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REGULAR ARTICLE

Short- and long-range behavior of the inner and outer densities

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Abstract We report the short- and long-range behavior of the inner $\rho_<(r)$ and outer $\rho_>(r)$ densities, which result from a rigorous partitioning of the spherically averaged one-electron density $\rho(r)$ in many-electron atoms. It is found that for a small r, $\rho_<(r)$ has one-electron nature but $\rho_>(r)$ has two-electron nature. For a large r, however, the opposite is true.

Keywords Short-range behavior · Long-range behavior · Inner density · Outer density

1 Introduction

In recent articles [1, 2] published in this Journal, it was found that the spherically averaged one-electron density $\rho(r)$ in many-electron atoms is rigorously separated into the inner $\rho_<(r)$ and outer $\rho_>(r)$ densities. The density $\rho(r)$ simply means the probability density of finding an electron at a radius r, but the inner density $\rho_<(r)$ represents the probability density that one electron moves with a radius r which is smaller than the radius of the other electrons and the outer density $\rho_>(r)$ is the probability density for the opposite situation. The inner and outer densities, multiplied by $4\pi r^2$, were examined [1, 3] for some ground- and excited-state atoms. In an article [1], it was noted without detailed mathematical analyses that when the radius r tends to zero, the inner density $\rho_<(r)$ approaches the total density $\rho(r)$ while the outer density $\rho_>(r)$ becomes zero. Also mentioned is that $\rho_>(r)$ tends to $\rho(r)$ whereas $\rho_<(r)$ becomes zero, when r goes to infinity.

In the present study, we report the small- and large-r asymptotic behavior of the inner and outer density functions. The results confirm the literature statements [1]. Furthermore, it will be found that for a small r, the inner density $\rho_<(r)$ has one-electron nature, but the outer density $\rho_>(r)$ has two-electron nature; the small-r behavior of $\rho_<(r)$ depends on the one-electron density $\rho(r)$ and its derivatives at the origin whereas that of $\rho_>(r)$ is intimately related with the two-electron density $\rho_2(r_1, r_2)$ and its derivatives at the origin. For a large r, on the contrary, $\rho_<(r)$ has two-electron nature but $\rho_>(r)$ has one-electron nature; the exponential decay of the correct $\rho_<(r)$ depends on the first two ionization potentials whereas that of the correct $\rho_>(r)$ on the first ionization potential only.

2 Definitions

For an N-electron atom ($N \geq 2$) described by a normalized, antisymmetric wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, the spherically averaged one-electron $\rho(r)$ and two-electron $\rho_2(r_1, r_2)$ density functions are defined by

$$\rho(r) = \frac{N}{4\pi} \int \mathrm{d}\Omega\, \mathrm{d}s\, \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}, \mathbf{x}_2, \cdots, \mathbf{x}_N)|^2, \tag{1a}$$

$$\rho_2(r_1, r_2) = \frac{N(N-1)}{2(4\pi)^2} \times \int \mathrm{d}\Omega_1\, \mathrm{d}s_1\, \mathrm{d}\Omega_2\, \mathrm{d}s_2\, \mathrm{d}\mathbf{x}_3 \cdots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2, \tag{1b}$$

where $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ is the combined position-spin coordinate of the electron i and (r_i, Ω_i) are polar coordinates of the

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vector $\mathbf{r}_i$. The densities $\rho(r)$ and $\rho_2(r_1, r_2)$ are normalized to N and $N(N-1)/2$, respectively.

In terms of $\rho_2(r_1, r_2)$, the one-electron density function $\rho(r)$ and its inner $\rho_<(r)$ and outer $\rho_>(r)$ components [1] are written as

$$\rho(r) = C\int_0^\infty \mathrm{d}r_2\, r_2^2\, \rho_2(r, r_2) = \rho_<(r) + \rho_>(r), \tag{2a}$$

$$\rho_<(r) = C\int_r^\infty \mathrm{d}r_2\, r_2^2\, \rho_2(r, r_2), \tag{2b}$$

$$\rho_>(r) = C\int_0^r \mathrm{d}r_2\, r_2^2\, \rho_2(r, r_2), \tag{2c}$$

where $C = (8\pi)/(N-1)$. Both the inner and outer densities are normalized to $N/2$.

3 Short- and long-range behavior of the inner and outer densities

3.1 Short-range behavior

We assume that all the density functions introduced above are continuous and infinitely differentiable. We then apply the Maclaurin expansion

$$f(r) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!}\, r^n \tag{3}$$

to the three densities $\rho(r)$, $\rho_<(r)$, and $\rho_>(r)$, where $f^{(n)}(r) = \mathrm{d}^n f(r)/\mathrm{d}r^n$.

Straightforward differentiations of Eqs. (2a)–(2c) give after some manipulation that the nth derivatives of $\rho(r)$, $\rho_<(r)$, and $\rho_>(r)$ are

$$\rho^{(n)}(r) = C\int_0^\infty \mathrm{d}r_2\, r_2^2\, \rho_2^{[n,0]}(r, r_2), \tag{4a}$$

$$\rho_<^{(n)}(r) = C\left\{\int_r^\infty \mathrm{d}r_2\, r_2^2\, \rho_2^{[n,0]}(r, r_2) - \sum_{k=0}^{n-1} \frac{\mathrm{d}^k}{\mathrm{d}r^k}\left[r^2 \rho_2^{[n-k-1,0]}(r, r)\right]\right\}, \tag{4b}$$

$$\rho_>^{(n)}(r) = C\left\{\int_0^r \mathrm{d}r_2\, r_2^2\, \rho_2^{[n,0]}(r, r_2) + \sum_{k=0}^{n-1} \frac{\mathrm{d}^k}{\mathrm{d}r^k}\left[r^2 \rho_2^{[n-k-1,0]}(r, r)\right]\right\}, \tag{4c}$$

where $\rho_2^{[m,n]}(r_1, r_2) = \partial^{m+n}\rho_2(r_1, r_2)/\partial r_1^m \partial r_2^n$. If $n = 0$, the second terms in the braces of Eqs. 4b and 4c do not appear. We then have

$$\rho_<^{(n)}(0) = \rho^{(n)}(0), \quad \rho_>^{(n)}(0) = 0, \tag{5a}$$

for $n = 0$, 1, 2 and

$$\rho_<^{(n)}(0) = \rho^{(n)}(0) - CA_n, \quad \rho_>^{(n)}(0) = CA_n, \tag{5b}$$

for $n \geq 3$, where

$$A_n = \sum_{k=2}^{n-1} k(k-1) \sum_{l=0}^{k-2} \binom{k-2}{l} \rho_2^{[n-k+l-1,k-l-2]}(0, 0). \tag{5c}$$

The first three values of A_n are

$$A_3 = 2\rho_2(0, 0), \tag{6a}$$

$$A_4 = 14\rho_2^{[1,0]}(0, 0), \tag{6b}$$

$$A_5 = 32\rho_2^{[2,0]}(0, 0) + 30\rho_2^{[1,1]}(0, 0), \tag{6c}$$

where we have used the fact that $\rho_2^{[m,n]}(0, 0) = \rho_2^{[n,m]}(0, 0)$.

The short-range behaviors of the inner $\rho_<(r)$ and outer $\rho_>(r)$ densities are now explicitly obtained as

$$\rho_<(r) = \rho(0) + \rho^{(1)}(0)r + \frac{\rho^{(2)}(0)}{2} r^2 + O(r^3), \tag{7a}$$

$$\rho_>(r) = \frac{C}{3}\left[\rho_2(0, 0)r^3 + \frac{7\rho_2^{[1,0]}(0, 0)}{4} r^4\right] + O(r^5), \tag{7b}$$

in terms of the two basic density functions $\rho(r)$ and $\rho_2(r_1, r_2)$. The results confirm the literature statement [1] that $\rho_<(r) \to \rho(r)$ and $\rho_>(r) \to 0$ when $r \to 0$.

Equation 7a implies that for a small r, the inner density $\rho_<(r)$ is identical with the usual one-electron density $\rho(r)$ to the order of r^2. In other words, $\rho_<(r)$ has one-electron nature for $r \ll 1$. If $\rho(r)$ has a cusp property, $\rho_<(r)$ also has exactly the same cusp property. Namely,

$$\rho_<^{(1)}(0)/\rho_<(0) = \rho^{(1)}(0)/\rho(0), \tag{8a}$$

which is valid for any approximate and exact wave functions. If the correct cusp condition [4, 5] is satisfied, the ratio in Eq. 8a is equal to $-2Z$ where Z is the nuclear charge.

On the other hand, Eq. 7b shows that the leading term of the outer density $\rho_>(r)$ is proportional to r^3. Moreover, the expansion coefficients of the first two terms explicitly depend on the two-electron density $\rho_2(r_1, r_2)$ and its first derivative $\rho_2^{[1,0]}(r_1, r_2)$ at the origin $r_1 = r_2 = 0$. The short-range behavior of the outer density $\rho_>(r)$ reveals two-electron nature. We obtain a relation

$$\left[\frac{\rho_>^{(4)}(0)}{4!}\right]\Big/\left[\frac{\rho_>^{(3)}(0)}{3!}\right]=\frac{7}{4}\frac{\rho_2^{[1,0]}(0,0)}{\rho_2(0,0)}=\frac{7}{8}\frac{\rho_2^{(1)}(0,0)}{\rho_2(0,0)}, \tag{8b}$$

for any approximate and exact wave functions, where $\rho_2^{(1)}(r,r)=\mathrm{d}\rho_2(r,r)/\mathrm{d}r$. When the Bingel expansion [6] of wave functions is applied, we find that for $r \ll 1$, the diagonal function $\rho_2(r,r)$ has the same behavior as the electron–electron coalescence function [7] $h_0(r)$. The latter function shows [7] a cusp property $h_0^{(1)}(0)/h_0(0)=-4Z$ at least for the exact and Hartree–Fock wave functions, where $h_0^{(1)}(r)=\mathrm{d}h_0(r)/\mathrm{d}r$. For wave functions with the correct cusp property, the ratio in Eq. 8b is evaluated to be $-7Z/2$.

3.2 Long-range behavior

Ahlrichs and coworkers reported [8] that for a large r, a general form of the asymptotically dominant exponential part of $\rho_2(r_1,r_2)$ is

$$\begin{aligned}\rho_2(r_1,r_2) \approx{}& \exp\left[-2\left(\sqrt{2\varepsilon_1}r_1+\sqrt{2\varepsilon_2}r_2\right)\right]\\ &+\exp\left[-2\left(\sqrt{2\varepsilon_1}r_1+\sqrt{2\varepsilon_2}r_2\right)\right],\end{aligned} \tag{9}$$

where ε_1 and ε_2 ($\varepsilon_1<\varepsilon_2$) are the first and second ionization potentials, respectively. The pre-exponential part is not considered. If Eq. 9 is combined with Eqs. 2a–2c, the dominant exponential decays of the three densities $\rho(r)$, $\rho_<(r)$ and $\rho_>(r)$ for a large r are obtained as

$$\rho(r)\approx\exp\left(-2\sqrt{2\varepsilon_1}r\right), \tag{10a}$$

$$\rho_<(r)\approx\exp\left[-2\left(\sqrt{2\varepsilon_1}+\sqrt{2\varepsilon_2}\right)r\right], \tag{10b}$$

$$\rho_>(r)\approx\exp\left(-2\sqrt{2\varepsilon_1}r\right), \tag{10c}$$

where the first relation was known in [8, 9]. Equations 10a–10c confirm the statement in [1] that $\rho_>(r)\to\rho(r)$ and $\rho_<(r)\to 0$ when $r\to\infty$: for a large r, the outer density $\rho_>(r)$ has the same exponential decay as $\rho(r)$. On the other hand, the inner density $\rho_<(r)$ has a faster decay than $\rho_>(r)$ and $\rho(r)$ by an exponential factor of $\exp\left(-2\sqrt{2\varepsilon_2}r\right)$. Moreover, we find the long-range behavior of the outer $\rho_>(r)$ and total $\rho(r)$ densities is related with the one-electron removal, while that of the inner density $\rho_<(r)$ with the two-electron removal.

The above results apply to the exact or correct large-r wave functions, and not to commonly used approximate wave functions with no special constraints. However, we anticipate that approximate wave functions also show a faster decay of $\rho_<(r)$ than $\rho_>(r)$ and $\rho(r)$ for a large r.

4 Simple illustration

We wish to illustrate the present results in a simple yet analytical manner, but we do not know analytical wave functions which have both the correct cusp and long-range properties simultaneously. Thus, we here use the Kellner approximation [10] for the He atom to show the equalities given in Eqs. 8a and 8b and the faster decay of $\rho_<(r)$ for a large r.

In the Kellner approximation, the wave function for the ground-state He atom is

$$\begin{aligned}\Psi(\mathbf{x}_1,\mathbf{x}_2)={}&\left(\zeta^3/\pi\right)\exp[-\zeta(r_1+r_2)]\\ &\times[\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)]/\sqrt{2},\end{aligned} \tag{11}$$

where the variationally optimum value of the parameter ζ is 27/16. Based on the definitions of the density functions, we analytically obtain $\rho_2(r_1,r_2)=(\zeta^3/\pi)^2\exp[-2\zeta(r_1+r_2)]$ and

$$\rho(r)=(2\zeta^3/\pi)\exp(-2\zeta r), \tag{12a}$$

$$\rho_<(r)=(2\zeta^3/\pi)\exp(-4\zeta r)[1+2\zeta r(1+\zeta r)], \tag{12b}$$

$$\begin{aligned}\rho_>(r)={}&(2\zeta^3/\pi)\exp(-4\zeta r)[-1+\exp(2\zeta r)\\ &-2\zeta r(1+\zeta r)].\end{aligned} \tag{12c}$$

For $r\ll 1$, the short-range behavior of the densities is then found to be

$$\rho(r)=\rho_<(r)=\left(2\zeta^3/\pi\right)\left(1-2\zeta r+2\zeta^2r^2\right)+O\left(r^3\right), \tag{13a}$$

$$\rho_>(r)=\left[8\zeta^6/(3\pi)\right]\left[r^3-(7\zeta/2)r^4\right]+O\left(r^5\right) \tag{13b}$$

and hence $\rho_>^{(0)}(0)=\rho_>^{(1)}(0)=\rho_>^{(2)}(0)=0$. We indeed observe the relations $\rho^{(1)}(0)/\rho(0)=\rho_<^{(1)}(0)/\rho_<(0)$ and $\left[\rho_>^{(4)}(0)/4!\right]/\left[\rho_>^{(3)}(0)/3!\right]=\left[7\rho_2^{[1,0]}(0,0)\right]/[4\rho_2(0,0)]$. In the present approximation, these ratios are -2ζ and $-7\zeta/2$, respectively. For $r\gg 1$, on the other hand, the long-range behavior is

$$\rho(r)\approx\rho_>(r)\approx\exp(-2\zeta r), \tag{14a}$$

$$\rho_<(r)\approx\exp(-4\zeta r), \tag{14b}$$

and the inner density has a faster decay by a factor of $\exp(-2\zeta r)$.

5 Summary

We have reported the short- and long-range behavior of the inner $\rho_<(r)$ and outer $\rho_>(r)$ densities of many-electron atoms in an analytical manner. Despite that $\rho_<(r)$ and $\rho_>(r)$ are components of the one-electron density $\rho(r)$, it has been found that $\rho_>(r)$ for a small r and $\rho_<(r)$ for a large r have two-electron nature.

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