Two-parameter partially correlated ground-state electron density of some light spherical atoms
from Hartree-Fock theory with nonintegral nuclear charge

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Partially correlated ground-state electron densities for some spherical light atoms are calculated, into which
nonrelativistic ionization potentials represent essential input data. The nuclear cusp condition of Kato is
satisfied precisely. The basic theoretical starting point, however, is Hartree-Fock (HF) theory for the N electrons
under consideration but with nonintegral nuclear charge Z' slightly different from the atomic number Z (=N). This HF density is scaled with a parameter λ, near to unity, to preserve normalization. Finally, some tests
are performed on the densities for the atoms Ne and Ar, as well as for Be and Mg.

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I. INTRODUCTION

In their celebrated theoretical study about adding Coulomb correlation effects to the Hartree-Fock (HF) approxi-
mation, Møller and Plesset [1] concluded by emphasizing the
accuracy of the HF ground-state electron density \( \rho(r) \) in
atomic physics. Their specific conclusion was that \( \rho(r) \) was
correct to second order in the difference between the correct
nonrelativistic ionization potential and scale the resulting density to satisfy Kato’s cusp condition for the
electron density at the nucleus [2].

The numerically calculated HF ground-state density for
species with nuclear charge Z' and N electrons, \( \rho_{\text{HF}}(Z',N,r) \), is well known to have an exponential factor in its decay at
large distances from the nucleus, taken as origin \( r=0 \), of the form

\[
\rho_{\text{HF}}(Z',N,r) \sim \exp\left(-2\sqrt{2I_K(Z',N)r}\right), \tag{1}
\]

in atomic units, where \( I_K(Z',N) \) is the appropriate Koop-
mans’ ionization potential, which in turn is the one-electron HF eigenvalue associated with the highest occupied atomic orbital (HOAO). In contrast, for a neutral atom with \( N=Z \), the exact exponential decay factor of the nonrelativistic ground-state electron density \( \rho_{\text{NR}}(r) \) is known to be [3]

\[
\rho_{\text{NR}}(Z,N,r) \sim \exp\left(-2\sqrt{2I_{\text{NR}}(Z,N)r}\right), \tag{2}
\]

where \( I_{\text{NR}}(Z,N) \) is the nonrelativistic ionization potential of
the neutral atom with atomic number \( Z \) under consideration.

Thus in Sec. II below we summarize an available method
which allows \( I_{\text{NR}} \) to be determined semiempirically. With
this nonrelativistic input information, we describe the basic
scaling proposal of this work. This will enable us to connect
uniquely the basic HF theoretical calculation of \( \rho_{\text{HF}}(Z',N,r) \)
cited in Eq. (1) to the desired (partially correlated) ground-state density \( \rho_{\text{NR}}(Z=N,r) \) of the neutral atom, cited in Eq.
(2). This section ends by analyzing our results of the two-
parameter \( \rho_{\text{NR}}(Z=N,r) \) proposed for Ne and Ar. Section III
compares and contrasts these results for rare gas atoms with
the divalent atoms Be and Mg chosen because they also have
spherical electron densities. Section IV gives some tests of
the proposed densities by comparison with quantum simulation
studies. A summary together with proposals for future
studies which should prove fruitful constitutes Sec. V.

II. SCALING APPROACH TO FORM CORRELATED
GROUND-STATE ELECTRON DENSITIES FROM
HARTREE-FOCK DENSITIES FOR Ne AND Ar

For a nonrelativistic atom with atomic number \( Z \) and \( N \)
(=N) electrons, the electronic density far from the nucleus
decays as in Eq. (2). Within the Hartree-Fock approximation,
the electronic density of a fictitious atom with atomic num-
ber \( Z' \) and \( N \) electrons falls off exponentially as given by Eq.
(1), where \( I_K(Z',N) \) is its ionization potential calculated
using Koopmans’ theorem [i.e., the eigenvalue of the
highest occupied atomic orbital, with the opposite sign
\( I_K(Z',N) = -e_{\text{HOAO}}(Z',N) \)].

If we scale this HF density using the norm-conserving ansatz

\[
\rho_{\lambda}(Z',N,r) = \lambda^3 \rho_{\text{HF}}(Z',N,\lambda r), \tag{3}
\]

where \( \lambda \) is a positive parameter, the asymptotic behavior of the
scaled density will be

\[
\rho_{\lambda}(Z',N,r) \sim \exp\left(-2\sqrt{2I_K(Z',N)\lambda r}\right). \tag{4}
\]

If we require the scaled density to decay in its long-range
behavior like the exact nonrelativistic one, \( \rho_{\lambda}(Z',N,r) \)
On the other hand, if we want this scaled density to satisfy Kato’s cusp condition at the nucleus [2] for the correct nuclear charge $Z$, we must have
\[
\frac{\partial \rho_\text{HF}(Z',N,r)}{\partial r} \bigg|_{r=0} = -\frac{2Z}{a_0} \rho_0(Z',N,r=0) = -\frac{2Z}{a_0} \lambda^3 \rho_\text{HF}(Z',N,r=0),
\]
and taking into account that
\[
\frac{\partial \rho_\text{HF}(Z',N,r)}{\partial r} \bigg|_{r=0} = \lambda^3 \frac{\partial \rho_\text{HF}(Z',N,r)}{\partial r} \bigg|_{r=0} = \lambda^4 \frac{\partial \rho_\text{HF}(Z',N,r)}{\partial r} \bigg|_{r=0} = -\lambda^4 \frac{2Z'}{a_0} \rho_\text{HF}(Z',N,r=0),
\]
we obtain
\[
Z'\lambda = Z.
\] (8)
This identity shows that the two parameters of the model are not independent. This means that our two-parameter model is in fact a one-parameter model. Eliminating $\lambda$ between Eqs. (5) and (8) one finds
\[
I_K(Z',N) = I_{\text{NR}}(Z,N) \frac{Z'^2}{Z^2}.
\] (9)
If we choose $Z'$ so that identity (9) is satisfied, we have a density $\rho_\lambda(Z',N,r)$ that has the correct nonrelativistic behavior both at the nucleus and very far from it, and so it must include some amount of Coulomb correlation and can be considered as an approximation to $\rho_{\text{NR}}(Z,N,r)$.

In order to calculate the nonrelativistic ionization potentials for Ne and Ar we have taken the experimental first ionization energies and made use of the relativistic corrections given by Chakravorty et al. [4]:
\[
I_{\text{NR}}(Z,N) = I_{\text{exp}}(Z,N) \frac{R_e}{R_Z} + \Delta E_{\text{iel}}(Z,N),
\] (10)
where
\[
\frac{R_e}{R_Z} = 1 + \frac{m_e}{M_Z} = 1 + \frac{m_e}{A - Zm_e}
\] (11)
with $M_Z$ the nuclear mass, $m_e$ the electron mass, and $A$ the atomic mass. All the experimental values were taken from [5], and the nonrelativistic ionization potentials calculated according to Eq. (10) appear in Table I.

We have slightly modified the Froese-Fischer HF code [6,7] to allow for noninteger atomic numbers and compute total densities in order to calculate $\rho_{\text{HF}}(Z,N,r)$ and $\rho_\lambda(Z',N,r)$. Table I also includes the fitted parameters $Z'$ and $\lambda$ for the spherical atoms Ne and Ar, as well as the Koopmans’ ionization potential for the atom with its original nuclear charge, $Z'\neq Z$ and the nonrelativistic ones $\lambda=Z/Z'$. Figure 2 and 3 show $\Delta(4\pi r^2\rho) = 4\pi r^2\rho(Z',N,r) - 4\pi r^2\rho_{\text{HF}}(Z,N,r)$ for Ne and Ar, respectively. In both cases $\rho_\lambda(Z',N,r) < \rho_{\text{HF}}(Z,N,r)$ close to the nucleus and, of course, $\int_0^\infty (4\pi r^2\rho)dr=0$ since the rescaling given by Eq. (3) is norm conserving, but there are two differences: $\Delta(4\pi r^2\rho)$ has one oscillation for Ne but two for Ar and is one order of magnitude smaller for the latter.

\begin{table}
\begin{tabular}{lcccccc}
\hline
Atom & $Z$ & $I_K(Z,N)$ & $I_{\text{exp}}(Z,N)$ & $I_{\text{NR}}(Z,N)$ & $Z'$ & $\lambda=Z/Z'$ & $I_K(Z',N)$
\hline
Ne & 10 & 0.850410 & 0.792482 & 0.794464 & 9.9128 & 1.0088 & 0.780612
Ar & 18 & 0.591017 & 0.579155 & 0.582173 & 17.9802 & 1.0011 & 0.580883
Be & 4 & 0.309270 & 0.342603 & 0.344332 & 4.1270 & 0.96922 & 0.366550
Mg & 12 & 0.253053 & 0.280994 & 0.280740 & 12.0960 & 0.99207 & 0.285245
\hline
\end{tabular}
\end{table}

FIG. 1. Scaled Hartree-Fock radial densities in atomic units.
III. COMPARISON BETWEEN RARE GAS ATOMS AND THE DIVALENT ELEMENTS Be AND Mg

The purpose of this section is to present partially correlated ground-state electron densities for Be and Mg and to compare and contrast with the results for Ne and Ar. For the latter purpose, we have added to Table I the values of \( \lambda \) and \( Z' \) for Be and Mg and the corresponding scaled radial densities to Fig. 1. The most important difference to be emphasized is that whereas, as stressed in Sec. II, the starting HF densities for Ne and Ar apply to “weakly negative” atomic ions, the opposite situation obtains for the “divalent” elements Be and Mg. While the values of the normalization scaling parameter \( \lambda \) are all within a few percent of unity, for Ne and Ar, \( \lambda \) is slightly greater than 1, while for Be and Mg, \( \lambda \) is slightly smaller than 1. However, with regard to the \( \lambda \) variation there is a common feature for the four atoms: \( Z' \) tends to \( Z \) in such a way that \( |\lambda - 1| \) decreases monotonically with \( Z \). In order to understand this result we must take into account that, although the Coulomb correlation contribution to the total energy of light neutral atoms increases roughly linearly with the number of pairings between antiparallel spin electrons (and thus with the atomic number) \[8,9\], the correlation contribution to the ionization potential is not a monotonic increasing function of \( Z \) \[10\]. For the four atoms considered here the last contribution is similar \[10\] and \( \lambda \) must get closer to unity as \( Z \) increases; otherwise, the correlation contribution to the ionization potential should increase with \( Z \), since the number of electrons increases.

All this means that the correlation effects become less important in correcting HF properties for the atoms considered as the atomic number \( Z \) increases. Thus, Be exhibits the largest deviations from HF results, as shown clearly in the departures of \( Z' \) and \( \lambda \) from \( Z \) and 1, respectively. Again, as with Ne and Ar displayed in Sec. II, radial density differences are also shown for Be and Mg in Figs. 4 and 5. In this case \( p_0(Z',N,r) > p_{HF}(Z,N,r) \), close to the nucleus, in contrast to what happened for Ne and Ar (owing to the different sign of \( \lambda - 1 \) and \( \Delta(4\pi^2\rho) \) has two oscillations for both Be and Mg.

IV. TESTS OF THE PROPOSED DENSITIES

Tables II-V present the density at the nucleus and the moments of the density calculated using the original Hartree-Fock density \( p_{HF}(Z,N,r) \) as well as the scaled one \( p_s(Z',N,r) \) for the four atoms under consideration. Monte Carlo and accurate configuration interaction (CI) results from different authors \[11–14\] are given for comparison. The mean relative error

\[
\Delta_{\text{rel}}(\rho^n) = \frac{1}{n_{\text{max}} + 2} \sum_{n=-2}^{n_{\text{max}}} \frac{\langle \rho^n \rangle - \langle \rho^n \rangle_{\text{accurate}}}{\langle \rho^n \rangle_{\text{accurate}}}
\]

and the mean relative error in absolute value,

\[
\Delta(4\pi^2\rho)\text{ (a.u.)}
\]
underestimate them for Ne

and a big improvement for higher-order moments. For the

appear at the bottom of the tables.

HF results consistently overestimate the moments of the
density for Be, Mg, and Ar ($\Delta_{\text{rel}}(r^n) = \Delta_{\text{rel}}(\langle r^n \rangle)$) while they
underestimate them for Ne ($\Delta_{\text{rel}}(r^n) = -\Delta_{\text{rel}}(\langle r^n \rangle)$). In the case
of Be (for which the greatest number of accurate moments
are available in the literature) our scaled density consistently
overestimates the moments but improves the results by
roughly one order of magnitude. This improvement is not
homogeneous; there is a slight worsening on $\langle r^{-2} \rangle$ and $\langle r^{-1} \rangle$
and a big improvement for higher-order moments. For the
rest of the atoms considered the scaled densities do not ex-
habit an overall underestimation or overestimation of the moments ($|\Delta_{\text{rel}}(r^n) + \Delta_{\text{rel}}(\langle r^n \rangle)|$). There is, however, a common
trend: although scaled HF values are better than HF ones
(except for Ar), they modestly improve (or slightly worsen)
low-order moments while clearly improve high-order ones.
This seems to imply that scaled densities are better than HF
ones overall but perform better far from the nucleus than
close to it. Regarding the comparison with Monte Carlo
results, scaled HF results are clearly competitive with them.

Liu et al. [15,16] have shown that the density at the
nucleus of an atom is in fact a nonlocal functional of the
electron density that can be calculated via four different
integrals:

$$\rho(0) = -\frac{1}{4\pi} \int \frac{\nabla^2 \rho(r)}{|r|} dr,$$

(12)

### Table II. Density at the nucleus and moments of the density (in a.u.) for the Be atom.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Scaled HF</th>
<th>VMCa</th>
<th>DMCb</th>
<th>VMC(v)c</th>
<th>VMC(e)d</th>
<th>ECGc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho(0)$</td>
<td>35.388</td>
<td>35.654</td>
<td>34.665(13)</td>
<td>35.32(8)</td>
<td>35.8(3)</td>
<td>35.3(1)</td>
<td>35.3116</td>
</tr>
<tr>
<td>$\langle r^{-2} \rangle$</td>
<td>57.618</td>
<td>58.001</td>
<td>56.79(2)</td>
<td>57.40(10)</td>
<td>58.3(5)</td>
<td>57.4(2)</td>
<td>57.59808</td>
</tr>
<tr>
<td>$\langle r^{-1} \rangle$</td>
<td>8.4088</td>
<td>8.4595</td>
<td>8.3734(14)</td>
<td>8.403(4)</td>
<td>8.408(2)</td>
<td>8.433(2)</td>
<td>8.42735</td>
</tr>
<tr>
<td>$\langle r \rangle$</td>
<td>6.1288</td>
<td>5.9766</td>
<td>5.9841(5)</td>
<td>6.065(7)</td>
<td>6.217(2)</td>
<td>5.985(1)</td>
<td>5.57256</td>
</tr>
<tr>
<td>$\langle r^2 \rangle$</td>
<td>17.319</td>
<td>16.330</td>
<td>16.197(3)</td>
<td>16.79(4)</td>
<td>16.154(8)</td>
<td>16.343(9)</td>
<td>16.2476</td>
</tr>
<tr>
<td>$\langle r^3 \rangle$</td>
<td>63.151</td>
<td>57.454</td>
<td>59.57(4)</td>
<td>57.43(6)</td>
<td>57.772</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\langle r^4 \rangle$</td>
<td>270.66</td>
<td>237.12</td>
<td>318.2(5)</td>
<td>236.7(4)</td>
<td>232.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $\Delta_{\text{rel}}(r^n)$ | 6.14% | 0.84% | -0.54% | 1.06% | 12.74% | 0.61% |
| $\Delta_{\text{rel}}(\langle r^n \rangle)$ | 6.22% | 0.84% | 0.64% | 1.38% | 12.82% | 0.72% |

aVariational Monte Carlo results from Langfelder et al. [11].

bDiffusion Monte Carlo results from Langfelder et al. [11].
cEnergy-optimized variational Monte Carlo results from Gálvez et al. [12].
dResults from Meyer et al. [14] using multireference singly and doubly excited configuration interaction that recovers 95.7% of the total correlation energy.

### Table III. Density at the nucleus and moments of the density (in a.u.) for the Ne atom.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Scaled HF</th>
<th>VMCa</th>
<th>DMCb</th>
<th>VMC(v)c</th>
<th>VMC(e)d</th>
<th>MR-SDCIc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho(0)$</td>
<td>619.92</td>
<td>619.37</td>
<td>609.83(17)</td>
<td>619.0(9)</td>
<td>615(2)</td>
<td>621(2)</td>
<td></td>
</tr>
<tr>
<td>$\langle r^{-2} \rangle$</td>
<td>414.89</td>
<td>414.35</td>
<td>409.69(12)</td>
<td>414.1(4)</td>
<td>412(2)</td>
<td>417(2)</td>
<td>414.8753</td>
</tr>
<tr>
<td>$\langle r^{-1} \rangle$</td>
<td>31.113</td>
<td>31.032</td>
<td>30.883(4)</td>
<td>31.03(2)</td>
<td>31.128(3)</td>
<td>31.134(5)</td>
<td>31.1093</td>
</tr>
<tr>
<td>$\langle r \rangle$</td>
<td>7.8911</td>
<td>7.9590</td>
<td>7.9844(5)</td>
<td>7.974(6)</td>
<td>7.935(1)</td>
<td>7.903(1)</td>
<td>7.9385</td>
</tr>
<tr>
<td>$\langle r^2 \rangle$</td>
<td>9.3718</td>
<td>9.5677</td>
<td>9.6640(13)</td>
<td>9.64(2)</td>
<td>9.567(3)</td>
<td>9.468(2)</td>
<td>9.5565</td>
</tr>
<tr>
<td>$\langle r^3 \rangle$</td>
<td>14.383</td>
<td>14.910</td>
<td>15.13(1)</td>
<td>14.94(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\langle r^4 \rangle$</td>
<td>27.188</td>
<td>28.709</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $\Delta_{\text{rel}}(r^n)$ | -0.63% | 0.00% | -0.07% | 0.22% | -0.14% | -0.20% |
| $\Delta_{\text{rel}}(\langle r^n \rangle)$ | 0.64% | 0.19% | 0.92% | 0.44% | 0.23% | 0.49% |

aVariational Monte Carlo results from Langfelder et al. [11].

bDiffusion Monte Carlo results from Langfelder et al. [11].
cEnergy-optimized variational Monte Carlo results from Gálvez et al. [12].
TWO-PARAMETER PARTIALLY CORRELATED GROUND-

\[ \rho(0) = -\frac{1}{4\pi} \int \frac{\mathbf{r} \cdot \nabla \rho(\mathbf{r})}{|\mathbf{r}|^3} d\mathbf{r}, \] (13)

\[ \rho(0)_3 = -\frac{1}{4\pi} \int \frac{e^{-\beta|\mathbf{r}|}}{|\mathbf{r}|^3} \left[ \nabla^2 \rho(\mathbf{r}) - \beta^2 \rho(\mathbf{r}) \right] d\mathbf{r}, \] (14)

\[ \rho(0)_4 = -\frac{1}{4\pi} \int \frac{e^{-\beta|\mathbf{r}|}}{|\mathbf{r}|^3} \left[ \mathbf{r} \cdot \nabla \rho(\mathbf{r}) - \beta \rho(\mathbf{r}) \right] d\mathbf{r}, \] (15)

where \( \alpha \) and \( \beta \) are arbitrary positive constants. If we particularize for a spherical atom \( \rho(\mathbf{r}) = \rho(r) \), these four identities read

\[ \rho(0)_1 = -\int_0^\infty [r \rho''(r) + 2 \rho'(r)] dr, \] (16)

\[ \rho(0)_2 = -\int_0^\infty \rho'(r) dr, \] (17)

\[ \rho(0)_3 = -\int_0^\infty e^{-\alpha r} [r \rho''(r) + 2 \rho'(r) - \alpha^2 \rho(r)] dr, \] (18)

\[ \rho(0)_4 = -\int_0^\infty e^{-\beta r} [\rho'(r) - \beta \rho(r)] dr, \] (19)

where \( \rho'(r) \) and \( \rho''(r) \) indicate the first and second derivatives of the density with respect to \( r \).

Liu et al. [15] tested these identities using the HF densities of Clementi and Roetti [17] obtaining an excellent agreement between values for these expressions and densities at the nucleus. Our results show that this agreement is maintained (within our numerical accuracy) for scaled HF densities. This is not surprising since, as has been noted by Liu et al. [16], Eqs. (16) and (17) demonstrate that the density at the origin \( \rho(0) \) is homogeneous of degree 3 with respect to coordinate scaling, just like the electron density \( \rho(r) \) itself.

V. SUMMARY AND FUTURE DIRECTIONS

The main content of this work is the use of the HF ground-state density \( \rho_{HF}(Z',N,r) \) as the starting point from which to construct partially correlated densities \( \rho(Z=N,r) \) for especially the rare gas atoms Ne and Ar. This is achieved via two parameters. The first one is the nonintegral nuclear charge \( Z' \) for chosen \( N \) (10 for Ne and 18 for Ar). Table I shows that \( Z' \) is slightly less than 10 and 18 for Ne and Ar, respectively. The second one is a scaling parameter \( \lambda \) (very near to unity in accord with the expectations of Møller and Plesset [1]). Choosing these parameters in order to reproduce (a) the nonrelativistic ionization potential and (b) Kato’s nuclear cusp condition [2] leads to a relationship between them turning in fact our two-parameter model into a single parameter one.

Comparison with the quantal simulation data [e.g., diffusion quantum Monte Carlo (QMC)] supports the quality of the partially correlated densities for Ne and Ar presented here. However, the proposed density still needs some modest refinement close to the nucleus and three methods will be mentioned below which may prove useful for future studies. Before that, we have thought it of interest to compare the atoms Be and Mg, which as for Ne and Ar also have spherical electron densities, with the rare gas atoms. One interesting difference is that the HF starting point, as seen in Table I, is now from (slightly) positive ions (i.e., \( Z>4 \) for Be and \( Z>12 \) for Mg) in contrast to the weak nonintegral negative ions for Ne and Ar.

As to future directions, it seems important to refine the method presented here for obtaining partially correlated densities to improve the nonrelativistic electron density \( \rho(0) \) at the (assumed) point nucleus. At least three approaches then

---

**TABLE IV. Density at the nucleus and moments of the density (in a.u.) for the Mg atom.**

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Scaled HF</th>
<th>MR-SDCI (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho(0) )</td>
<td>1093.7</td>
<td>1094.8</td>
<td></td>
</tr>
<tr>
<td>( \langle r^{-2} \rangle )</td>
<td>614.85</td>
<td>615.63</td>
<td>614.7719</td>
</tr>
<tr>
<td>( \langle r^{-1} \rangle )</td>
<td>39.920</td>
<td>40.012</td>
<td>39.9303</td>
</tr>
<tr>
<td>( \langle r \rangle )</td>
<td>12.258</td>
<td>12.058</td>
<td>12.1357</td>
</tr>
<tr>
<td>( \langle r^2 \rangle )</td>
<td>29.612</td>
<td>28.189</td>
<td>28.5698</td>
</tr>
<tr>
<td>( \langle r^3 \rangle )</td>
<td>114.30</td>
<td>104.83</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{rel}(\rho^0) )</td>
<td>1.16%</td>
<td>-0.41%</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{rel}(\rho^3) )</td>
<td>1.17%</td>
<td>0.58%</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Results from Meyer et al. [14] using multireference singly and doubly excited configuration interaction that recovers 93.7% of the total correlation energy.

**TABLE V. Density at the nucleus and moments of the density (in a.u.) for the Ar atom.**

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Scaled HF</th>
<th>MR-SDCI (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho(0) )</td>
<td>3839.8</td>
<td>3839.4</td>
<td></td>
</tr>
<tr>
<td>( \langle r^{-2} \rangle )</td>
<td>1465.0</td>
<td>1464.8</td>
<td>1464.9102</td>
</tr>
<tr>
<td>( \langle r^{-1} \rangle )</td>
<td>69.725</td>
<td>69.704</td>
<td>69.7426</td>
</tr>
<tr>
<td>( \langle r \rangle )</td>
<td>16.071</td>
<td>16.097</td>
<td>16.0382</td>
</tr>
<tr>
<td>( \langle r^2 \rangle )</td>
<td>26.034</td>
<td>26.144</td>
<td>25.9344</td>
</tr>
<tr>
<td>( \langle r^3 \rangle )</td>
<td>55.988</td>
<td>56.397</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{rel}(\rho^0) )</td>
<td>0.14%</td>
<td>0.28%</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{rel}(\rho^3) )</td>
<td>0.15%</td>
<td>0.31%</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Results from Meyer et al. [14] using multireference singly and doubly excited configuration interaction that recovers 91.4% of the total correlation energy.

This fact does not mean that our scaled densities at the origin for the atoms studied are \( \lambda^3 \) times the HF ones (as can be checked using the data in Tables II–V) because we have modified the nuclear charge in order to recover the nonrelativistic ionization potential of the neutral atom.
offer promise. The first is associated with the Hiller-Sucher-Feinberg (HSF) identity (see, for example, Cioslowski et al. [18,19] and Holas and March [20], the latter work casting the HSF study in the general context of density functional theory). Particularly the work of Cioslowski et al. points to the possible use of the HSF identity in refining $\rho(0)$. The other is the older study of “bounds” of $\rho(0)$ by Hoffmann-Ostenhof et al. [3,21]. The third and most recent study is that of Liu [16] who has shown that the electron density of a spherical atom must satisfy some integral rules that involve the atomic number $Z$. Besides, analysis of the phase equation of Hartree-Fock theory [22,23] could give some insight into the differences between HF and scaled HF densities. Also, for the future, generalizations of the present approach to “rather spherical” molecules like SiH$_4$ and GeH$_4$ (see, e.g., the early work of March [24]) would seem worthwhile, especially based on HF calculations on SiH$_4$ such as those of Carter [25].

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