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Radial electron-pair densities in momentum space and shell structure of atoms

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Abstract. The radial electron-pair intracule (relative motion) $H(u)$ and extracule (center-of-mass motion) $D(R)$ densities in position space were known to reveal four types of maxima which are related to the four inner electron shells, K, L, M, and N, of atoms. The corresponding radial electron-pair intracule $\bar{H}(v)$ and extracule $\bar{D}(P)$ densities in momentum space are studied for the 102 atoms from He (atomic number $Z = 2$) to Lr ($Z = 103$). The densities $\bar{H}(v)$ and $\bar{D}(P)$ are found to have either one maximum or two maxima, and the numbers of maxima in $\bar{H}(v)$ and $\bar{D}(P)$ are the same for 98 atoms. For these atoms, the locations $v_{\max}$ and $P_{\max}$ and the heights $\bar{H}_{\max}$ and $\bar{D}_{\max}$ of the corresponding maxima satisfy the approximate relations $v_{\max} \cong 2P_{\max}$ and $\bar{H}_{\max} \cong \bar{D}_{\max}/2$. On the basis of their Z-dependence, the maxima in $\bar{H}(v)$ and $\bar{D}(P)$ of the 102 atoms are classified into five types. Shell-pair decompositions of the radial densities show that these maxima reflect five outer electron shells of atoms.

Key words: Radial electron-pair densities – Intracule and extracule – Momentum space – Shell structure – Atoms

1 Introduction

In a recent article [1], the characteristics of the radial electron-pair intracule (relative motion) $H(u)$ and extracule (center-of-mass motion) $D(R)$ densities, defined [2, 3] by

$$H(u) \equiv \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \delta(u - |\mathbf{r}_1 - \mathbf{r}_2|)\Gamma(\mathbf{r}_1, \mathbf{r}_2) \ , \tag{1}$$

$$D(R) \equiv \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \delta(R - |\mathbf{r}_1 + \mathbf{r}_2|/2)\Gamma(\mathbf{r}_1, \mathbf{r}_2) \ , \tag{2}$$

were studied, where $\delta(x)$ is the one-dimensional Dirac delta function and

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{N(N-1)}{2} \int \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 d\mathbf{x}_3 \ldots\, d\mathbf{x}_N |\Psi t.(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 . \tag{3}$$

is the spin-reduced two-electron density function [4] associated with an N-electron wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, with $\mathbf{x}_\mathrm{i} \equiv (\mathbf{r}_\mathrm{i}, \sigma_\mathrm{i})$ being the combined position-spin coordinates of the electron i. The intracule $H(u)$ and extracule $D(R)$ densities are [1–3] the probability density functions for the relative distance $|\mathbf{r}_i - \mathbf{r}_j|$ and the center-of-mass radius $|\mathbf{r}_i + \mathbf{r}_j|/2$ of any pair of electrons i and j, respectively. For the 102 neutral atoms from He to Lr, it was found [1] that the radial densities $H(u)$ and $D(R)$ in position space reveal four different types of maxima, which are related to the inner four electron shells, K, L, M, and N, of atoms.

The corresponding radial intracule $\bar{H}(v)$ and extracule $\bar{D}(P)$ densities are defined in momentum space as well:

$$\bar{H}(v) \equiv \int \mathrm{d}\mathbf{p}_1 \mathrm{d}\mathbf{p}_2 \delta(v - |\mathbf{p}_1 - \mathbf{p}_2|)\, \bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2) \ , \tag{4}$$

$$\bar{D}(P) \equiv \int \mathrm{d}\mathbf{p}_1 \mathrm{d}\mathbf{p}_2 \delta(P - |\mathbf{p}_1 + \mathbf{p}_2|/2) \bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2) \ , \tag{5}$$

where $\bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2)$ is the two-electron density function resulting from a momentum wave function $\Phi(\mathbf{y}_1, \ldots, \mathbf{y}_N)$, with $\mathbf{y}_\mathrm{i} \equiv (\mathbf{p}_i, \sigma_i)$ being the combined momentum–spin coordinates of the electron i. The intracule $\bar{H}(v)$ and extracule $\bar{D}(P)$ densities have the physical meaning analogous to that of $H(u)$ and $D(R)$, but in momentum space, and are probability density functions for the relative $|\mathbf{p}_i - \mathbf{p}_j|$ and center-of-mass $|\mathbf{p}_i + \mathbf{p}_j|/2$ momenta. In the literature [2, 3, 5–7], various properties and the physical significance of the spherically averaged intracule and extracule densities, corresponding to $\bar{H}(v)/(4\pi v^2)$ and the extracule $\bar{D}(P)/(4\pi P^2)$, have been reported. In particular, the presence of three different types of modalities in the spherical averages was reported [8–10] for neutral atoms, reflecting the differ-

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ences in the valence electronic configurations. However, little is known about the radial electron-pair momentum densities $\bar{H}(v)$ and $\bar{D}(P)$, which incorporate the effect of the surface areas $4\pi v^2$ and $4\pi P^2$ into the spherical averages.

In the present work, we study the characteristics of the momentum-space radial intracule $\bar{H}(v)$ and extracule $\bar{D}(P)$ densities in a systematic manner for the 102 neutral atoms from He (atomic number $Z = 2$) to Lr ($Z = 103$) in their ground states, with our particular interest in the shell structure of atomic electrons as observed in their position-space counterparts. In the next section, our numerical procedure is summarized for the analysis of the radial densities. The results are presented and discussed in Sect. 3. It is found that all the radial densities have either one maximum or two maxima. The locations $v_{\max}$ and $P_{\max}$ and the heights $\bar{H}_{\max}$ and $\bar{D}_{\max}$ of two corresponding maxima in $\bar{H}(v)$ and $\bar{D}(P)$ have approximate but interesting relations. Examination of the Z-dependence of these locations and heights shows that the maxima are classified into five types. Decomposition of the radial densities $\bar{H}(v)$ and $\bar{D}(P)$ into shell-pair contributions clarifies that these five types of maxima are related to the outer-shell structure of atomic electrons, in contrast to the inner shells detected in position space. Hartree atomic units are used throughout.

2 Computational outline

The experimental ground electronic configurations and *LS* terms [11, 12] were considered for all the 102 atoms from He to Lr. The intracule densities $\bar{H}(v)$ were constructed from the spherical averages reported in Ref. [13] for the 53 lighter atoms from He to Xe and in Ref. [10] for the 49 heavier atoms from Cs to Lr. The extracule densities $\bar{D}(P)$ were constructed from the spherical averages reported in Ref. [14] for the atoms from He to Xe and in Ref. [10] for the atoms from Cs to Lr. All these electron-pair densities were constructed by the numerical Hartree–Fock method [15, 16] and, hence, the radial densities $\bar{H}(v)$ and $\bar{D}(P)$ were obtained as numerical tables. The search for extrema was made using analytical quintic polynomials designed to interpolate three data points on each side of the target extremum.

3 Results and discussion

3.1 Radial intracule densities

Examination of the radial intracule densities $\bar{H}(v)$ shows that 74 atoms with $Z = 2$, 3, 5–13, 21–40, 49–88, and 101–103 have a single maximum, whereas 28 atoms with $Z = 4$, 14–20, 41–48, and 89–100 have two maxima. No densities with three or more maxima were observed. Examples are given in Fig. 1 for the Ne atom ($Z = 10$) with a single maximum and for the Ru atom ($Z = 44$) with two maxima. However, we did not find any regularities for the appearance of one maximum or two maxima in the radial intracule densities.

We next examined the locations $v_{\max}$ and heights $\bar{H}_{\max} \equiv \bar{H}(v_{\max})$ of these maxima as a function of atomic number Z. The results are depicted in Fig. 2. Clearly, different Z-dependences of $v_{\max}$ and $\bar{H}_{\max}$ distinguish the maxima into five types: type A for $Z = 2$–4, type B for $Z = 4$–20, type C for $Z = 14$–48, type D for $Z = 41$–100, and type E for $Z = 89$–103. For the maxima with the same type, both the location $v_{\max}$ and the height $\bar{H}_{\max}$ increase with increasing Z, though there are a few exceptions. Thus, the four groups of atoms with two maxima are characterized by the combinations of two different types of maxima: A + B for $Z = 4$, B + C for $Z = 14$–20, C + D for $Z = 41$–48, and D + E for $Z = 89$–100.

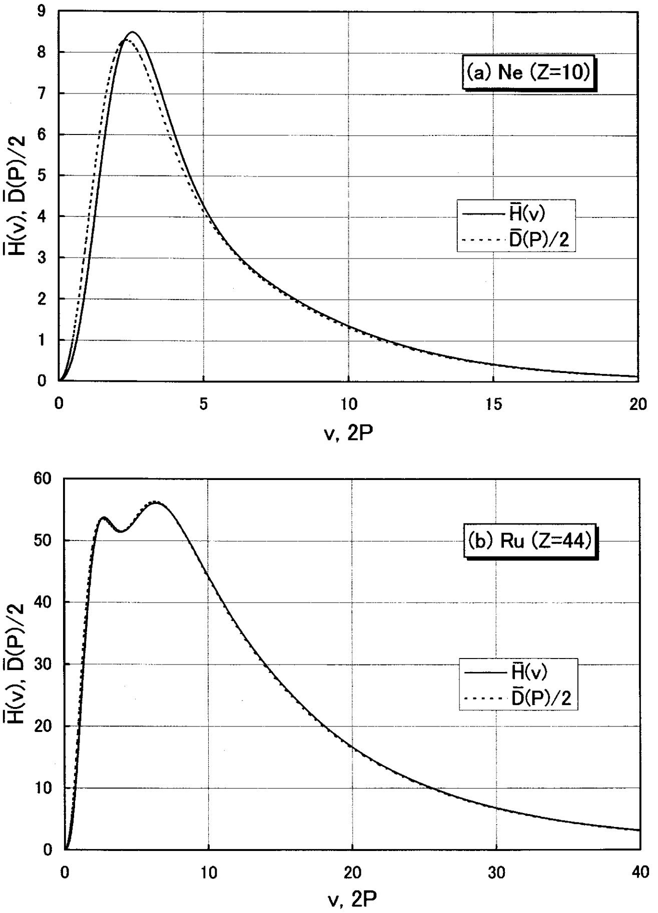

Fig. 1a, b. Examples of the radial intracule and extracule densities in momentum space. **a** Ne atom ($Z = 10$) with a single maximum. **b** Ru atom ($Z = 44$) with two maxima

To identify the origin of the five different types of maxima, we applied shell-pair decomposition to $\bar{H}(v)$, as was done in Ref. [1] in position space. We then found that particular combinations of a few outer shell pairs explain well the five different types of maxima in $\bar{H}(v)$. The major shell-pair components of $\bar{H}(v)$ which generate the two maxima in Ru are exemplified in Fig. 3. We find that the type C maximum of Ru originates from MM, MN, and MO shell pairs, while the type D maximum originates from NN and NO shell pairs. In other words, the type C (D) maximum is due to one electron in the M (N) shell and the other electron in the same or an outer shell, suggesting that the M and N shells are characteristic shells of the type C and D maxima, respectively.

The results of analogous examinations of the 102 atoms are summarized in Table 1. The table clarifies that the type A maxima originate from the KK + KL shell pairs, the type B from LL + LM + LN shell pairs, the type C from MM + MN + MO shell pairs, the type D from NN + NO + NP + NQ shell pairs, and the type E from OO + OP + OQ shell pairs. (If some shells are vacant, the corresponding shell pairs are absent from the previously mentioned contributions.) When the location and the height of the peaks of the shell-pair contributions are examined, the *Z*-dependences of $v_{\max}$ and $\bar{H}_{\max}$ observed in Fig. 2 are well reproduced with average relative errors of 12 and 24%, respectively. Namely, the five different types of maxima in $\bar{H}(v)$ can be interpreted as the reflection of electron pairs in different shell pairs specified by two principal quantum numbers *n* and $n'(n \le n')$ and are characterized by the smaller quantum number *n*. Thus, the maxima in the radial intracule densities are indicative of the five shells K, L, M, N, and O, which occupy the outer part of the electron shells in atoms.

For heavier atoms, the outer shells P and Q, corresponding to $n = 6$ and 7, are occupied as well; however, the shell-pair analysis shows that the peaks from these contributions are buried in the distribution of inner-shell

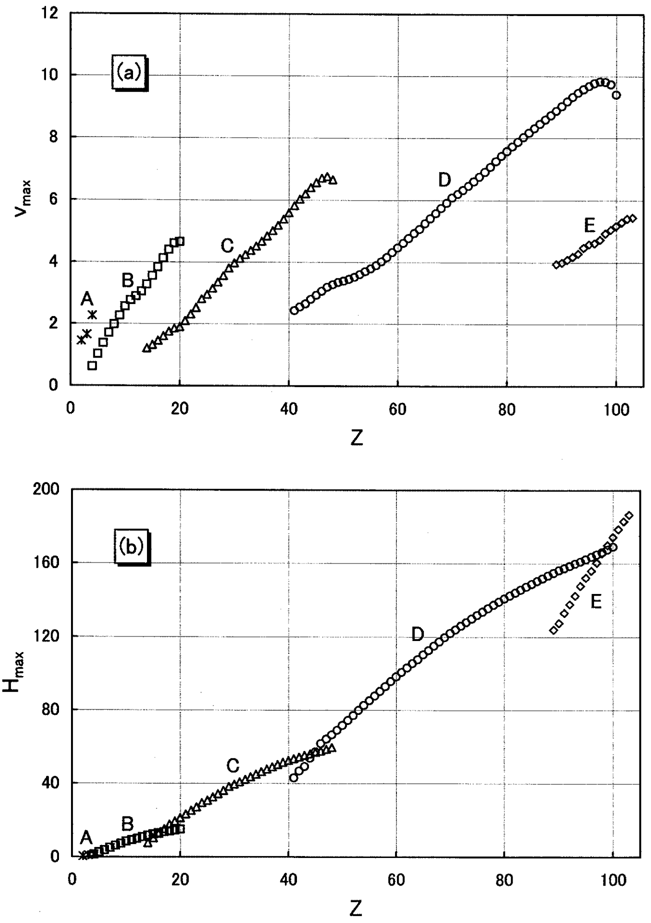

Fig. 2a, b. *Z*-dependences of the locations and the heights of the maxima in the radial intracule densities. **a** Locations $v_{\max}$. **b** Heights $\bar{H}_{\max}$

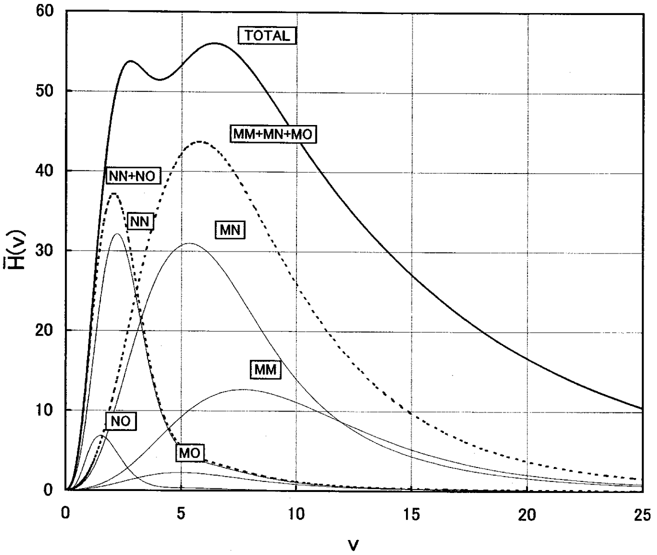

Fig. 3. Shell-pair decomposition of the radial intracule density of the Ru atom

Table 1. Predominant shell pairs which generate the five types of maxima in the radial intracule density

Period	Atoms	A	B	C	D	E
1	He	KK				
2	Li	KK + KL				
	Be	KK + KL	LL			
	B–Ne		LL			
3	Na–Al		LL + LM			
	Si–Ar		LL + LM	MM		
4	K, Ca		LL + LM + LN	MM + MN		
	Sc–Kr			MM + MN		
5	Rb–Zr			MM + MN + MO		
	Nb–Rh, Ag, Cd			MM + MN + MO	NN + NO	
	Pd			MM + MN	NN	
	In–Xe				NN + NO	
6	Cs–Rn				NN + NO + NP	
7	Fr, Ra				NN + NO + NP + NQ	
	Ac–Fm				NN + NO + NP + NQ	OO + OP + OQ
	Md–Lr					OO + OP + OQ

pairs with more numbers of electron pairs, and the components arising from the P and Q shells do not reveal their own maxima in the total radial density. Thus, the occupation of a particular electron shell does not necessarily imply the appearance of the corresponding maximum in the radial intracule density. Another example is the fact that the type A maximum corresponding to the K shell is absent for atoms with $Z \geq 5$, though the shell is fully occupied in all the atoms. We could not obtain any strict index for the appearance and disappearance of these maxima in the radial intracule density from our study. However, the ratio $R_n = N_n/N$ of the number of electrons N_n in the relevant shell n to the total number of electrons N is empirically found to be an important factor: When there is a single maximum, a shell n with the largest R_n and larger n reveals the maximum in $\bar{H}(v)$. When there are two maxima, two shells with the largest ratios generate the corresponding maxima. If we assign the shells n and n' to the maxima with larger and smaller $v_{\max}$, respectively, then R_n is the largest and $R_{n'}$ is the second largest among the ratios, yet $n' = n + 1$ with no exceptions. The value of $R_{n'}$ never exceeds R_n and the maximum corresponding to the shell n disappears after $R_{n'}$ reaches R_n in $\bar{H}(v)$. Outer electron shells with more electrons are concluded to yield the maxima in the radial intracule density in momentum space.

3.2 Radial extracule densities

The relative motion and the center-of-mass motion of two particles are completely independent. Nevertheless, the Coulombic binding of electrons in an atomic system is known [17] to generate nontrivial relations between the intracule and extracule properties. In particular, an approximate isomorphic relation,

$$\bar{H}(v) \cong \frac{1}{2}\bar{D}(v/2) \ , \tag{6}$$

is derived from the results of Ref. [17] between the radial intracule and extracule densities.

As anticipated from Eq. (6), our examination of the radial extracule densities $\bar{D}(P)$ showed that for all 102 atoms the behavior of $\bar{D}(P)$ is very similar to that of $\bar{H}(v)$, if the abscissa and ordinate are scaled. Examples are given in Fig. 1 for the Ne and Ru atoms. All the extracule densities have either one maximum (70 atoms with $Z = 2$, 3, 6–13, 21–38, 49–87, and 101–103) or two maxima (32 atoms with $Z = 4$, 5, 14–20, 39–48, and 88–100). The numbers of maxima in $\bar{H}(v)$ and $\bar{D}(P)$ are common to 98 atoms; four atoms with $Z = 5$, 39, 40, and 88 have two maxima in $\bar{D}(P)$ and a single maximum in $\bar{H}(v)$. The different numbers of maxima in the latter four atoms is due to a larger deviation in the isomorphism (Eq. 6) owing to the contributions of particular pairs of spin-orbitals [17].

Equation (6) also suggests that the locations $P_{\max}$ and the heights $\bar{D}_{\max} \equiv \bar{D}(P_{\max})$ of the maxima in the extracule densities $\bar{D}(P)$ would be related by

$$v_{\max} \cong 2P_{\max}, \quad \bar{H}_{\max} \cong \bar{D}_{\max}/2 \tag{7}$$

to the maximum characteristics $v_{\max}$ and $\bar{H}_{\max}$ of the intracule densities $\bar{H}(v)$. Indeed, numerical examinations showed these relations are true; we have $v_{\max}/P_{\max} = 2.062$ and $\bar{H}_{\max}/\bar{D}_{\max} = 0.498$, when averaged over the 98 atoms with the same number of maxima in $\bar{H}(v)$ and $\bar{D}(P)$.

Apart from the factor 2 appearing in Eq. (7), the Z-dependences of $P_{\max}$ and $\bar{D}_{\max}$ are thus analogous to those of $v_{\max}$ and $\bar{H}_{\max}$, and the maxima in the extracule densities $\bar{D}(P)$ are again classified into five types A, B, C, D, and E: type A appears for $Z = 2$–5, type B for $Z = 4$–20, type C for $Z = 14$–48, type D for $Z = 39$–100, and type E for $Z = 88$–103. On basis of the shell-pair decomposition, the origin of these five types of maxima in $\bar{D}(P)$ was found to be the same as that of maxima in $\bar{H}(v)$, resulting in the conclusion that the maxima in the radial extracule densities also reflect outer five shells K, L, M, N, and O.

4 Summary

The maxima in the radial intracule $\bar{H}(v)$ and extracule $\bar{D}(P)$ densities in momentum space were analyzed for the 102 atoms from He to Lr. They were found to be classified into five types, which reflect the five outer shells, K, L, M, N, and O, of atoms, respectively, in contrast to the inner shells detected in position space. The ratio of the number of shell electrons to the total number of electrons was suggested to be an index for the appearance and disappearance of the maximum corresponding to the shell.

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