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

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

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 $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ 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.¹ For the evaluation of V_{ee} , on the other hand, the spherically averaged electron-pair intracule (relative motion) density $h(r_{12})$ is required, which is defined by

$$h(r_{12}) = (4\pi r_{12}^2)^{-1} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(r_{12} - |\mathbf{r}_i - \mathbf{r}_j|) \right\rangle.$$
(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.²⁻⁴ 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,⁵ 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 $V = V_{en} + V_{ee}$ 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,

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

was introduced²⁻⁴ 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 reported⁶⁻⁸ between the intracule and extracule densities of atoms.

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

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

has been introduced in a recent article,⁵ 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):

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

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

where the second equality in Eq. (5b) follows from a scaling relation⁵

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

in which c is any nonzero real number.

Originally, the generalized electron-pair density function g(q;a,b) is defined⁵ for nonzero values of *a* and *b*. However, if we allow the parameter *b* to be zero, we obtain

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

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

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

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

The electron-pair density g(q;a,b) defined by Eq. (4) can be rewritten⁵ as

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

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

$$X(s;a,b) \equiv (4\pi)^{-1} \int d\Omega_s \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \exp(-ia\mathbf{s} \cdot \mathbf{r}_j) \times \exp(-ib\mathbf{s} \cdot \mathbf{r}_k) \right\rangle,$$
(9b)

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

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

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

We then find

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

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

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

corresponding to Eqs. (8a), (8b), and (8c), where singleelectron $\langle r^n \rangle$, 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

$$\frac{\partial}{\partial a} \langle q^n \rangle_{(a,b)} \bigg|_{\substack{a=0\\b\neq 0}} = \frac{\partial}{\partial b} \langle q^n \rangle_{(a,b)} \bigg|_{\substack{b=0\\a\neq 0}} = 0, \tag{13}$$

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

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

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

the potential energy V can be expressed as

$$V = \int_0^\infty dq G(q), \tag{15a}$$

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.⁹ The Kellner wave function for a helium-like atom is given by

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

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

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

$$g(q;a,b) = (\zeta^{2}/\pi)(B^{2}-A^{2})^{-3} \{2A^{2}B^{2}q^{-1} \\ \times [\exp(-2\zeta q/A) - \exp(-2\zeta q/B)] \\ + \zeta(B^{2}-A^{2})[A\exp(-2\zeta q/A) \\ + B\exp(-2\zeta q/B)]\},$$
(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

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

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



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 $|b| \le 1$. 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 $0 \le q < 0.59$ 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 4.35×10^{-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

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

for n = -2, and

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



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

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

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

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

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

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

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

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

for b = 0 and

$$\langle q^n \rangle_{(a,\pm a)} = \frac{(n+2)!}{48} (n^2 + 10n + 24) \left(\frac{A}{2\zeta}\right)^n \quad (n \ge -2)$$
(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 ± 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 $\langle q^{-1} \rangle_{(1,0)} = -V_{\rm en}/(2Z)$ is the maximum whereas the electron repulsion $\langle q^{-1} \rangle_{(1,-1)} = V_{\rm ee}$ is the minimum of $\langle q^{-1} \rangle_{(1,b)}$ in the region $-1 \le b \le +1$. 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 $-1 \le b \le +1$.

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 singleelectron 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 known¹⁰⁻¹⁴ 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.

- ¹P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).
- ²A. J. Coleman, Int. J. Quantum Chem., Symp. 1, 457 (1967).
- ³A. J. Thakkar, in *Density Matrices and Density Functionals*, edited by R.
- M. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), pp. 553-581.
- ⁴R. J. Boyd and J. M. Ugalde, in *Computational Chemistry*, edited by S. Fraga (Elsevier, Amsterdam, 1992), Part A, pp. 273–299.
- ⁵T. Koga, Theor. Chem. Acc. **105**, 96 (2000).
- ⁶T. Koga and H. Matsuyama, J. Chem. Phys. 108, 3424 (1998).
- ⁷T. Koga, H. Matsuyama, E. Romera, and J. S. Dehesa, Phys. Rev. A 57, 4212 (1998).
- ⁸T. Koga and H. Matsuyama, J. Chem. Phys. **111**, 9191 (1999).
- ⁹G. W. Kellner, Z. Phys. 44, 91 (1927).
- ¹⁰T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
- ¹¹E. Steiner, J. Chem. Phys. **39**, 2365 (1963).
 - ¹²A. J. Thakkar and V. H. Smith, Jr., Chem. Phys. Lett. 42, 476 (1976).
 - ¹³J. C. Kimball, Phys. Rev. A 7, 1648 (1973).
 - ¹⁴A. E. Carlsson and N. W. Ashcroft, Phys. Rev. B 25, 3474 (1982).