many-body systems containing two electrons which interact among themselves in addition to their interaction with the nucleus. The two-electron systems are therefore the ideal candidates for studying the electron correlation effects.

Several theoretical approaches have been employed in the past in dealing with the electron correlation problem. Some of the approaches include the variational Hylleraas method [1,2], coupled channels method [3], the configuration interaction method [4], explicitly correlated basis and complex scaling method [5]. At present only the Hylleraas method, which includes the interelectronic distance as an additional free co-ordinate, yields the known absolute accuracy of the groundstate energy of the helium atom [6].

Configuration interaction methods have also been proved to be accurate but they are quite expensive computationally. To overcome the computational challenges especially for really large systems, single active electron (SAE) methods become advantageous, although some approximations are necessary in developing the model potentials [7,8]. Reasonably accurate eigenvectors and energies can be generated using the model potentials. The major limitation of SAE approximations is the inability to explain multiple electron features like double excitation, simultaneous excitation and ionization, double ionization, and innershell transitions. However, progress is being made towards the realization of these features.

The development of the single particle potentials is an active field of study taking different approximations [9] like the independent particle approximation (IPA), multi-configurational Hartree-Fock (HF) [10], density functional theory (DFT) [11], random phase approximation (RPA) [12], and many others.

In our previous works [13–16], we have developed a theory for resolving the electron-electron interacting term with a goal of making the Hamiltonian separable. The separated Hamiltonian makes it possible to reduce the complex system to a one particle problem. The theory advanced requires the use of a suitable partition function for the results to be accurate. In reference [14,15], a classical partition function is suggested but the method required the use of an approximation to make the Hamiltonian fully separable. The classical partition function resulted into a central pseudopotential yielding reliable energies for excited states of $n$–electron atoms for $2 \leq n \leq 12$, although it performed poorly for groundstate energies. The equal partitioning of the correlation energy on the other hand resulted into a perfectly separable Hamiltonian and was quite successful in predicting the non-relativistic groundstate energies for helium, lithium, and beryllium atoms, all having spherical symmetry in their groundstate. The equal partitioning is however poor in predicting energies of non-spherical states.

In reference [16], a quantum mechanical symmetry-dependent partition function is suggested for $n$–electron atoms where $2 \leq n \leq 12$. This partition function yields the expected groundstate energies for the atoms and reasonable excited state energies for lithium atom. The partition function however does not yield the expected accuracy for the excited states of helium atom.

In this work, a symmetry-dependent partition function for helium atom is suggested. With the partition function, the corresponding non-relativistic Hamiltonian is completely separable resulting into an independent particle problem. We obtain reliable results for the groundstate, excited states, and the doubly excited states of helium atom using the present method.

II. THEORY

The non-relativistic Hamiltonian of a two-electron system with a nuclear charge $Z$ is given by

$$H = \frac{1}{2} \left[ p_1^2 + p_2^2 \right] - Z \left[ \frac{1}{r_1} + \frac{1}{r_2} \right] + \frac{1}{|r_1 - r_2|} \tag{1}$$

where the first term correspond to the sum of the kinetic energy of each of the two electrons, the second term to the sum of the interactions between each of the electrons and the nucleus, and the last term to the electron-electron repulsion between the two electrons. The second and the
last term form the potential energy function of a bound two-electron system.

In our previous work [13], it was shown that the electron-electron interaction analytically simplifies to
\[ \frac{1}{|r_i - r_j|} = \frac{1}{\sqrt{r_i^2 + r_j^2}} \]  
(2)
because of orthogonality of the two interacting quantum states. In the independent particle method, the single particle potential function
\[ V(r_i, r_j) = -\frac{Z}{r_i} + \eta_i \frac{1}{\sqrt{r_i^2 + \eta_i^2}} \]  
(3)
for a two-electron system, using the mean field, can be completely separated [13, 16] as
\[ V(r_i) = -\left[ \frac{Z - \eta_i \sqrt{\eta_i}}{r_i} \right] \]  
(4)
by minimizing the function with respecting to the scaling parameter \( r_i \). Factor \( \eta_i \) in equations (3) and (4) corresponds to a partition function which ensures the sharing of the electron-electron interaction energy between the two interacting electrons as a function the orbital angular momentum of the \( i \)th electron. We have seen in our previous works [13, 16] that the equal sharing \( \eta_i = 1/2 \) of the electron-electron interaction is quite successful in approximating the groundstate ionization potentials of helium, lithium, and beryllium because of their spherical symmetry.

In this work, a symmetry-dependent partition function
\[ \eta_i = \frac{\sqrt{l_i} + 1}{\sqrt{l_i} + 2} \]  
(5)
for helium atom is suggested. The partition function is based on the mean value theory advanced in our previous paper [16] but with the mean values empirically determined for helium atom. With this partition function, the corresponding non-relativistic Hamiltonian is completely separable resulting into an independent particle problem.

With this potential, the single particle Hamiltonian
\[ h(r_i) = \frac{p_i^2}{2} + V(r_i) \]  
(6)
for helium atom is defined. The eigenvalues of a two-electron system can then be evaluated as [13]
\[ \langle E_{\alpha\alpha'} \rangle = \begin{cases} 4 \varepsilon_{\alpha\alpha'} & \text{if } \alpha = \alpha' \\ \varepsilon_{\alpha\alpha} + \varepsilon_{\alpha'\alpha'} & \text{if } \alpha \neq \alpha' \end{cases} \]  
(7)
where \( \varepsilon_{\alpha\alpha} = \langle h(r_i) \rangle \) is the eigenvalue of a single electron orbital. Factor 4 in the above equation arises from both exchange and degeneracy consideration for states with \( \alpha = \alpha' \). For a helium atom with one electron considered to be in the ground state and the other electron occupying an excited state \( \alpha' \), \( \varepsilon_{\alpha\alpha} \) is approximately equal to the core energy eigenvalue, \( E_{\text{core}} = -2.00000 \), for the helium ion in its ground state.

### III. RESULTS AND DISCUSSIONS

We have developed a single electron potential for helium atom given by equation \( [4] \). The pseudopotential is used to calculate the 1s\( nl \) eigenvalues for helium atom as shown in table \( [1] \) for angular momenta of up to \( l_{\text{max}} = 7 \). The results are presented for the first five principal quantum numbers for each angular momentum values. In generating our results, a B-spline radial box of 600 B-splines, \( r_{\text{max}} = 200 \), \( k = 10 \), and a non-linear knot sequence is used.

| State | Present | Trip. | Sing. | Rel. |
|-------|---------|-------|-------|------|
| \( L = 0 \) | -2.91031 | -2.90394 | -2.90372 |
| \( L = 1 \) | -2.13481, -2.13320 | -2.12838, -2.12387 | -2.12341, -2.12391 |
| \( L = 2 \) | -2.05991, -2.05850, -2.05516, -2.05514 | -2.03124, -2.03129, -2.03128, -2.03127 | -2.01999, -2.02002, -2.02002, -2.02001 |
| \( L = 3 \) | -2.01388, -2.01390, -2.01390, -2.01389 | -2.01015, -2.01020, -2.01020, -2.01020 | -2.00777, -2.00781, -2.00781 |
| \( L = 4 \) | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01388, -2.01389, -2.01389, -2.01388 | -2.01020, -2.01020, -2.01020, -2.01020 |
| \( L = 5 \) | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01388, -2.01389, -2.01389, -2.01388 | -2.01020, -2.01020, -2.01020, -2.01020 |
| \( L = 6 \) | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01020, -2.01020, -2.01020, -2.01020 |
| \( L = 7 \) | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01389, -2.01389, -2.01389, -2.01389 | -2.01020, -2.01020, -2.01020, -2.01020 |

TABLE I: Some numerically calculated eigenvalues using the present method potential versus the experimentally determined triplet and singlet values [17] and the non-relativistic reference values for helium atom [3].

The results generated with the potential presented is in good agreement with the references values [3] at larger
values of $n$ and $l$ as expected. The singlet and triplet values are the reference experimental results. We can observe that the present results are close to the triplet values while the reference theoretical data are close to the singlet values. It is also clearly visible in the present results that the accidental degeneracy, where states having the same principal quantum numbers but different angular momentum quantum numbers have the same energies, is completely removed. This is a consequence of the symmetry-dependent interaction potential used.

The largest discrepancy between the present results and the literature values stem from the lowest lying spherically symmetric states. This discrepancy seems to stem from the influence of coherences, which are vanishing in our non-relativistic case. The coherences also help in distinguishing between the singlet and triplet states of helium.

From equation (4), it can be deduced that the nuclear charge screening effect of the other electron can be determined exactly. The charge screening can be seen to depend on the nuclear charge and the angular momentum of the active electron. This work therefore modifies the existing theory of charge screening by introducing the symmetry dependence in it.

In table II, we present the eigenvalues of autoionizing levels of helium relative to the groundstate energy. The eigenvalues have been evaluated using equation (7). We have also determined the non-relativistic excitation energies of the $2s^2$ and $2p^2$ autoionizing states from the present method to be 59.19 eV and 64.31 eV respectively against the known experimental values of 57.8 eV and 62.2 eV respectively. The excitation energy for the $2p^2$ autoionizing state is an improvement of the value presented in ref. 13 since the current separable Hamiltonian for helium breaks the degeneracy of states with equal principle quantum number but different orbital angular momentum quantum numbers.

From table II, one can observe that our $ns^2 1S$ states and $2s2p 1P$ state results compare well with ref. 1 values while $np^2 1S$ states results are lower compared to the reference values. This observation forms a complementary relationship with table II results in that singly excited states with $s$ symmetry are poorly described while doubly excited states with $s$ symmetry are well described by the present potential. Conversely, single excited states with $p$ symmetry are well described while doubly excited states with $p$ symmetry are underestimated by the present potential.

The present method is advantageous in that, unlike other methods tackling electron correlation, there is no inherent approximation involved in the treatment of the electron-electron interaction and all the effects including electron exchange and correlation are evaluated exactly. The validity of the current method lies in the suggested partition function which in turn determines the quality of the results obtained.

Within the non-relativistic solution framework, the present results are in good comparison to the literature values can be deemed to be reliable especially for non-spherical ($l \neq 0$) symmetry states. For states with spherical ($l = 0$) symmetry, the method is only accurate for the groundstate and autoionizing states while it overestimates the binding energies of the singly excited states. The inaccuracy arises because of the non-inclusion of coherences. The relative importance of these coherences is expected to vanish within the framework of non-relativistic quantum mechanics. In ref. 13, it was shown that with the inclusion of some relativistic corrections, the groundstate energy of the helium atom is accurately reproduced.

With the symmetry-dependent partition function, the electron correlation problem is exactly solved. For helium atom, we are led to a conclusion that the non-relativistic ground state energy is $−2.9103$. This implies that the accurate value of $−2.9037$ can only be achieved if the higher-order corrections are incorporated into the Hamiltonian of helium atom. The success of the present method validates the use of equation (3) derived in our previous paper. It is important to note that the same equation is also the basis of hyperspherical co-ordinates method developed by Macek [21]. We can therefore the present method as a modification of the hyperspherical co-ordinates method.

### IV. CONCLUSION

Accurate treatment of the electron-electron interaction is the key to resolving uncertainties in many-body physics. Many existing methods for solving the many-body problems are quite expensive computationally. In this work, a symmetry-dependent partition function for helium atom is suggested. A simple separable parameter-free Hamiltonian for helium atom yielding reasonable and degenerate non-relativistic eigenvalues is consequently obtained. The singly and doubly excited state energies

| State   | Present ref 1 | ref 2 |
|---------|---------------|-------|
| $2s^2 1S$ | $-0.7775$     | $-0.7333$  |
| $3s^2 1S$ | $-0.3233$     | $-0.3265$  |
| $4s^2 1S$ | $-0.1818$     | $-0.1838$  |
| $5s^2 1S$ | $-0.1164$     | $-0.1177$  |
| $6s^2 1S$ | $-0.0808$     | $-0.0817$  |
| $7s^2 1S$ | $-0.0593$     | $-0.0600$  |
| $2p^2 1P$ | $-0.6343$     | $-0.6587$  |
| $2p^2 1S$ | $-0.5392$     | $-0.6314$  |
| $3p^2 1S$ | $-0.2396$     | $-0.2933$  |
| $4p^2 1S$ | $-0.1348$     | $-0.1671$  |
| $5p^2 1S$ | $-0.0862$     | $-0.1075$  |
| $6p^2 1S$ | $-0.0599$     | $-0.0749$  |
| $7p^2 1S$ | $-0.0440$     | $-0.0551$  |

TABLE II: Some numerically calculated eigenvalues (in atomic units) using the present potential versus the literature values for helium autoionizing levels. Ref. 1 results were generated using DFT calculations while ref. 2 are reference data reported in the paper for comparison purposes.
obtained by the separable potential compare well with literature values. It is our belief that the suggested method will go along way in improving the solutions of the complex multi-electron problems.

[1] E. A. Hylleraas, Zeitschrift für Physik 54, 347 (1929).
[2] G. W. F. Drake, Physica Scripta 1999, 83 (1999).
[3] J. F. Barna and J. M. Rost, Eur. Phys. J. D 27, 287 (2003).
[4] R. Hasbani, E. Cormier, and H. Bachau, Journal of Physics B: Atomic, Molecular and Optical Physics 33, 2101 (2000).
[5] A. Scrinzi and B. Piriaux, Phys. Rev. A 58, 1310 (1998).
[6] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).
[7] J. S. Parker, L. R. Moore, E. S. Smyth, and K. T. Taylor, Journal of Physics B: Atomic, Molecular and Optical Physics 33, 1057 (2000).
[8] J. S. Parker, E. S. Smyth, and K. T. Taylor, Journal of Physics B: Atomic, Molecular and Optical Physics 31, L571 (1998).
[9] T. N. Chang and U. Fano, Phys. Rev. A 13, 263 (1976).
[10] A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (Dover Publishing, Newyork, 1996).
[11] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[12] J. Linderberg, Physica Scripta 21, 373 (1980).
[13] E. O. Jobunga, arXiv p. 1704.02009 (2017).
[14] E. O. Jobunga, arXiv p. 1708.04061 (2017).
[15] E. O. Jobunga, arXiv p. 1711.07645 (2017).
[16] E. O. Jobunga, arXiv p. 1712.06286 (2017).
[17] NIST, Experimental Energy Values for Helium (accessed April 20, 2018), URL http://physics.nist.gov/PhysRefData/ASD/levels-form.html
[18] E. Clementi and D. L. Raimondi, The Journal of Chemical Physics 38, 2686 (1963).
[19] M. E. Rudd, Phys. Rev. Lett. 13, 503 (1964).
[20] R. Singh and B. M. Deb, The Journal of Chemical Physics 104, 5892 (1996).
[21] J. Macek, Journal of Physics B: Atomic and Molecular Physics 1, 831 (1968).