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REGULAR ARTICLE

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Inner and outer radial density functions in many-electron atoms

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Abstract When any two electrons are considered simultaneously, the radial density function $D(r)$ in many-electron atoms is shown to be rigorously separated into inner $D_<(r)$ and outer $D_>(r)$ radial densities. Accordingly, radial properties such as the electron–nucleus attraction energy V_{en} and the diamagnetic susceptibility χ_{d} are the sum of the inner and outer contributions. The electron–electron repulsion energy V_{ee} has an approximate relation with the minus first moment of the outer density $D_>(r)$. For the 102 atoms He through Lr in their ground states, different characteristics of local maxima in the radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ are reported based on the numerical Hartree-Fock wave functions. Relative contributions of the inner and outer components to V_{en} and χ_{d} are also discussed for these atoms.

Keywords Inner and outer radial densities · Nuclear attraction energy · Diamagnetic susceptibility · Electron shells · Atoms

1 Introduction

The radial density function $D(r)$ is defined (see, e.g., [1]) as:

$$D(r) = r^2 \int \mathrm{d}\Omega \; \rho(\mathbf{r}) \,, \tag{1a}$$

where (r, Ω) are polar coordinates of the vector $\mathbf{r}$ and

$$\rho(\mathbf{r}) = N \int \mathrm{d}s \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \,, \tag{1b}$$

is the single-electron density associated with a normalized N-electron 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 radial density $D(r)$ represents the probability density function of finding an electron at a distance between r and $r + \mathrm{d}r$ from the coordinate origin, and is normalized as:

$$\int_0^\infty \mathrm{d}r \; D(r) = N \,. \tag{2}$$

Though $D(r)$ is a one-dimensional condensation of the wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ with $4N$ variables, radial physical properties which depend solely on the radial variable r are completely determined by the knowledge of $D(r)$. Two typical examples for atomic systems are the electron–nucleus attraction energy $V_{\text{en}} = -Z < r^{-1} >$ and the diamagnetic susceptibility $\chi_{\text{d}} = - < r^2 > /(6c^2)$, where Z and c are the nuclear charge and the speed of light. Another important aspect of the atomic radial density $D(r)$ is that it is [2] a Hankel transform of the isotropic form factor $F(k)$ and exhibits (see, e.g., Refs. [2–6]) several local maxima corresponding to the electron shells. For the Ar atom, good agreement [2] of the $D(r)$ from electron diffraction experiments and from Hartree-Fock calculations is well-known [1], where three local maxima are clearly observed in both $D(r)$, reflecting the occupied K, L, and M shells.

In the present paper, we point out that if any two electrons are considered simultaneously, the radial density $D(r)$ is rigorously partitioned into two component functions, inner $D_<(r)$ and outer $D_>(r)$ radial density functions. The inner radial density function $D_<(r)$ represents the probability density that one electron moves with a radius r which is smaller than the radius of the other electron, and the outer radial density function $D_>(r)$ is the probability density for the opposite situation. The partitioning of $D(r)$ into two components results in the corresponding partitioning of any radial properties, including V_{en} and χ_{d}. The electron–electron repulsion energy V_{ee} is shown to have an approximate relation with the minus first moment of the outer density $D_>(r)$. For the 102 atoms He through Lr in their ground states, the three radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ are examined and the differences in their maximum characteristics are clarified based on the numerical Hartree-Fock wave functions. Relative contributions of the inner and outer components to V_{en}

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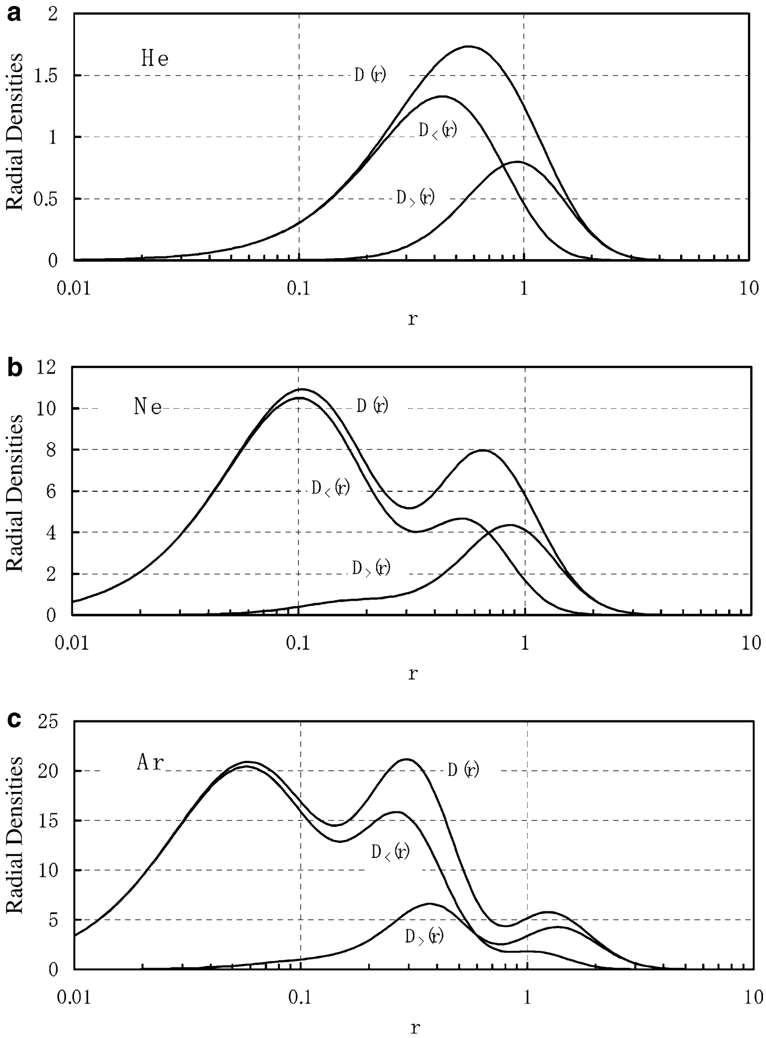

Fig. 1 Hartree-Fock radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ for **a** He, **b** Ne, and **c** Ar atoms

and χ_d as well as an approximation to V_{ee} are also discussed for these atoms. Hartree atomic units are used throughout.

2 Inner and outer radial density functions

We first introduce (see, e.g., [7]) the two-electron radial density function $D_2(r_1, r_2)$ given by

$$D_2(r_1, r_2) = r_1^2 r_2^2 \int \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \Gamma(\mathbf{r}_1, \mathbf{r}_2)\,, \tag{3a}$$

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

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \times \int \mathrm{d}s_1 \mathrm{d}s_2 \mathrm{d}\mathbf{x}_3 \ldots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2\,, \tag{3b}$$

is the spinless two-electron density function normalized to $N(N-1)/2$, the number of electron pairs. The function $D_2(r_1, r_2)$ is the probability density that one electron is at radius r_1 and the other electron at radius r_2, when any two electrons are considered simultaneously, and is normalized as

$$\int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2\, D_2(r_1, r_2) = \frac{N(N-1)}{2}\,. \tag{4}$$

Then the single-electron radial density $D(r)$, defined by Eq. (1a), is alternatively obtained from $D_2(r_1, r_2)$ as

$$D(r) = \frac{2}{N-1} \int_0^\infty \mathrm{d}r_2\, D_2(r, r_2)\,. \tag{5}$$

Into the integrand of Eq. (5), we now insert an identity relation

$$H(r - r_2) + H(r_2 - r) = 1\,, \tag{6a}$$

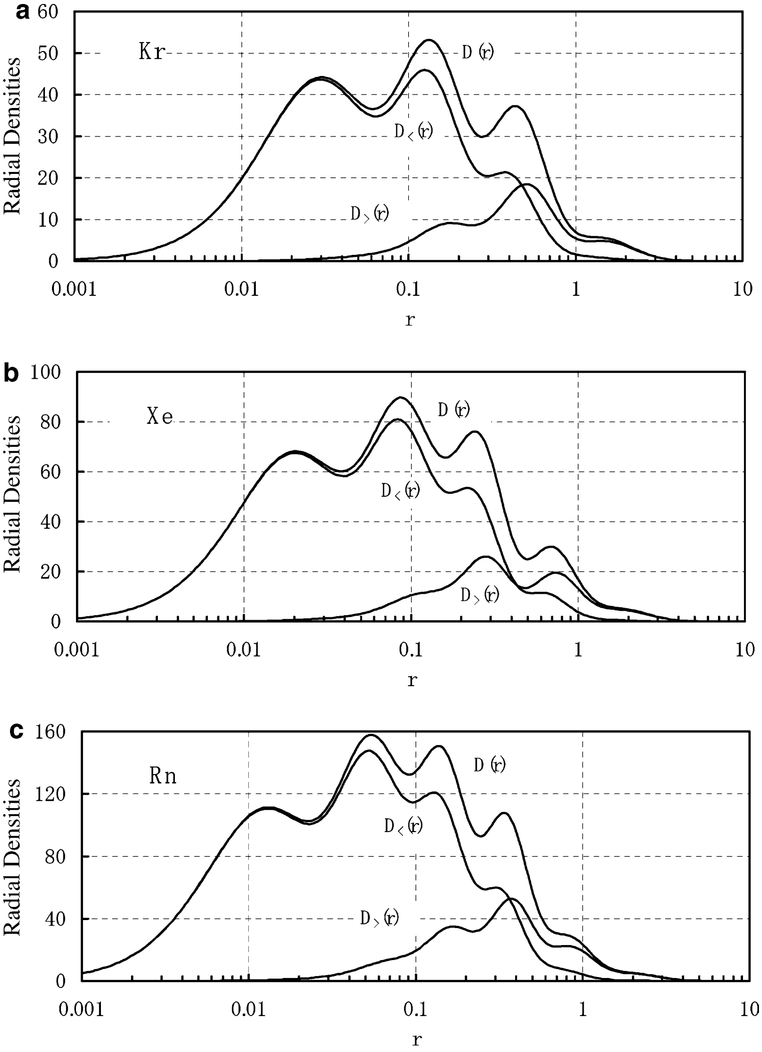

Fig. 2 Hartree-Fock radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ for **a** Kr, **b** Xe, and **c** Rn atoms

of the Heaviside function [8] $H(x-a)$ defined by

$$H(x-a)=\begin{cases}0\,, & x<a\\ \frac{1}{2}\,, & x=a\\ 1\,, & x>a\end{cases}. \tag{6b}$$

We then have

$$D(r)=D_<(r)+D_>(r)\,, \tag{7}$$

where

$$D_<(r)=\frac{2}{N-1}\int\limits_0^\infty \mathrm{d}r_2\ H(r_2-r)\ D_2(r,r_2)$$
$$=\frac{2}{N-1}\int\limits_r^\infty \mathrm{d}r_2\ D_2(r,r_2)\,, \tag{8a}$$

$$D_>(r)=\frac{2}{N-1}\int\limits_0^\infty \mathrm{d}r_2\ H(r-r_2)\ D_2(r,r_2)$$
$$=\frac{2}{N-1}\int\limits_0^r \mathrm{d}r_2\ D_2(r,r_2)\,. \tag{8b}$$

The function $D_<(r)$ is called inner radial function, since it represents the probability density that one electron moves with a radius r which is smaller than the radius of the other

Table 1 Atomic numbers Z of ground-state atoms for which electron shells are detected as the local maxima in the three radial densities

Shell	$D_<(r)$	$D_>(r)$	$D(r)$
K	2–103	2–8	2–103
L	4–103	3–42	3–103
M	17–103	11–103	11–103
N	49–103	36–103	40–103
O	None	82–103	92–103

electron. The function $D_>(r)$ is the probability density for the opposite situation and is called outer radial function. The inner and outer radial functions are normalized as

$$\int_0^\infty \mathrm{d}r\, D_<(r) = \int_0^\infty \mathrm{d}r\, D_>(r) = \frac{N}{2}\,, \tag{9}$$

in accord with Eqs. (2) and (7). From the comparison of Eqs. (5), (8a), and (8b), we see that $D_<(r)$ is a more important component function of $D(r)$ when r is small while $D_>(r)$ is when r is large. If we consider the spherically-averaged densities $\rho(r) = D(r)/(4\pi r^2)$, $\rho_<(r) = D_<(r)/(4\pi r^2)$, and $\rho_>(r) = D_>(r)/(4\pi r^2)$ corresponding to the three radial densities, we find that

$$\rho_<(r) \to \rho(r) \text{ and } \rho_>(r) \to 0, \quad \text{when } r \to 0, \tag{10a}$$

$$\rho_<(r) \to 0 \text{ and } \rho_>(r) \to \rho(r), \text{ when } r \to \infty. \tag{10b}$$

Thus the electron–nucleus cusp property [9,10] of $\rho(r)$ appears only in the inner density $\rho_<(r)$, whereas the long-range asymptotic behavior [11–16] of $\rho(r)$ appears only in the outer density $\rho_>(r)$.

Since the radial density $D(r)$ is rigorously separated into the inner $D_<(r)$ and outer $D_>(r)$ densities, any radial property $f(r)$ which depends only on the radial variable r is partitioned correspondingly. As a simple example, we have for the radial moments $f(r) = r^n$ that

$$< r^n > = < r_<^n > + < r_>^n >\,, \tag{11a}$$

where

$$< r^n > = \int_0^\infty \mathrm{d}r\; r^n\; D(r)\,, \tag{11b}$$

$$< r_<^n > = \int_0^\infty \mathrm{d}r\; r^n\; D_<(r) = \frac{1}{N-1}\int_0^\infty \mathrm{d}r_1 \int_0^\infty dr_2\; r_<^n\; D_2(r_1, r_2)\,, \tag{11c}$$

$$< r_>^n > = \int_0^\infty \mathrm{d}r\; r^n\; D_>(r) = \frac{1}{N-1}\int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2\; r_>^n\; D_2(r_1, r_2)\,, \tag{11d}$$

in which $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. A few important cases of Eq. (11a) are: when $n = -1$, we obtain a partitioning of the electron–nucleus attraction energy $V_{\mathrm{en}} = -Z < r^{-1} >$ of atoms, where the nuclear position is the natural choice of the coordinate origin. When $n = 1$, we have the inner $< r_< >$ and outer $< r_> >$ electron radii studied in [17–19], under the condition that all the radial densities are normalized to unity. When $n = 2$, Eq. (11a) shows that the diamagnetic susceptibility $\chi_{\mathrm{d}} = - < r^2 > /(6c^2)$ is the sum of the inner and outer contributions.

Another useful relation follows from the Laplace expansion (see, e.g., [20]) of the reciprocal interelectronic distance,

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{n=0}^{\infty} \frac{r_<^n}{r_>^{n+1}} P_n(\cos\,\alpha)\,, \tag{12}$$

where α is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ and $P_n(x)$ is the Legendre function. If we keep only the leading term of Eq. (12), we obtain for the electron–electron repulsion energy $V_{\mathrm{ee}} = < r_{12}^{-1} >$ that

$$V_{\mathrm{ee}} \cong (N-1)\int_0^\infty \mathrm{d}r\; r^{-1}\; D_>(r) = (N-1) < r_>^{-1} >\,, \tag{13}$$

where the equality holds when only s orbitals are involved such as the ground-state He, Li, and Be atoms in the Hartree-Fock approximation. Equation (13) provides us with an approximate relation between the electron repulsion energy V_{ee} and the minus first moment $< r_>^{-1} >$ of the outer radial density $D_>(r)$. The relation was previously discussed [21] for the He atom, but the connection to the outer radial density was not mentioned.

Except for the expression of V_{en}, the above discussion is valid not only for atoms but also for molecules and solids. For the latter cases, however, the meanings of the inner $D_<(r)$ and outer $D_>(r)$ radial densities are less unique, since they depend on the choice of the coordinate origin.

3 Results and discussion for atoms

Using a modified version of the MCHF72 program [22], we have calculated the Hartree-Fock radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ for the 102 atoms He (atomic number Z = 2) through Lr (Z = 103) in their ground states [23].

Figures 1 and 2 exemplify the radial densities $D_<(r)$, $D_>(r)$, and $D(r)$ for the six group-18 atoms. As mentioned in the previous section, we find in the figures that the inner density $D_<(r)$ is a more important component of $D(r)$ for a small r, while the outer density $D_>(r)$ is for a large r. Accordingly, the characteristics of local maxima are different among the three densities, though the largest number of local maxima is always found in $D(r)$. When we examine the inner or core region, local maxima in $D(r)$ originate mainly from $D_<(r)$. For example, the innermost maximum corresponding to the K shell is observed for all the atoms Z = 2–103 in $D_<(r)$ and $D(r)$, but only for 7 atoms Z = 2–8 in $D_>(r)$. When we consider the outer or valence region, on the other hand, local maxima and shoulders in $D(r)$ are mainly due to $D_>(r)$. Moreover $D_>(r)$ detects new maxima missing in $D(r)$ for some atoms. An example is that the fifth maximum corresponding to the O shell is found for Z = 92–103 in $D(r)$, but for Z = 82–103 in $D_>(r)$. For the 102 atoms examined, Table 1 summarizes how local maxima appear in the three radial densities.

For $n = -2, -1, 1$, and 2, the ratios $< r_<^n > / < r^n >$ of the inner moments $< r_<^n >$ relative to the total moments

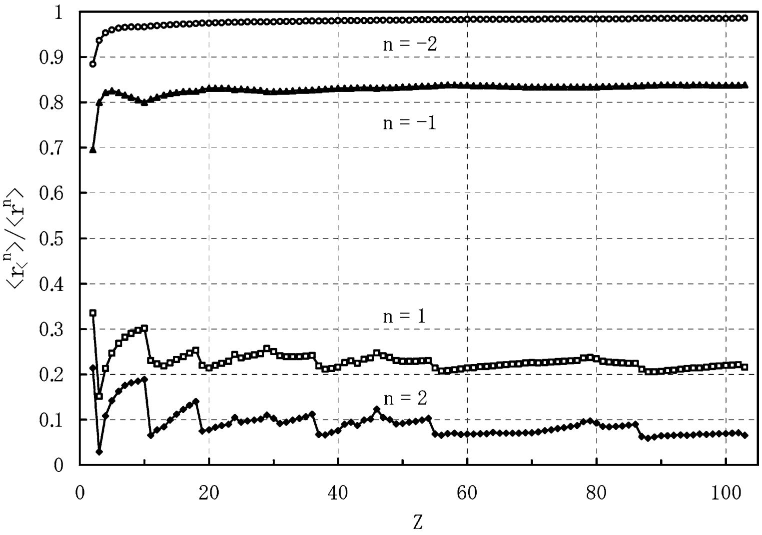

Fig. 3 The ratios $< r_<^n > / < r^n >$ of the inner moments $< r_<^n >$ relative to the total moments $< r^n >$ for $n = -2, -1, 1$, and 2

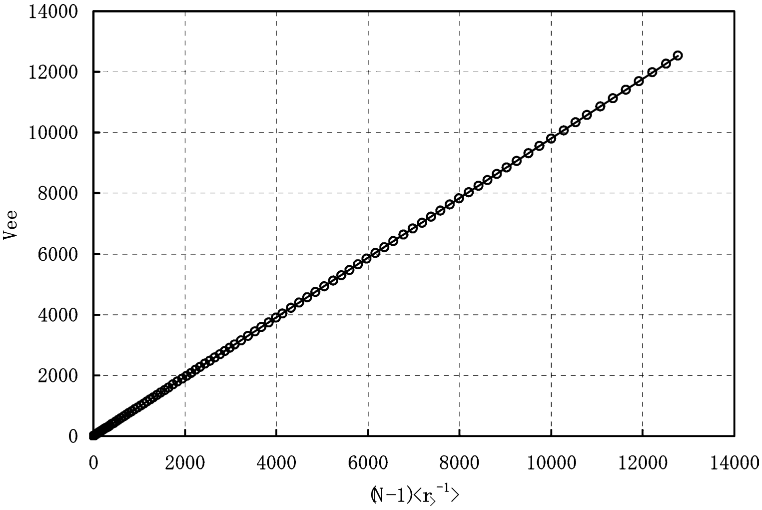

Fig. 4 Correlation between the electron–electron repulsion energies V_{ee} and the minus first moments $(N-1) < r_>^{-1} >$ of the outer radial densities

$< r^n >$ are depicted in Fig. 3 as a function of Z. When $n < 0$, the ratios are almost constants (0.98 for $n = -2$ and 0.83 for $n = -1$) except for the first several atoms and show that the major parts of the moments come from the inner radial density $D_<(r)$. In fact, the inner contribution occupies 82.9% of the electron–nucleus attraction energy V_{en} on an average, with the minimum 69.6% at $Z = 2$ and the maximum 83.8% at $Z = 58$. On the other hand, when $n > 0$, the inner contributions are smaller than the outer ones. The average values of the ratios are only 0.23 for $n = 1$ and 0.09 for $n = 2$. However, the ratios show a periodical Z-dependence reflecting the valence electron configuration of atoms. In particular, we have local minima for the group-1 or -2 atoms with diffuse s orbitals, whereas we have local maxima for the group-18 atoms with fully-occupied orbitals. On an average, the outer radial density $D_>(r)$ is responsible to 91.0% of the diamagnetic susceptibility χ_d, with the minimum 78.6% at $Z = 2$ and the maximum 97.2% at $Z = 3$.

We have also examined a possible correlation between the electron–electron repulsion energies V_{ee} and the minus first moments $(N - 1) < r_>^{-1} >$ of the outer radial densities $D_>(r)$, suggested by Eq. (13). Figure 4 demonstrates that there is an excellent linear correlation between the two properties. For the 102 atoms, a least-square fitting indeed gives

$$V_{ee} \cong 0.981307(N-1) < r_>^{-1} > -7.942473\,, \tag{14}$$

with correlation coefficient 0.999999. A finer analysis shows that $V_{ee} = (N - 1) < r_>^{-1} >$ when $Z = 2$–4, but $V_{ee} < (N - 1) < r_>^{-1} >$ when $Z = 5$–103. For the latter case, however, $(N - 1) < r_>^{-1} >$ is only 2.5% larger than V_{ee} on an average, with the minimum 1.4% at $Z = 5$ and the maximum 3.7% at $Z = 10$. Thus the electron–electron repulsion energies V_{ee} are simply approximated by $(N-1) < r_{>}^{-1} >$ themselves, if we accept at most 4% relative errors.

For the He atom, we have performed a pilot examination of the electron correlation effect on the distributions of the inner and outer density functions, based on multi-configuration Hartree-Fock calculations. The results show that the inner and outer densities shift towards the inner and outer directions, respectively, though the magnitudes are very small. Namely, the electron correlation works to separate the two density distributions from each other. We wish to report whether such correlation effect is common, when appropriate correlated wave functions are available for a series of atoms.

4 Concluding remarks

When any two electrons are considered simultaneously, the radial density function $D(r)$ in many-electron atoms is separated into the inner $D_{<}(r)$ and outer $D_{>}(r)$ radial densities. Accordingly, radial properties such as the electron–nucleus attraction energy V_{en} and the diamagnetic susceptibility χ_{d} are the sum of the inner and outer contributions. The electron–electron repulsion energy V_{ee} has an approximate relation with the minus first moment of the outer density $D_{>}(r)$. Based on Hartree-Fock calculations, numerical results have been discussed for the 102 atoms He through Lr in their ground states.

In the present study, the inner and outer densities have been introduced by decomposing the two-electron density into two parts based on the property of the Heaviside function $H(x-a)$. A possible generalization is to separate the density into three or more parts by the repeated use of a window function $H(x-a) - H(x-b)$, which clips out only the region $a < x < b$ of an operand function. In this case, however, the assignment of meaningful boundary values will be important from the physical point of view.

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