A generalized electron-pair density function for atoms

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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_{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.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

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

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.^{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 $V = V_{\text{en}} + V_{\text{ee}}$ 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^{2–4} 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 reported^{6–8} between the intracule and extracule densities of atoms.

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

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

has been introduced in a recent article,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 $g(q;a,b)$:

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

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

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

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

in which c is any nonzero real number.

Originally, the generalized electron-pair density function $g(q; a, b)$ is defined⁵ 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 rewritten⁵ 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, Ω_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.⁹ 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 ξ 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 4.35×10^{-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 ± 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 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.

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