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# A generalized electron-pair density function for atoms

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For many-electron atoms, we discuss a generalized electron-pair density function  $g(q;a,b)$  that represents the probability density function for the magnitude  $|a\mathbf{r}_i+b\mathbf{r}_j|$  of the two-electron vector  $a\mathbf{r}_i+b\mathbf{r}_j$  to be  $q$ , where  $a$  and  $b$  are real-valued parameters. It is pointed out that the function  $g(q;a,b)$  connects smoothly the single-electron density  $\rho(r)$ , the electron-pair intracule (relative motion) density  $h(r_{12})$ , and the electron-pair extracule (center-of-mass motion) density  $d(R)$ . Moreover,  $\rho(r)$  is found to be a local extremum function of  $g(q;1,b)$  with respect to the parameter  $b$ . Analogously, the single-electron moments  $\langle r^n \rangle$  are local extrema of the moments  $\langle q^n \rangle_{(a,b)}$  associated with  $g(q;a,b)$ . An illustrative example is given for the helium atom within the Kellner approximation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1328750]

## I. INTRODUCTION

The potential energy  $V$  of an  $N$ -electron atom ( $N \geq 2$ ) consists of two different contributions: the electron–nucleus attraction energy  $V_{\text{en}} = -\langle Z/r \rangle$  and the electron–electron repulsion energy  $V_{\text{ee}} = \langle 1/r_{12} \rangle$ , where  $Z$  is nuclear charge. For the evaluation of  $V_{\text{en}}$ , we need the spherically averaged electron density function  $\rho(r)$  defined by

$$\rho(r) \equiv (4\pi r^2)^{-1} \left\langle \sum_{i=1}^N \delta(r-|\mathbf{r}_i|) \right\rangle, \quad (1)$$

where  $\delta(x)$  is the one-dimensional Dirac delta function and the angular brackets  $\langle \rangle$  stand for the expectation value over the wave function  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  with  $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$  being the combined position–spin coordinates of the electron  $i$ . The electron density  $\rho(r)$  represents the probability density function for the distance  $|\mathbf{r}_i|$  of any electron  $i$  from the nucleus to be  $r$ , and is normalized to  $N$ , the number of electrons.<sup>1</sup> For the evaluation of  $V_{\text{ee}}$ , on the other hand, the spherically averaged electron-pair intracule (relative motion) density  $h(r_{12})$  is required, which is defined by

$$h(r_{12}) \equiv (4\pi r_{12}^2)^{-1} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(r_{12}-|\mathbf{r}_i-\mathbf{r}_j|) \right\rangle. \quad (2)$$

The intracule density  $h(r_{12})$  is the probability density function for the relative distance  $|\mathbf{r}_i-\mathbf{r}_j|$  of any pair of electrons  $i$  and  $j$  to be  $r_{12}$ , and is normalized to  $N(N-1)/2$ , the number of electron pairs.<sup>2–4</sup> Apparently, the two density functions  $\rho(r)$  and  $h(r_{12})$  are different quantities in the sense that they result from one- and two-electron operators,  $\delta(r-|\mathbf{r}_i|)$  and  $\delta(r_{12}-|\mathbf{r}_i-\mathbf{r}_j|)$ , respectively.

In the present article, however, we point out that apart from a constant factor, the electron  $\rho(r)$  and electron-pair intracule  $h(r_{12})$  densities are two particular cases of a generalized electron-pair density  $g(q;a,b)$  introduced very recently,<sup>5</sup> and appear below. In other words, there exists a smooth connection between the two densities  $\rho(r)$  and  $h(r_{12})$ , which determine the potential energy  $V = V_{\text{en}} + V_{\text{ee}}$  of atoms. In the next section, the implication of the function  $g(q;a,b)$  and the associated moments  $\langle q^n \rangle_{(a,b)}$  is discussed.

An illustrative example is given in Sec. III for the helium atom. Hartree atomic units are used throughout.

## II. GENERALIZED ELECTRON-PAIR DENSITY

The motion of two particles in space is characterized by the relative and center-of-mass coordinates. Correspondingly, the electron-pair extracule (center-of-mass motion) density,

$$d(R) \equiv (4\pi R^2)^{-1} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(R-|\mathbf{r}_i+\mathbf{r}_j|/2) \right\rangle, \quad (3)$$

was introduced<sup>2–4</sup> as a partner of the intracule density  $h(r_{12})$  defined by Eq. (2). The extracule density  $d(R)$  represents the probability density function for the center-of-mass radius  $|\mathbf{r}_i+\mathbf{r}_j|/2$  of any pair of electrons  $i$  and  $j$  to be  $R$ . Based on a systematic examination of the 102 ground-state neutral atoms from He ( $Z=2$ ) to Lr ( $Z=103$ ), an approximate isomorphism has been reported<sup>6–8</sup> between the intracule and extracule densities of atoms.

For deeper understanding of the observed isomorphism, a generalized electron-pair density function,

$$g(q;a,b) \equiv (4\pi q^2)^{-1} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(q-|a\mathbf{r}_i+b\mathbf{r}_j|) \right\rangle, \quad (4)$$

has been introduced in a recent article,<sup>5</sup> where parameters  $a$  and  $b$  are assumed to be nonzero real numbers. The density  $g(q;a,b)$  represents the probability density function for the magnitude  $|a\mathbf{r}_i+b\mathbf{r}_j|$  of the two-electron vector  $a\mathbf{r}_i+b\mathbf{r}_j$  of any pair of electrons  $i$  and  $j$  to be  $q$ , and is normalized to  $N(N-1)/2$ . Clearly, the intracule  $h(r_{12})$  and extracule  $d(R)$  densities are two special cases of  $g(q;a,b)$ :

$$h(r_{12}) = g(r_{12}; 1, -1), \quad (5a)$$

$$d(R) = g(R; \frac{1}{2}, \frac{1}{2}) = 8g(2R, 1, 1), \quad (5b)$$

where the second equality in Eq. (5b) follows from a scaling relation<sup>5</sup>

$$g(q; a, b) = |c|^3 g(|c|q; ac, bc), \quad (6)$$

in which  $c$  is any nonzero real number.

Originally, the generalized electron-pair density function  $g(q; a, b)$  is defined<sup>5</sup> for nonzero values of  $a$  and  $b$ . However, if we allow the parameter  $b$  to be zero, we obtain

$$\begin{aligned} g(q; a, 0) &= (4\pi q^2)^{-1} \frac{N-1}{2} \left\langle \sum_{i=1}^N \delta(q - |a\mathbf{r}_i|) \right\rangle \\ &= (4\pi |a|q^2)^{-1} \frac{N-1}{2} \left\langle \sum_{i=1}^N \delta\left(\frac{q}{|a|} - |\mathbf{r}_i|\right) \right\rangle \\ &= \frac{1}{|a|^3} \frac{N-1}{2} \rho\left(\frac{q}{|a|}\right). \end{aligned} \quad (7)$$

Namely, a particular case of the density  $g(q; a, b)$  for  $b=0$  (and  $a \neq 0$ ) reduces to the electron density  $\rho(r)$  scaled by  $|a|$  and multiplied by a constant  $(N-1)/2$ .

When Eqs. (5a), (5b), and (7) are combined together, we find that the generalized electron-pair density  $g(q; a, b)$  with  $a=1$  connects the three separately-defined densities,  $\rho(r)$ ,  $h(r_{12})$ , and  $d(R)$ , in a smooth manner as a function of the parameter  $b$ . Explicitly, we have

$$g(q; 1, -1) = h(q), \quad (8a)$$

$$g(q; 1, 0) = \frac{N-1}{2} \rho(q), \quad (8b)$$

$$g(q; 1, +1) = \frac{1}{8} d\left(\frac{q}{2}\right). \quad (8c)$$

The electron-pair density  $g(q; a, b)$  defined by Eq. (4) can be rewritten<sup>5</sup> as

$$g(q; a, b) = (2\pi^2)^{-1} \int_0^\infty ds s^2 j_0(qs) X(s; a, b), \quad (9a)$$

where  $j_l(x)$  is the spherical Bessel function of the first kind and

$$\begin{aligned} X(s; a, b) &\equiv (4\pi)^{-1} \int d\Omega_s \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^N \exp(-ias \cdot \mathbf{r}_j) \right. \\ &\quad \left. \times \exp(-ibs \cdot \mathbf{r}_k) \right\rangle, \end{aligned} \quad (9b)$$

in which  $(s, \Omega_s)$  with  $\Omega_s \equiv (\theta_s, \phi_s)$  are the polar coordinates of the vector  $\mathbf{s}$ . Then we obtain

$$\frac{\partial}{\partial a} g(q; a, b) \Big|_{a=0} = \frac{\partial}{\partial b} g(q; a, b) \Big|_{b=0} = 0, \quad (10)$$

which implies that apart from a constant  $(N-1)/2$ , the electron density  $\rho(r)$  is a local extremum function of the electron-pair density  $g(q; 1, b)$  with respect to the parameter  $b$ . We could not determine whether  $\rho(r)$  is a local maximum or minimum based on the analysis of the second derivative. However, the density  $g(q; 1, 0) = [(N-1)/2] \rho(q)$  should have both  $q$  regions where it is local maximum and minimum of  $g(q; 1, b)$  with respect to  $b$ , since the function  $g(q; a, b)$  is always normalized to  $N(N-1)/2$ , independent

of the values of the parameters  $a$  and  $b$ . The density  $g(q; 1, 0)$  can be neither a local maximum nor minimum of  $g(q; 1, b)$  for all values of the variable  $q$ .

We define moments  $\langle q^n \rangle_{(a,b)}$  of the electron-pair density  $g(q; a, b)$  by

$$\langle q^n \rangle_{(a,b)} \equiv 4\pi \int_0^\infty dq q^{n+2} g(q; a, b). \quad (11)$$

We then find

$$\langle q^n \rangle_{(1,-1)} = \langle r_{12}^n \rangle, \quad (12a)$$

$$\langle q^n \rangle_{(1,0)} = \frac{N-1}{2} \langle r^n \rangle, \quad (12b)$$

$$\langle q^n \rangle_{(1,+1)} = 2^n \langle R^n \rangle, \quad (12c)$$

corresponding to Eqs. (8a), (8b), and (8c), where single-electron  $\langle r^n \rangle$ , intracule  $\langle r_{12}^n \rangle$ , and extracule  $\langle R^n \rangle$  moments are defined by equations analogous to Eq. (11). Combination of Eq. (11) with Eqs. (9a) and (9b) gives

$$\frac{\partial}{\partial a} \langle q^n \rangle_{(a,b)} \Big|_{a=0} = \frac{\partial}{\partial b} \langle q^n \rangle_{(a,b)} \Big|_{b=0} = 0, \quad (13)$$

which corresponds to Eq. (10). For given values of  $n (\neq 0)$  and  $a=1$ , the single-electron moment  $\langle r^n \rangle$  is thus a local extremum of the electron-pair moment  $\langle q^n \rangle_{(1,b)}$  with respect to  $b$ , apart from a constant  $(N-1)/2$ . We expect that the maximum and minimum characteristics of the moments  $\langle q^n \rangle_{(1,0)} = [(N-1)/2] \langle r^n \rangle$  switch depending on whether  $n$  is positive or negative. For example, the moments  $\langle q^n \rangle_{(1,0)}$  are local maxima when  $n < 0$  and local minima when  $n > 0$  of the generalized moments  $\langle q^n \rangle_{(1,b)}$ , if the density  $g(q; 1, 0)$  is a local maximum for a small  $q$  and a local minimum for a large  $q$  of the function  $g(q; 1, b)$ .

Since

$$V_{\text{en}} = -\frac{2Z}{N-1} \langle q^{-1} \rangle_{(1,0)}, \quad (14a)$$

$$V_{\text{ee}} = \langle q^{-1} \rangle_{(1,-1)}, \quad (14b)$$

the potential energy  $V$  can be expressed as

$$V = \int_0^\infty dq G(q), \quad (15a)$$

where the ‘‘potential energy density’’  $G(q)$  is given by

$$G(q) = 4\pi q \left[ -\frac{2Z}{N-1} g(q; 1, 0) + g(q; 1, -1) \right], \quad (15b)$$

which is the radial distribution of the sum of the electron–nucleus attraction and electron–electron repulsion contributions.

### III. AN ILLUSTRATION

Some analytical and numerical results for a simple system are helpful to grasp the relations and properties of the densities and moments discussed in Sec. II. For this purpose,

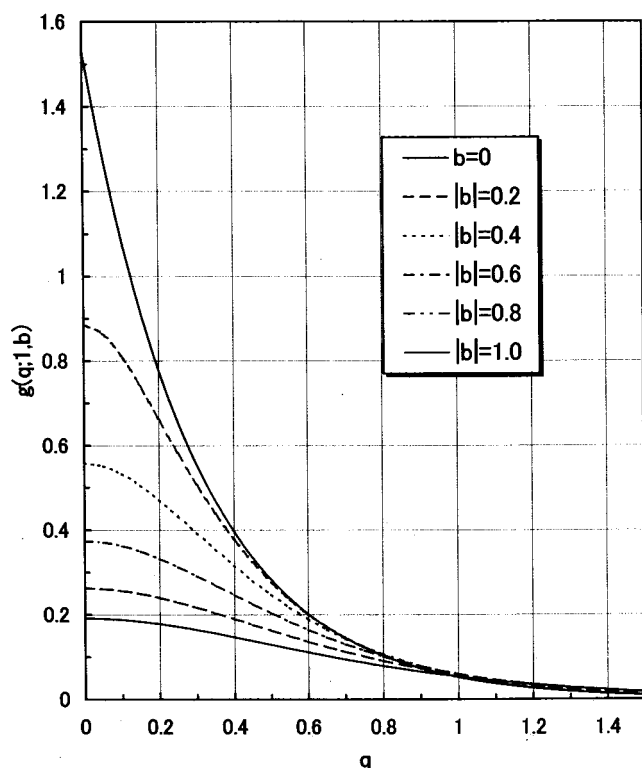


FIG. 1. Examples of the generalized electron-pair density  $g(q; a, b)$  for the helium atom.

we examine the ground-state helium atom ( $N=Z=2$ ) within the Kellner approximation.<sup>9</sup> The Kellner wave function for a helium-like atom is given by

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = (\xi^3/\pi) \exp[-\xi(r_1 + r_2)], \quad (16)$$

where we have suppressed the two-electron singlet spin function. The variationally optimum value of the exponent  $\xi$  is  $Z - (5/16)$ .

For Eq. (16), the generalized electron-pair density  $g(q; a, b)$  is obtained after some manipulation as

$$\begin{aligned} g(q; a, b) = & (\xi^2/\pi)(B^2 - A^2)^{-3} \{ 2A^2B^2q^{-1} \\ & \times [\exp(-2\xi q/A) - \exp(-2\xi q/B)] \\ & + \xi(B^2 - A^2)[A \exp(-2\xi q/A) \\ & + B \exp(-2\xi q/B)] \}, \end{aligned} \quad (17a)$$

where  $A = |a|$  and  $B = |b|$ . In this case, the density  $g(q; a, b)$  is an even function both for the parameters  $a$  and  $b$ , and hence the intracule ( $a=1$  and  $b=-1$ ) and extracule ( $a=1$  and  $b=+1$ ) densities satisfy an equality  $d(R) = 8h(2R)$  precisely. Appropriate limiting procedures give

$$g(q; a, 0) = \frac{1}{\pi} \left( \frac{\xi}{A} \right)^3 \exp(-2\xi q/A), \quad (17b)$$

$$\begin{aligned} g(q; a, \pm a) = & \frac{1}{24\pi} \left( \frac{\xi}{A} \right)^3 \left( 3 + \frac{6\xi q}{A} + \frac{4\xi^2 q^2}{A^2} \right) \\ & \times \exp(-2\xi q/A), \end{aligned} \quad (17c)$$

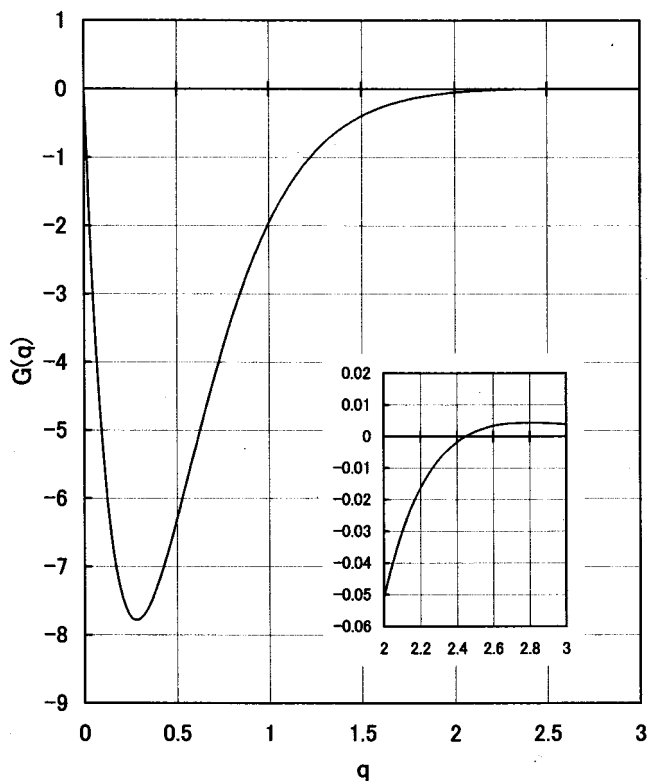


FIG. 2. The potential energy density  $G(q)$  for the helium atom.

as special cases of Eq. (17a) for  $b=0$  and  $|a|=|b|$ . When  $Z=2$  and  $a=1$ , Fig. 1 depicts the density  $g(q; a, b)$  for several values of  $b$  with  $|b| \leq 1$ . Since  $b=-1, 0$ , and  $+1$  correspond to the intracule, single-electron, and extracule densities (apart from constant factors), respectively, Fig. 1 shows how these different densities are connected as a smooth function of the parameter  $b$ . Also, we find in the figure that the electron density  $\rho(r)$  (corresponding to  $b=0$ ) is an extremum function of  $g(q; a, b)$ , when  $b$  is varied for  $a=1$ . A finer analysis shows that  $g(q; 1, 0) = [(N-1)/2]\rho(q)$  is a local maximum for  $0 \leq q < 0.59$  and a local minimum for  $q > 0.59$  of the function  $g(q; 1, b)$ .

The potential energy density  $G(q)$  is plotted in Fig. 2. The density is negative for  $0 < q < 2.45$  with a minimum  $-7.78$  at  $q=0.28$ , due to the predominant nuclear attraction contribution. For  $q > 2.45$ , however, the electron repulsion contribution is larger than the nuclear attraction and  $G(q)$  is positive. A very small maximum  $4.35 \times 10^{-3}$  is found at  $q=2.80$ .

From Eq. (17a), the moments  $\langle q^n \rangle_{(a,b)}$  of the density  $g(q; a, b)$  are found to be

$$\langle q^{-2} \rangle_{(a,b)} = \frac{2\xi^2}{(B^2 - A^2)^3} [B^4 - A^4 + 4A^2B^2 \ln(A/B)], \quad (18a)$$

for  $n = -2$ , and

$$\begin{aligned} \langle q^n \rangle_{(a,b)} = & \frac{(n+1)!}{2(2\xi)^n (B^2 - A^2)^3} [(n+2)(B^{n+6} - A^{n+6}) \\ & - (n+6)A^2B^2(B^{n+2} - A^{n+2})], \end{aligned} \quad (18b)$$

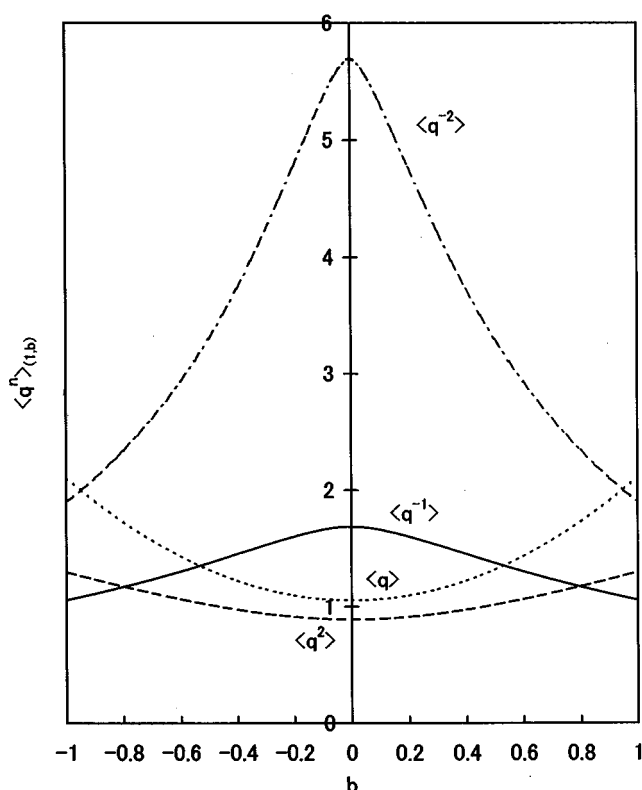


FIG. 3. Examples of the generalized electron-pair moments  $\langle q^n \rangle_{(a,b)}$  for the helium atom.

for  $n \geq -1$  in general. A few particular cases of Eq. (18b) are

$$\langle q^{-1} \rangle_{(a,b)} = \zeta \frac{A^2 + 3AB + B^2}{(A+B)^3}, \quad (18c)$$

$$\langle q^0 \rangle_{(a,b)} = 1, \quad (18d)$$

$$\langle q \rangle_{(a,b)} = \frac{1}{2\zeta} \frac{3A^4 + 9A^3B + 11A^2B^2 + 9AB^3 + 3B^4}{(A+B)^3}, \quad (18e)$$

$$\langle q^2 \rangle_{(a,b)} = \frac{3}{\zeta^2} \frac{A^5 + 3A^4B + 4A^3B^2 + 4A^2B^3 + 3AB^4 + B^5}{(A+B)^3}. \quad (18f)$$

When appropriate limiting procedures are applied, Eqs. (18a) and (18b) reduce to

$$\langle q^n \rangle_{(a,0)} = \frac{(n+2)!}{2} \left( \frac{A}{2\zeta} \right)^n \quad (n \geq -2) \quad (19a)$$

for  $b = 0$  and

$$\langle q^n \rangle_{(a,\pm a)} = \frac{(n+2)!}{48} (n^2 + 10n + 24) \left( \frac{A}{2\zeta} \right)^n \quad (n \geq -2) \quad (19b)$$

for  $|a| = |b|$ .

In the case of  $Z=2$  and  $a=1$ , the moments  $\langle q^n \rangle_{(a,b)}$  are depicted in Fig. 3 for  $n = \pm 1$  and  $\pm 2$  as a function of the parameter  $b$ . We find in the figure that the generalized moments  $\langle q^n \rangle_{(1,b)}$  smoothly connect the intracule (when  $b = -1$ ), single-electron (when  $b=0$ ), and extracule (when  $b = +1$ ) moments apart from the constant factors mentioned

in Eqs. (12b) and (12c). For the helium atom in the Kellner approximation, the moments are even functions of  $b$ , and therefore the intracule moments  $\langle r_{12}^n \rangle$  (when  $b = -1$ ) are exactly the same as the extracule moments  $\langle R^n \rangle$  (when  $b = +1$ ) multiplied by a factor  $2^n$ . As discussed in Sec. II, the moments  $\langle q^n \rangle_{(1,b)}$  take extremum values at  $b=0$ , which correspond to the single-electron moments  $\langle r^n \rangle$ . Moreover, the numerical results for the helium atom show that  $\langle q^n \rangle_{(1,b)}$  at  $b = 0$  are maximum if  $n < 0$  and minimum if  $n > 0$ . When the case of  $n = -1$  is examined, in particular, we find that the nuclear attraction  $\langle q^{-1} \rangle_{(1,0)} = -V_{en}/(2Z)$  is the maximum whereas the electron repulsion  $\langle q^{-1} \rangle_{(1,-1)} = V_{ee}$  is the minimum of  $\langle q^{-1} \rangle_{(1,b)}$  in the region  $-1 \leq b \leq +1$ . On the other hand, the average electron-nucleus distance  $\langle q \rangle_{(1,0)} = \langle r \rangle / 2$  is the minimum whereas the average electron-electron distance  $\langle q \rangle_{(1,-1)} = \langle r_{12} \rangle$  is the maximum of the first moment  $\langle q \rangle_{(1,b)}$  for  $-1 \leq b \leq +1$ .

#### IV. CONCLUDING REMARKS

We have discussed a generalized electron-pair density function  $g(q; a, b)$  that represents the probability density function for the magnitude  $|a\mathbf{r}_j + b\mathbf{r}_k|$  of the two-electron vector  $a\mathbf{r}_j + b\mathbf{r}_k$  of any pair of electrons  $j$  and  $k$  to be  $q$ , where  $a$  and  $b$  are real-valued parameters. The function  $g(q; a, b)$  connects smoothly the single-electron density  $\rho(r)$ , the electron-pair intracule density  $h(r_{12})$ , and the electron-pair extracule density  $d(R)$ . The associated moments  $\langle r^n \rangle$ ,  $\langle r_{12}^n \rangle$ , and  $\langle R^n \rangle$  are also obtained as special cases of the generalized moments  $\langle q^n \rangle_{(a,b)}$ . Both the single-electron density and moments have been found to be local extrema of the generalized density and moments with respect to the parameter  $b$ . An illustrative example has been given for the helium atom within the Kellner approximation.

For the exact and some approximate wave functions, the electron  $\rho(r)$  and intracule  $h(r_{12})$  densities are known<sup>10-14</sup> to satisfy the cusp conditions  $d\rho/dr|_{r=0} = -2Z\rho(0)$  and  $dh/dr_{12}|_{r_{12}=0} = h(0)$ , respectively. These relations imply  $dg(q; 1, 0)/dq|_{q=0} = -2Zg(0; 1, 0)$  and  $dg(q; 1, -1)/dq|_{q=0} = g(0; 1, -1)$  for the generalized electron-pair density  $g(q; a, b)$ . We could not derive a general relation for  $dg(q; a, b)/dq|_{q=0}$  in the present study, but the examination of the derivative as a function of the parameters  $a$  and  $b$  would be useful for a unified understanding of the single-electron and electron-pair densities.

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