Partitioning of the Electron-Electron Interaction

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Abstract Electron-electron correlation forms the basis of difficulties encountered in many-body problems. 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 classical partition function for the electron-electron correlation between two interacting states is proposed in this study. Using this partition function, a model potential for a two-electron system is derived. The model potential can accurately reproduce the singlet states of a singly excited neutral helium atom with one of its electrons frozen in the $1s$ orbital.

Keywords: electron-electron interaction, correlation energy, helium, partitioning, multipole expansion.

1 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 Hyleraas 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 development of the SAE 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. 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 non-relativistic Hamiltonian of a two-electron system with a nuclear charge Z is given by

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

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 interaction for the two-electron systems. The second and the last terms form the potential energy function of a bound two-electron system.

In our previous work [13], it was shown that the electron correlation interaction analytically simplifies to

$$\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \approx \frac{1}{\sqrt{r_i^2 + r_j^2}} \tag{2}$$

in the lowest-order alternative multipole expansion. In the independent particle approximation method, the potential function

$$V(r_i, r_j) = -\frac{Z}{r_i} + \frac{1}{2} \frac{1}{\sqrt{r_i^2 + r_j^2}} \tag{3}$$

for a two-electron system, using the mean field, can be completely separated [13] as

$$V(r_i) = -\frac{Z}{r_i} + \frac{1}{2} \frac{\sqrt[3]{2Z}}{r_i}. \tag{4}$$

Factor $1/2$ in equation (3) assumes an equal sharing of the correlation energy between the two interacting electrons. While this may be true if the interacting electrons occupy identical quantum states, the validity of the equal sharing assumption is lost for a pair of interacting electrons occupying different quantum states. In ref.[13], it can be seen that accurate groundstate energy of helium atom and reasonable eigenvalues of autoionizing levels of identical symmetry have been obtained using the equal partitioning of the correlation energy. On the other hand, singly excited states of helium atom with one electron frozen in the ground state is poorly represented by this partioning of the correlation energy.

In this work, a more appropriate energy sharing relation based on the geometry of the problem is proposed. This is used in generating a pseudopotential by separating the electron-electron interaction for a two-electron system within a mean-field approach. The pseudopotential is consequently used to determine the energy eigenvalues corresponding to various eigenstates that the electrons occupy.

2 Theory

From the physics of oscillations, it is known that the potential energy of a vibrating particle is proportional to the square of the amplitude of vibration. That is, $\epsilon = 1/2\, k\, r^2$, where k in this case is equivalent to a spring constant, and r is the vibration amplitude. The total potential energy for two interacting electrons would therefore be given by $\epsilon_{tot} = 1/2\, k\, [r_i^2 + r_j^2]$, if each of the electron is considered as an independent classically vibrating particle. It can be hypothesized that the electron-electron interaction energy between two electrons is shared in proportion to their corresponding non-interacting potential energies. That is, the electron-electron energy due to the ith electron is,

$$\delta E_i^{(\text{e-e})} = \frac{r_i^2}{r_i^2 + r_j^2} \delta E_{\text{tot}}^{(\text{e-e})} = \frac{r_i^2}{r_i^2 + r_j^2} \frac{1}{\sqrt{r_1^2 + r_2^2}} \tag{5}$$

where $\delta E_{\text{tot}}^{(e-e)}$ is the total electron-electron interaction energy as given in equation (2) and its prefactor is the classical partition function. The potential energy function for the ith electron in the independent particle approximation can then be expressed as

$$V(r_i, r_j) = -\frac{Z}{r_i} + \frac{r_i^2}{\left[r_i^2 + r_j^2\right]^{\frac{3}{2}}}. \tag{6}$$

Equation (6) if minimised with respect to r_i leads to

$$\frac{\partial V(r_i, r_j)}{\partial r_i} = \frac{Z}{r_i^2} + \frac{2\, r_i}{\left[r_i^2 + r_j^2\right]^{\frac{3}{2}}} - \frac{3\, r_i^3}{\left[r_i^2 + r_j^2\right]^{\frac{5}{2}}} = 0. \tag{7}$$

or

$$\frac{Z}{r_i^2} + \frac{2\, r_i\, r_j^2 - r_i^3}{\left[r_i^2 + r_j^2\right]^{\frac{5}{2}}} = 0, \tag{8}$$

as the condition for an extremum potential. Equation (8) can be reorganized further by reversing the sign of the coefficient of $r_i\, r_j^2$ and incrementing the coefficient of r_i^3 by 1. The reorganization introduces an inequality

$$\frac{Z}{r_i^2} - \frac{\left[2\, r_i\, r_j^2 + 2\, r_i^3\right]}{\left[r_i^2 + r_j^2\right]^{\frac{5}{2}}} \leq 0, \tag{9}$$

which ensures the potential is minimized while treating the co-ordinates r_i and r_j with an equal weighting. The equality condition in equation (9) guarantees a minimum potential. It is from this condition that the correlation term

$$\frac{1}{\sqrt{r_i^2 + r_j^2}} = \frac{1}{r_i} \left[\frac{Z}{2} \frac{r_i^2}{r_i^2 + r_j^2} \right]^{\frac{1}{5}} \tag{10}$$

is evaluated and equation (6) simplifies as

$$V(r_i, r_j) = -\frac{Z}{r_i} + \frac{[(Z/2) f(r_i, r_j)]^{\frac{3}{5}}}{r_i} \tag{11}$$

where the correlated two-dimensional function

$$f(r_i, r_j) = \frac{r_i^2}{r_i^2 + r_j^2} \tag{12}$$

is equivalent to the partition function already introduced in equation (5). With regards to SAE, the value of the function $f(r_i, r_j)^{\frac{3}{5}}$ in equation (11) cannot be evaluated exactly but can only be approximated by taking its expectation value relative to the some trial wavefunction of the jth electron. In our case, we have used the hydrogenic wavefunction of the $1s$ orbital as the trial wavefuction and the conditions $0 \leq r_j \leq r_i$ and $r_i \leq r_j \leq \infty$ in evaluating the expectation value of the function in terms of the radial co-ordinate r_i.

In our working, the expectation value of the correlated function, expressed in terms of one of the radial co-ordinate, is evaluated approximately as

$$\langle f(r_i, r_j)^{\frac{3}{5}} \rangle \approx 1 - \left[\frac{27}{25} + \frac{6}{5} Z r_i - \frac{6}{125 Z r_i} \right] \exp(-2Z r_i). \tag{13}$$

Appendix A shows the explicit method used in arriving at this expectation value. A further empirical and intuitive optimization of the expectation value given by equation (13) is employed to obtain

$$\langle f(r_i, r_j)^{\frac{3}{5}} \rangle \approx 1 - \alpha \left[1 + 3Z r_i \right] \exp(-2Z r_i) \tag{14}$$

with the parameter $\alpha = 0.46135$ set to include other significant corrections. The approximation in equation (14) if employed in the independent electron potential, defined in equation (11), is found to be of a better agreement with the experimental results for the singly excited helium atom as compared to equation (13). Substituting the expectation value obtained into equation (11) reduces the correlated problem into a single electron model potential

$$V(r_i) = -\frac{Z}{r_i} + \frac{[Z/2]^{\frac{3}{5}} \zeta(r_i)}{r_i} \tag{15}$$

with $\zeta(r_i)$ given by equations (13) or (14). With this potential, the SAE Hamiltonian

$$H(r_i) = \frac{p_i^2}{2} + V(r_i) \tag{16}$$

is defined. It is evident that the first term of the SAE potential defined in equation (15) is the electron-nuclear interaction, and the second term yields the screening potential of the active electron from the other electron. The eigenvalues of a two-electron system can then be evaluated as [13]

$$\langle E_{\alpha\alpha'} \rangle = \begin{cases} 4\,\varepsilon_\alpha & \text{if } \alpha = \alpha' \\ \varepsilon_\alpha + \varepsilon_{\alpha'} & \text{if } \alpha \neq \alpha' \end{cases} \tag{17}$$

where $\varepsilon_\alpha = \langle H(r_i) \rangle$ is the eigenvalue of a single electron eigenstate. Factor 4 in the above equation arises from both exchange and permutation symmetry 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 α, $\varepsilon_{\alpha'}$ is approximately equal to the core energy eigenvalue, $E_{\text{core}} = -2.00000$, for the helium ion in its ground state.

3   Results and Discussions

Table 1. Some numerically calculated eigenvalues using the present pseudopotentials versus the reference values for helium atom [5]. The H_1 and H_2 are the single-electron Hamiltonian with equations (13) and (14) as the distribution function used in the pseudopotential in equation (15) respectively. The results presented are truncated to 6 s.f.

State	H_1	H_2	Ref.
$L = 0$	-3.29443	-2.90367	-2.90372
	-2.15290	-2.14580	-2.14597
	-2.06325	-2.06136	-2.06127
	-2.03439	-2.03364	-2.03358
	-2.02158	-2.02120	
$L = 1$	-2.12631	-2.12617	-2.12384
	-2.05600	-2.05595	-2.05514
	-2.03144	-2.03142	-2.03106
	-2.02010	-2.02009	-2.01991
	-2.01394	-2.01394	
$L = 2$	-2.05555	-2.05555	-2.05562
	-2.03125	-2.03125	-2.03127
	-2.02000	-2.02000	-2.02001
	-2.01388	-2.01388	-2.01389
	-2.01020	-2.01020	
$L = 3$	-2.03125	-2.03125	-2.03125
	-2.02000	-2.02000	-2.02000
	-2.01388	-2.01388	-2.01389
	-2.01020	-2.01020	-2.01020
	-2.00781	-2.00781	
$L = 4$	-2.02000	-2.02000	-2.02000
	-2.01388	-2.01388	-2.01388
	-2.01020	-2.01020	-2.01020
	-2.00781	-2.00781	
	-2.00617	-2.00617	
$L = 5$	-2.01388	-2.01388	-2.01388
	-2.01020	-2.01020	-2.01020
	-2.00781	-2.00781	-2.00781
	-2.00617	-2.00617	
	-2.00500	-2.00499	
$L = 6$	-2.01020	-2.01020	-2.01020
	-2.00781	-2.00781	-2.00781
	-2.00617	-2.00617	-2.00617
	-2.00499	-2.00500	
	-2.00413	-2.00413	
$L = 7$	-2.00781	-2.00781	-2.00781
	-2.00617	-2.00617	-2.00617
	-2.00499	-2.00500	-2.00499
	-2.00413	-2.00413	
	-2.00347	-2.00347	

We have developed a single-electron pseudopotential for a two-electron system given by equation (15). The pseudopotential is used to calculate the $1snl$ eigenvalues for helium atom as shown in table 1 for angular momenta of up to $l_{\max} = 7$. In the table, we use the two alternative relations expressed in

equations (13) and (14) to evaluate the eigenvalues given by H_1 and H_2 respectively. 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, radius $r_{\max} = 200$, order $k = 10$, and a non-linear knot sequence is used.

The results generated with the model potentials presented are in good agreement with the references values [5] at larger values of n and l as expected. At these higher quantum numbers, the spatial extent of the orbitals is larger reducing the significance of the electron-electron interaction. In particular, one can see that for $l \geq 2$, the three sets of results are in good agreement with each other. The discrepancy between the set of results essentially manifest at lower values of n and l. The disparities are quite evident for $l = 0$ and $l = 1$ states presented. These lower angular momentum states usually provide the stringest test of accuracy for any model potential for helium atom.

As can be seen, the groundstate yields the largest deviation in the results. The H_1 interaction yields an unphysical tight binding potential to the groundstate helium atom. This emanates from the confinement introduced by the shortrange term $1/r^2$ in the correlation term. In the H_2 interaction, the shortrange confinement is removed. The eigenvalues generated using the model potential in H_2 are in good agreement with reference values.

The removal of the shortrange interaction in the SAE model potential in H_2 is motivated by its absence in the exactly separable symmetric term $V_{\alpha\alpha}$ as given in equation (4). The good agreement between the eigenvalues in the model potential of equation (14) and the reference results attests to the credibility of the method introduced in ref. [13] and advanced in this paper.

4 Conclusion

The exact partitioning of the electron-electron interaction energy between two electrons in different orbitals is tackled in this paper. A partition function which depends on the spatial extent of the interacting electrons in different states is suggested. In our working, we obtain a non-separable correlated function whose expectation value is approximated as a function of one of the radial coordinates. This leads to quasi-separability of the corrrelated term in the two-electron Hamiltonian. The partition function introduced and the consequently optimized single-electron pseudopotential developed in this work proves to be reasonably accurate in the calculated eigenvalues. The method can be extended further to treat a general n-electron system.

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Appendix A

The method through which the expectation value in equation (13) has been evaluated is shown in this appendix. The integral

$$
\begin{aligned}
\langle f(r_i, r_j)^{\frac{3}{5}} \rangle =& \langle \phi(r_j) | \left[\frac{r_j^2}{r_i^2 + r_j^2} \right]^{\frac{3}{5}} | \phi(r_j) \rangle \\
=& \int_0^{r_i} \mathrm{d}r_j \left[r_j^2 \, t^{\frac{6}{5}} \left(1 + t^2\right)^{-\frac{3}{5}} \right] \exp(-2Zr_j) \\
&+ \int_{r_i}^{\infty} \mathrm{d}r_j \left[r_j^2 \left(1 + t^2\right)^{-\frac{3}{5}} \right] \exp(-2Zr_j)
\end{aligned}
\tag{A.1}
$$

is evaluated in parts where we consider that $0 \leq r_j \leq r_i$, $r_i \leq r_j \leq \infty$, $t = r_</r_>$, $r_< = \min(r_i, r_j)$, and $r_> = \max(r_i, r_j)$. We have used the hydrogenic orbital $\phi(r_j) = \exp(-Zr_i)$ and a binomial expansion of

$$
(1 + t^2)^{-\frac{3}{5}} = \sum_{k=0}^{\infty} \binom{-3/5}{k} t^{2k}
\tag{A.2}
$$

to evaluate this expectation value assuming that one of the electrons is localized inside the ground state ionic core. Equation (A.1) together with the series in equation (A.2) yield an integral that cannot be evaluated exactly. In our case, only $k = 0$ and $k = 1$ are used for estimation. It is important to note that the expectation value in this case provides a dynamic mean-field contribution of the correlated term to the active electron.