Average electron radii in many-electron atoms

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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

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

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 \(r_\text{<} \) and outer radius \(r_\text{>}\), to reduce the electron-electron repulsion, as motivated the introduction of the Kellner\(^2\) and Eckart\(^3\) wave functions for the He atom. The present paper examines the average radii \(\langle r_\text{<} \rangle\) and \(\langle r_\text{>}\rangle\) 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 \(\langle r_\text{<} \rangle\) and outer \(\langle r_\text{>}\rangle\) radii would be

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

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

where \(r_\text{<} = \min(r_1, r_2)\), \(r_\text{>} = \max(r_1, r_2)\), 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 \(r_\text{<}\) and \(r_\text{>}\) in Eq. (2) are two-electron operators. Since \(r_\text{<} + r_\text{>} = r_1 + r_2\) and \(r_\text{>} - r_\text{<} = |r_1 - r_2|\), we find

\[
\langle r_\text{<} \rangle = \langle r \rangle - \frac{3}{2} |r_1 - r_2|, \quad \langle r_\text{>} \rangle = \langle r \rangle + \frac{3}{2} |r_1 - r_2|,
\]

as well as \(\langle (r_\text{<} + r_\text{>)}/2 = \langle r \rangle\), 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 \(\langle r_\text{<} \rangle\) and \(\langle r_\text{>}\rangle\) separated by \(\langle |r_1 - r_2|\rangle\).

Using a modified version of the MCHF\textsuperscript{88} program\(^5\) we have calculated the Hartree-Fock values of the inner \(\langle r_\text{<} \rangle\) and outer \(\langle r_\text{>}\rangle\) 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 \(\langle r_\text{<} \rangle\), \(\langle r_\text{>}\rangle\), and \(\langle r \rangle\) show a trend to decrease as \(Z\) increases. The splitting of \(\langle r \rangle\) into \(\langle r_\text{<} \rangle\) and \(\langle r_\text{>}\rangle\) 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 \(\langle r_\text{>} \rangle/\langle r_\text{<} \rangle\) are 1.982 and 5.610, respectively. In the largest case of the Li atom, the inner \(\langle r_\text{<} \rangle\) and outer \(\langle r_\text{>}\rangle\) radii are 69.7% smaller and larger than the usual average radius \(\langle r \rangle\), respectively. The inner radius \(\langle r_\text{<} \rangle\) 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 \(\langle r_\text{>}\rangle\) 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 \(\langle r_\text{>}\rangle\) due to the very diffuse 2s orbital. Local maxima in \(\langle r_\text{<} \rangle\) 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, \(\langle r_\text{<} \rangle\) 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 \(\langle r_\text{>}\rangle\), since \(\langle r \rangle\) is the arithmetic mean of \(\langle r_\text{<} \rangle\) and \(\langle r_\text{>}\rangle\).

To examine the correlation effect on \(\langle r_\text{<} \rangle\) and \(\langle r_\text{>}\rangle\), we have performed multiconfiguration Hartree-Fock calculations for the first five members of two-electron atoms, using a modified version of the MCHF\textsuperscript{88} program\(^5\) and the best combination of 30 configurations.\(^7,8\) In Table I, the correlated

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**FIG. 1.** The Hartree-Fock average radii \(\langle r_\text{<} \rangle\), \(\langle r_\text{>}\rangle\), and \(\langle r \rangle\) as a function of \(Z\).
results are summarized and compared with the Hartree-Fock values. The electron correlation is found to decrease the inner radius \( r_{<} \) and increase the outer radius \( r_{>} \) with no exceptions, which leads to an increase in the radial separation \( r_{1} - r_{2} \). The largest changes in \( r_{<} \) and \( r_{>} \) are seen for the H\(_{2}^{+} \) ion in accord with a common observation in the literature \(^{9-13} \) that the radial correlation is more important for H\(_{2}^{+} \) than for He and heavier ions. In the case of the H\(_{2}^{-} \) ion, the correlated radii \( r_{<} \) and \( r_{>} \) 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 \( r_{<} \) and \( r_{>} \), 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 \( r_{<} \) and outer \( r_{>} \) radii for 102 atoms, He through Lr, at the Hartree-Fock limit level. The effect of electron correlations on \( r_{<} \) and \( r_{>} \) has also been discussed for the He atom and its isoelectronic ions.

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

\(^a\text{Ratio means the correlated value divided by the Hartree-Fock value.}\)