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REGULAR ARTICLE

Average inner and outer radii in singly-excited 1*snl* states of the He atom

Hisashi Matsuyama · Toshikatsu Koga

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Abstract Average inner $< r_< >$ and outer $< r_> >$ radii are studied for 28 singly-excited 1 *snl* singlet and triplet states ($0 \leq l < n \leq 5$) of the He atom. In all the cases, the average inner radius $< r_< >$ is close to 0.75 bohr, which indicates that one of the two electrons behaves like the 1*s* electron in He^+. On the other hand, an analysis of the average outer radius $< r_> >$ shows that the other electron of the 1*snl* states behaves approximately like an *nl* electron in the hydrogen atom. The average outer radius $< r_> >$ reflects more diffuse character of the singlet electron distribution.

Keywords Inner radius · Outer radius · Singly excited states · He atom

1 Introduction

The helium atom in its ground $1s^2$ and singly excited 1*snl* states has been (see, e.g., [1]) a subject of extensive studies for two reasons, where *n* and *l* are the principal and azimuthal quantum numbers, respectively. The first reason is that these constitute simple targets to test a new idea or a method for the description of the electronic structure. The second reason is that they are the starting point to examine the correlation between electrons. The singly excited 1*snl* states are experimentally observed [2–6] in an electron-transfer collision process of the He^+ cation with an alkali atom, and their physical and chemical properties have been theoretically studied from various viewpoints such as Hund rules [7–11], Coulomb holes [12–14], correlation coefficients [15–17], and intracule densities [18–21].

For the ground-state He atom, the one-electron radial density $D(r)$ is (see, e.g., [22]) a compact unimodal function, where r is the distance of an electron from the nucleus. Accordingly, the average electron radius $< r >$ is a good representative of the distribution $D(r)$. For the singly excited states, however, $D(r)$ is (see, e.g., [22]) a multimodal function and hence $< r >$ dose not provide (see, e.g., [7]) us with useful information about the characteristics of $D(r)$. In these cases, we need alternative physical quantities, instead of $< r >$, to characterize the electron density distribution.

The average inner $< r_< >$ and outer $< r_> >$ radii have been recently proposed [23,24] to clarify the characteristics of the distribution of electrons with different motions. For 102 ground-state atoms, the average inner $< r_< >$ and outer $< r_> >$ radii have been reported [23] in the Hartree–Fock (HF) approximation. The radius $< r_< >$ decreases gradually as atomic number increases. In contrast, $< r_> >$ shows a clear periodical structure reflecting the valence electron configurations, which demonstrates that $< r_> >$ is more sensitive to the density distribution than $< r >$. For the ground state of two-electron atoms, the electron correlation was found [23] to decrease the inner radius $< r_< >$ and increase the outer radius $< r_> >$ compared with the corresponding HF values.

In the present paper, we study the average inner $< r_< >$ and outer $< r_> >$ radii for the 28 singly excited 1*snl* states ($0 \leq l < n \leq 5$) of the He atom at the HF and correlated levels. Both the singlets and triplets are considered. The next section outlines the definition of the average inner and outer radii and summarizes the accuracy of correlated wave functions used in this study. Then, we discuss the radii

Contribution to the Serafin Fraga Memorial Issue.

This paper is dedicated to the late Professor Serafin Fraga for his great contribution to quantum sciences.

H. Matsuyama · T. Koga (✉)
Department of Applied Chemistry,
Muroran Institute of Technology,
Muroran, Hokkaido 050-8585, Japan
e-mail: koga@mmm.muroran-it.ac.jp

$< r_< >$ and $< r_> >$ of the 1*snl* states. We will find that $< r_< >$ and $< r_> >$ well characterize the two electrons with different natures in the singly excited states of the He atom. Also found is a good correlation between the outer radius $< r_> >$ and the average interelectronic separation $< r_{12} >$, where r_{12} is the distance between two electrons. Hartree atomic units are used throughout this paper.

2 Definitions and wave functions

For an N-electron system ($N \geq 2$), we first introduce (see, e.g., [25]) the two-electron radial density function $D_2(r_1, r_2)$ defined by

$$D_2(r_1, r_2) = r_1^2 r_2^2 \int \mathrm{d}\,\Omega_1 \mathrm{d}\,\Omega_2 \Gamma(\mathbf{r}_1, \mathbf{r}_2), \tag{1a}$$

where (r_i, Ω_i) are the polar coordinates of position vector $\mathbf{r}_i$ and

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int \mathrm{d}\,s_1 \mathrm{d}\,s_2 \mathrm{d}\,\mathbf{x}_3 \ldots \mathrm{d}\,\mathbf{x}_N |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2, \tag{1b}$$

is the spinless two-electron density function [26] associated with a normalized wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ with $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ being the combined position-spin coordinates of the electron i. The function $D_2(r_1, r_2)$ is the probability density that one electron is at a radius r_1 and the other electron at a radius r_2, when any two electrons are considered simultaneously, and is normalized to the number of electron pairs as

$$\int_0^\infty \mathrm{d}\,r_1 \int_0^\infty \mathrm{d}\,r_2\; D_2(r_1, r_2) = \frac{N(N-1)}{2}. \tag{2}$$

We then define [23,24] the average inner $< r_< >$ and outer $< r_> >$ radii as

$$< r_< > = \frac{2}{N(N-1)} \int_0^\infty \mathrm{d}\,r_1 \int_0^\infty \mathrm{d}\,r_2 r_< D_2(r_1, r_2), \tag{3a}$$

$$< r_> > = \frac{2}{N(N-1)} \int_0^\infty \mathrm{d}\,r_1 \int_0^\infty \mathrm{d}\,r_2\; r_> \; D_2(r_1, r_2), \tag{3b}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. The inner radius $< r_< >$ is the average of an electron radius which is smaller than that of another electron, when any two electrons are considered simultaneously. The outer radius $< r_> >$ is the average radius of an electron with a larger radius.

For the 28 singly excited 1*snl* states of the He atom, HF and correlated wave functions were generated by the multi-configuration Hartree–Fock (MCHF) method using a modified version of the MCHF88 program [27]. For the MCHF correlated wave function of each state, the combination of configurations was optimized, and the number N_c of configurations was chosen such that the difference ΔE between the MCHF and near exact [28] total energies is never larger than 10 microhartree. Table 1 lists the N_c and ΔE values for the 28 states examined in this study. Following Eqs. (1) and (3), we then constructed the HF and MCHF $D_2(r_1, r_2)$ densities and calculated the inner and outer radii.

Table 1 Numbers N_c of the configurations used in MCHF calculations and the total energy errors ΔE in microhartree

Electron configuration	Singlet		Triplet	
	N_c	ΔE	N_c	ΔE
1*s*2*s*	30	9.7	15	0.7
1*s*3*s*	26	3.6	14	0.2
1*s*4*s*	25	1.5	10	0.1
1*s*5*s*	25	0.8	10	0.1
1*s*2*p*	35	9.8	15	9.0
1*s*3*p*	15	8.1	10	5.8
1*s*4*p*	12	4.8	9	2.8
1*s*5*p*	8	4.1	6	2.5
1*s*3*d*	9	0.8	8	0.9
1*s*4*d*	7	0.5	7	0.5
1*s*5*d*	6	0.3	6	0.3
1*s*4*f*	6	0.0	6	0.0
1*s*5*f*	6	0.0	6	0.0
1*s*5*g*	4	0.0	4	0.0

3 Results and discussion

Table 2 shows the average inner radius $< r_< >$ for the 28 singly excited 1*snl* states of the helium atom calculated by the HF and MCHF methods. All the HF and MCHF $< r_< >$ values are close to 0.75 bohr, particularly when n is large. There are no significant differences in the $< r_< >$ values between the singlet and the triplet states. The correlation effect is also small, but slightly increases $< r_< >$, except for the 1*snp* triplet states.

In order to explain the fact that the inner radius $< r_< >$ for the singly excited states of the He atom is nearly equal to 0.75 bohr, irrespective of the quantum numbers n and l, spin states, or the HF and MCHF methods, we consider a crude independent electron model (see, e.g., [1,29]); when the interaction between the two electrons in the He atom can be disregarded, an electron with a smaller radius behaves like the 1*s* electron of He^+ because of the bare Coulomb field of the nucleus. In such a model, $< r_< >$ may be approximated by the average electron radius $< r >_{Z,n,l}$ (see, e.g., [30])

Table 2 The HF and MCHF inner radii $< r_< >$ for the 28 singly excited $1snl$ states of the He atom

Electron configuration	Singlet		Triplet	
	HF	MCHF	HF	MCHF
$1s2s$	0.747813	0.749162	0.729261	0.729461
$1s3s$	0.749581	0.749948	0.745130	0.745171
$1s4s$	0.749852	0.750001	0.748135	0.748150
$1s5s$	0.749931	0.750005	0.749095	0.749102
$1s2p$	0.746841	0.747950	0.753195	0.752957
$1s3p$	0.749010	0.749325	0.750819	0.750680
$1s4p$	0.749576	0.749708	0.750326	0.750259
$1s5p$	0.749782	0.749848	0.750162	0.750126
$1s3d$	0.749973	0.750063	0.750019	0.750084
$1s4d$	0.749985	0.750026	0.750010	0.750038
$1s5d$	0.749991	0.750013	0.750006	0.750020
$1s4f$	0.750000	0.750006	0.750000	0.750006
$1s5f$	0.750000	0.750004	0.750000	0.750004
$1s5g$	0.750000	0.750001	0.750000	0.750001

of the hydrogen-like atom with a nuclear charge Z and the quantum numbers n, l as

$$< r >_{Z,n,l} = \frac{1}{2Z}[3n^2 - l(l+1)]. \quad (4)$$

For an electron with a smaller radius, substitution of $Z = 2$, $n = 1$, and $l = 0$ into Eq. (4) results in $< r >_{2,1,0} = 0.75$ bohr. When we compare the $< r_< >$ radii shown in Table 2 with the $< r >_{2,1,0}$ value, the averages of ratios $< r_< > / < r >_{2,1,0}$ are 0.999 (HF) and 1.000 (MCHF) in the singlets and 0.998 (HF and MCHF) in the triplets. This confirms that the inner radius $< r_< >$ detects an electron which behaves as the $1s$ electron of the helium cation.

Table 3 summarizes the average outer radius $< r_> >$ of the singly excited states of the He atom at the HF and MCHF levels. For a fixed l, $< r_> >$ increases with increasing n at both levels. The correlation effect decreases $< r_> >$, which is opposite [23] to the ground state of the He atom. At present, we do not have any physical interpretation for the different correlation effects. Unlike the inner radius $< r_< >$, the outer radius $< r_> >$ is larger for the singlets than for the triplets both in the HF and the MCHF calculations. The result is closely related to the difference in the electron–nucleus attraction energy V_{en} between the singlet and triplet states; $|V_{\mathrm{en}}|$ is smaller in the singlet than in the triplet, and the electron distribution of the singlet state is more diffuse than that of the triplet state, as reported in the literature [7–11]. The radius $< r_> >$ reflects an outer part of the electron distribution sensitively.

In the model mentioned above, it is expected that one electron with a larger radius behaves like an nl electron of the hydrogen atom because of an almost completely screened Coulomb field by the other electron with a smaller radius. The average radius of the former electron may be approximated by $< r >_{Z,n,l}$ (Eq. 4) with $Z = 1$, which is listed in the last column of Table 3 for different values of n and l. A comparison of $< r_> >$ with $< r >_{1,n,l}$ finds that the averages of ratios $< r_> > / < r >_{1,n,l}$ are 0.983 (HF) and 0.977

Table 3 The HF and MCHF outer radii $< r_> >$ for the 28 singly excited $1snl$ states of the He atom as well as the hydrogenic electron radius $< r >_{1,n,l}$

Electron configuration	Singlet		Triplet		$< r >_{1,n,l}$
	HF	MCHF	HF	MCHF	
$1s2s$	5.287329	5.197300	4.390464	4.371480	6
$1s3s$	12.415822	12.274120	10.996798	10.966805	13.5
$1s4s$	22.546451	22.354399	20.615199	20.574333	24
$1s5s$	35.677355	35.435239	33.235506	33.183682	37.5
$1s2p$	5.142186	5.073943	4.659455	4.595312	5
$1s3p$	12.711222	12.611940	11.995842	11.892938	12.5
$1s4p$	23.280732	23.149741	22.329086	22.189181	23
$1s5p$	36.850491	36.689902	35.661437	35.487156	36.5
$1s3d$	10.503423	10.481671	10.493908	10.476029	10.5
$1s4d$	21.005299	20.975446	20.990466	20.966648	21
$1s5d$	34.506868	34.469284	34.487596	34.457784	34.5
$1s4f$	18.000027	17.995104	17.999954	17.995071	18
$1s5f$	31.500045	31.493662	31.499921	31.493605	31.5
$1s5g$	27.500000	27.498319	27.500000	27.498319	27.5

(MCHF) in the singlets and 0.938 (HF) and 0.935 (MCHF) in the triplets. All these ratios are close to (but slightly smaller than) unity, showing that the outer electron is well (but not perfectly) screened by the inner electron. Because the singlet states have more diffuse electron distributions and larger $< r_> >$ than the triplet states, the outer electron in the singlets experiences more screened nuclear charge. Thus, the ratio between $< r_> >$ and $< r >_{1,n,l}$ is closer to unity in the singlets than in the triplets. We conclude that the outer radius $< r_> >$ detects an electron which behaves approximately as the *nl* electron of the hydrogen atom.

For the 102 atoms He through Lr in their ground states, a good correlation between the outer radius $< r_> >$ and the average interelectronic distance $< r_{12} >$ was found [31], where $< r_{12} >$ is defined by

$$< r_{12} >= \frac{2}{N(N-1)} \int \mathrm{d}\,\mathbf{r}_1 \int \mathrm{d}\,\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2| \Gamma(\mathbf{r}_1, \mathbf{r}_2). \quad (5)$$

The interelectronic distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ between two electrons is expanded [32] in terms of the product of a radial function and a Legendre polynomial $P_k(\cos\theta_{12})$ as

$$r_{12} = \sum_{k=0}^{\infty} \left(\frac{1}{2k+3} \frac{r_<^{k+2}}{r_>^{k+1}} - \frac{1}{2k-1} \frac{r_<^{k}}{r_>^{k-1}} \right) P_k(\cos\theta_{12}), \quad (6)$$

where θ_{12} is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. If we consider only the leading term with $k = 0$ and neglect the $r_<^2/r_>$ term, we find an approximate relation $r_{12} \cong r_>$.

We have additionally calculated $< r_{12} >$ using the MCHF wave functions in Table 1 and plotted the resultant $< r_{12} >$ against $< r_> >$ in Fig. 1. We find that a correlation between $< r_{12} >$ and $< r_> >$ is also good for the excited states, as is the case [31] of the 102 ground-state atoms. For the 14 singlet states, a linear regression analysis yields

$$< r_{12} > \cong 0.998450 < r_> > +0.057663, \quad (7a)$$

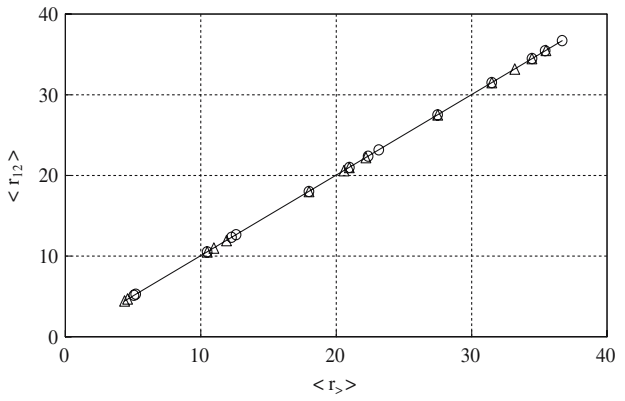

Fig. 1 Linear correlation between the average interelectronic distance $< r_{12} >$ and the average outer radius $< r_> >$ at the MCHF level. *Circles* and *triangles* correspond to the singlet and triplet states, respectively

with the correlation coefficient 1.000000, and for the 14 triplet states,

$$< r_{12} > \cong 0.997940 < r_> > +0.071538, \quad (7b)$$

with the correlation coefficient 0.999999. The slopes and intercepts in Eqs. (7a) and (7b) are close to unity and zero, respectively. When the interelectronic distance $< r_{12} >$ is estimated simply by the outer radius $< r_> >$ itself, the average relative errors are at most 0.28% (singlets) and 0.39% (triplets). The radius $< r_> >$ is larger in the singlets and so is $< r_{12} >$. This does not contradict with the fact that the electron-electron repulsion energy $V_{ee} = < 1/r_{12} >$ is smaller in the singlets (see also [7–11]).

4 Summary

The average inner $< r_< >$ and outer $< r_> >$ radii for the 28 singly excited $1snl$ states ($0 \le l < n \le 5$) of the helium atom were studied based on the HF and MCHF wave functions. Since all $< r_< >$ values are about 0.75 bohr, an electron with a smaller radius behaves as the $1s$ electron in the helium cation. On the other hand, $< r_> >$ is in reasonable agreement with the average electron radius of the hydrogen atom, and hence an electron with a larger radius behaves like an *nl* electron of the hydrogen atom. The present results of the inner $< r_< >$ and outer $< r_> >$ radii support the screened hydrogenic model [18,19,22] for the electron density distribution of the singly excited states of the He atom.

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