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# Average electron radii in many-electron atoms

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In an  $N$ -electron ( $N \geq 2$ ) atom, the average distance of an electron from the nucleus (i.e., the coordinate origin) is given by the average electron radius  $\langle r \rangle$  defined by

$$\langle r \rangle = \frac{1}{N} \int_0^\infty dr r D(r), \quad (1)$$

where  $D(r)$  is the single-electron radial density (see, e.g., Ref. 1) normalized to  $N$ , the number of electrons. The quantity  $\langle r \rangle$  represents the mean radius of an electron orbital when all the interelectronic interactions are averaged and only a *single* electron is focused upon. If any *two* electrons are considered simultaneously, however, the electrons would prefer different radii, inner radius  $r_<$  and outer radius  $r_>$ , to reduce the electron-electron repulsion, as motivated the introduction of the Kellner<sup>2</sup> and Eckart<sup>3</sup> wave functions for the He atom. The present paper examines the average radii  $\langle r_< \rangle$  and  $\langle r_> \rangle$  for the ground-state atoms He through Lr at the Hartree-Fock limit level. The effect of the electron correlation is discussed for some two-electron atoms. Hartree atomic units are used.

Naive definitions of the average inner  $\langle r_< \rangle$  and outer  $\langle r_> \rangle$  radii would be

$$\langle r_< \rangle = \frac{2}{N(N-1)} \int_0^\infty dr_1 \int_0^\infty dr_2 r_< D_2(r_1, r_2), \quad (2a)$$

$$\langle r_> \rangle = \frac{2}{N(N-1)} \int_0^\infty dr_1 \int_0^\infty dr_2 r_> D_2(r_1, r_2), \quad (2b)$$

where  $r_< = \min(r_1, r_2)$ ,  $r_> = \max(r_1, r_2)$ , and  $D_2(r_1, r_2)$  is the two-electron radial density (see, e.g., Ref. 4) normalized to  $N(N-1)/2$ , the number of electron pairs. Note that  $r_<$  and  $r_>$  in Eq. (2) are two-electron operators. Since  $r_< + r_> = r_1 + r_2$  and  $r_> - r_< = |r_1 - r_2|$ , we find

$$\langle r_< \rangle = \langle r \rangle - \frac{1}{2} \langle |r_1 - r_2| \rangle, \quad \langle r_> \rangle = \langle r \rangle + \frac{1}{2} \langle |r_1 - r_2| \rangle, \quad (3)$$

as well as  $(\langle r_< \rangle + \langle r_> \rangle)/2 = \langle r \rangle$ , where the definition of  $\langle |r_1 - r_2| \rangle$  is analogous to Eq. (2). Namely, the explicit consideration of the electron-electron interaction splits the radius  $\langle r \rangle$  into the radii  $\langle r_< \rangle$  and  $\langle r_> \rangle$  separated by  $\langle |r_1 - r_2| \rangle$ .

Using a modified version of the MCHF72 program,<sup>5</sup> we have calculated the Hartree-Fock values of the inner  $\langle r_< \rangle$  and outer  $\langle r_> \rangle$  radii for the 102 atoms, He through Lr, in

their ground states. The results are plotted in Fig. 1 as a function of atomic number  $Z$ . All the radii  $\langle r_< \rangle$ ,  $\langle r_> \rangle$ , and  $\langle r \rangle$  show a trend to decrease as  $Z$  increases. The splitting of  $\langle r \rangle$  into  $\langle r_< \rangle$  and  $\langle r_> \rangle$  is smallest at  $Z=2$  and largest at  $Z=3$ , where the values of  $\langle |r_1 - r_2| \rangle$  are 0.611 and 2.334 bohrs, and the ratios  $\langle r_> \rangle / \langle r_< \rangle$  are 1.982 and 5.610, respectively. In the largest case of the Li atom, the inner  $\langle r_< \rangle$  and outer  $\langle r_> \rangle$  radii are 69.7% smaller and larger than the usual average radius  $\langle r \rangle$ , respectively. The inner radius  $\langle r_< \rangle$  distributes between 0.267 ( $Z=102$ ) and 0.671 bohrs ( $Z=5$ ), but its  $Z$  dependence is rather smooth except for the first several atoms. In marked contrast, the outer radius  $\langle r_> \rangle$  distributes between 0.905 ( $Z=79$ ) and 2.840 bohrs ( $Z=3$ ) and is found to show a periodical structure reflecting the electronic configuration of atoms. The Li atom has an exceptionally large  $\langle r_> \rangle$  due to the very diffuse  $2s$  orbital. Local maxima in  $\langle r_> \rangle$  are observed at  $Z=3$  (Li), 13 (Al), 20 (Ca), 38 (Sr), 56 (Ba), and 88 (Ra). Except for the first two, these atoms belong to group 2 with the valence  $s^2$  configuration. After these atoms,  $\langle r_> \rangle$  generally decreases towards the group 18 atoms within respective periods, unless the irregularity in the ground electronic configuration appears. The  $Z$  dependence of the average radius  $\langle r \rangle$  is parallel to that of the outer radius  $\langle r_> \rangle$ , since  $\langle r \rangle$  is the arithmetic mean of  $\langle r_< \rangle$  and  $\langle r_> \rangle$ .

To examine the correlation effect on  $\langle r_< \rangle$  and  $\langle r_> \rangle$ , we have performed multiconfiguration Hartree-Fock calculations for the first five members of two-electron atoms, using a modified version of the MCHF88 program<sup>6</sup> and the best combination of 30 configurations.<sup>7,8</sup> In Table I, the correlated

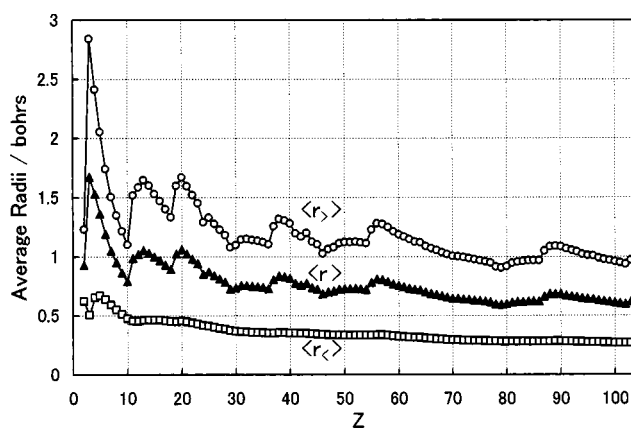


FIG. 1. The Hartree-Fock average radii  $\langle r_< \rangle$ ,  $\langle r_> \rangle$ , and  $\langle r \rangle$  as a function of  $Z$ .

TABLE I. Correlation effect on the average radii (in bohrs) of two-electron atoms.

Atom	$\langle r_{<} \rangle$			$\langle r \rangle$			$\langle r_{>} \rangle$		
	Hartree-Fock	Correlated	Ratio <sup>a</sup>	Hartree-Fock	Correlated	Ratio <sup>a</sup>	Hartree-Fock	Correlated	Ratio <sup>a</sup>
H <sup>-</sup>	1.586 010	1.427 870	0.900	2.503 960	2.710 955	1.083	3.421 910	3.994 040	1.167
He	0.622 000	0.602 438	0.969	0.927 273	0.929 487	1.002	1.232 547	1.256 535	1.019
Li <sup>+</sup>	0.387 816	0.380 565	0.981	0.572 367	0.572 776	1.001	0.756 918	0.764 986	1.011
Be <sup>2+</sup>	0.281 799	0.278 045	0.987	0.414 141	0.414 283	1.000	0.546 482	0.550 522	1.007
B <sup>3+</sup>	0.221 314	0.219 022	0.990	0.324 489	0.324 556	1.000	0.427 665	0.430 090	1.006

<sup>a</sup>Ratio means the correlated value divided by the Hartree-Fock value.

results are summarized and compared with the Hartree-Fock values. The electron correlation is found to decrease the inner radius  $\langle r_{<} \rangle$  and increase the outer radius  $\langle r_{>} \rangle$  with no exceptions, which leads to an increase in the radial separation  $\langle |r_1 - r_2| \rangle$ . The largest changes in  $\langle r_{<} \rangle$  and  $\langle r_{>} \rangle$  are seen for the H<sup>-</sup> ion in accord with a common observation in the literature<sup>9-13</sup> that the radial correlation is more important for H<sup>-</sup> than for He and heavier ions. In the case of the H<sup>-</sup> ion, the correlated radii  $\langle r_{<} \rangle$  and  $\langle r_{>} \rangle$  are 10.0% smaller and 16.7% larger than the Hartree-Fock results, respectively, which should be compared with the corresponding values 3.1% and 1.9% for the He atom. On the other hand, the correlation effect on the average radius  $\langle r \rangle$  is smaller than those on  $\langle r_{<} \rangle$  and  $\langle r_{>} \rangle$ , in agreement with a perturbation theoretical conclusion that Hartree-Fock one-electron properties are correct to first order as a consequence of Brillouin's theorem (see, e.g., Ref. 14).

In summary, we have systematically examined the splitting of the average radius  $\langle r \rangle$  into the inner  $\langle r_{<} \rangle$  and outer

$\langle r_{>} \rangle$  radii for 102 atoms, He through Lr, at the Hartree-Fock limit level. The effect of electron correlations on  $\langle r_{<} \rangle$  and  $\langle r_{>} \rangle$  has also been discussed for the He atom and its isoelectronic ions.

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