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REGULAR ARTICLE

On the inner and outer radial density functions

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Abstract Starting from the two-electron radial density $D_2(r_1, r_2)$, a generalized partitioning of the one-electron radial density function $D(r)$ into two component densities $D_a(r)$ and $D_b(r)$ is discussed for many-electron systems. The literature partitioning (Koga and Matsuyama Theor Chem Acc 115:59, 2006) of $D(r)$ into the inner $D_<(r)$ and outer $D_>(r)$ radial densities is shown to minimize the average variance $(\sigma_a^2 + \sigma_b^2)/2$ of the two component density functions $D_a(r)$ and $D_b(r)$. It is also found that the average radial separation halved, $\langle|r_1 - r_2|\rangle/2$, constitutes a lower bound to the standard deviation σ of $D(r)$.

Keywords Radial density · Partitioning · Inner density · Outer density · Variance

1 Introduction

The radial density $D(r)$ represents (see, e.g., [1]) the probability density function of finding an electron at a distance r $(0 \leq r < \infty)$ from the coordinate origin, and is normalized to the number N of electrons as

$$\int_0^\infty \mathrm{d}r\, D(r) = N. \tag{1}$$

In a recent paper [2] published in this Journal, it was shown that for systems with $N \geq 2, D(r)$ is rigorously separated into inner $D_<(r)$ and outer $D_>(r)$ densities,

$$D(r) = D_<(r) + D_>(r), \tag{2a}$$

where

$$D_<(r) = \frac{2}{N-1}\int_0^\infty \mathrm{d}r_2\, H(r_2 - r)\, D_2(r, r_2) = \frac{2}{N-1}\int_r^\infty \mathrm{d}r_2\, D_2(r, r_2), \tag{2b}$$

$$D_>(r) = \frac{2}{N-1}\int_0^\infty \mathrm{d}r_2\, H(r - r_2)\, D_2(r, r_2) = \frac{2}{N-1}\int_0^r \mathrm{d}r_2\, D_2(r, r_2), \tag{2c}$$

in which

$$H(x - c) = \begin{cases} 0\,, & x < c \\ \frac{1}{2}\,, & x = c\,, \\ 1\,, & x > c \end{cases} \tag{3}$$

is the Heaviside function [3] and $D_2(r_1, r_2)$ is the two-electron radial density function (see, e.g., [2,4]). The latter function represents the probability density that one electron is at a radius r_1 and the other electron at a radius r_2, when any two electrons are considered simultaneously, and is normalized to the number of electron pairs as

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

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In Eq. (2a), the inner density $D_<(r)$ is the probability density that one electron moves with a radius r which is smaller than the radius of the other electron, while the outer density $D_>(r)$ is the probability density for the opposite situation. These radial densities are normalized as

$$\int_0^\infty \mathrm{d}r D_<(r) = \int_0^\infty \mathrm{d}r D_>(r) = \frac{N}{2}, \tag{5}$$

in accordance with Eqs. (1) and (2a). The partitioning (2a) is based on a relation

$$D(r) = \frac{2}{N-1}\int_0^\infty \mathrm{d}r_2\ D_2(r, r_2), \tag{6}$$

between the one- and two-electron density functions and an identity

$$H(x-c) + H(c-x) = 1 \tag{7}$$

of the Heaviside function for any real values of x and c. In the present article, we discuss a generalized partitioning of the radial density $D(r)$ into two component densities $D_a(r)$ and $D_b(r)$, based on a generalization of the Heaviside identity (7). Hartree atomic units are used throughout.

2 A generalized density partitioning

For any real-valued parameters a, b, a', and b', which satisfy $a + b = a' + b' = 1$, we have a general identity relation

$$G_{a,a'}(x-c) + G_{b,b'}(x-c) = 1, \tag{8a}$$

where

$$G_{a,a'}(x-c) = aH(x-c) + a'H(c-x). \tag{8b}$$

If we insert Eq. (8a) with $x = r_2$ and $c = r$ into the integrand of Eq. (6), we obtain a generalized partitioning of the radial density $D(r)$,

$$D(r) = d_{a,a'}(r) + d_{b,b'}(r), \tag{9a}$$

where

$$d_{a,a'}(r) = \frac{2}{N-1}\int_0^\infty \mathrm{d}r_2\ G_{a,a'}(r_2 - r)\ D_2(r, r_2). \tag{9b}$$

Because of Eqs. (2b) and (c), Eq. (9b) is rewritten as

$$d_{a,a'}(r) = aD_<(r) + a'D_>(r) \tag{9c}$$

in terms of the inner $D_<(r)$ and outer $D_>(r)$ densities.

We impose a condition that the two component densities $d_{a,a'}(r)$ and $d_{b,b'}(r)$ are equally normalized as

$$\int_0^\infty \mathrm{d}r\ d_{a,a'}(r) = \int_0^\infty \mathrm{d}r\ d_{b,b'}(r) = \frac{N}{2}. \tag{10}$$

Then the parameters should satisfy the relations $a' = 1 - a$ and $b' = 1 - b$ due to Eqs. (9c) and (5). We further add a restriction $0 \le a,\ b \le 1$ so that the component functions $d_{a,a'}(r)$ and $d_{b,b'}(r)$ are non-negative for any values of r and are referred to as “densities”. Now, the generalized partitioning of the density $D(r)$ given by Eqs. (9a)–(c) reads

$$D(r) = D_a(r) + D_b(r), \tag{11a}$$

$$D_a(r) = d_{a,1-a}(r) = aD_<(r) + (1-a)D_>(r), \tag{11b}$$

$$D_b(r) = d_{b,1-b}(r) = bD_<(r) + (1-b)D_>(r), \tag{11c}$$

where $a + b = 1$ and $0 \le a,\ b \le 1$. The component densities are weighted sums of the inner and outer densities. In particular, $D_0(r) = D_>(r), D_{1/2}(r) = D(r)/2$, and $D_1(r) = D_<(r)$.

3 Variances of densities

We first define the moments $\langle r^n\rangle$, $\langle r^n\rangle_a$, and $\langle r^n\rangle_b$ of the densities $D(r), D_a(r)$, and $D_b(r)$ by

$$\langle r^n\rangle = \frac{1}{N}\int_0^\infty \mathrm{d}r\ r^n\ D(r), \tag{12a}$$

$$\langle r^n\rangle_i = \frac{2}{N}\int_0^\infty \mathrm{d}r\ r^n\ D_i(r) \quad (i = a, b), \tag{12b}$$

so that $\langle r^0\rangle = \langle r^0\rangle_i = 1$. From Eq. (11a), we find that these moments satisfy

$$\langle r^n\rangle = \tfrac{1}{2}\left(\langle r^n\rangle_a + \langle r^n\rangle_b\right), \tag{13}$$

for any values of a and b. Then the variances σ^2, σ_a^2, and σ_b^2 of the densities $D(r), D_a(r)$, and $D_b(r)$ are given by

$$\sigma^2 = \langle r^2\rangle - \langle r\rangle^2, \tag{14a}$$

$$\sigma_i^2 = \langle r^2\rangle_i - \langle r\rangle_i^2 \quad (i = a, b). \tag{14b}$$

Using Eq. (13) and $b = 1 - a$, we obtain, after some manipulation, that the average variance $(\sigma_a^2 + \sigma_b^2)/2$ of the two component density functions $D_a(r)$ and $D_b(r)$ is expressed as

$$\tfrac{1}{2}(\sigma_a^2 + \sigma_b^2) = \sigma^2 - (a - \tfrac{1}{2})^2\left(\langle r\rangle_0 - \langle r\rangle_1\right)^2. \tag{15}$$

The average variance takes the maximal value σ^2 when $a = 1/2$, which corresponds to $D_a(r) = D_b(r) = D(r)/2$.

For other values of a, $(\sigma_a^2 + \sigma_b^2)/2$ is smaller than σ^2. Since we have put the restriction $0 \le a \le 1$, the average variance is minimal when $a = 0$ or $a = 1$. By virtue of Eqs. (11a)–(c), both cases are found to correspond to the separation of $D(r)$ into $D_<(r)$ and $D_>(r)$. In other words, the literature partitioning [2] of the radial density into the inner and outer densities has a characteristics that it minimizes the average variance $(\sigma_a^2 + \sigma_b^2)/2$ of the two component densities, and is most informative for the radial distribution of electrons among the decompositions given in the form of Eqs. (11a)–(c).

The quantities $\langle r\rangle_0$ and $\langle r\rangle_1$ appeared in Eq. (15) are identical to the average outer $\langle r_>\rangle$ and inner $\langle r_<\rangle$ radii previously introduced [5–7], respectively, and their difference $\langle r_>\rangle - \langle r_<\rangle$ is [5] nothing but the average radial separation $\langle|r_1 - r_2|\rangle$ between two electrons,

$$\langle|r_1 - r_2|\rangle = \frac{2}{N(N-1)}\int_0^\infty \mathrm{d}r_1 \times \int_0^\infty \mathrm{d}r_2\, |r_1 - r_2| D_2(r_1, r_2). \tag{16}$$

For $a = 0$ or $a = 1$, Eq. (15) then gives

$$\sigma^2 - \tfrac{1}{2}(\sigma_0^2 + \sigma_1^2) = \tfrac{1}{4}\langle|r_1 - r_2|\rangle^2, \tag{17}$$

and the reduction of the variance by the decomposition of the radial density into the inner and outer densities is just a quarter of the radial separation squared. Namely, the partitioning into the inner and outer densities adds more information on the specification of the electron radius r, when the radial separation $\langle|r_1 - r_2|\rangle$ is larger. From Eq. (17), we also have an inequality

$$\sigma \ge \tfrac{1}{2}\langle|r_1 - r_2|\rangle, \tag{18}$$

which implies that in general, the average radial separation halved bounds the standard deviation σ of $D(r)$ from below.

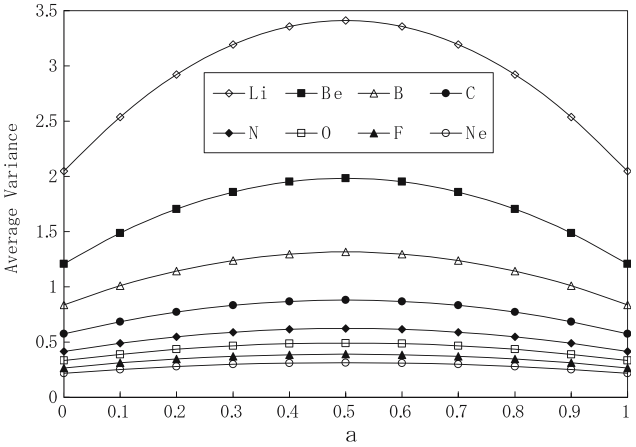

Fig. 1 The average variance $(\sigma_a^2 + \sigma_b^2)/2$ as a function of the parameter $a\,(= 1 - b)$ for the second-period atoms

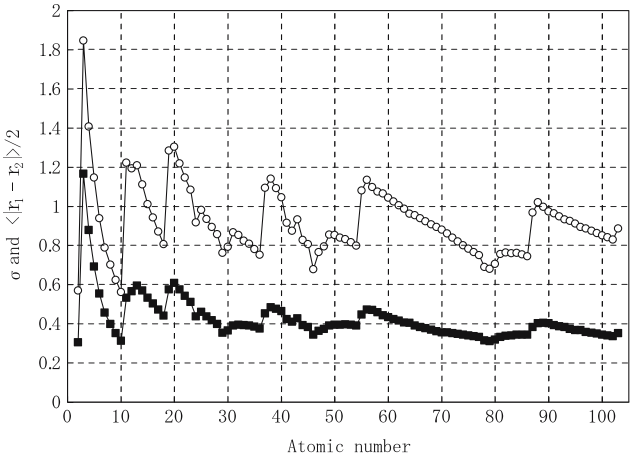

Fig. 2 The standard deviation σ of $D(r)$ (*open circle*) and the average radial separation halved $\langle|r_1 - r_2|\rangle/2$ (*closed square*) as a function of atomic number

4 Numerical illustrations

In atomic systems, the nuclear position is the natural choice of the coordinate origin for the radius r of an electron. Figure 1 exemplifies the average variance $(\sigma_a^2 + \sigma_b^2)/2$ of the component densities $D_a(r)$ and $D_b(r)$ as a function of the parameter a $(= 1 - b)$ for the eight second-period atoms, for which different dependences on atomic number Z are most clear among six periods examined. The required moment data were taken from Refs. [2,5], which report the results of numerical Hartree–Fock calculations. For any value of a $(0 \le a \le 1)$, the variance gradually decreases as Z increases or we move from the left to the right on the second period. Analogous trends are observed for the other periods. Among the eight atoms, the Li atom has an exceptionally large variance due to the simultaneous presence of the tight 1*s* and very diffuse 2*s* electrons. As discussed above, all the average variances are maximal $\left(\sigma_{1/2}^2 = \sigma^2\right)$ when $a = 1/2$, and minimal $[(\sigma_0^2 + \sigma_1^2)/2]$ when $a = 0$ or $a = 1$. The difference Δ between the maximal and minimal average variances is largest (1.362) for Li and is smallest (0.098) for Ne in the second period. In the other periods, Δ is mainly largest at group 2 atoms with two diffuse outermost *s* electrons and is smallest at group 18 atoms with all closed subshells as is the case of the Ne atom.

For the 102 atoms with $Z = 2 - 103$ in their ground states [8], we plot in Fig. 2 the standard deviation σ of the radial density $D(r)$ and the average radial separation halved $\langle|r_1 - r_2|\rangle/2$ as a function of Z. The standard deviation σ shows a periodical structure reflecting the configuration of valence electrons. Within a period, σ is maximal either at a group 1 or 2 atom, decreases gradually with increasing Z, and is minimal at a group 18 atom in most cases. Several irregularities in the dependence of σ on Z come from irregular electron occupations of the outermost d or f subshell of the corresponding transition or inner transition atoms in the ground state [8]. The average radial separation halved $\langle|r_1 - r_2|\rangle/2$ shows a similar Z dependence, and Fig. 2 demonstrates the validity of the inequality (18). When the ratio $\sigma/(\langle|r_1 - r_2|\rangle/2)$ is examined, however, its average over the 102 atoms is 2.211, with the minimum (1.582) at Li and the maximum (2.531) at Ra. The lower bound to σ by $\langle|r_1 - r_2|\rangle/2$ is not very tight.

5 Summary

We discussed a generalized partitioning of the radial density $D(r)$ into two components $D_a(r)$ and $D_b(r)$, based on a generalization of a Heaviside identity. The literature partitioning [2] of $D(r)$ into the inner $D_<(r)$ and outer $D_>(r)$ densities was found to minimize the average variance $(\sigma_a^2 + \sigma_b^2)/2$ of the two component density functions. The average radial separation halved $\langle|r_1 - r_2|\rangle/2$ bounds the standard deviation σ of $D(r)$ from below.

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