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Symmetry Dependent Analytical Pseudopotential for Helium Atom

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May 28, 2020

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 pseudopotential for helium atom derived using the alternative multipole expansion, a variational technique, and the mean-field theory. We have calculated the non-relativistic groundstate energy for helium atom to be -2.9059 . The suggested pseudopotential 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 pseudopotential emanates from the higher-order terms of the multipole series expansion. The higher-order multipole interactions are fully included via the exchange correlation processes where the operator exchanges angular momentum with the atom. With the derived potential, we can claim that an analytical solution to helium atom has been found. Our results are in reasonable agreement with literature values.

1 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. The electron-nuclei interaction is usually much simpler to deal with because they are separable in spatial coordinates. The electron-electron interactions on the other hand are quite challenging to deal with because of the electronic correlations. 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 already been made in developing techniques to deal 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 also quite accurate depending on the size and quality of configurations included but it is also 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]. Pseudopotential method 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 [12].

A pseudopotential can 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 [13]. Hellmann [14] subsequently developed a pseudopotential model for atoms which has been extensively used in atomic scattering [15]. 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.

In this study, a symmetry-dependent pseudopotential for helium atom of the form

$$V(r) = -\frac{Z^{dir} + Z_h^{xc}(r)\delta_{l_i}}{r} \quad (1)$$

, with the lowest-order effective nuclear charge Z^{dir} and a higher-order multipole correction Z_h^{xc} , is derived using our alternative multipole expansion [16–20], a variational technique, and a mean-field theory. The higher-order multipole potential accounts for the exchange correlation effects which includes the separation into singlet and triplet states. In equation (1), l and l_i correspond to the orbital angular momentum quantum numbers of the operator and the i^{th} -electron respectively. The analytical separation of spatial coordinates is exact without any inherent approximations involved. The Schrödinger equation for helium atom is solved using the derived pseudopotential in this study and the results compared with literature values.

2 Theory

In our previous manuscripts [16–20], we formulated the alternative multipole expansion of the Coulomb repulsion term

$$\begin{aligned} \frac{1}{|\vec{r}_i - \vec{r}_j|} &= (r_i^2 - 2r_i r_j x + r_j^2)^{-1/2} \\ &= \frac{4\pi}{\sqrt{r_i^2 + r_j^2}} \sum_l \tilde{j}_l(r_i, r_j) Y_l^{m*}(\hat{r}_i) Y_l^{m*}(\hat{r}_j) \end{aligned} \quad (2)$$

where

$$\tilde{j}_l(r_i, r_j) = \sum_{k=l, l+2, \dots} \frac{(2k-1)!!}{(k-l)!! (k+l+1)!!} \left(\frac{r_i r_j}{r_i^2 + r_j^2} \right)^k \quad (3)$$

is a spherical Bessel-like function. We use this expansion to express the single-electron interaction potential for a two-electron system as

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

where

$$\gamma_{l_i} = \frac{1 + \sqrt[l_i]{l_i}}{2 + \sqrt[l_i]{l_i} + \delta_2} \quad (5)$$

is a general symmetry-dependent partition function [17–19] representing the fraction of the electron-electron interaction energy belonging to i^{th} -electron. The parameters in equation (5) are determined to be

$$\begin{aligned} \delta_1 &= \left(n - \frac{1}{2}\right) \times \left(l_i + \frac{1}{2}\right) \\ \delta_2 &= \frac{l_v}{2^{(2l_v-1)}} \end{aligned} \quad (6)$$

with n representing the number of electrons in the atom and l_v representing the orbital angular momentum of the valent electron in case of a many-electron system. For helium atom, $n = 2$ and $l_v = 0$. The symmetry-dependent partition function was obtained by empirical analysis of the calculated eigenvalues relative to experimental results. It has been further improved by observing the convergence pattern of the non-local part of the potential. The single-electron interaction potential can then be rewritten in multipole moments as

$$V(r_i, r_j) = \sum_{l,m,k} V_{l,m}^k(\vec{r}_i, \vec{r}_j) \quad (7)$$

with

$$V_{0,0}^0(\vec{r}_i, \vec{r}_j) = -\frac{Z}{r_i} + \gamma_{l_i} \frac{1}{\sqrt{r_i^2 + r_j^2}} \quad (8)$$

as the leading-order term of the multipole potential and

$$V_{l,m}^k(\vec{r}_i, \vec{r}_j) = 4\pi \gamma_{li} \beta_l^k \frac{r_i^k r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}} Y_l^{m*}(\hat{r}_i) Y_l^{m*}(\hat{r}_j) \quad (9)$$

for higher-order terms of the interaction potential with β_l^k representing the coefficients in the summation in equation (3). Subjecting the multipole potential moments $V_{l,m}^k$ to the minimization condition

$$\frac{\partial V_{l,m}^k}{\partial r_i} = 0 \quad (10)$$

leads to the potential terms

$$V_{0,0}^0(\vec{r}_i) = -\frac{Z}{r_i} + \gamma_{li} \frac{\sqrt[3]{\frac{Z}{\gamma_{li}}}}{r_i} \quad (11)$$

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

, as shown in appendix A1 with the spatial coordinates completely separated. We utilize the separation of coordinates and the mean-field theory (in appendix A2)

$$V_{l,m}^k(\vec{r}_i) = 4\pi \gamma_{li} \left(\frac{k}{(2k+1)} \right)^{k+\frac{1}{2}} \frac{\beta_l^k}{r_i^{k+1}} Y_l^{m*}(\hat{r}_i) \langle r_j^k Y_l^{m*}(\hat{r}_j) \rangle \quad (12)$$

to evaluate the symmetry-dependent single-electron pseudopotential

$$V_0^0(\vec{r}_i) = -\frac{\left(Z - \gamma_{li} \sqrt[3]{\frac{Z}{\gamma_{li}}} \right)}{r_i} \quad (13)$$

$$V_l^k(\vec{r}_i) = \frac{\tilde{\beta}_l^k(Z)}{r_i^{k+1}} \delta_{ll_i}$$

for the two-electron system with the coefficient

$$\tilde{\beta}_l^k(Z) = \gamma_{li} \frac{(2k-1)!!}{(k-l)!!(l+k+1)!!} \left(\frac{k}{2k+1} \right)^{k+\frac{1}{2}} \left[\frac{(l+1)}{(l+2)Z} \right]^{l+k+3} \quad (14)$$

when the corresponding double integral for the correlated two-electron is solved. Slater-type orbitals with angular momentum quantum number l and principal quantum number $k+1$ have been used in equation (13) as the trial wavefunctions. The higher-order multipole potentials $V_l^k(\vec{r}_i)$ can be added perturbatively to increase the accuracy of the single-potential.

The summation of the higher order potentials in equation (13) simplify to a fully analytical single-electron potential function

$$V(r_i) = -\frac{Z^{dir} + Z_h^{xc}(r_i)\delta_{ll_i}}{r_i} \quad (15)$$

where

$$Z^{dir} = Z - \gamma_{li} \sqrt[3]{\frac{Z}{\gamma_{li}}} \quad (16)$$

$$Z_h^{xc}(r_i) = \gamma_{li} \left[\gamma_{li} \frac{(l+1)}{(l+2)Z} \right]^{(l+3)} \cos \left[\gamma_{li} \frac{(l+1)}{(l+2)Zr} \right]$$

are the parameters for the two-component function.

One can see that our derived potential has a local Coulomb potential part and a non-local component that scales with radial distance (r) from the nuclear coordinate via a cosine function. The charge screening parameter, if all the non-relativistic interaction are included, can be seen to be partly constant and partly varies as a cosine function of the scaled radial distance.

3 Results

An ab initio analytical pseudopotential for two-electron atoms or ions free from any fitting parameters is presented in equation (15). This pseudopotential is consequently used in a B-spline code to solve the Schrödinger equation for helium atom. The quality of the energy eigenvalues obtained using the leading-order $V_0^0(r)$ as well as the multipole-order $V_h(r)$ pseudopotential are tested.

Table 1 shows our non-relativistic results for the leading-order and the higher multipole-order pseudopotential in comparison with literature values. It can be observed that our 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 significant differences between our results and the reference values stem majorly from s states. Our calculated s states are significantly lower than the corresponding literature data. One can observe that $2s$ singlet state has the largest deviation (≈ 0.0356 au). This deviation reduces as the principal and orbital angular momentum quantum numbers increase. For example, the deviation is ≈ 0.009 au for $2p$ singlet state and ≈ 0.003 au for $3d$ singlet state. In general, the deviations for triplet states are less than corresponding deviations for spherically symmetric singlet states with the groundstate yielding the least deviation for the first five principal quantum numbers of the s states shown in the table. For non-spherical states, the deviations from triplet states are higher than the singlet states. Table 2 gives a summary of deviations for the first four angular momenta states. We can attribute the difference in results to the alternative multipole expansion method used in our case which treats the non-relativistic interactions exactly without any approximation. The calculated ground state energy eigenvalue shows some significant difference when the non-local higher-order multipole potential V_h^{corr} corrections are included. The non-local potential enables the resolution of both singlet and triplet states and consequently the correlation energy for each case. The present calculated groundstate energy eigenvalue -2.9059 can be considered as the non-relativistic limit of the groundstate energy eigenvalue for helium atom, given the exact nature of our alternative multipole expansion. The difference between our calculated value and the expected groundstate energy -2.9037 may be attributed to relativistic effects. In deed if the spin-spin interaction and the finite mass corrections are included, we get -2.9040 which is quite close to the expected groundstate energy of -2.9037 . We intend to probe relativistic effects further in our subsequent work.

The present method, besides resolving the influence of the exchange potential in revealing the singlet and triplet states within the framework of non-relativistic quantum mechanics, also yields the expected degeneracy of states even for highly excited states.

State	V_0^0	$V_h^{trip.}$	$V_h^{sing.}$	Trip.	Sing.	Ref.
$L = 0$	-2.91031	-	-2.90597	-	-2.90394	-2.90372
	-2.18189	-2.18217	-2.18161	-2.17528	-2.14601	-2.14597
	-2.08084	-2.08096	-2.08071	-2.06871	-2.06128	-2.06127
	-2.04547	-2.04554	-2.04540	-2.03652	-2.03359	-2.03358
	-2.02910	-2.02914	-2.02905	-2.02262	-2.02118	
$L = 1$	-2.13481	-2.13670	-2.13292	-2.13320	-2.12387	-2.12384
	-2.05991	-2.06076	-2.05907	-2.05809	-2.05516	-2.05514
	-2.03370	-2.03417	-2.03323	-2.03233	-2.03107	-2.03106
	-2.02156	-2.02187	-2.02126	-2.02055	-2.01991	-2.01991
	-2.01497	-2.01519	-2.01476	-2.01421	-2.01383	
$L = 2$	-2.05760	-2.05894	-2.05627	-2.05565	-2.05563	-2.05562
	-2.03240	-2.03315	-2.03165	-2.03129	-2.03128	-2.03127
	-2.02073	-2.02122	-2.02026	-2.02002	-2.02002	-2.02001
	-2.01440	-2.01473	-2.01406	-2.01390	-2.01390	-2.01389
	-2.01058	-2.01082	-2.01033	-2.01021	-2.01021	
$L = 3$	-2.03223	-2.03316	-2.03131	-2.03126	-2.03126	-2.03125
	-2.02062	-2.02122	-2.02004	-2.02000	-2.02000	-2.02000
	-2.01432	-2.01473	-2.01391	-2.01389	-2.01389	-2.01389
	-2.01052	-2.01082	-2.01022	-2.01020	-2.01020	-2.01020
	-2.00805	-2.00829	-2.00782	-2.00781	-2.00781	
$L = 4$	-2.02064	-2.02131	-2.01998	-2.02000	-2.02000	-2.02000
	-2.01433	-2.01480	-2.01387	-2.01389	-2.01389	-2.01388
	-2.01053	-2.01087	-2.01019	-2.01020	-2.01020	-2.01020
	-2.00806	-2.00832	-2.00780	-2.00781	-2.00781	
	-2.00637	-2.00657	-2.00616	-2.00617	-2.00617	
$L = 5$	-2.01436	-2.01487	-2.01387	-2.01389	-2.01389	-2.01388
	-2.01055	-2.01092	-2.01019	-2.01020	-2.01020	-2.01020
	-2.00808	-2.00836	-2.00780	-2.00781	-2.00781	-2.00781
	-2.00638	-2.00661	-2.00616	-2.00617	-2.00617	
	-2.00517	-2.00535	-2.00499	-2.00500	-2.00500	
$L = 6$	-2.01058	-2.01097	-2.01019	-2.01020	-2.01020	-2.01020
	-2.00810	-2.00840	-2.00780	-2.00781	-2.00781	-2.00781
	-2.00640	-2.00663	-2.00616	-2.00617	-2.00617	-2.00617
	-2.00518	-2.00537	-2.00499	-2.00500	-2.00500	
	-2.00428	-2.00444	-2.00412			
$L = 7$	-2.00812	-2.00843	-2.00781	-2.00781	-2.00781	-2.00781
	-2.00641	-2.00666	-2.00617	-2.00617	-2.00617	-2.00617
	-2.00519	-2.00539	-2.00500	-2.00500	-2.00500	-2.00499
	-2.00429	-2.00446	-2.00413			
	-2.00360	-2.00374	-2.00347			

Table 1: Some energy eigenvalues corresponding to non-relativistic (V_0^0), singlet ($V_h^{sing.}$) and triplet ($V_h^{trip.}$) states of helium atom are numerically calculated using the derived potential. The results are compared with the experimentally determined triplet and singlet values [21] and the non-relativistic reference values for helium atom [22].

State	Dev.(Trip)	Dev.(sing)	State	Dev.(Trip)	Dev.(Sing)
$L = 0$	-	0.00203	$L = 2$	0.00329	0.00064
	0.00689	0.03560		0.00186	0.00037
	0.01225	0.01943		0.00120	0.00024
	0.00902	0.01181		0.00083	0.00016
	0.00652	0.00787		0.00061	0.00012
$L = 1$	0.00350	0.00905	$L = 3$	0.00190	0.00005
	0.00267	0.00391		0.00122	0.00004
	0.00084	0.00216		0.00084	0.00002
	0.00132	0.00135		0.00062	0.00002
	0.00098	0.0093		0.00048	0.00000

Table 2: Deviations in energy eigenvalues corresponding to our calculated singlet ($V_h^{sing.}$) and triplet ($V_h^{trip.}$) states of helium atom relative to the experimentally determined triplet and singlet values [21].

4 Conclusion

In this study, an alternative multipole expansion has been used to derive an analytical symmetry pseudopotential for helium atom. The success of this study lies on the demonstrated separability of the two-electron Hamiltonian using the the variational technique employed in this work as well as the choice of the partition function which has been determined intuitively and empirically. The local and non-local Coulomb potentials obtained describes the single-electron interaction potential. The effect of the other electron in charge screening is also manifested in the derived pseudopotential. The non-local component of the analytical pseudopotential can be seen to be an effect of the higher-order terms of the multipole expansion. Nuclear charge screening is determined from the derived analytical potential to be partly constant and partly varies as a cosine function of radial distance. With this method, the influence of electron correlation can be determined. Further investigation may need to focus on the effect of the relativistic corrections on the groundstate as well as the excited states as well as its extension to other many-electron systems.

5 Acknowledgement

We are grateful to Prof. C. Singh of Department of Physics, Kenyatta University and Prof. Dr. Alejandro Saenz of Institute of physics, Humboldt University-Berlin for useful discussions. We are also grateful for CIM GmbH for partial funding of the project.

A 1

In this section we show that the interaction potentials are separable in spatial coordinates by evaluating the potentials subject to the minimization condition stated in

equation (10).

$$\begin{aligned}
V_{0,0}^0(\vec{r}_i, \vec{r}_j) &= -\frac{Z}{r_i} + \gamma_{l_i} \frac{1}{\sqrt{r_i^2 + r_j^2}} \\
\frac{\partial V_{0,0}^0(\vec{r}_i, \vec{r}_j)}{\partial r_i} &= \frac{Z}{r_i^2} - \frac{1}{2} \gamma_{l_i} \frac{2r_i}{(r_i^2 + r_j^2)^{\frac{3}{2}}} = 0 \\
\frac{1}{(r_i^2 + r_j^2)^{\frac{3}{2}}} &= \frac{Z}{\gamma_{l_i} r_i^3} \\
\frac{1}{(r_i^2 + r_j^2)^{\frac{1}{2}}} &= \frac{\sqrt[3]{Z}}{\gamma_{l_i}} \\
V_{0,0}^0(\vec{r}_i, \vec{r}_j) &= -\frac{Z}{r_i} + \gamma_{l_i} \frac{\sqrt[3]{Z}}{r_i}
\end{aligned} \tag{17}$$

Likewise,

$$\begin{aligned}
V_{l,m}^{k>0}(\vec{r}_i, \vec{r}_j) &= 4\pi \gamma_{l_i} \beta_l^k \frac{r_i^k r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}} Y_l^{m*}(\hat{r}_i) Y_l^{m*}(\hat{r}_j) \\
\frac{\partial V_{l,m}^{k>0}(\vec{r}_i, \vec{r}_j)}{\partial r_i} &= 4\pi \gamma_{l_i} \beta_l^k Y_l^{m*}(\hat{r}_i) Y_l^{m*}(\hat{r}_j) \left[\frac{k r_i^{k-1} r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}} - \left(k + \frac{1}{2}\right) \frac{2r_i^{k+1} r_j^k}{(r_i^2 + r_j^2)^{k+\frac{3}{2}}} \right] = 0
\end{aligned} \tag{18}$$

Equation (18) implies that

$$\begin{aligned}
\frac{1}{(r_i^2 + r_j^2)} &= \frac{k}{(2k+1)r_i^2} \\
\left(\frac{1}{r_i^2 + r_j^2}\right)^{k+\frac{1}{2}} &= \left(\frac{k}{2k+1}\right)^{k+\frac{1}{2}} \frac{1}{r_i^{2k+1}} \\
\left(\frac{r_i^k r_j^k}{(r_i^2 + r_j^2)^{k+\frac{1}{2}}}\right) &= \left(\frac{k}{2k+1}\right)^{k+\frac{1}{2}} \frac{r_j^k}{r_i^{k+1}}
\end{aligned} \tag{19}$$

Hence

$$V_{l,m}^k(\vec{r}_i, \vec{r}_j) = 4\pi \gamma_{l_i} \beta_l^k \left(\frac{k}{2k+1}\right)^{k+\frac{1}{2}} \frac{r_j^k}{r_i^{k+1}} Y_l^{m*}(\hat{r}_i) Y_l^{m*}(\hat{r}_j) \tag{20}$$

A 2

In this section, we describe the mean-field theory employed in equation (12) to evaluate the expectation value

$$\begin{aligned}
\langle r_j^k Y_l^{m*}(\hat{r}_j) \rangle &= \langle \phi_{1s} | r_j^k Y_l^{m*}(\hat{r}_j) | \phi_{l+1,l} \rangle \\
&= \frac{1}{\sqrt{4\pi}} \int_0^\infty r_j^{2+l+k} \exp\left[-\left(\frac{l+2}{1+1}\right) Z r_j\right] dr_j \delta_{l_j} \\
&= \frac{1}{\sqrt{4\pi}} \frac{(l+k+2)! (k+1)^{(l+k+3)}}{[(k+2)Z]^{(l+k+3)}} \delta_{l_j}
\end{aligned} \tag{21}$$

using laplace transform method and Slater-type orbitals

$$R_{nl}(r) = r^l \exp\left(-\frac{Zr}{l+1}\right) \text{ and } R_{1s}(r) = \exp(-Zr) \quad (22)$$

as our trial wavefunctions. In our working, evaluating this expectation value proved to be the most challenging task. First, the choice of the trial wavefunctions is not trivial. Second, the alternative multipole expansion of the electron-electron interaction converges theoretically as expected from equations (4) and (5). In reality, after the separation of spatial coordinates, the potential diverges with numerical inclusion of higher-order multipole interactions. We therefore sought an analytical function as a limit of convergence of the expansion series.

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