

Electron-pair shell density approximation applied to inner and outer densities of atoms

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Abstract The shell density approximation to the electron-pair radial density of atoms is applied to the inner $D_{<}(r)$ and outer $D_{>}(r)$ densities, which are two components of the single-electron density $D(r)$. The inner and outer densities are found to be expressed by product sums of shell densities and shell distributions or their complements. The expressions clarify physical meaning of the two densities and give examples for constructing two-electron properties from single-electron properties. Examination of the 53 atoms He through Xe shows that the quantum similarity indices between the original and approximate densities, bounded by 0 (complete dissimilarity) and 1 (complete similarity), are never smaller than 0.99998 and 0.99987 for the inner and outer densities, respectively. The local nature of the shell density and the monotonically increasing property of the shell distribution are used to derive simple shellwise lower and upper bounds to $D_{<}(r)$ and $D_{>}(r)$ in terms of $D(r)$ and the numbers of shell electrons. Numerical tests of the bounds demonstrate their utility.

Keywords Inner and outer densities · Electron-pair densities · Shell densities · Shell distributions

1 Introduction

When a normalized N -electron ($N \geq 2$) wave function $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ is given, the electron-pair radial density function (see, e.g., [1–7]) $D^{(2)}(r_1, r_2)$ is defined by

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$$D^{(2)}(r_1, r_2) = \frac{N(N-1)}{2} r_1^2 r_2^2 \int ds_1 ds_2 d\Omega_1 d\Omega_2 dx_3 \dots dx_N |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2, \quad (1)$$

where $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ is the combined position-spin coordinate of the electron i , (r_i, Ω_i) with $\Omega_i = (\theta_i, \phi_i)$ is the polar coordinate of the position vector \mathbf{r}_i , and $\int d\Omega_i$ stands for the angular integration $\int_0^{2\pi} d\phi_i \int_0^\pi d\theta_i \sin\theta_i$. The function $D^{(2)}(r_1, r_2)$ represents the probability density that among N electrons, one electron is located at a radius r_1 and the other electron at a radius r_2 simultaneously. It is normalized in this work to the number $N(N-1)/2$ of electron pairs. The familiar single-electron radial density (see, e.g., [8–11]) $D(r)$ is straightforwardly obtained from $D^{(2)}(r_1, r_2)$ by

$$D(r) = \frac{2}{N-1} \int_0^\infty dr_2 D^{(2)}(r, r_2). \quad (2)$$

The radial density $D(r)$, normalized to the number N of electrons in this work, implies the probability density of any single electron among N electrons being on the sphere with a radius r . The physical significance of the densities $D^{(2)}(r_1, r_2)$ and $D(r)$ as well as their connection to experimental measurements are described in [7].

If any two electrons are considered simultaneously, the radial density $D(r)$ is rigorously partitioned [12] into two component functions, the inner $D_{<}(r)$ and outer $D_{>}(r)$ density functions:

$$D(r) = D_{<}(r) + D_{>}(r), \quad (3a)$$

$$D_{<}(r) = \frac{2}{N-1} \int_r^\infty dr_2 D^{(2)}(r, r_2), \quad (3b)$$

$$D_{>}(r) = \frac{2}{N-1} \int_0^r dr_2 D^{(2)}(r, r_2). \quad (3c)$$

The inner density $D_{<}(r)$ 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 density $D_{>}(r)$ is the probability density for the opposite situation. Both the inner and outer densities are normalized to $N/2$. The partitioning of $D(r)$ into $D_{<}(r)$ and $D_{>}(r)$ was shown [13] to minimize the average variance of two component densities when a generalized partitioning of $D(r)$ is considered. The short- and long-range behavior of $D_{<}(r)$ and $D_{>}(r)$ was clarified in [12, 14] and an examination of $D_{<}(r)$ and $D_{>}(r)$ for singly-excited states of the He atom was reported in [15].

Based on subshell and shell analysis of the electron-pair radial density $D^{(2)}(r_1, r_2)$ of atoms, it was recently found [16] that $D^{(2)}(r_1, r_2)$ is well expressed by a set of shell densities $d_n(r)$ in the Hartree-Fock theory, where n denotes the principal quantum number. In the present paper, we apply the shell density approximation of $D^{(2)}(r_1, r_2)$ to the inner $D_{<}(r)$ and outer $D_{>}(r)$ density functions. The resultant expressions clar-

ify physical meaning of the two densities that the inner and outer densities are product sums of shell densities $d_n(r)$ and shell distributions $f_n^<(r)$ or their complements $f_n^>(r)$. For the 53 atoms He through Xe in their ground states [17], numerical examinations show that the quantum similarity indices between the original and approximate densities are never smaller than 0.99998 and 0.99987 for the inner and outer densities, respectively, where the index is bounded by 0 (complete dissimilarity) and 1 (complete similarity). The result implies a quantitatively acceptable construction of two-electron properties from single-electron properties. The local nature [16, 18] of the shell density $d_n(r)$ and the monotonically increasing property of the shell distribution $f_n^<(r)$ are used to derive simple shellwise lower and upper bounds to $D_<(r)$ and $D_>(r)$ in terms of $D(r)$ and the numbers N_n of shell electrons. Numerical tests of the bounds demonstrate their utility. All the numerical results in this work have been obtained by numerical Hartree-Fock calculations based on a modified version of the MCHF88 program [19]. Atomic units are used throughout.

2 Shell density approximation of inner and outer densities

The shell density approximation of the electron-pair density $D^{(2)}(r_1, r_2)$ reads [16]

$$D^{(2)}(r_1, r_2) \cong \frac{1}{2} \left[D(r_1)D(r_2) - \sum_n N_n d_n(r_1)d_n(r_2) \right], \quad (4a)$$

where

$$D(r) = \sum_n N_n d_n(r), \quad (4b)$$

$d_n(r)$ is the electron shell density (normalized to unity), and N_n is the number of electrons of the shell n . The shell density is exemplified in Fig. 1a for the four shells of the Kr atom. Equations (4a) and (4b) are consistent with the relation (2), since $\sum_n N_n = N$. We note that Eq. (4a) is correct (not approximate) for the ground-state He atom in the Hartree-Fock approximation, since the atom has only one occupied shell.

Inserting Eq. (4a) into Eqs. (3b) and (3c), we find

$$\begin{aligned} D_<(r) &\cong \frac{1}{N-1} \left[D(r)F^>(r) - \sum_n N_n d_n(r)f_n^>(r) \right], \\ &= \frac{1}{N-1} \sum_n N_n [D(r) - d_n(r)]f_n^>(r), \end{aligned} \quad (5a)$$

$$\begin{aligned} D_>(r) &\cong \frac{1}{N-1} \left[D(r)F^<(r) - \sum_n N_n d_n(r)f_n^<(r) \right], \\ &= \frac{1}{N-1} \sum_n N_n [D(r) - d_n(r)]f_n^<(r), \end{aligned} \quad (5b)$$

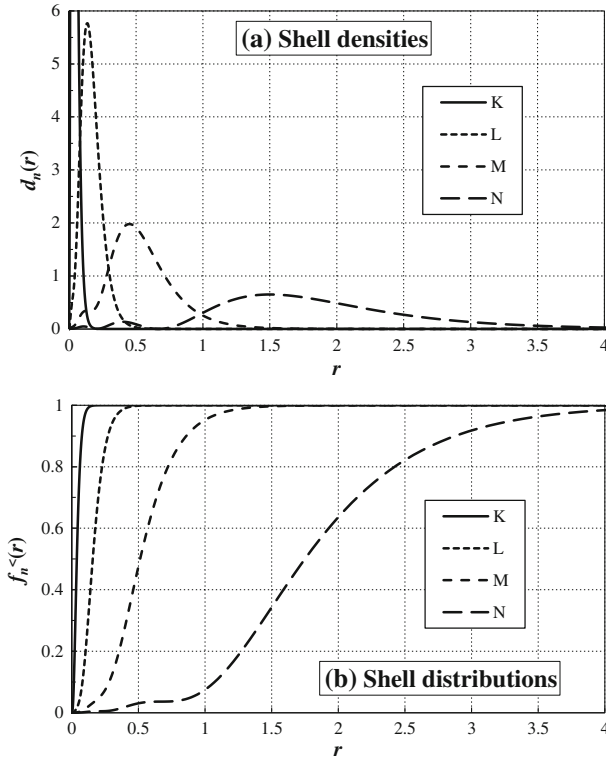


Fig. 1 **a** The shell density $d_n(r)$ and **b** the shell distribution $f_n^<(r)$ exemplified for the four shells of the Kr atom

for the inner and outer densities, where

$$f_n^<(r) = \int_0^r dr' d_n(r'), \tag{6a}$$

$$f_n^>(r) = \int_r^\infty dr' d_n(r'), \tag{6b}$$

are the cumulative distribution function of the n shell electron and its complementary function and

$$F^<(r) = \int_0^r dr' D(r') = \sum_n N_n f_n^<(r), \tag{6c}$$

$$F^>(r) = \int_r^\infty dr' D(r') = \sum_n N_n f_n^>(r), \tag{6d}$$

are the cumulative distribution function of all electrons and its complementary function. Since $D(r)$ and $d_n(r)$ are nonnegative, the distributions $F^<(r)$ and $f_n^<(r)$ are monotonically increasing functions from 0 to N and from 0 to 1, respectively, while the complements $F^>(r)$ and $f_n^>(r)$ are monotonically decreasing functions from N to 0 and from 1 to 0, respectively, when r varies from 0 to ∞ . Examples of the shell distribution $f_n^<(r)$ are given in Fig. 1b for the four shells of the Kr atom. The above distributions and complements satisfy sum rules

$$f_n^<(r) + f_n^>(r) = 1, \quad (7a)$$

$$F^<(r) + F^>(r) = N, \quad (7b)$$

for any value of r . The sum rules guarantee that Eqs. (5a) and (5b) satisfy Eq. (3a). It is also confirmed that the right-hand sides of Eqs. (5a) and (5b) are correctly normalized to $N/2$, because

$$\int_0^{\infty} dr d_n(r) f_n^<(r) = \int_0^{\infty} dr d_n(r) f_n^>(r) = \frac{1}{2}, \quad (8a)$$

$$\int_0^{\infty} dr [d_n(r) f_{n'}^<(r) + d_{n'}(r) f_n^<(r)] = \int_0^{\infty} dr [d_n(r) f_{n'}^>(r) + d_{n'}(r) f_n^>(r)] = 1, \quad (8b)$$

$$\int_0^{\infty} dr D(r) F^<(r) = \int_0^{\infty} dr D(r) F^>(r) = \frac{N^2}{2}. \quad (8c)$$

The above application of the shell density approximation to the inner and outer densities gives physical interpretation of the two densities as follows: The first lines of Eqs. (5a) and (5b) show that if the total density and the total distribution are expanded by their shell contributions (see Eqs. (4b), (6c), and (6d)), the inner and outer densities are weighted product sums of shell densities and shell distributions, where the weight factors depend on the numbers of electrons in two relevant shells. In the second line of Eq. (5a), the inner density $D_<(r)$ is clarified to originate from a product of the electron density $D(r) - d_n(r)$ of $N - 1$ electrons with a radius r , arising from the removal of an electron in the shell n , and the complementary cumulative distribution $f_n^>(r)$ of the removed electron, which has a radius larger than r of the $N - 1$ electrons. Analogously, the second line of Eq. (5b) shows that the outer density $D_>(r)$ comes from a product of the electron density $D(r) - d_n(r)$ of $N - 1$ electrons and the cumulative distribution $f_n^<(r)$ of an electron removed from the shell n . The removed electron has a radius smaller than r of the $N - 1$ electrons.

We next examine the accuracy of Eqs. (5a) and (5b) for the 53 atoms He through Xe in their ground states [17]. When the original and approximate densities are plotted and compared for the inner and outer densities of these atoms, we have found that the two curves are so similar that they are apparently superimposed and it is hard to distinguish the original and approximate densities by using figures. An example is

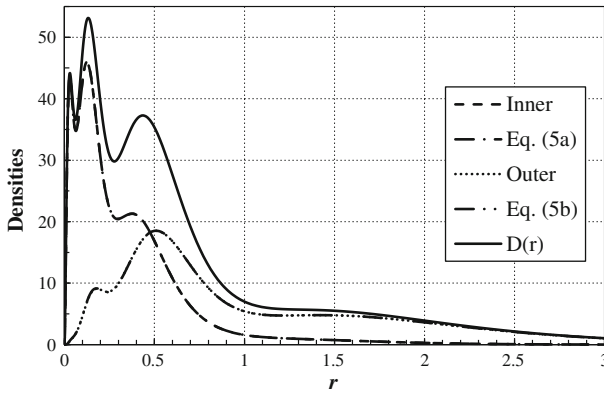


Fig. 2 The original and the shell density approximated inner and outer densities exemplified for the Kr atom

given in Fig. 2 for the Kr atom. To see the difference in a distinct way and to check the similarity in a quantitative manner, we then use the quantum similarity index [20,21] $S[f, g]$ of two nonnegative functions $f(r)$ and $g(r)$ defined by

$$S[f, g] = \left(\int_0^\infty dr f(r)g(r) \right) / \left[\left(\int_0^\infty dr f^2(r) \right) \left(\int_0^\infty dr g^2(r) \right) \right]^{1/2}. \quad (9)$$

The index is bounded as $0 \leq S[f, g] \leq 1$, where 0 means the complete dissimilarity while 1 means complete similarity. The calculated indices for the 53 atoms He through Xe are plotted in Fig. 3 as a function of atomic number Z . The indices for the inner density are never smaller than 0.99998 and are larger than 0.99999 for all atoms with $Z > 5$; the minimal value is 0.999984 for Be and the maximal value is 1 for He. The presence of equally occupied two shells (K and L) appears to be the origin of the largest dissimilarity for the Be atom. On the other hand, the similarity indices for the outer density are slightly worse. Nonetheless, they are never smaller than 0.99987 and larger than 0.99998 for all atoms with $Z > 6$; the minimal value is 0.999878 for Be and the maximal value is 1 for He. These values demonstrate that the shell density approximations to the inner and outer densities are highly accurate and quantitatively acceptable.

3 Shellwise behavior of inner and outer densities

In the literature [16,18,22–26], it was reported that atomic shell densities are quite dissimilar and well localized depending on the radial value r . When we consider a radial value r which lies in the n shell region bounded by two radii $r_n^{(\min)}$ and $r_n^{(\max)}$, we neglect the density contributions from all shells other than the n shell and have approximate relations

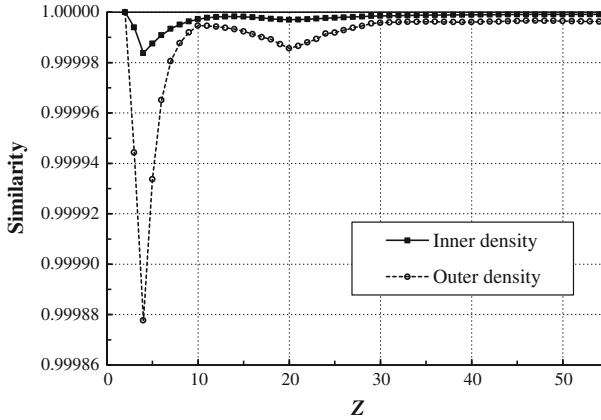


Fig. 3 Similarity indices between the original and the shell density approximated inner and outer densities as a function of atomic number Z

$$D(r) \cong N_n d_n(r), \tag{10a}$$

$$F^<(r) \cong N_n^< + N_n f_n^<(r), \tag{10b}$$

$$F^>(r) \cong N_n^> + N_n f_n^>(r), \tag{10c}$$

where

$$N_n^< = \sum_{k=1}^{n-1} N_k, \quad N_n^> = \sum_{k=n+1}^{n_{\max}} N_k, \tag{11}$$

are the numbers of electrons inside and outside the n shell, respectively, and n_{\max} stands for the principal quantum number of the outermost shell. Naturally, these numbers satisfy a relation $N_n^< + N_n + N_n^> = N$. Combining Eqs. (10a) – (10c) with Eqs. (5a) and (5b), we find for the n shell region that

$$D_{<}(r) \cong \frac{(N_n - 1) f_n^>(r) + N_n^>}{N - 1} D(r), \tag{12a}$$

$$D_{>}(r) \cong \frac{(N_n - 1) f_n^<(r) + N_n^<}{N - 1} D(r), \tag{12b}$$

whose sum fulfills the correct relation $D_{<}(r) + D_{>}(r) = D(r)$ because of Eq. (7a).

If we are reminded of the fact that the distribution $f_n^<(r)$ is a monotonically increasing function, whereas the complement $f_n^>(r)$ is a monotonically decreasing function when r increases in the n shell region, Eqs. (12a) and (12b) show that the relative contributions $D_{<}(r)/D(r)$ and $D_{>}(r)/D(r)$ of the inner and outer densities are monotonically decreasing and increasing, respectively, in that region. Successively connecting such monotonicity for all occupied shells, the overall monotonicity is expected for the relative contributions in the entire region of r . The anticipation is confirmed to be true for all the atoms, as exemplified in Fig. 4 for the Kr atom where the relevant

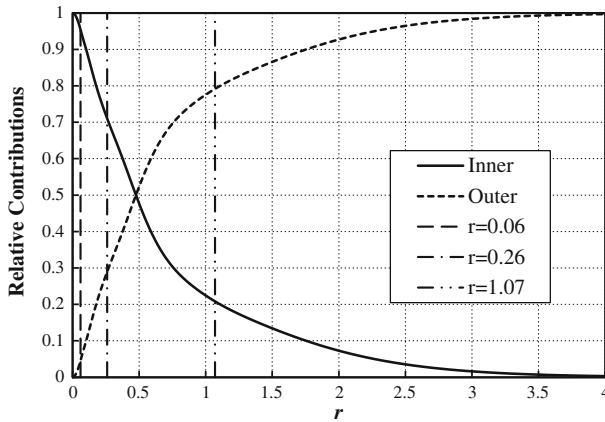


Fig. 4 The relative contributions $D_{<}(r)/D(r)$ and $D_{>}(r)/D(r)$ of the inner and outer densities for the Kr atom calculated by the original electron-pair density. The three vertical lines separate the four shell regions in the atom

data have been taken from the original electron-pair density [12]. Equations (12a) and (12b) also tell us that the curves of the inner $D_{<}(r)$ and outer $D_{>}(r)$ density functions would cross at a single point $r^{(c)}$ in a particular n shell region where a relation $(N_n - 1)f_n^{>}(r^{(c)}) + N_n^{>} = (N_n - 1)f_n^{<}(r^{(c)}) + N_n^{<}$ is satisfied. For the Kr atom, Figs. 2 and 4 show that the two density curves indeed have a single cross point in the M shell region, where $f_{n=3}^{<}(r^{(c)}) = 1 - f_{n=3}^{>}(r^{(c)}) \cong 15/34$. Examples of the single crossing nature of the inner and outer densities are also found in figures of [12] for other atoms.

Furthermore, since the functions $f_n^{<}(r)$ and $f_n^{>}(r)$ are bounded by 0 and 1, we obtain from Eqs. (12a) and (12b) lower and upper bounds to the inner and outer densities in the n shell region (i.e. $r_n^{(\min)} < r < r_n^{(\max)}$) as

$$\frac{N_n^{>}}{N - 1} D(r) \leq D_{<}(r) \leq \frac{N_n - 1 + N_n^{>}}{N - 1} D(r), \tag{13a}$$

$$\frac{N_n^{<}}{N - 1} D(r) \leq D_{>}(r) \leq \frac{N_n - 1 + N_n^{<}}{N - 1} D(r). \tag{13b}$$

Note that two cross sums of the four bounds (i.e., the lower bound in an inequality plus the upper bound in another inequality) in Eqs. (13a) and (13b) reduce to $D(r)$ as is the sum of $D_{<}(r)$ and $D_{>}(r)$. A particular case of these inequalities for $n = 1$ (K shell) reads

$$\frac{N - 2}{N - 1} D(r) \leq D_{<}(r) \leq D(r), \tag{14a}$$

$$0 \leq D_{>}(r) \leq \frac{1}{N - 1} D(r), \tag{14b}$$

Table 1 The numerical values of the shellwise lower and upper bounds to the relative contributions $D_{<}(r)/D(r)$ and $D_{>}(r)/D(r)$ for the Kr atom

Shell	$N_n^{<}$	N_n	$N_n^{>}$	$r_n^{(b)}$	$D_{<}(r)/D(r)$			$D_{>}(r)/D(r)$		
					Lower bound	Value at $r_n^{(b)}$	Upper bound	Lower bound	Value at $r_n^{(b)}$	Upper bound
				0	–	1	–	–	0	–
K ($n = 1$)	0	2	34	–	34/35 (= 0.971)	–	1	0	–	1/35 (= 0.029)
				0.06	–	0.952	–	–	0.048	–
L ($n = 2$)	2	8	26	–	26/35 (= 0.743)	–	33/35 (= 0.943)	2/35 (= 0.057)	–	9/35 (= 0.257)
				0.26	–	0.707	–	–	0.293	–
M ($n = 3$)	10	18	8	–	8/35 (= 0.229)	–	5/7 (= 0.714)	2/7 (= 0.286)	–	27/35 (= 0.771)
				1.07	–	0.209	–	–	0.791	–
N ($n = 4$)	28	8	0	–	0	–	1/5 (= 0.200)	4/5 (= 0.800)	–	1
				∞	–	0	–	–	1	–

since $N_1^{<} = 0$, $N_1 = 2$, and $N_1^{>} = N - 2$. The relations do not contradict with the short-range behavior of the inner and outer densities reported in the literature [12, 14] that $D_{<}(r) = [1 + O(r^3)]D(r)$ and $D_{>}(r) = [0 + O(r^3)]D(r)$. Another particular case of Eqs. (13a) and (13b) for $n = n_{\max}$ (outermost shell) is

$$0 \leq D_{<}(r) \leq \frac{N_{n_{\max}} - 1}{N - 1} D(r), \tag{15a}$$

$$\frac{N - N_{n_{\max}}}{N - 1} D(r) \leq D_{>}(r) \leq D(r), \tag{15b}$$

since $N_{n_{\max}}^{<} = N - N_{n_{\max}}$ and $N_{n_{\max}}^{>} = 0$. The inequalities are consistent with the known long-range behavior [12, 14] that $D_{<}(r) \rightarrow 0$ and $D_{>}(r) \rightarrow D(r)$ when $r \rightarrow \infty$.

To check the utility of the shellwise bounds to the inner and outer densities, we have performed numerical tests for various atoms. We first separated radial regions of occupied shells in an atom by defining boundary radii $r_n^{(b)}$, at which two neighboring n and $n + 1$ shells have equal density contributions $N_n d_n(r_n^{(b)}) = N_{n+1} d_{n+1}(r_n^{(b)})$. In the case of the Kr atom, for example, the values of $r_n^{(b)}$ for $n = 1, 2, 3$ are 0.06, 0.26, 1.07, respectively, which are illustrated in Fig. 4. Note that $r_n^{(\max)} < r_n^{(b)} < r_{n+1}^{(\min)}$ by the definition. We then calculated the relative contributions $D_{<}(r)/D(r)$ and $D_{>}(r)/D(r)$ at $r_n^{(b)}$ from the original densities, and the values were compared with the coefficients of $D(r)$ appearing in the upper and lower bounds in Eqs. (13a) and (13b). The results have shown both the lower and upper bounds work in a satisfactory manner. A detailed

numerical example is given in Table 1 for the Kr atom. We find the shellwise lower and upper bounds are well bounded by the relative contributions at two neighboring values of $r_n^{(b)}$. A minor exception is the upper bound $5/7$ for $D_{<}(r)/D(r)$ (or the lower bound $2/7$ for $D_{>}(r)/D(r)$) of the M shell, which is slightly larger than 0.707 (or slightly smaller than 0.293) obtained from the original densities at $r_{n=2}^{(b)}$. The nontrivial overlap of the L and M shell densities, as observed in Fig. 1a, seems to be the origin of these small discrepancies. Analogous small inversions were found for the M shell of the other fourth period atoms and for the M and N shells of the fifth period atoms, but were not found for the second and third period atoms. Though we encounter cases where the shell density approximation is not highly quantitative, Eqs. (13a) and (13b) are demonstrated to be very useful since we can predict the relative contributions of the inner and outer densities only from the knowledge of the numbers of shell electrons.

4 Summary

We have applied the shell density approximation of $D^{(2)}(r_1, r_2)$ to the inner $D_{<}(r)$ and outer $D_{>}(r)$ density functions. The resultant expressions clarify physical meaning of the two densities that the inner and outer densities originate from products of shell densities $d_n(r)$ and shell distributions $f_n^{<}(r)$ or their complements $f_n^{>}(r)$. Examinations of the quantum similarity indices between the original and approximate densities have shown high accuracy of the approximation for the 53 atoms He through Xe. The local nature of the shell density $d_n(r)$ and the monotonically increasing property of the shell distribution $f_n^{<}(r)$ have been used to derive simple shellwise lower and upper bounds to $D_{<}(r)$ and $D_{>}(r)$ in terms of $D(r)$ and the numbers N_n of shell electrons. Numerical tests of the bounds have demonstrated their utility.

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