

# Electron-pair radial density functions

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**Abstract** We introduce and discuss a generalized electron-pair radial density function  $G(q; a)$  that represents the probability density for the electron-pair radius  $|r_1 + ar_2|$  to be  $q$ , where  $a$  is a real-valued parameter. The density function  $G(q; a)$  is a projection of the two-electron radial density  $D_2(r_1, r_2)$  along lines  $r_1 + ar_2 \pm q = 0$  in the  $r_1 r_2$  plane onto a point in the  $qa$  plane, and connects three densities  $S(s)$ ,  $D(r)$ , and  $T(t)$ , defined independently in the literature, as a smooth function of  $a$ : For an  $N$ -electron ( $N \geq 2$ ) system,  $S(s) = G(s; +1)$ ,  $D(r) = 2G(r; 0)/(N - 1)$ , and  $T(t) = G(|t|; -1)/2$ , where  $S(s)$  and  $T(t)$  are the electron-pair radial sum and difference densities, respectively, and  $D(r)$  is the single-electron radial density. Simple illustrations are given for the helium atom in the ground  $1s^2$  and the first excited  $1s2s$   $^3S$  states.

**Keywords** Electron-pair densities · Radial densities · Radial holes · Helium atom

## 1 Introduction

The electron-electron radial hole [1–10] implies that under certain conditions, any two electrons in many-electron atoms cannot be on the same sphere centered on the nucleus, irrespective of its radial value. In a recent paper [11], the electron-pair radial sum  $S(s)$  and difference  $T(t)$  density functions, defined by

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$$S(s) = \int_0^\infty dr_1 \int_0^\infty dr_2 \delta[s - (r_1 + r_2)] D_2(r_1, r_2), \tag{1a}$$

$$T(t) = \int_0^\infty dr_1 \int_0^\infty dr_2 \delta[t - (r_1 - r_2)] D_2(r_1, r_2), \tag{1b}$$

were introduced and examined to obtain deeper insights into the electron-electron radial hole, which results in  $T(0) = 0$ . In Eq. 1,  $\delta(x)$  is the one-dimensional Dirac delta function (see, e.g., Ref. [12]) and  $D_2(r_1, r_2)$  is the two-electron radial density function (see, e.g., Ref. [7] and Sect. 2). The density functions  $S(s)$  and  $T(t)$  are the probability densities for the sum  $r_1 + r_2$  and difference  $r_1 - r_2$  of two electron radii  $r_1$  and  $r_2$ , respectively. The domains of the variables  $s$  and  $t$  are  $0 \leq s < \infty$  and  $-\infty < t < \infty$ , and the density  $T(t)$  is an even function of  $t$ .

In the present paper, we introduce and study a generalized electron-pair radial density function  $G(q; a)$  defined by

$$G(q; a) = \int_0^\infty dr_1 \int_0^\infty dr_2 \delta(q - |r_1 + ar_2|) D_2(r_1, r_2), \tag{2}$$

where  $a$  is a real-valued parameter and the domain of the variable  $q$  is  $0 \leq q < \infty$ . The replacement of  $\delta(q - |r_1 + ar_2|)$  with  $\delta(q - |r_2 + ar_1|)$  in Eq. 2 does not alter the definition of  $G(q; a)$ , corresponding to the indistinguishability of electrons. The density function  $G(q; a)$  represents the probability density for the electron-pair radius  $|r_1 + ar_2|$ , and hence the electron-pair radial sum  $S(s)$  and difference  $T(t)$  density functions are two particular cases of  $G(q; a)$ :  $S(s) = G(s; +1)$  and  $T(t) = G(|t|; -1)/2$ . Another interesting case occurs when  $a = 0$ : we have  $D(r) = 2G(r; 0)/(N - 1)$  where  $D(r)$  is the single-electron radial density defined by

$$D(r) = \frac{2}{N - 1} \int_0^\infty dr_1 \int_0^\infty dr_2 \delta(r - r_1) D_2(r_1, r_2) = \frac{2}{N - 1} \int_0^\infty dr_2 D_2(r, r_2), \tag{3}$$

and  $N(\geq 2)$  is the number of electrons. The electron-pair  $S(s)$  and  $T(t)$  densities and the single-electron  $D(r)$  density are essentially different in nature. Nevertheless, the new density  $G(q; a)$  connects them as a smooth function of the parameter  $a$ . Mathematical properties of the generalized electron-pair radial density  $G(q; a)$  are examined in the next section. Derivatives of  $G(q; a)$  with respect to  $q$  and  $a$  are discussed in Sect. 3, as well as extremum properties of  $G(q; a)$ . In Sect. 4, simple illustrations are given for the helium atom in the ground  $1s^2$  and the first excited  $1s2s\ ^3S$  states. Throughout this paper, the normalization of the densities is

$$\int_0^{\infty} dr_1 \int_0^{\infty} dr_2 D_2(r_1, r_2) = \int_0^{\infty} dq G(q; a) = \frac{N-1}{2} \int_0^{\infty} dr D(r) = \frac{N(N-1)}{2}, \quad (4)$$

where  $N(N-1)/2$  is nothing but the number of electron pairs. Hartree atomic units are used in Sect. 4.

## 2 Electron-pair radial density functions

### 2.1 Two-electron radial density

We first summarize the properties of the two-electron density  $D_2(r_1, r_2)$ , based on which the generalized electron-pair radial density  $G(q; a)$  is defined in Eq. 2. For a normalized  $N$ -electron ( $N \geq 2$ ) wave functions  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  with  $\mathbf{x}_i = (\mathbf{r}_i, s_i)$  being the combined position-spin coordinate of the electron  $i$ , the two-electron radial density function  $D_2(r_1, r_2)$  is given by

$$D_2(r_1, r_2) = \frac{N(N-1)}{2} r_1^2 r_2^2 \int d\Omega_1 d\Omega_2 ds_1 ds_2 d\mathbf{x}_3 \dots d\mathbf{x}_N |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2, \quad (5)$$

where  $(r_i, \Omega_i)$  is the polar coordinate of the vector  $\mathbf{r}_i$ . The two-electron radial density represents the probability density that one electron is located at a radius  $r_1$  and the other electron at a radius  $r_2$  simultaneously.

The function  $D_2(r_1, r_2)$  is meaningful only when  $r_1 \geq 0$  and  $r_2 \geq 0$ , and for such values of  $r_1$  and  $r_2$ ,  $D_2(r_1, r_2) \geq 0$ . The density is symmetric,  $D_2(r_2, r_1) = D_2(r_1, r_2)$ , due to the antisymmetry of the parent wave function. We consider atomic systems and hence the density vanishes if either or both of  $r_1$  and  $r_2$  is 0 or  $\infty$ ;

$$D_2(0, r) = D_2(r, 0) = D_2(\infty, r) = D_2(r, \infty) = 0 \quad (6a)$$

for any  $r$ . We assume that  $D_2(r_1, r_2)$  is infinitely differentiable with respect to  $r_1$  and  $r_2$ . Since  $D_2(r_1, r_2)$  is proportional to  $r_1^2 r_2^2$ , partial derivatives of  $D_2(r_1, r_2)$  satisfy

$$D_2^{(0,k)}(0, r) = D_2^{(k,0)}(r, 0) = D_2^{(1,k)}(0, r) = D_2^{(k,1)}(r, 0) = 0 \quad (6b)$$

for any values of  $r$  and  $k$ , where  $f^{(m,n)}(x, y) = \partial^{m+n} f(x, y) / \partial x^m \partial y^n$ .

### 2.2 Generalized electron-pair radial density

By the definition (Eq. 2), the generalized electron-pair radial density function  $G(q; a)$  is the probability density for the electron-pair radius  $|r_1 + ar_2|$  to be  $q$  for a given real-valued parameter  $a$ . An alternative statement is that the density function  $G(q; a)$  is a projection of the two-electron radial density  $D_2(r_1, r_2)$  along lines

$r_1 + ar_2 \pm q = 0$  in the  $r_1r_2$  plane onto a point in the  $qa$  plane. If we assume that the original variables  $r_1$  and  $r_2$  are along the vertical and horizontal directions in the  $r_1r_2$  plane, respectively, then the new variable  $q$  defines the vertical intercepts and the parameter  $a$  sign reversed does the slope of the “probe” lines  $r_1 + ar_2 \pm q = 0$ . Depending on the values of  $q$  and  $a$ , the probe line covers all possible lines in the  $r_1r_2$  plane except for  $r_2 =$  positive constant lines, which give the same results as  $r_1 =$  positive constant lines.

From Eq. 2, it immediately follows that the generalized electron-pair radial density function  $G(q; a)$  explicitly takes the form

$$G(q; a) = \begin{cases} G_+(q; a), & a > 0 \\ G_0(q), & a = 0 \\ G_-(q; a), & a < 0 \end{cases} \quad (7a)$$

where

$$G_+(q; a) = \int_0^{q/a} dr D_2(q - ar, r), \quad (7b)$$

$$G_0(q) = \int_0^{\infty} dr D_2(q, r), \quad (7c)$$

$$G_-(q; a) = \int_{-q/a}^{\infty} dr D_2(-q - ar, r) + \int_0^{\infty} dr D_2(q - ar, r). \quad (7d)$$

If appropriate limiting procedures  $a \rightarrow \pm\infty$  are applied to Eq. 7b and d, respectively, we find  $G_+(q; \infty) = 0$  and  $G_-(q; -\infty) = 0$  for any value of  $q$ . When  $a = +1$ , we see that the density  $G(q; a)$  is identical to the electron-pair radial sum density  $S(s)$  given by Eq. 1a or  $G_+(s; +1) = S(s)$ . When  $a = -1$ , on the other hand, we have a relation  $G_-(t; -1) = 2T_+(t)$ , where  $T_+(t)$  is the  $t \geq 0$  part of the electron-pair radial difference density  $T(t)$  given by Eq. 1b. Since  $T(t)$  is [11] an even function of  $t$ , we also obtain an alternative relation  $T(t) = G_-(|t|; -1)/2$ . As clear from Eq. 3, the density  $G(q; a)$  with  $a = 0$  is nothing but the single-electron radial density  $D(r)$  multiplied by  $(N - 1)/2$  or  $G_0(r) = (N - 1)D(r)/2$ . At present, we do not know whether the density  $G(q; a)$  has “good” physical significance for other values of  $a$ .

From Eq. 6a, we see  $G_+(0; a) = G_+(\infty; a) = 0$  for any  $a (> 0)$ ,  $G_0(0) = G_0(\infty) = 0$ , and  $G_-(\infty; a) = 0$  for any  $a (< 0)$ , but  $G_-(0; a) > 0$  in general. We find from Eq. 7b–d that  $G_+(q; a) \rightarrow G_0(q)$  when  $a \rightarrow 0+$  and  $G_-(q; a) \rightarrow G_0(q)$  when  $a \rightarrow 0-$ . Namely, the generalized electron-pair density  $G(q; a)$  is a smooth function of the real-valued parameter  $a$ . The result implies that apart from some constant factors, the three different densities  $S(s)$ ,  $T(t)$  and  $D(r)$  are smoothly connected via the

value of the parameter  $a$ . It is interesting to observe that the densities  $S(s)$  and  $T(t)$  are two-electron in nature, while the density  $D(r)$  is one-electron in nature. Nevertheless, the parameter  $a$  in  $G(q; a)$  combines them together.

### 3 Derivatives of $G(q; a)$ and extremum properties

#### 3.1 Derivatives with respect to $q$

Consider the function  $G_+(q; a)$  first. From Eq. 7b, we obtain after some manipulation that the  $n$ th derivative ( $n \geq 1$ )  $G_+^{(n)}(q; a)$  of  $G_+(q; a)$  with respect to  $q$  is

$$G_+^{(n)}(q; a) = \int_0^{q/a} dr D_2^{(n,0)}(q - ar, r) + \sum_{k=0}^{n-1} a^{k-n} D_2^{(k, n-k-1)}(0, q/a). \quad (8a)$$

At the origin  $q = 0$ , we then have

$$G_+^{(n)}(0; a) = \sum_{k=0}^{n-1} a^{k-n} D_2^{(k, n-k-1)}(0, 0), \quad (8b)$$

in general. However, combination of Eq. 8b and Eq. 6a–b with  $r = 0$  results in an important fact that  $G_+^{(n)}(0; a)$  always vanishes for  $n = 0 - 4$ , and the first nonzero term is  $G_+^{(5)}(0; a) = a^{-3} D_2^{(2,2)}(0, 0)$ . In other words, the Maclaurin expansion of the function  $G_+(q; a)$  reads

$$G_+(q; a) = \frac{a^{-3} D_2^{(2,2)}(0, 0)}{5!} q^5 + O(q^6), \quad (8c)$$

and  $G_+(q; a)$  shows a quintic behavior at the origin. The value of the parameter  $a$  changes the coefficient value, but does not affect the quintic dependence on  $q$ , as long as  $a$  is positive.

Next, the  $n$ th derivative  $G_0^{(n)}(q)$  of  $G_0(q)$  is

$$G_0^{(n)}(q) = \int_0^{\infty} dr D_2^{(n,0)}(q, r). \quad (9a)$$

Because of Eq. 6a and b,  $G_0^{(n)}(0)$  vanishes for  $n = 0, 1$  and the Maclaurin series of  $G_0(q)$  is

$$G_0(q) = \frac{1}{2} \left[ \int_0^{\infty} dr D_2^{(2,0)}(0, r) \right] q^2 + O(q^3), \quad (9b)$$

and  $G_0(q)$  shows a quadratic behavior at the origin.

Finally, the  $n$ th derivative  $G_-^{(n)}(q; a)$  of  $G_-(q; a)$  with respect to  $q$  is obtained as

$$G_-^{(n)}(q; a) = (-1)^n \left[ \int_{-q/a}^{\infty} dr D_2^{(n,0)}(-q - ar, r) - \sum_{k=0}^{n-1} a^{k-n} D_2^{(k,n-k-1)}(0, -q/a) \right] + \int_0^{\infty} dr D_2^{(n,0)}(q - ar, r). \tag{10a}$$

At the origin  $q = 0$ , Eq. 10a gives

$$G_-^{(n)}(0; a) = [1 + (-1)^n] \left[ \int_0^{\infty} dr D_2^{(n,0)}(-ar, r) \right] - (-1)^n \sum_{k=0}^{n-1} a^{k-n} D_2^{(k,n-k-1)}(0, 0). \tag{10b}$$

If Eq. 10b with  $n = 1$  is combined with Eq. 6a and b, we find  $G_-^{(1)}(0; a) = 0$  for any  $a$  ( $< 0$ ). Therefore  $G_-(q; a)$  always has a local extremum at  $q = 0$ . The leading term of  $G_-(q; a)$  for a small value of  $q$  is a positive constant and

$$G_-(q; a) = 2 \left[ \int_0^{\infty} dr D_2(-ar, r) \right] + O(q^2), \tag{10c}$$

in general. The value of the parameter  $a$  changes the constant in Eq. 10c, but does not change the leading  $q$  dependence so far as  $a$  is negative.

The above analysis shows that the density  $G(q; a)$  and its first derivative  $G^{(1)}(q; a)$  with respect to  $q$  are continuous functions of the parameter  $a$ .

The continuity in the value of  $a$  does not results in the continuity of the power of the leading term in the Maclaurin series of the density function  $G(q; a)$  with respect to the variable  $q$ . The power jumps among 0 ( $a < 0$ ), 2 ( $a = 0$ ), and 5 ( $a > 0$ ) depending on the sign of  $a$ . We also note that the leading term in the Maclaurin  $q$  series of  $G(q; a)$  is related to a derivative at the origin of the two-electron density  $D_2(r_1, r_2)$  when  $a > 0$ , but is to a definite integral of  $D_2(r_1, r_2)$  when  $a \leq 0$ .

If there exists an electron-electron radial hole [1–10], we have  $D_2(r, r) = 0$  for any value of  $r$ . The  $n$ th derivative of the relation implies

$$D_2^{(n)}(r, r) = \sum_{k=0}^n \binom{n}{k} D_2^{(k,n-k)}(r, r) = 0 \tag{11}$$

for any values of  $n$  and  $r$ , in addition to the properties given in Eq. 6a and b. Accordingly, the appearance of the radial hole “shifts” the Maclaurin series of  $G(q; a)$ : When  $a > 0$ ,  $G_+^{(5)}(0; a)$  vanishes and Eq. 8c must be modified as

$$G_+(q; a) = \frac{a^{-4}D_2^{(2,3)}(0, 0) + a^{-3}D_2^{(3,2)}(0, 0)}{6!} q^6 + O(q^7). \quad (12a)$$

Moreover,  $G_+^{(6)}(0; a)$  or the leading term of Eq. 12a is zero if  $a = +1$  and hence

$$G_+(q; +1) = \frac{2D_2^{(2,4)}(0, 0) + D_2^{(3,3)}(0, 0)}{7!} q^7 + O(q^8). \quad (12b)$$

as reported in Ref. [11] for the electron-pair radial sum function  $S(s)$ . The property  $D_2(r, r) = 0$  makes the constant term in Eq. 10c vanish for  $a = -1$ , and the Maclaurin series of  $G_-(q; -1)$  reads

$$G_-(q; -1) = 2 \left[ \int_0^\infty dr D_2^{(2,0)}(r, r) \right] q^2 + O(q^4), \quad (12c)$$

as known [11] for the electron-pair radial difference function  $T(t)$ . However, Eq. 12c is not true for other values of  $a (< 0)$ . The series for  $G_0(q)$  (Eq. 9b) remain unchanged by the radial hole. When there are radial holes, we conclude that the power of the leading term in the Maclaurin series of the function  $G(q; a)$  jumps among 0 ( $a < 0$  except  $-1$ ),  $2(a = 0$  and  $-1)$ ,  $6(a > 0$  except  $+1$ ), and  $7(a = +1)$ . The presence of radial holes has significant meaning in the Maclaurin  $q$  series of the generalized electron-pair radial density. Though it depends on a particular value of the parameter  $a$ , the radial hole generally shifts the density  $G(q; a)$  towards larger  $q$  and the probability of finding a larger value of the radius  $|r_1 + ar_2|$  increases, as long as  $q$  is not large. The result further suggests that when  $a > 0$ , the probability of finding electrons in the vicinity of the nucleus is small, if there is an electron-electron radial hole.

### 3.2 Derivatives with respect to $a$

A general expression for the  $n$ th derivative  $G_+^{[n]}(q; a)$  of  $G_+(q; a)$  with respect to the parameter  $a$  is not simple. Therefore, we show the first two cases instead.

$$G_+^{[1]}(q; a) = -qa^{-2}D_2(0, q/a) - \int_0^{q/a} dr r D_2^{(1,0)}(q - ar, r), \quad (13a)$$

$$G_+^{[2]}(q; a) = 2qa^{-3}D_2(0, q/a) + q^2a^{-3}D_2^{(1,0)}(0, q/a) + q^2a^{-4}D_2^{(0,1)}(0, q/a)$$

$$+ \int_0^{q/a} dr r^2 D_2^{(2,0)}(q - ar, r), \tag{13b}$$

where all the terms except the two definite integrals vanish due to the property (Eq. 6a and b) of  $D_2(r_1, r_2)$ . For a small value of  $a (> 0)$  and  $q \neq 0$ , we thus obtain

$$G_+(q; a) = \left[ \int_0^\infty dr D_2(q, r) \right] - \left[ \int_0^\infty dr r D_2^{(1,0)}(q, r) \right] a + O(a^2), \tag{14}$$

where the first term is identical to the function  $G_0(q)$ . The result is consistent with the previous statement that  $G_+(q; a) \rightarrow G_0(q)$  when  $a \rightarrow 0+$ .

Analogously, the first  $G_-^{[1]}(q; a)$  and second  $G_-^{[2]}(q; a)$  derivatives of  $G_-(q; a)$  with respect to  $a$  are found to be

$$G_-^{[1]}(q; a) = -qa^{-2}D_2(0, -q/a) - \int_{-q/a}^\infty dr r D_2^{(1,0)}(-q - ar, r) - \int_0^\infty dr r D_2^{(1,0)}(q - ar, r), \tag{15a}$$

$$G_-^{[2]}(q; a) = 2qa^{-3}D_2(0, -q/a) - q^2a^{-3}D_2^{(1,0)}(0, -q/a) - q^2a^{-4}D_2^{(0,1)}(0, -q/a) + \int_{-q/a}^\infty dr r^2 D_2^{(2,0)}(-q - ar, r) + \int_0^\infty dr r^2 D_2^{(2,0)}(q - ar, r), \tag{15b}$$

where all the terms except the four definite integrals vanish again. Taking the limit  $a \rightarrow 0-$ , we find the Maclaurin  $a$  series of  $G_-(q; a)$  for  $q > 0$  reads

$$G_-(q; a) = \left[ \int_0^\infty dr D_2(q, r) \right] - \left[ \int_0^\infty dr r D_2^{(1,0)}(q, r) \right] a + O(a^2), \tag{16}$$

which is identical to that of  $G_+(q; a)$  or Eq. 14. The density  $G(q; a)$  and its first  $G^{[1]}(q; a)$  and second  $G^{[2]}(q; a)$  derivatives with respect to  $a$  are continuous functions of the parameter  $a$ .

For a small positive value of  $a$ , Eqs. 14 and 16 imply that if  $q > 0$ ,

$$G(q; a) + G(q; -a) = 2G_0(q) + O(a^2), \tag{17}$$

and the functions  $G(q; a)$  and  $G(q; -a)$  are approximately “inversion symmetric” with respect to  $G(q; 0) = G_0(q)$  in the sense that  $G(q; a) - G_0(q; 0) \cong$



$G_0(q; 0) - G(q; -a)$  for any  $q (>0)$ . An alternative view of Eq. 17 is that interestingly, the sum of the *two-body* densities  $G(q; a)$  and  $G(q; -a)$  is twice the *one-body* density  $G_0(q)$  to the first order of  $a$ . For a special case of  $q = q_0$ , which is defined in the next paragraph, the linear coefficients in Eqs. 14 and 16 vanish and hence  $G(q; a) \cong G(q; -a) \cong G_0(q)$  to the first order of  $a$ .

In addition to the properties given by Eq. 6a and b, the work of Ahlrichs et al. [13] shows that the two-electron density  $D_2(r_1, r_2)$  includes exponentially decaying factors  $\exp[-(\alpha r_1 + \beta r_2)]$  and its  $r_1 \leftrightarrow r_2$  substitution, where the positive constants  $\alpha$  and  $\beta$  are related to the ionization potentials in the exact case. Then the first derivative  $D_2^{(1,0)}(r_1, r_2)$  should have both positive and negative values depending on  $r_1$  and  $r_2$ . For particular values of  $q = q_0$ , it is possible to happen

$$G_+^{[1]}(q_0; 0+) = G_-^{[1]}(q_0; 0-) = \int_0^{\infty} dr r D_2^{(1,0)}(q_0, r) = 0, \quad (18)$$

where the definite integral means the first moment of the derivative  $D_2^{(1,0)}(r_1, r_2)$  at  $r_1 = q_0$ . When Eq. 18 holds, the Maclaurin series (14) and (16) are quadratic functions of  $a$ , and the one-electron density value  $G_0(q_0)$  is a local maximum or minimum of the two-electron density values  $G(q_0; a)$  as a function of the parameter  $a$ . In this case, the  $a = 0$  line in the  $qa$  plane, which generates the single-electron density  $D(r)$ , always passes local minima and/or maxima of the electron-pair function  $G(q; a)$ , though we cannot theoretically predict the numbers of such local minima and maxima. In other words, local minima and maxima appearing in the single-electron radial density  $D(r)$  are candidates of local minima and maxima in the electron-pair radial density  $G(q; a)$ .

Analogous consideration about the first derivative  $D_2^{(1,0)}(r_1, r_2)$  shows that at  $q = 0$ , there will be a particular value  $a_0 (<0)$  for which

$$G_-^{[1]}(0; a_0) = -2 \int_0^{\infty} dr r D_2^{(1,0)}(-a_0 r, r) = 0, \quad (19)$$

and hence the function  $G_-(q; a)$  is locally maximal or minimal at  $(q, a) = (0, a_0)$ , i.e., the condensation of the two-electron density  $D_2(r_1, r_2)$  along the line  $r_1 + a_0 r_2 = 0$  ( $a_0 < 0$ ) has a local maximum or minimum compared to the other lines passing the origin  $(r_1, r_2) = (0, 0)$ .

As mentioned in Sect. 2.2, the density function  $G(q; a)$  reduces to the electron-pair radial difference density  $T(t)$ , the single-electron radial density  $D(r)$ , and the electron-pair radial sum density  $S(s)$ , when the parameter  $a$  takes the values  $-1, 0$ , and  $+1$ , respectively. The analyses of the function  $G(q; a)$  in this Section show that the electron-pair density  $G(q; a)$  and its  $a = 0$  cross-section  $D(r)$  share some of their own local minima and maxima. However, the remaining two values of the parameter  $a$  do not provide cross-sections of the function  $G(q; a)$  with any particular mathematical characteristics.

### 4 Simple illustrations

We first illustrate analytical aspects of the density function  $G(q; a)$  using an approximate wave function. In the Kellner approximation [14], the wave function for the ground-state He atom is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = (\zeta^3/\pi) \exp[-\zeta(r_1 + r_2)][\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]/\sqrt{2}, \quad (20)$$

where  $\zeta$  is a positive-valued parameter. The associated two-electron radial density function  $D_2(r_1, r_2)$  is found to be

$$D_2(r_1, r_2) = 16\zeta^6 r_1^2 r_2^2 \exp[-2\zeta(r_1 + r_2)]. \quad (21)$$

Based on Eq. 7b–d, the three functions  $G_+(q; a)$ ,  $G_0(q)$  and  $G_-(q; a)$  are obtained as

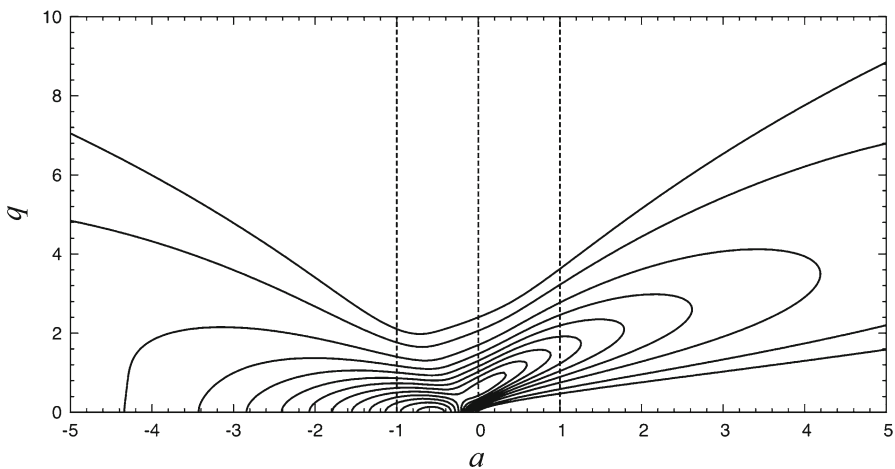
$$G_+(q; a) = 4\zeta b^{-5}[(3a^2 - 3ab\zeta q + b^2\zeta^2 q^2) \exp(-2\zeta q/a) - (3a^2 + 3ab\zeta q + b^2\zeta^2 q^2) \exp(-2\zeta q)], \quad (22a)$$

$$G_0(q) = 4\zeta^3 q^2 \exp(-2\zeta q), \quad (22b)$$

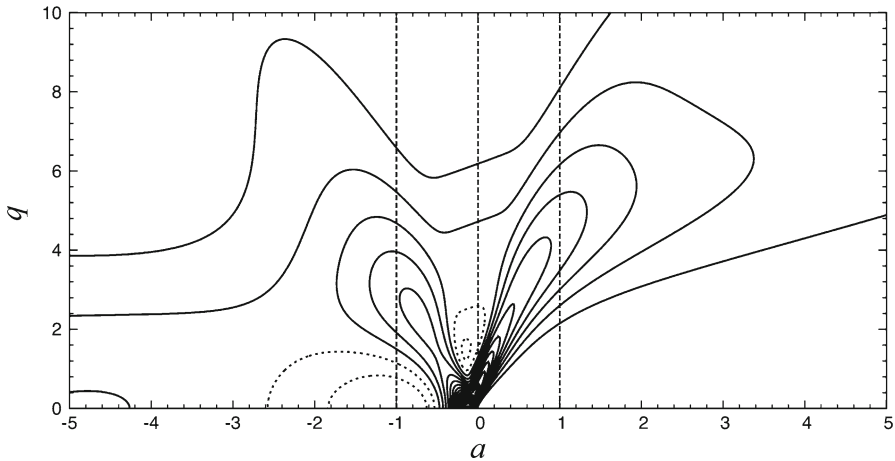
$$G_-(q; a) = -4\zeta b^{-5}(3a^2 + 3ab\zeta q + b^2\zeta^2 q^2)[\exp(-2\zeta q) + \exp(2\zeta q/a)], \quad (22c)$$

where  $b = a - 1$ . Analyses of these functions explicitly confirm various properties of the density function  $G(q; a)$  discussed in the previous sections. Note that an appropriate limiting procedure yields  $G_+(q; +1) = (8/15)\zeta^6 q^5 \exp(-2\zeta q)$ .

To catch a graphical idea about the new density function  $G(q; a)$ , we examine the  $1s^2$  ground state of the helium atom using a configuration interaction (CI) wave



**Fig. 1** The electron-pair radial density  $G(q; a)$  for the  $1s^2$  ground state of the helium atom. The contour values are 0.05, 0.1(0.1)1.2 from the outermost contour



**Fig. 2** The electron-pair radial density  $G(q; a)$  for the  $1s2s^3S$  state of the helium atom. The contour values are 0.05(0.05)0.95 from the outermost contour. Dotted contours mean valleys

function with the Clementi–Roetti function [15] supplemented by extra four s, five p, and five d Slater-type functions. Figure 1 shows a contour plot of the electron-pair density  $G(q; a)$ . We find the contour surface has no definite symmetry. Three vertical cross-sections along the dashed lines give the known densities  $T(t)$ ,  $D(r)$ , and  $S(s)$ , respectively, which are indeed found to be connected by the function  $G(q; a)$  in a smooth manner. In the present approximation, the global maximum of  $G(q; a)$  is observed at  $q = 0$  and  $a_0 = -0.55$  where Eq. 19 is valid. There is a secondary local maximum at  $q = 0.64$  and  $a = 0.07$ , but there are no local minima. Thus, the probability density  $D_2(r_1, r_2)$  is largest along the line  $r_1 = 0.55r_2$  or  $r_2 = 0.55r_1$  among various lines in the  $r_1r_2$  plane. The secondary local maximum of  $G(q; a)$  lies close to the global maximum of  $D(r)$  given by  $a = 0$  and  $q = 0.57$ . The approximate inversion symmetry given by Eq. 17 is also observed in Fig. 1 around  $a = 0$ ; contours in the vicinity of  $a = 0$  are well approximated by straight lines.

We next consider the  $1s2s^3S$  state of the helium atom in a CI calculation with the same basis set as the ground state. The  $1s2s^3S$  state has a radial hole in any approximate or exact descriptions, and our major concern is how the radial hole emerges in the function  $G(q; a)$ . Figure 2 plots a contour map of  $G(q; a)$  for the  $^3S$  state. When compared with the ground state map, we first find that the contours extend to larger  $q$  values in the  $^3S$  state, reflecting the diffuser character of the excited state density distribution. The density function  $G(q; a)$  is rather complicated in the  $^3S$  state: it has four local maxima and two local minima. The local maxima are located at  $(q, a) = (0, -0.11)$ ,  $(0.50, 0)$ ,  $(2.29, -0.72)$ , and  $(0, -4.80)$  in the order of higher peak. The first coordinates give the global maximum implying that two electrons are most probable on the line  $r_1 - 0.11r_2 = 0$  in the  $r_1r_2$  plane. The secondary maximum of  $G(q; a)$  at  $(q, a) = (0.50, 0)$  is nothing but the global maximum of the single-electron density  $D(r)$  due to electrons in 1s region. The secondary and broader maximum in  $D(r)$  due to electrons in 2s region, appearing at  $r = 3.54$ , lies merely on a ridge of  $G(q; a)$ . The local minima are located at  $(q, a) = (0, -1)$  and  $(1.45, -0.16)$  in the order

of deeper valley. At the first minimum, the density  $G(0; -1)$  is exactly zero and this point is the radial hole of the  $1s2s\ ^3S$  state. The two electrons have zero probability density to be on the  $r_1 - r_2 = 0$  line or the two electrons cannot be on the same sphere. The  $G(q; a)$  contour map shows that there exists the secondary local minimum which can be regarded as a “quasi radial hole”: At the point  $(q, a) = (1.45, -0.16)$  or along the line  $r_1 - 0.16r_2 = \pm 1.45$ , the two electrons are less probable compared to neighboring points or lines, though the probability density is not zero. The presence of the quasi radial hole is found for the first time by the use of the electron-pair radial density  $G(q; a)$  introduced in this study.

## 5 Summary and remarks

We have studied a generalized electron-pair radial density function  $G(q; a)$  that represents the probability density for the electron-pair radius  $|r_1 + ar_2|$  to be  $q$ , and is a projection of the two-electron radial density  $D_2(r_1, r_2)$  along lines  $r_1 + ar_2 \pm q = 0$  in the  $r_1r_2$  plane onto a point in the  $qa$  plane. The density  $G(q; a)$  connects the electron-pair radial sum density  $S(s)$ , the electron-pair radial difference density  $T(t)$ , and the single-electron radial density  $D(r)$ , defined independently in the literature, as a smooth function of real-valued parameter  $a$ . Simple illustrations of the density function  $G(q; a)$  have been given for the helium atom in the ground  $1s^2$  and the first excited  $1s2s\ ^3S$  states, and the presence of the quasi radial hole has been pointed out for the first time. We hope the present results are useful in density functional studies based on the spherically-averaged pair density (see, e.g., [16, 17]).

It is possible to introduce another electron-pair radial density function  $g(q; a, b)$  with two real-valued parameters  $a$  and  $b$ ,

$$g(q; a, b) = \int_0^{\infty} dr_1 \int_0^{\infty} dr_2 \delta(q - |ar_1 + br_2|) D_2(r_1, r_2), \quad (23)$$

which is apparently more general than  $G(q; a)$  examined in this study. However, a scaling relation [12] of the Dirac delta function yields that if  $a \neq 0$ ,  $g(q; a, b) = \frac{1}{|a|} G\left(\frac{q}{|a|}; \frac{b}{a}\right)$  and hence  $g(q; a, b)$  is isomorphic to  $G(q; a)$ . If  $a = 0$  and  $b \neq 0$ , we have  $g(q; 0, b) = \frac{1}{|b|} G_0\left(\frac{q}{|b|}\right)$ . The information contents of  $g(q; a, b)$  and  $G(q; a)$  are equivalent.

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