Symmetry-dependent analytical all-electron potential for helium atom

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ABSTRACT

Electron–electron interaction is the origin of the many-body problems usually encountered in physics and chemistry. Helium atom and other two-electron systems are the simplest many-body systems in nature. The Schrödinger equation even for such simple systems cannot be solved exactly without resorting to approximate methods. In this study, we have suggested a symmetry-dependent analytical all-electron potential for helium atom derived using an alternative multipole expansion, a variational technique, and a mean-field approximation. We have calculated the non-relativistic groundstate energy for helium atom to be −2.90422284. The suggested all-electron potential has a local Coulomb potential with embedded nuclear charge screening effect in the leading term of the multipole potential. A non-local component of the potential emanates from the higher-order angular momentum terms of the multipole series expansion. The higher-order multipole interactions are fully included through the exchange correlation processes where the interacting electrons exchange their angular momenta via the operator. With the derived potential, the effects of the local long-range and non-local short-range components, and the finite nuclear mass corrections are tested. Our results are in reasonable agreement with literature values. Indeed with the finite nuclear mass correction, we obtain the groundstate energy of helium atom to be −2.90382769.

Introduction

Helium atom and other two-electron systems are the simplest many-body systems in nature. The dominant interactions in many-body systems are the electron-nuclei and the electron–electron interactions. Within the fixed nuclear geometry, with the position of the nucleus taken as the point of reference in the coordinate system, the electron-nuclei interaction and the kinetic energy operators in the Schrödinger equation are usually much simpler to deal with because they are separated in spatial and momentum coordinates respectively. The electron–electron interactions, on the other hand, are quite challenging to deal with because of the correlations in the spatial coordinates. These challenges often lead to the use of approximation methods in solving the Schrödinger equations for the many-body systems encountered in atomic and molecular physics, condensed matter physics, nuclear physics, and quantum chemistry.

It is already known that the electron–electron interaction is the origin of many interesting phenomena in materials like the metal–insulator transitions, magnetic ordering, and superconductivity [1]. Significant progress has since been made in developing techniques to deal with the electron correlation problem. Hartree–Fock method is usually a good starting point in solving the many-body problem, but it is not good enough for chemistry and spectroscopy of an *n*-electron systems [2]. Random Phase Approximation methods are emerging rapidly

as effective validation tools for semi-local density functional computations. These methods have the ability to capture approximately static correlations in molecules [3,4]. Hylleraas method [5–7] which employs explicitly correlated wavefunctions is quite accurate but computationally very expensive and hence tractable for helium atom and other small quantum systems only. Configuration Interaction (CI) is also an alternative method which is quite accurate depending on the size and quality of configurations included, but it is computationally demanding. Density Function Theory (DFT) [8] is currently the method of choice in computational quantum chemistry and condensed matter physics owing to its use of single-particle non-interacting Hamiltonian and Kohn–Sham orbitals which yield reasonably accurate groundstate energies [9]. Despite employing minimal computational resources, the challenge with DFT rests with evaluating the unknown exchange correlation functional [10] and a poor description of excited states [11].

Besides other theoretical methods, a pseudopotential can also be used as an approximation for the simplified description of complex atoms, molecules, and other quantum systems. The use of pseudopotentials was first introduced by Fermi [12]. Hellmann [13] subsequently developed a pseudopotential model for atoms which has been extensively used in atomic scattering [14]. The use of pseudopotential method in the many-body problems is convenient, computationally less expensive and has the potential of revealing the underlying processes in the interaction dynamics. Pseudopotentials can be conveniently adapted to the codes for single-electron systems.

An optimized effective potential (OEP) method, as an alternative to the use of pseudopotentials, employs an effective potential for a single particle but carefully designed using mean-field theories to incorporate the dynamical features of the other electrons in a many-body problem [15]. The optimized potential bears all the practical advantages of a pseudopotential in addition to its ability to describe a quantum system in a more realistic way. The use of the effective potentials is also justified by the understanding that when more accurate energy levels are obtained, the wavefunctions obtained from the resulting boundary conditions will closely approximate the exact values when solving the atomic and molecular problems [16]. With the energy eigenvalues and the corresponding wavefunctions determined, other spectroscopic properties of a system, for example, bond lengths, ionization potentials, dissociation energies, and polarizabilities, can also be determined [17].

In this study, an optimized symmetry-dependent single-particle all-electron potential for helium atom of the form

$$V(r_i) = -\frac{(Z - \sigma_{l_i})}{r_i} \tag{1}$$

with the screening parameter σ_{l_i}, originally suggested by Slater and Zener [16,18–20] in their pioneering works, is derived using our alternative multipole expansion [21–25], a variational technique, and a mean-field approximation. The higher-order non-spherical terms of the electron–electron multipole interaction account for the exchange correlation effects which are non-local and short-range. In Eq. (1), r_i and l_i refer to the radial co-ordinate and the orbital angular momentum of the ith electron respectively. The screening parameter σ_{l_i}, which is a function of l_i, is obtained by summing over the l and m quantum numbers of the electron–electron interaction term in the Hamiltonian operator. The analytical separation of spatial coordinates is achieved through a mean-field approximation of the higher-order multipole terms. The Schrödinger equation for helium atom is solved using the derived all-electron potential in this study and the results compared with literature values. This paper should be considered as an extension to our previous study [21] which solved the Schrödinger equation for helium atom using the lowest-order approximation of the electron–electron interaction. The goal of the paper is therefore to develop a systematic method of including the higher-order multipole interactions, not incorporated in Ref. [21].

Theory

The time-independent Schrödinger equation for a two-electron system is given by

$$H\Psi(\vec{r}_i, \vec{r}_2) = E\Psi(\vec{r}_i, \vec{r}_2), \tag{2}$$

where H is the non-relativistic Hamiltonian operator of the system, E is the total energy of the system corresponding to the Hamiltonian, and $\Psi(\vec{r}_i, \vec{r}_2)$ is the two-electron wavefunction. The Hamiltonian, in atomic units and in fixed nuclear coordinates, can be expressed as

$$H = \frac{1}{2}\left[p_1^2 + p_2^2\right] - Z\left[\frac{1}{r_1} + \frac{1}{r_2}\right] + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \tag{3}$$

where the first term corresponds to the kinetic energy operators, the second term corresponds to the interaction between nucleus and each of the atomic electrons, and the last term corresponds to the electron–electron interaction between the two atomic electrons.

In our previous articles [21–25], we formulated the alternative multipole expansion of the Coulomb repulsion term,

$$\frac{1}{|\vec{r}_i - \vec{r}_j|} = (r_i^2 - 2r_i r_j x + r_j^2)^{-1/2}$$
$$= \frac{4\pi}{\sqrt{r_i^2 + r_j^2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \tilde{j}_l(r_i, r_j) Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j), \tag{4}$$

where $x = \cos\theta$, θ is the angle between vectors $\vec{r}_i$ and $\vec{r}_j$, the unit vector $\hat{r}$ specifies the angular coordinates of vector $\vec{r}$, and

$$\tilde{j}_l(r_i, r_j) = \sum_{k=l,l+2,\dots} \frac{(2k-1)!!}{(k-l)!!\,(k+l+1)!!} \left(\frac{r_i r_j}{r_i^2 + r_j^2}\right)^k \tag{5}$$

is a spherical Bessel-like function. For $l = 0$, the first term of the series is unity. We use the function in Eq. (5) to express the single-electron interaction potential for a two-electron system as

$$V(\vec{r}_i, \vec{r}_j) = -\frac{Z}{r_i} + \gamma_{l_i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$
$$= -\frac{Z}{r_i} + \gamma_{l_i} \frac{4\pi}{\sqrt{r_i^2 + r_j^2}} \sum_{l,m} \tilde{j}_l(r_i, r_j) Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j), \tag{6}$$

where the parameter

$$\gamma_{l_i} = \frac{1 + \delta_1}{2 + \delta_1 + \delta_2} \tag{7}$$

is a general symmetry-dependent partitioning fraction [21,24] representing the proportion of the electron–electron interaction energy corresponding to ith-electron. The parameters in Eq. (7) are empirically determined to be

$$\delta_1 = \begin{cases} 0 & \text{if} \quad l_i = 0 \\ \sqrt[l_i]{l_i} & \text{if} \quad l_i \neq 0 \end{cases} \tag{8}$$

and

$$\delta_2 = \frac{l_v}{2^{(2l_v - 1)}} \tag{9}$$

with l_i representing the orbital angular momentum quantum number of the ith-electron in the atom and l_v representing the orbital angular momentum of the groundstate valent electron in the case of an arbitrary many-electron system. For helium atom, $l_v = 0$.

In the empirical determination of Eq. (7), the suggested partitioning is argued on the basis that the two interacting electrons share the electron–electron interaction energy, not on equal basis, but with the sharing fractions determined by the proportion of each of their intrinsic energies [21]. The interacting electrons are assumed to be exhibiting quantum harmonic oscillations with each of their intrinsic energies given by

$$\epsilon_i = \left[\tilde{l}_i + \frac{1}{2}\right]\hbar\omega, \tag{10}$$

where $\tilde{l}_i$ is a discrete quantum number corresponding to the orbital angular momentum of the harmonic oscillator, $\hbar$ is the Planck's constant divided by 2π, and ω is the fundamental angular frequency of oscillations of the electrons. Consequently, the partitioning fraction corresponding to the ith-electron becomes

$$\gamma_{l_i} = \frac{\epsilon_i}{\epsilon_i + \epsilon_j}, \tag{11}$$

which simplifies to the form given by Eq. (7). The empirical task is then reduced to the determination of the explicit forms of δ_i as given by Eqs. (8) and (9).

The single-electron interaction potential given by Eq. (6) can then be rewritten in multipole moments as

$$V(\vec{r}_i, \vec{r}_j) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{k=l,l+2,\dots}^{\infty} V_{l,m}^k(\vec{r}_i, \vec{r}_j) \tag{12}$$

with

$$V_{0,0}^0(\vec{r}_i, \vec{r}_j) = -\frac{Z}{r_i} + \gamma_{l_i} \frac{1}{\sqrt{r_i^2 + r_j^2}} \tag{13}$$

as the leading-order term of the multipole potential and

$$V_{l,m}^k(\vec{r}_i, \vec{r}_j) = 4\pi\,\gamma_{l_i}\,\beta_l^k \frac{r_i^k r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}} Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j) \tag{14}$$

for the higher-order terms of the multipole potential with β_l^k representing the coefficients in the power series in Eq. (5). Subjecting the lowest-order multipole term $V_{0,0}^0$ to the optimization condition,

$$\frac{\partial V_{0,0}^0}{\partial r_i} = 0, \tag{15}$$

leads to the potential terms

$$V_{0,0}^0(\vec{r}_i) = -\frac{Z}{r_i} + \gamma_{l_i} \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}$$

$$V_{l,m}^k(\vec{r}_i, \vec{r}_j) = 4\pi \gamma_{l_i} \frac{\beta_l^k \sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i} \left(\frac{r_i r_j}{r_i^2 + r_j^2}\right)^k Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j), \tag{16}$$

as shown in appendix A1, with the spatial coordinates completely separated in the lowest-order term. Since $\vec{F} = -\vec{\nabla}V$, where $\vec{F}$ is the net force acting on a body and V is the potential energy function for that body, the optimization condition is equivalent to requiring that the forces associated with the leading-order interaction to be vanishing.

To simplify Eq. (16) further, We then utilize a mean-field approximation and a summation over the k-index (as shown in appendix A2) to evaluate the symmetry-dependent single-electron multipole potential

$$V(\vec{r}_i) = \sum_{l=0}^\infty \sum_{m=-l}^l V_l^m(\vec{r}_i), \tag{17}$$

for the two-electron system where

$$V_0^0(\vec{r}_i) = -\frac{\left(Z - \gamma_{l_i} B_0^0(Z) \sqrt[3]{\frac{Z}{\gamma_{l_i}}}\right)}{r_i},$$

$$V_l^m(\vec{r}_i) = \gamma_{l_i} B_l^m(Z) \sqrt[3]{\frac{Z}{\gamma_{l_i}}} \frac{\exp\left[-\frac{lZr_i}{(l_i+1)(l_i-l+1)}\right]}{r_i^{l+1}} \delta_{l_i,l_j+l}\delta_{m_i,m_j+m}, \tag{18}$$

and the coefficient

$$B_l^m(Z) = \frac{(2l_i - l + 2)!}{(2l_i - 2l + 2)!} \left(\frac{2Z}{l_i - l + 1}\right)^{(2l_i-2l+3)}$$

$$\times \left[\frac{(l_i+1)(l_i-l+1)}{(2+2l_i-l)Z}\right]^{2l_i-l+3} A_l^m \langle \tilde{j}_l(r_i, r_j)\rangle. \tag{19}$$

The angular factors A_l^m in Eq. (19), evaluated in Eq. (38) in appendix A2, arise when the corresponding double integral for the correlated two-electron is solved. Hydrogenic orbitals with angular momentum quantum number l' and principal quantum number $l' + 1$, where $l' = l_i$ or l_j, have been used in Eq. (18) as the trial wavefunctions to solve the non-local exchange integral. The higher-order multipole potentials $V_l^m(\vec{r}_i)$ can then be added perturbatively to increase the accuracy of the single-electron potential.

The summation of all orders of the multipole potential in Eqs. (17) and (18) simplify to a fully analytical single-electron potential function given by Eq. (1) where the electron screening parameter σ_{l_i} is evaluated as

$$\sigma_{l_i} = \gamma_{l_i} \sqrt[3]{\frac{Z}{\gamma_{l_i}}} \sum_{l=0}^\infty \sum_{m=-l}^{+l} B_l^m(Z) \frac{\exp\left[-\frac{lZr}{(l_i+1)(l_i-l+1)}\right]}{r_i^l} \delta_{l_i,l_j+l}\delta_{m_i,m_j+m}. \tag{20}$$

One can see that our derived potential has a local long-range Coulomb potential part ($l = 0$) and a non-local short-range exchange correlation potential component ($l \neq 0$) that scales with radial distance (r_i) from the nucleus. The charge screening parameter, if all the non-relativistic interactions are included, can be seen to be partly constant and partly varies as a decaying exponential function scaled by the radial distance r_i raised to power l.

With the potential given by Eq. (17), the Hamiltonian given by Eq. (3) is fully separable and the non-relativistic single-electron Hamiltonian can then be written as

$$h_\infty(\vec{r}_i) = \frac{p_i^2}{2} + V(\vec{r}_i) \tag{21}$$

within the infinite nuclear mass approximation. With the finite nuclear mass correction, the Hamiltonian becomes

$$h(\vec{r}_i) = h_\infty(\vec{r}_i) - \frac{1}{M_{ion}} h_\infty(\vec{r}_i) \tag{22}$$

where $1/M_{ion} = 1.3606048 \times 10^{-4}$ is the electron-helium nuclear mass ratio. The influence of the nuclear mass in Eq. (22) reduces to a mass scaling parameter which linearly scales all the energy eigenvalues in the same way.

Within the independent particle Hamiltonian given by Eqs. (21) and (22), the energy eigenvalues of a two-electron system can then be evaluated as [21,22]

$$\langle E_{\alpha\alpha'}\rangle = \langle \Psi(\mathbf{q}_i, \mathbf{q}_j)|\mathrm{H}|\Psi(\mathbf{q}_i, \mathbf{q}_j)\rangle = \begin{cases} 4\,\varepsilon_{\alpha\alpha'} & \text{if } \alpha = \alpha' \\ \varepsilon_{\alpha\alpha} + \varepsilon_{\alpha'\alpha'} & \text{if } \alpha \neq \alpha' \end{cases} \tag{23}$$

using the total Hamiltonian, $\mathrm{H} = \sum_{i=1}^2 h(\vec{r}_i)$, and an anti-symmetric determinant expansion,

$$\Psi(\mathbf{q}_i, \mathbf{q}_j) = \frac{1}{\sqrt{2}}\left[\phi_\alpha(\mathbf{q}_i)\phi_{\alpha'}(\mathbf{q}_j) - \phi_{\alpha'}(\mathbf{q}_i)\phi_\alpha(\mathbf{q}_j)\right], \tag{24}$$

of the total wavefunction of the two-electron system, where $\mathbf{q} = (\vec{r}, \vec{s})$ incorporates both the spatial and the spin coordinates respectively. In Eq. (23), $\varepsilon_{\alpha\alpha} = \langle \phi_\alpha|h(r_i)|\phi_\alpha\rangle$ is the spin averaged energy eigenvalue of a single electron orbital, with an eigenfunction $\phi_\alpha(r_i)$ and a unique quantum number $\alpha = \{n_i, l_i, m_i\}$. The factor 4 in Eq. (23) arises from both exchange and permutation symmetry consideration for states with $\alpha = \alpha'$. In our simplification, we have used

$$\langle \uparrow | \uparrow\rangle = \langle \downarrow | \downarrow\rangle = 1 \quad \text{and} \quad \langle \uparrow | \downarrow\rangle = \langle \downarrow | \uparrow\rangle = i \tag{25}$$

to evaluate the spin integrals noting that our separable Hamiltonian operator is free of spin. The imaginary number $i = \sqrt{-1}$ is used as defined in complex numbers. The set $\{\uparrow, \downarrow\}$ consists of the spin-up and spin-down states respectively. The two electrons are considered to be indistinguishable in the treatment. For the other cases where $\alpha \neq \alpha'$, the inner electron sees the unscreened nuclear charge Z while the outer electron sees the screened nuclear charge as a result of the inner electron. The infinite nuclear mass energy eigenvalue, corresponding to the principal quantum number n, for the inner electron can therefore be computed as a hydrogenic eigenvalue

$$\varepsilon_n = -\frac{Z_{\text{eff}}^2}{2n^2} \tag{26}$$

with unscreened effective nuclear charge $Z_{\text{eff}} = Z$, whereas that for the outer electron can also be computed in a similar way but with a screened effective nuclear charge $Z_{\text{eff}} = Z - \sigma$. For a helium atom with one electron considered to be in the $1s$ state and the other electron occupying an excited state α', $\varepsilon_{1s} = -2.00000$, which is equal to the infinite nuclear mass groundstate energy of helium ion, since the inner electron is assumed to be unshielded. The computation in Eq. (26) can be evaluated analytically for a spatially independent nuclear charge screening parameter, as is the case for spherical approximation when only the $l = 0$ term in Eq. (20) is considered.

For comparison purposes, we have also included results calculated using a derived central potential [22,23]

$$V_{cen}(r_i) = -\frac{Z}{r_i} + \langle \tilde{j}_0\rangle \frac{\left[\frac{Z f(r_i, r_j)}{2}\right]^{3/5}}{r_i} \tag{27}$$

where the function

$$f(r_i, r_j) = \frac{r_i^2}{r_i^2 + r_j^2} \tag{28}$$

is the radial partitioning fraction. The expectation value

$$\langle f(r_i, r_j)^{\frac{3}{5}}\rangle \approx \left(1 + \frac{\exp\left[\sqrt{\frac{5}{3}}\ln\sqrt{\frac{5}{3}} - \sqrt{\frac{5}{3}}\right]}{Z^2 r_i^2}\right)^{-\frac{3}{5}} \tag{29}$$

is approximately optimized by evaluating the integral using a trial function for hydrogenic system in the $1s$ state and the Stirling's approximation, $\ln N! \approx (N \ln N - N)$.

Results and discussion

An ab initio analytical all-electron separable potential for two-electron atoms or ions is presented in Eq. (17). Higher orders of the multipole expansion series of the electron–electron interaction are systematically included in the potential. In the derivation, an empirically determined partitioning fraction and an optimization procedure has been used to express the lowest-order term of the electron–electron interaction as a function of a single-electron radial distance. Subsequently, a mean-field approximation has been used to include the effects of the higher-order multipole interactions. The mean-field approximation employs a root mean value in evaluating the spherical Bessel-like functions emanating from the electron–electron interaction. Also, the hydrogenic trial functions have been used to evaluate the non-local potentials. The results evaluated using the symmetry-dependent partitioning fractions are compared with the results calculated using a radially-dependent partitioning fraction, given by Eq. (27), and with literature values [26]. Analytically calculated results, evaluated using Eq. (26) within the spherical approximation, are also presented.

The effect of electron–electron interaction term on the single-electron potential can be seen, from Eqs. (1) and (20), to reduce to a well defined screening parameter that depends on the nuclear charge Z, orbital angular momentum l_i and the radial distance r_i of the screened electron, as well as the multipole orders l and m of the electron–electron interaction operator. From Eq. (18), the $l = 0$ term of the multipole potential can be seen to be a Coulombic long-range interaction from our derivation while the higher order non-spherical, $l \neq 0$, terms can be seen to be short-range in nature and equivalent to the non-local exchange correlation potentials. From the derived short-range potentials, the multipole polarizabilities and the cut-off parameters can be explicitly determined.

The derived potential is consequently used in a B-spline code to solve the Schrödinger equation for helium atom numerically. The Schrödinger equation is also solved analytically using Eqs. (20) and (26), within the spherical approximation of the electron–electron interaction, to elucidate the effects of the short-range terms of the potential.

The quality of the energy eigenvalues obtained using the lowest-order $V_{0,0}^0(r)$ potential given by Eq. (16), the multipole-order $V_h(r)$ potential given by Eq. (17), as well as the multipole-order potential with finite nuclear mass correction $V_{fnm}(r)$ of the Hamiltonian given by Eq. (22) are tested.

Table 1 shows our non-relativistic energy results (in hartrees) for the lowest-order potential ($V_{0,0}^0$), the lowest- plus higher-order multipole potential (V_h), and the lowest- plus higher-order multipole potential with finite nuclear mass corrections (V_{fnm}) in comparison with analytical results (V_0), values obtained using a central potential (V_{cen}), and some literature values [26]. The results correspond to the states $1snl$, where n takes the values of the lowest five principal quantum numbers in ascending order, for each total orbital angular momentum quantum number L. It can be observed that our lowest-order ($V_{0,0}^0$) results are lower but comparable to the literature values for all the energy eigenvalues shown in the table. This is contrary to Hartree–Fock approximation which yields an upper limit in the energy eigenvalues.

The addition of the higher-order terms of the multipole potential leads to a good agreement of our V_h groundstate results with the literature value. The calculated groundstate energy eigenvalue shows some significant difference when the local ($l = 0$) higher-order multipole potential V_h corrections are included. The present calculated groundstate energy eigenvalue -2.904222848 can be hypothesized to be the infinite nuclear mass non-relativistic limit of the groundstate energy eigenvalue for helium atom within the mean-field approximation employed in this

work. It is important to note that, from the selection rule imposed in the derived potential, the spherically symmetric states are only affected by the spherically symmetric multipole potential.

Non-spherical states, on the other hand, can benefit from both the spherical and non-spherical multipole potential provided that $l \leq l_i$ and $m \leq m_i$, where l and m are the orbital angular momentum and the projection quantum numbers of the multipole operator while l_i and m_i are the orbital angular momentum and the projection quantum numbers of the screened atomic electron respectively. The difference between our calculated value and the expected groundstate energy may be attributed to the relativistic effects. Indeed if the finite nuclear mass corrections are included, we get $-2.903827\,E_h$. Besides the s and p states, our results with the finite nuclear mass corrections included tends to be higher than the experimental and other literature data. We recognize that the finite nuclear mass corrections are in the same order of magnitude with other relativistic interactions and should therefore treated together. The effects of relativistic and other higher order interactions shall be probed further in our subsequent works.

The significant difference between our V_h results, with the higher multipole-order terms included and without the finite nuclear mass correction, and the reference values stems majorly from $L = 0$ states. Our calculated energies for the $L = 0$ states are significantly lower than the corresponding literature data. Our calculated energies for the $L = 1$ and $L = 7$ states are also slightly lower than the reference data. However, for $2 \leq L \leq 5$ states, our calculated values are slightly higher than the literature values. We get the best agreement with literature values for $L = 6$ states. We can attribute the discrepancy in results to the derived symmetry-dependent all-electron potential method used in this work. To validate the accuracy of the numerical results and to test the effects of the non-local interactions, we included the analytically calculated infinite nuclear mass (V_0) results in Table 1. The analytical calculations are evaluated using Eq. (26) and with the values of the effective nuclear charge given by Table 2.

The analytical results are only feasible within the spherical approximation ($l = 0$) of the multipole expansion series. The numerically calculated (V_h) values, on the other hand, have been obtained without the spherical approximation and with an expansion of angular momentum in the range $0 \leq l \leq 4$ in the multipole series for converged results. Using the analytical results, one can determine the influence of the non-local short-range potentials in the calculated energy eigenvalues.

Except for the $2p$ and $4f$ states where the non-local interactions are relatively significant, it can be seen that the disparity between local and non-local terms in the calculated results in Table 1 manifests at the fourth decimal place for low-lying states for each non-spherical symmetry. Their significance decays as the principal quantum number increases. Within the non-relativistic limit, these non-local short-range potentials can be neglected. The derived potential can consequently be reasonably approximated by the spherically symmetric terms of the electron–electron interactions only, unless one is interested in probing the effects of the non-local short-range interactions further. This has the additional advantage that the Schrödinger equation for helium atom can be evaluated fully analytically, using the suggested symmetry-dependent potential, within the spherical approximation as can be seen in Table 1 results. However, the role of the short-range potentials may still be important especially in removing the energy degeneracy of the d and g states with the same principal quantum number as can be observed in the table.

From the results obtained, it can also be seen that the effect of the higher-order terms of the multipole potential is more significant for the groundstate eigenvalue, and less significant for the excited states. The effect of the finite nuclear mass correction leads to be better description of the groundstate. It, however, distorts the agreement between our results and the literature values for $L \geq 2$ singly excited states.

In attempting to investigate further the disparity between our symmetry dependent all-electron potential results and the reference values, we included calculations generated by an improved central potential,

Table 1

Some energy eigenvalues (in E_{h}) for the states of helium atom, five lowest principal quantum numbers for each symmetry L, calculated using the derived non-relativistic lowest-order ($V_{0,0}^0$) interaction, lowest- plus higher-order (V_h) interactions, and the lowest- plus higher-order interactions with finite nuclear mass correction (V_{fnm}). The calculations have been done with the projection quantum number $m_\alpha = 0$ for each of the orbitals. The results are compared with our analytically (V_0) calculated values within the spherical approximation using Eq. (26), with the values calculated using a central potential (V_{cen}) expressed in Eq. (27), and with the non-relativistic reference values for helium atom [26].

State	$V_{0,0}^0$	V_h	V_{fnm}	V_0	V_{cen}	Ref.
$L = 0$	−2.91031	−2.90422	−2.90382	−2.90422	−2.90357	−2.90372
	−2.18189	−2.18151	−2.18121	−2.18151	−2.14661	−2.14597
	−2.08084	−2.08067	−2.08038	−2.08038	−2.06151	−2.06127
	−2.04547	−2.04537	−2.04510	−2.04537	−2.03367	−2.03358
	−2.02910	−2.02904	−2.02876	−2.02120	−2.02151	
$L = 1$	−2.13481	−2.13367	−2.13338	−2.13441	−2.12691	−2.12384
	−2.05991	−2.05950	−2.05922	−2.05973	−2.05605	−2.05514
	−2.03370	−2.03350	−2.03322	−2.03360	−2.03143	−2.03106
	−2.02156	−2.02145	−2.02117	−2.02150	−2.02008	−2.01991
	−2.01497	−2.01490	−2.01463	−2.01493	−0.01392	
$L = 2$	−2.05555	−2.05506	−2.05478	−2.05537	−2.05552	−2.05562
	−2.03124	−2.03100	−2.03073	−2.03115	−2.03121	−2.03127
	−2.01999	−2.01986	−2.01958	−2.01993	−2.01996	−2.02001
	−2.013888	−2.01380	−2.01352	−2.01384	−2.01386	−2.01389
	−2.01020	−2.01014	−2.00986	−2.01017	−2.01018	
$L = 3$	−2.03110	−2.03081	−2.03054	−2.03101	−2.03117	−2.03125
	−2.01991	−2.01974	−2.01946	−2.01984	−2.01994	−2.02000
	−2.01382	−2.01372	−2.01344	−2.01378	−2.01385	−2.01389
	−2.01015	−2.01008	−2.00981	−2.01012	−2.01017	−2.01020
	−2.00777	−2.00772	−2.00745	−2.00775	−2.00779	
$L = 4$	−2.01999	−2.01980	−2.01953	−2.01993	−2.01994	−2.02000
	−2.01388	−2.01376	−2.01349	−2.01384	−2.01384	−2.01388
	−2.01020	−2.01012	−2.00984	−2.01017	−2.01017	−2.01020
	−2.00781	−2.00775	−2.00748	−2.00778	−2.00778	
	−2.00617	−2.00612	−2.00585	−2.00615	−2.00615	
$L = 5$	−2.01396	−2.01382	−2.01355	−2.01392	−2.01384	−2.01388
	−2.01026	−2.01016	−2.00989	−2.01022	−2.01017	−2.01020
	−2.00785	−2.00778	−2.00751	−2.00783	−2.00778	−2.00781
	−2.00620	−2.00615	−2.00588	−2.00618	−2.00615	
	−2.00502	−2.00499	−2.00471	−2.00501	−2.00498	
$L = 6$	−2.01031	−2.01019	−2.00992	−2.01028	−2.01017	−2.01020
	−2.00789	−2.00782	−2.00754	−2.00787	−2.00778	−2.00781
	−2.00624	−2.00617	−2.00590	−2.00622	−2.00615	−2.00617
	−2.00505	−2.00500	−2.00473	−2.00503	−2.00498	
	−2.00417	−2.00414	−2.00386	−2.00416	−2.00411	
$L = 7$	−2.00793	−2.00783	−2.00756	−2.00791	−2.00778	−2.00781
	−2.00626	−2.00621	−2.00594	−2.00625	−2.00615	−2.00617
	−2.00507	−2.00506	−2.00479	−2.00506	−2.00498	−2.00499
	−2.00419	−2.00418	−2.00391	−2.00418	−2.00411	
	−2.00360	−2.00350	−2.00323	−2.00351	−2.00346	

given by Eq. (27), derived using the classical radially dependent partitioning fractions [22,23]. The central potential results have been evaluated within the infinite nuclear mass approximation, but including higher spherically symmetric multipole interactions using the mean-field approximation, $\langle \bar{j}_0 \rangle$. The expectation value given by Eq. (29) is presented for the first time in this work. With the new expectation value, we find better agreement between our present central potential (V_{cen}) results and the reference values. The difference between our analytical (V_0) and central potential (V_{cen}) interactions stems from the use of the symmetry-dependent and radially dependent partitioning fractions respectively. The difference in the interactions is significantly manifested in Table 1 results, with the symmetry-dependent results closely predicting the triplet results while the radially-dependent results closely predicting the singlet results for helium atom [27]. Also, the central potential results tend to have degenerate energy eigenvalues for states with the same principal quantum number for highly excited states. The symmetry-dependent potential, on the other hand, removes such degeneracies.

Table 2 presents the symmetry-dependent partitioning fractions (γ_{l_i}) and the spherically symmetric, radially independent, nuclear charge

Table 2

Symmetry-dependent partitioning fractions (γ_{l_i}), the corresponding spherically symmetric, radially independent, nuclear charge screening parameters (σ_{l_i}), and the effective screened nuclear charge, $Z_{\text{eff}} = Z - \sigma_{l_i}$, for helium atom calculated using Eqs. (7) and (20) respectively. The values are truncated to 6 d.p.

l_i	P.F. (γ_{l_i})	Scr. Par.(σ_{l_i})	Z_{eff}
0	0.500000	0.794964	1.205036
1	0.666667	0.963030	1.036970
2	0.707106	1.001591	0.998409
3	0.709492	1.002247	0.997753
4	0.707106	1.001591	0.998409
5	0.704118	0.998767	1.001233
6	0.701314	0.996115	1.003885
7	0.698837	0.993768	1.006232

screening parameters (σ_{l_i}) and effective screened nuclear charge ($Z_{\text{eff}} = Z - \sigma_{l_i}$) calculated using Eqs. (7) and (20) respectively.

From these calculations, it can be observed that the *s* states have the least nuclear charge shielding effect, followed by $l = 7$ states, while

the f states have the highest. It is also interesting to note that the d and g states have equivalent partitioning fractions and charge screening parameters. This implies that, in the absence of the non-spherical short-range potentials, the d and g states with the same principal quantum number are degenerate in the energy eigenvalue. The calculated nuclear charge screening parameters are consequently used in the analytical evaluation of the energy eigenvalues using Eqs. (20) and (26), within the spherical approximation of the electron–electron interaction. The nuclear shielding effect can explain why the $l = 0$ and the $l = 7$ states experience significantly lower energies than the reference values and the central potential calculations.

Conclusion

In this study, an alternative multipole expansion has been used to derive an analytical symmetry all-electron potential for helium atom. The success of this study lies on the demonstrated separability of the two-electron Hamiltonian employed in this work as well as in the choice of an empirically determined partitioning fraction. The local and non-local Coulomb potential terms obtained completely describe the non-relativistic single-electron interaction potential. The effect of the other electron in charge screening is also manifested in the derived potential. The non-local component of the analytical potential can be seen to be an effect of the higher-order non-spherical ($l \neq 0$) terms of the multipole expansion. Nuclear charge screening is determined from the derived analytical potential to be partly constant and partly varies as a decaying exponential function scaled by the radial distance to power l. Our results are in reasonable agreement with literature values. Indeed with and without the finite nuclear mass scaling correction, we obtain the groundstate energy of helium atom to be -2.90382769 and -2.90422284 respectively. It is important to note that the finite nuclear mass correction is in the same order of magnitude with the relativistic interactions like the spin–orbit coupling and the spin–spin coupling and should therefore be considered together for a complete treatment. With the suggested symmetry-dependent partitioning fractions, the influence of electron–electron interaction can be precisely determined within the framework of non-relativistic quantum mechanics. This is already evident in the relative accuracy of the calculated energy of helium atom in its groundstate. We have also shown that within the spherical approximation, the Schrödinger equation for helium atom can be solved analytically, just like the case for hydrogen-like systems. The use of a radially-dependent partitioning fraction, on the other hand, leads to a central potential which can also be made separable using additional mean-field approximations. The results generated using the central potential interaction are in better agreement, though, with the reference results for all orbitals. Using the central potential, we obtain the groundstate energy of -2.90357835. Resolving the influence of the nature of the partitioning fraction used in the separation of the electron–electron interaction in electronic structure calculations is a good candidate for further investigation.

The present symmetry-dependent method, besides accounting for the influence of the higher-order terms of the multipole potential in the non-relativistic states of helium atom, also yields the expected non-degeneracy of states even for the highly excited states. The central potential method, on the other hand, closely predicts the non-relativistic results for helium atom evaluated with a Hylleraas-like potential and wavefunctions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is embedded in the article.

Acknowledgment

Appendix

A1

In this section, we show that the lowest-order term of the interaction potential, due to a single electron in a two-electron system, is separable in spatial coordinates. This is achieved by evaluating the lowest-order potential term subject to the optimization condition stated in Eq. (15). That is,

$$
\begin{aligned}
V_{0,0}^0(\vec{r}_i, \vec{r}_j) &= -\frac{Z}{r_i} + \gamma_{l_i} \frac{1}{\sqrt{r_i^2 + r_j^2}} \\
\frac{\partial V_0^0(\vec{r}_i, \vec{r}_j)}{\partial r_i} &= \frac{Z}{r_i^2} - \frac{1}{2} \gamma_{l_i} \frac{2r_i}{(r_i^2 + r_j^2)^{\frac{3}{2}}} = 0 \\
\frac{1}{(r_i^2 + r_j^2)^{\frac{3}{2}}} &= \frac{Z}{\gamma_{l_i} r_i^3} \\
\frac{1}{(r_i^2 + r_j^2)^{\frac{1}{2}}} &= \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}
\end{aligned}
\tag{30}
$$

$$
V_{0,0}^0(\vec{r}_i, \vec{r}_j) = -\frac{Z}{r_i} + \gamma_{l_i} \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}.
$$

Likewise,

$$
\begin{aligned}
V_{l,m}^{k>0}(\vec{r}_i, \vec{r}_j) &= 4\pi \gamma_{l_i} \beta_l^k \frac{r_i^k r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}} Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j) \\
&= 4\pi \gamma_{l_i} \beta_l^k \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i} \left(\frac{r_i r_j}{r_i^2 + r_j^2} \right)^k Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j).
\end{aligned}
\tag{31}
$$

A2

In this section, we describe the method employed in Eq. (18) to evaluate the expectation value of both local ($l = 0$) and non-local exchange integral ($l \neq 0$)

Making use of the root mean value,

$$
t_{av} = \left\langle \frac{r_i r_j}{r_i^2 + r_j^2} \right\rangle \approx \frac{1}{4\pi\sqrt{2}},
\tag{32}
$$

approximated by determining the squareroot of the peak value ($r_i = r_j$) per solid angle, Eq. (31) implies that

$$
\langle V_{l,m}^{k>0}(\vec{r}_i, \vec{r}_j) \rangle = 4\pi \gamma_{l_i} \beta_l^k \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i} \left(\frac{1}{4\pi\sqrt{2}} \right)^k Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j).
\tag{33}
$$

Summing over index k, the mean multipole interaction potential can be expressed as

$$
V_0(\vec{r}_i, \vec{r}_j) = -\frac{Z}{r_i} + \gamma_{l_i} \tilde{j}_0(t) \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}
\tag{34}
$$

$$
V_l(\vec{r}_i, \vec{r}_j) = 4\pi \gamma_{l_i} \tilde{j}_l(t) \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i} \sum_{m=-l}^{+l} Y_l^{m*}(\hat{r}_i) Y_l^m(\hat{r}_j)
$$

Table 3
Mean values of the first few spherical Bessel-like functions, $\langle \tilde{j}_l(t) \rangle$, evaluated using Eqs. (32) and (35).

$\langle \tilde{j}_l(t) \rangle$	Mean value
$\tilde{j}_0(t_{av})$	1.001591982×10^0
$\tilde{j}_1(t_{av})$	$2.822460800 \times 10^{-2}$
$\tilde{j}_2(t_{av})$	$7.966284926 \times 10^{-4}$
$\tilde{j}_3(t_{av})$	$2.997936894 \times 10^{-5}$
$\tilde{j}_4(t_{av})$	$1.269233885 \times 10^{-6}$
$\tilde{j}_5(t_{av})$	$5.208375019 \times 10^{-8}$
$\tilde{j}_6(t_{av})$	$2.486752189 \times 10^{-9}$
$\tilde{j}_7(t_{av})$	$1.216089476 \times 10^{-10}$

where the spherical Bessel-like function, written as

$$\tilde{j}_l(t) = t^l \sum_{k=0,2,\ldots}^{\infty} \frac{(2l+2k-1)!!}{k!!(2l+k+1)!!} t^k, \tag{35}$$

is evaluated using the mean value of t given in Eq. (32). Table 3 shows the first few mean values of the spherical Bessel-like functions, $\langle \tilde{j}_l(t) \rangle$, evaluated using Eqs. (32) and (35).

From the treatment of the electron–electron interaction, the multipole potential terms,

$$
\begin{aligned}
V_l^m(r_i) &= 4\pi\, \gamma_{l_i}\, A_l^m \langle \tilde{j}_l(t) \rangle\, \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}\, \frac{R_{n_j,l_j}}{R_{n_i,l_i}} \left(R_{n_i,l_i}(r_j) | R_{n_j,l_j}(r_j) \right) \\
&= 4\pi\, \gamma_{l_i}\, A_l^m \langle \tilde{j}_l(t) \rangle\, \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i}\, | N_{n_j,l_j} |^2\, \frac{r_i^{l_j}}{r_i^{l_i}} \exp\left[-\left(\frac{l_i - l_j}{(l_i+1)(l_j+1)} \right) Z r_i \right] \\
&\quad \times \int_0^\infty r_j^{2+l_i+l_j} \exp\left[-\left(\frac{2+l_i+l_j}{(l_i+1)(l_j+1)} \right) Z r_j \right] \mathrm{d}r_j\, \delta_{l_i,l_j+l}\delta_{m_i,m_j+m} \\
&= 4\pi\, \gamma_{l_i}\, A_l^m \langle \tilde{j}_l(t) \rangle\, \frac{\sqrt[3]{\frac{Z}{\gamma_{l_i}}}}{r_i^{l+1}}\, | N_{n_j,l_j} |^2 \exp\left[-\left(\frac{l}{(l_i+1)(l_i-l+1)} \right) Z r_i \right] \\
&\quad \times \frac{(2l_i-l+2)!\, \left[(l_i+1)(l_i-l+1) \right]^{(2l_i-l+3)}}{\left[(2l_i-l+2)Z \right]^{(2l_i-l+3)}}\, \delta_{l_i,l_j+l}\delta_{m_i,m_j+m},
\end{aligned}
\tag{36}
$$

emanating from the inner integral of the double integration (in space coordinates) are evaluated using the Laplace transform method and hydrogenic radial wavefunctions,

$$R_{n'l'}(r) = N_{n',l'}\, r^{l'} \exp\left(-\frac{Zr}{l'+1} \right), \tag{37}$$

as our trial functions, where $N_{n',l'}$ are the normalization factors and $n' = l' + 1$ is the principal quantum number. In Eq. (36), we have imposed the conditions $l_i = l_j + l$ and $m_i = m_j + m$ in the triangular relations of the angular momentum algebra. The angular factor A_l^m arises from the angular integral and can be evaluated with the help of the Wigner-$3j$ symbols as

$$
\begin{aligned}
A_l^m &= \int Y_{l_j}^{m_j} Y_l^{m*} Y_{l_i}^{m_i}\, \mathrm{d}\Omega_i \times \int Y_{l_i}^{m_i} Y_l^m Y_{l_j}^{m_j}\, \mathrm{d}\Omega_j \\
&= (-1)^m \frac{(2l_i+1)(2l+1)(2l_j+1)}{4\pi} \begin{pmatrix} l_i & l & l_j \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_i & l & l_j \\ m_i & m & m_j \end{pmatrix}^2.
\end{aligned}
\tag{38}
$$

In principle, the triangular relations allow $l_i = l_j \pm l$ but the inclusion of $l_i = l_j - l$ leads to divergences in the Hamiltonian. This can be explained that the exchange of quantum numbers between the electrons is mediated by the operator and can go only in one direction such that $l_i = l_j + l$.

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