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Atomic one- and two-electron subshell moments in position and momentum spaces

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Abstract. For 357 subshells of the 53 neutral atoms He through Xe in their ground states, the two-electron intracule (relative motion) $\langle u^k \rangle_{nl}$ and extracule (center-of-mass motion) $\langle R^k \rangle_{nl}$ subshell moments in position space are examined as well as their counterparts $\langle v^k \rangle_{nl}$ and $\langle P^k \rangle_{nl}$ in momentum space, where n and l are the principal and azimuthal quantum numbers of the atomic subshell, respectively. It is clarified that between the intracule and extracule moments the "2^k-rule" is strictly valid, which means $\langle u^k \rangle_{nl} = 2^k \langle R^k \rangle_{nl}$ and $\langle v^k \rangle_{nl} = 2^k \langle P^k \rangle_{nl}$ for any nl subshell. Theoretical analysis also proves that for a particular case of $k = +2$, two relations $\langle u^2 \rangle_{nl} = (N_{nl} - 1)\langle r^2 \rangle_{nl}$ and $\langle v^2 \rangle_{nl} = (N_{nl} - 1)\langle p^2 \rangle_{nl}$ hold exactly, where N_{nl} (≥ 2) is the number of electrons in the subshell nl, and $\langle r^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ are the familiar one-electron subshell moments in position and momentum spaces, respectively. The latter equality establishes a new and rigorous relation between the second electron-pair moments in momentum space and the total energy of an atom through the virial theorem. For $k = +1$, -1, and -2, the numerical Hartree-Fock results for the 357 subshells show that there are approximate but accurate linear relations between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ and between $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$, in which the proportionality constant in each space depends on n, l, and k.

Key words: Intracule density – Extracule density – Two-electron moments – One-electron moments – Position space – Momentum space

1 Introduction

The intracule (relative motion) $I(\mathbf{u})$ and extracule (center-of-mass motion) $E(\mathbf{R})$ densities [1], as well as their spherical averages $h(u)$ and $d(R)$, are a couple of electron-pair densities useful to analyze the motion of a pair of electrons in atoms and molecules (see, for example, Ref. [2] for a review). The intracule densities $I(\mathbf{u})$ and $h(u)$ are the probability density functions for the relative vector $\mathbf{u} = \mathbf{r}_i - \mathbf{r}_j$ and its magnitude $u = |\mathbf{r}_i - \mathbf{r}_j|$ of any pair of electrons i and j. On the other hand, the extracule densities $E(\mathbf{R})$ and $d(R)$ represent the probability density functions for the center-of-mass vector $\mathbf{R} = (\mathbf{r}_i + \mathbf{r}_j)/2$ and its magnitude $R = |\mathbf{r}_i + \mathbf{r}_j|/2$ of any pair of electrons i and j. The corresponding intracule $\bar{I}(\mathbf{v})$ and $\bar{h}(v)$ densities and extracule $\bar{E}(\mathbf{P})$ and $\bar{d}(P)$ densities are also introduced in momentum space, and represent the probability density functions for the relative and center-of-mass momentum vectors and their magnitudes for a pair of electrons. As reviewed in Refs. [2–4], for example, studies on the two-electron intracule and extracule densities are limited compared with the familiar one-electron position $\rho(\mathbf{r})$ and momentum $\Pi(\mathbf{p})$ densities or their spherical averages $\rho(r)$ and $\Pi(p)$. Within the Hartree-Fock framework, however, systematic examinations of the spherically averaged intracule $h(u)$ and extracule $d(R)$ densities, together with their momentum-space counterparts $\bar{h}(v)$ and $\bar{d}(P)$, have been performed very recently for the neutral atoms from He to Xe in their ground states [5, 6].

The one-electron position $\langle r^k \rangle$ and momentum $\langle p^k \rangle$ moments follow immediately from the one-electron position $\rho(r)$ and momentum $\Pi(p)$ densities, respectively, and characterize the distributions of their parent densities. Analogously, the intracule densities $h(u)$ and $\bar{h}(v)$ are accompanied by the two-electron intracule moments $\langle u^k \rangle$ and $\langle v^k \rangle$, respectively, and the extracule densities $d(R)$ and $\bar{d}(P)$ with the two-electron extracule moments $\langle R^k \rangle$ and $\langle P^k \rangle$, respectively. Accurate Hartree-Fock values of the intracule moments $\langle u^k \rangle$ and $\langle v^k \rangle$ and the extracule moments $\langle R^k \rangle$ and $\langle P^k \rangle$, based on numerical Hartree-Fock calculations, have been reported for the atoms He through Xe [3, 4]. Though these intracule and extracule moments characterize the distributions of the parent electron-pair densities, the practical significance of the four kinds of two-electron moments is not yet known in many-electron systems except for two particular cases. The position-space in-

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tracule moment $\langle u^{-1}\rangle$ is just the electron-electron repulsion energy, and the first moments $\langle u\rangle$ and $\langle v\rangle$ are the average interelectronic distances in position and momentum spaces, respectively. The role of the two-electron moments in atomic and molecular quantum theory is quite different from that of the one-electron moments $\langle r^k\rangle$ and $\langle p^k\rangle$, many of which are directly connected with important physical properties of atoms and molecules.

Recently however, we have found that in position space the two-electron intracule $\langle u^k\rangle$ and extracule $\langle R^k\rangle$ moments of atoms have good linear correlation with the familiar one-electron moments $\langle r^l\rangle^{k/l}$ for some combinations of small positive integers k and l [7]. The same is true in momentum space for the corresponding intracule $\langle v^k\rangle$ and extracule $\langle P^k\rangle$ moments and the one-electron moments $\langle p^l\rangle^{k/l}$. The correlation is generally better in momentum space than in position space and also when $k = l$ than when $k \neq l$. The best linear correlation is observed between $\langle v^2\rangle$ and $\langle p^2\rangle$ and between $\langle P^2\rangle$ and $\langle p^2\rangle$ with a correlation coefficient of 0.999999. Though these results suggest hidden structural relationships between the one- and two-electron densities, we could not find any appropriate model to explain the observed linearity [7].

In the present paper, we decompose the intracule and extracule moments of atoms according to subshells specified by the principal n and azimuthal l quantum numbers, and study the contributions arising from a pair of electrons in a subshell. The 53 neutral atoms from He to Xe in their ground states are the subject of our study, and hence there is a total of 357 subshells which contain two or more electrons. The next section summarizes the definitions of various one- and two-electron density functions and the associated moments as well as their subshell decompositions. The 2^k rule for the kth intracule and extracule moments for a subshell nl will be proved. An interesting yet rigorous relation will also be clarified between the second one- and two-electron moments. In Sect. 3, we describe our computational procedures based on the numerical Hartree-Fock method. The results are presented and discussed in Sect. 4. Hartree atomic units are used throughout this paper.

2 Theoretical structure of one- and two-electron densities and their moments

2.1 One-electron densities and their moments

For an N-electron system ($N \geq 1$), the spin-reduced one-electron density $\rho(\mathbf{r})$ and its spherical average $\rho(r)$ in position space are defined [8] by

$$\rho(\mathbf{r}) \equiv N \int d\sigma\, d\mathbf{x}_2 \ldots d\mathbf{x}_N |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \ , \tag{1a}$$

$$\rho(r) \equiv (4\pi)^{-1} \int d\Omega_r \rho(\mathbf{r}) \ , \tag{1b}$$

where $\mathbf{r} \equiv (r, \Omega_r)$ with $\Omega_r \equiv (\theta_r, \phi_r)$, $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is the electronic wave function of the system under consideration, and $x_i \equiv (\mathbf{r}_i, \sigma_i)$ is the combined position-spin coordinate of the electron i. The associated one-electron position moments $\langle r^k\rangle$ are defined by

$$\begin{aligned} \langle r^k\rangle &\equiv \int d\mathbf{r}\, r^k \rho(\mathbf{r}) \\ &= 4\pi \int_0^\infty dr\, r^{k+2}\, \rho(r) \ . \end{aligned} \tag{1c}$$

For a single Slater determinant Hartree-Fock wave function composed of N orthonormal spin orbitals $\psi_j(\mathbf{r})\eta_j(\sigma)$, Eq. (1a) is rewritten as a sum of orbital contributions $|\psi_j(\mathbf{r})|^2$. For atoms and atomic ions, we can generally assume that the spatial function $\psi_j(\mathbf{r})$ has a form

$$\psi_j(\mathbf{r}) = R_{n_j l i_j}(r) Y_{l_j m_j}(\Omega_r) \ , \tag{2}$$

where $Y_{lm}(\Omega)$ is a spherical harmonic. Then the one-electron densities $\rho(\mathbf{r})$ and $\rho(r)$ for atoms are decomposed into contributions from different subshells specified by a set of the principal n and azimuthal l quantum numbers.

$$\rho(\mathbf{r}) = \sum_{nl} \rho_{nl}(\mathbf{r}), \quad \rho_{nl}(\mathbf{r}) = \sum_{j=1}^{N} \delta_{nn_j}\delta_{ll_j}|\psi_j(\mathbf{r})|^2 \ , \tag{3a}$$

$$\begin{aligned} \rho(r) &= \sum_{nl} \rho_{nl}(r), \\ &\rho_{nl}(r) = (4\pi)^{-1} \sum_{j=1}^{N} \delta_{nn_j}\delta_{ll_j}|R_{n_j l_j}(r)|^2, \end{aligned} \tag{3b}$$

where δ_{ij} denotes the Kronecker delta. The associated subshell moments $\langle r^k\rangle_{nl}$ are given by

$$\langle r^k\rangle_{nl} \equiv \int d\mathbf{r}\, r^k \rho_{nl}(\mathbf{r}) = 4\pi \int_0^\infty dr\, r^{k+2}\, \rho_{nl}(r) \ , \tag{3c}$$

where the normalization is $\langle r^0\rangle_{nl} = N_{nl}$, the number of electrons in the subshell nl.

If we start from a momentum-space N-electron wave function $\Phi(\mathbf{y}_1, \ldots, \mathbf{y}_N)$, where $\mathbf{y}_i \equiv (\mathbf{p}_i, \sigma_i)$ is the combined momentum-spin coordinate of the electron i, the exactly analogous procedure defines the momentum-space one-electron density $\Pi(\mathbf{p})$, its spherical average $\Pi(p)$, and one-electron momentum moments $\langle p^n\rangle$. The Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, provided that the one-electron spatial function $\psi_j(\mathbf{r})$ is replaced with

$$\phi_j(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r}\, \exp(-i\mathbf{p}\cdot\mathbf{r})\psi_j(\mathbf{r}) \ . \tag{4a}$$

For the position-space atomic orbital given by Eq. (2), the corresponding momentum-space orbital is

$$\phi_j(\mathbf{p}) = P_{n_j l_j}(p) Y_{l_j m_j}(\Omega_p) \ , \tag{4b}$$

where $\mathbf{p} \equiv (p, \Omega_p)$ and

$$P_{n_j l_j}(p) = (-i)^{l_j} \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2 j_{l_j}(pr) R_{n_j l_j}(r) \ , \tag{4c}$$

in which $j_l(x)$ is the lth order spherical Bessel function of the first kind. Then the subshell components $\Pi_{nl}(\mathbf{p})$,

$\Pi_{nl}(p)$, and $\langle p^k \rangle_{nl}$ in momentum space are immediately obtained from equations analogous to Eqs. (3a)–(3c).

2.2 Two-electron intracule densities and their moments

For an N-electron system ($N \geq 2$), the intracule density $I(\mathbf{u})$, its spherical average $h(u)$, and the intracule moments $\langle u^k \rangle$ are defined [1, 2] by

$$I(\mathbf{u}) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \ \delta[\mathbf{u} - (\mathbf{r}_1 - \mathbf{r}_2)]\Gamma(\mathbf{r}_1, \mathbf{r}_2) \ , \tag{5a}$$

$$h(u) \equiv (4\pi)^{-1} \int d\Omega_u I(\mathbf{u}) \ , \tag{5b}$$

$$\langle u^k \rangle \equiv \int d\mathbf{u} \ u^k \ I(\mathbf{u}) = 4\pi \int_0^\infty du \ u^{k+2} \ h(u) \ , \tag{5c}$$

where $\mathbf{u} \equiv (u, \Omega_u)$ with $\Omega_u \equiv (\theta_u, \phi_u), \delta(\mathbf{r})$ is the three-dimensional Dirac delta function, and $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the spin-reduced two-electron density function [8],

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) \equiv \binom{N}{2} \int d\sigma_1 d\sigma_2 d\mathbf{x}_3 \ldots d\mathbf{x}_N |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 \ . \tag{6}$$

For a single Slater determinant wave function composed of N orthonormal spin orbitals $\psi_j(\mathbf{r})\eta_j(\sigma)$, $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ reduces to a sum of spin-orbital-pair contributions,

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \ \Gamma_{jk}(\mathbf{r}_1, \mathbf{r}_2) \ , \tag{7a}$$

$$\begin{aligned} \Gamma_{jk}(\mathbf{r}_1, \mathbf{r}_2) =& |\psi_j(\mathbf{r}_1)|^2 |\psi_k(\mathbf{r}_2)|^2 \\ &- \delta_s(j,k)[\psi_j^*(\mathbf{r}_1)\psi_k(\mathbf{r}_1)][\psi_k^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)] \ , \end{aligned} \tag{7b}$$

where $\delta_s(j,k)$ is unity if the two spin orbitals j and k have the same spin and is zero if they have opposite spins. Accordingly, the intracule densities $I(\mathbf{u})$ and $h(u)$ are decomposed into spin-orbital-pair components $I_{jk}(\mathbf{u})$ and $h_{jk}(u)$, respectively. When we use the kernel of three-dimensional Fourier transformation for the Dirac delta function,

$$\delta(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{s} \exp(+i\mathbf{r} \cdot \mathbf{s}) \ , \tag{8}$$

the spin-orbital-pair components $I_{jk}(\mathbf{u})$ and $h_{jk}(u)$ are expressed as the Fourier and Hankel transforms of their characteristic functions $F_{jk}(\mathbf{s})$ and $H_{jk}(s)$,

$$I_{jk}(\mathbf{u}) = (2\pi)^{-3} \int d\mathbf{s} \exp(+i\mathbf{u} \cdot \mathbf{s}) \ F_{jk}(\mathbf{s}) \ , \tag{9a}$$

$$h_{jk}(u) = (2\pi^2)^{-1} \int_0^\infty ds \ s^2 j_0(us) H_{jk}(s) \ , \tag{9b}$$

where

$$F_{jk}(\mathbf{s}) \equiv F_{kk}^{jj}(\mathbf{s}) - \delta_s(j,k) F_{kj}^{kj}(\mathbf{s}) \ , \tag{9c}$$

$$H_{jk}(s) \equiv H_{kk}^{jj}(s) - \delta_s(j,k) H_{kj}^{kj}(s) \ , \tag{9d}$$

in which

$$F_{\mu\nu}^{\kappa\lambda}(\mathbf{s}) \equiv f_{\kappa\lambda}^*(\mathbf{s}) f_{\mu\nu}(\mathbf{s}),$$

$$H_{\mu\nu}^{\kappa\lambda}(s) \equiv (4\pi)^{-1} \int d\Omega_s \ F_{\mu\nu}^{\kappa\lambda}(\mathbf{s}), \tag{9e}$$

$$f_{\kappa\lambda}(\mathbf{s}) \equiv \int d\mathbf{r} \exp(+i\mathbf{s} \cdot \mathbf{r}) \psi_\kappa^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) = f_{\lambda\kappa}^*(-\mathbf{s}) \ , \tag{9f}$$

and $\mathbf{s} \equiv (\mathrm{s}, \Omega_s)$.

For atomic systems with the spatial function (2), we obtain [3, 9]

$$\begin{aligned} f_{\kappa\lambda}(\mathbf{s}) = \sqrt{4\pi} \sum_{l=|l_\kappa - l_\lambda|}^{l_\kappa + l_\lambda} & i^l \sqrt{2l+1} \, c^l(\kappa; \lambda) Y_{l, m_\kappa - m_\lambda}^*(\Omega_s) \\ & \times W_{l\kappa\lambda}(s) \ , \end{aligned} \tag{10a}$$

where

$$W_{l\kappa\lambda}(s) \equiv \int_0^\infty dr \, r^2 j_l(sr) R_\kappa^*(r) R_\lambda(r) = W_{l\lambda\kappa}^*(s) \ , \tag{10b}$$

and $c^l(\kappa; \lambda) \equiv c^l(l_\kappa m_\kappa; l_\lambda m_\lambda)$ is the Condon-Shortley parameter [10]. Note that due to the property of $c^l(\kappa; \lambda)$, the summation in Eq. (10a) runs over every other integer between the specified values. Based on (10a), the angular integration in the function $H_{\mu\nu}^{\kappa\lambda}(s)$ is performed analytically. We have

$$\begin{aligned} H_{\mu\nu}^{\kappa\lambda}(s) = \sum_{l=\max(|l_\kappa - l_\lambda|, |l_\mu - l_\nu|)}^{\min(l_\kappa + l_\lambda, l_\mu + l_\nu)} & (2l+1) c^l(\kappa; \lambda) \\ & \times c^l(\mu; \nu) W_{l\kappa\lambda}^*(s) W_{l\mu\nu}(s) \ , \end{aligned} \tag{11a}$$

if $(l_\kappa + l_\lambda + l_\mu + l_\nu)$ is even and $m_\kappa - m_\lambda = m_\mu - m_\nu$. When either or both of these conditions are not satisfied, $H_{\mu\nu}^{\kappa\lambda}(s)$ vanishes. Two special cases of Eq. (11a) are

$$H_{kk}^{jj}(s) = \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1) a^l(j; k) W_{ljj}^*(s) W_{lkk}(s) \ , \tag{11b}$$

$$H_{kj}^{kj}(s) = \sum_{l=|l_j - l_k|}^{l_j + l_k} (2l+1) b^l(k; j) \left| W_{lkj}(s) \right|^2 \ , \tag{11c}$$

which appear in Eq. (9d), where $a^l(\kappa; \mu) \equiv c^l(\kappa; \kappa) c^l(\mu; \mu)$ and $b^l(\kappa; \mu) \equiv [c^l(\kappa; \mu)]^2$ are Condon-Shortley parameters [10]. The summations in Eqs. (11a)–(11c) run over every other integer between the specified values.

The subshell intracule densities $I_{nl}(\mathbf{u})$ and $h_{nl}(u)$ are defined by

$$I_{nl}(\mathbf{u}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta_{nn_j} \delta_{ll_j} \delta_{nn_k} \delta_{ll_k} \ I_{jk}(\mathbf{u}) \ , \tag{12a}$$

$$h_{nl}(u) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta_{nn_j} \delta_{ll_j} \delta_{nn_k} \delta_{ll_k} h_{jk}(u) \ . \tag{12b}$$

The associated subshell intracule moments $\langle u^k \rangle_{nl}$ are given by

$$\langle u^k\rangle_{nl} \equiv \int d\mathbf{u}\, u^k\, I_{nl}(\mathbf{u}) = 4\pi \int_0^\infty du\, u^{k+2} h_{nl}(u) \ , \tag{12c}$$

where $\langle u^0\rangle_{nl} = N_{nl}(N_{nl}-1)/2$, the number of electron pairs in the subshell nl. For integer values of k, the moments can also be derived from the characteristic function directly. Explicit formulas are obtained immediately from the relations reported in Refs. [3, 4]. Note that the subshell densities $I_{nl}(\mathbf{u})$ and $h_{nl}(u)$ are meaningful only when there are two or more electrons in a subshell.

Exactly analogous definitions apply to the momentum-space intracule $\bar{I}(\mathbf{v})$ and $\bar{h}(v)$ densities, the associated moments $\langle v^k\rangle$, and their subshell components, if we start from a momentum-space N-electron wave function $\Phi(\mathbf{y}_1,\ldots,\mathbf{y}_N)$, spin-orbitals $\phi_j(\mathbf{p})\eta_j(\sigma)$, and atomic radial functions $P_{n_j l_j}(p)$.

2.3 Two-electron extracule densities and their moments

The extracule density $E(\mathbf{R})$, its spherical average $d(R)$, and moments $\langle R^k\rangle$ are defined [1, 2] by

$$E(\mathbf{R}) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2\ \delta[\mathbf{R}-(\mathbf{r}_1+\mathbf{r}_2)/2]\Gamma(\mathbf{r}_1,\mathbf{r}_2) \ , \tag{13a}$$

$$d(R) \equiv (4\pi)^{-1}\int d\Omega_R\, E(\mathbf{R}) \ , \tag{13b}$$

$$\langle R^k\rangle \equiv \int d\mathbf{R}\, R^k E(\mathbf{R}) = 4\pi\int_0^\infty dR\, R^{k+2} d(R) \tag{13c}$$

where $\mathbf{R} \equiv (R,\Omega_R)$ with $\Omega_R \equiv (\theta_R,\phi_R)$.

For single determinant wave functions, the spin-orbital-pair components $E_{jk}(\mathbf{R})$ and $d_{jk}(R)$ read

$$E_{jk}(\mathbf{R}) = \pi^{-3}\int d\mathbf{s}\exp(+2i\mathbf{R}\cdot\mathbf{s})G_{jk}(\mathbf{s}) \ , \tag{14a}$$

$$d_{jk}(R) = (4/\pi^2)\int_0^\infty ds\, s^2 j_0(2Rs) D_{jk}(s) \ , \tag{14b}$$

where the characteristic functions $G_{jk}(\mathbf{s})$ and $D_{jk}(s)$ have the same mathematical structure as Eqs. (9c) and (9d), and are simply obtained if we replace $F^{\kappa\lambda}_{\mu\nu}(\mathbf{s})$ with

$$G^{\kappa\lambda}_{\mu\nu}(\mathbf{s}) \equiv f^*_{\kappa\lambda}(\mathbf{s}) f_{\mu\nu}(-\mathbf{s}) = f^*_{\kappa\lambda}(\mathbf{s}) f^*_{\nu\mu}(\mathbf{s}) \ , \tag{14c}$$

and $H^{\kappa\lambda}_{\mu\nu}(s)$ with

$$D^{\kappa\lambda}_{\mu\nu}(s) \equiv (4\pi)^{-1}\int d\Omega_s\, G^{\kappa\lambda}_{\mu\nu}(\mathbf{s}) \ . \tag{14d}$$

The explicit form of $D^{\kappa\lambda}_{\mu\nu}(s)$ for atomic systems has been obtained [9] as

$$D^{\kappa\lambda}_{\mu\nu}(s) = \sum_{l=\max(|l_\kappa-l_\lambda|,|l_\mu-l_\nu|)}^{\min(l_\kappa+l_\lambda,l_\mu+l_\nu)} (-1)^l(2l+1)c^l(\kappa;\lambda)c^l(\mu;\nu) \times W^*_{l\kappa\lambda}(s)W_{l\mu\nu}(s) \ , \tag{15a}$$

if $(l_\kappa + l_\lambda + l_\mu + l_\nu)$ is even and $m_\kappa - m_\lambda = m_\mu - m_\nu$. When these two conditions are not satisfied simultaneously, $D^{\kappa\lambda}_{\mu\nu}(s)$ vanishes. The two particular cases of Eq. (15a) corresponding to Eqs. (11b) and (11c) are

$$D^{jj}_{kk}(s) = \sum_{l=0}^{\min(2l_j,2l_k)} (2l+1)a^l(j;k)W^*_{\ell jj}(s)W_{lkk}(s) \ , \tag{15b}$$

$$D^{kj}_{kj}(s) = \sum_{l=|l_j-l_k|}^{l_j+l_k} (-1)^l(2l+1)b^l(k;j)|W_{lkj}(s)|^2 \ , \tag{15c}$$

which were also derived in Ref. [4]. The summations in Eqs. (15a)–(15c) run over every other integer between the specified values.

The subshell extracule densities $E_{nl}(\mathbf{R})$ and $d_{nl}(R)$ and the associated moments $\langle R^k\rangle_{nl}$ are defined by equations analogous to Eqs. (12a)–(12c).

Exactly the same procedures as above define the corresponding extracule properties $\bar{E}_{nl}(\mathbf{P}), \bar{d}_{nl}(P)$, and $\langle P^k\rangle_{nl}$ for an nl subshell in the momentum representation.

2.4 Isomorphism and 2^k-rule of two-electron subshell properties

Comparison of the characteristic functions $H_{jk}(s)$ and $D_{jk}(s)$ of the spin-orbital-pair intracule $h_{jk}(u)$ and extracule $d_{jk}(R)$ densities for Hartree-Fock atoms shows [see Eq. (9d)] that the first terms are identical, $H^{jj}_{kk}(s) = D^{jj}_{kk}(s)$, as seen from Eqs. (11b) and (15b). On the other hand, the second terms $H^{kj}_{kj}(s)$ and $D^{kj}_{kj}(s)$ with the spin factor $\delta_s(j,k)$ differ by a sign factor $(-1)^l$ in the summation over l as seen in Eqs. (11c) and (15c). If the spin-orbitals j and k belong to the same subshell nl, however, the sign factor is always unity leading to

$$H_{nl}(s) = D_{nl}(s) \ , \tag{16a}$$

for the characteristic functions of the subshell intracule $h_{nl}(u)$ and extracule $d_{nl}(R)$ densities. Equation (16a) combined with Eqs. (9b) and (14b) results in a rigorous relation,

$$d_{nl}(R) = 8h_{nl}(2R) \ . \tag{16b}$$

The proportionality constant is $8 = 2^3$, where the factor 2 comes from the denominator in the Dirac delta function in Eq. (13a) and the exponent 3 originates from the three dimensionality of space. The relative and center-of-mass motions of a pair of electrons are essentially different even if the electrons are bound in an atom. Nevertheless, Eq. (16b) implies an interesting fact, namely, that the density distributions of the relative and center-of-mass motions are isomorphic with each other when the two electrons are in the same atomic subshell. Equation (16b) further yields a "2^k rule",

$$\langle u^k\rangle_{nl}/\langle R^k\rangle_{nl} = 2^k \ , \tag{16c}$$

between the intracule and extracule moments of any subshell nl, where k is a real number for which the moments are well defined.

The exact relations between the subshell intracule and extracule properties discussed above in position space are also valid in momentum space, and we have a set of corresponding equations, $\bar{H}_{nl}(s) = \bar{D}_{nl}(s)$, $\bar{d}_{nl}(P) = 8\bar{h}_{nl}(2P)$, and $\langle v^k \rangle_{nl} / \langle P^k \rangle_{nl} = 2^k$.

2.5 Second one- and two-electron subshell moments

For integer values of k, we can obtain the intracule $\langle u^k \rangle_{ij}$ and $\langle v^k \rangle_{ij}$ moments and the extracule $\langle R^k \rangle_{ij}$ and $\langle P^k \rangle_{ij}$ moments, arising from a pair of spin orbitals i and j, directly from the respective characteristic functions, by using the techniques developed in Refs. [3, 4]. When k is a non-negative *even* integer, the results are simplest and the expression for $\langle u^k \rangle_{ij}$, for example, is given by

$$\langle u^k \rangle_{ij} = (-1)^{k/2}(k+1)H_{ij}^{(k)}(0) \ , \tag{17}$$

where $H_{ij}^{(k)}(s)$ is the kth derivative of the characteristic function $H_{ij}(s)$. If we are reminded that $j_l(0) = \delta_{l0}$, we obtain from Eqs. (9d), (10b), (11b), and (11c) that for $k = 0$,

$$\langle u^0 \rangle_{ij} = H_{ij}(0) = a^0(i;j) - \delta_s(i,j)|X_{0ij}|^2 = 1 \ , \tag{18}$$

since $a^0(i;j) = 1$ and either or both of $\delta_s(i,j)$ and X_{0ij} are zero for any i and $j(\neq i)$, where

$$X_{kij} \equiv \int_0^\infty dr\, r^{k+2}\ R_i^*(r) R_j(r) = X_{kji}^* \ . \tag{19}$$

When $k = +2$ in Eq. (17), we have

$$\begin{aligned} \langle u^2 \rangle_{ij} = & \left[X_{2ii} + X_{2jj}\right] \\ & - \delta_s(i,j) \sum_{l=|l_i-l_j|}^{l_i+l_j} (2l+1) b^l(i;j) \\ & \times \left[\delta_{l0}(X_{0ij}X_{2ji} + X_{0ji}X_{2ij}) - \frac{2}{3}\delta_{l1}|X_{1ij}|^2\right] \ . \end{aligned} \tag{20}$$

If the spin orbitals i and j constitute the same atomic subshell nl, the last term with the spin factor $\delta_s(i,j)$ of Eq. (20) vanishes. Then the summation over such spin-orbital pairs gives for the second intracule subshell moment $\langle u^2 \rangle_{nl}$

$$\langle u^2 \rangle_{nl} = (N_{nl} - 1)\langle r^2 \rangle_{nl} \ , \tag{21a}$$

where N_{nl} (≥ 2) is the number of electrons in the subshell nl and we have used $X_{kii} = \langle r^k \rangle_i$. Analogously, we obtain in momentum space the corresponding equality,

$$\langle v^2 \rangle_{nl} = (N_{nl} - 1)\langle p^2 \rangle_{nl} \ . \tag{21b}$$

Combination of Eqs. (21a, b) with Eq. (16c) and its momentum-space analog further yields

$$\langle R^2 \rangle_{nl} = (N_{nl} - 1)\langle r^2 \rangle_{nl}/4 \ , \tag{21c}$$

$$\langle P^2 \rangle_{nl} = (N_{nl} - 1)\langle p^2 \rangle_{nl}/4 \ . \tag{21d}$$

Equations (21a)–(21d) imply that when two electrons belong to the same subshell, the second intracule and extracule moments are exactly proportional to the second one-electron moment of that subshell. To our knowledge, rigorous relations of this kind are not reported in the literature between one- and two-electron properties.

The Hartree-Fock approximation satisfies the quantum-mechanical virial theorem which states that the total energy E is equal to the negative of the kinetic energy T for atomic systems. Since the kinetic energy is the sum of the second one-electron momentum moments $\langle p^2 \rangle_{nl}$ divided by two, Eqs. (21b) and (21d) further give

$$E = -\frac{1}{2}\sum_{nl} \frac{\langle v^2 \rangle_{nl}}{N_{nl} - 1} = -2\sum_{nl} \frac{\langle P^2 \rangle_{nl}}{N_{nl} - 1} \ , \tag{22}$$

if all the occupied subshells contain two or more electrons. Namely, both the second intracule and extracule moments in momentum space are directly and explicitly connected with the total energy of an atom. It is also important that Eqs. (21) and (22) are valid within the Hartree-Fock framework for any LS term of any electronic configuration of a subshell nl specified by any set of the quantum numbers n and l.

Though the expressions are much involved, rigorous relations similar to Eq. (20) can be derived between higher two-electron moments with even k and one-electron moments of spin-orbital-pair densities. When $k = +4$, for example, we obtain

$$\begin{aligned} \langle u^4 \rangle_{ij} = & \sum_{l=0}^{\min(2l_i,2l_j)} (2l+1) a^l(i;j) \\ & \times \left[\delta_{l0}\left(X_{4ii} + X_{4jj} + \tfrac{10}{3}X_{2ii}X_{2jj}\right) + \tfrac{8}{15}\delta_{l2}X_{2ii}X_{2jj}\right] \\ & - \delta_s(i,j) \sum_{l=|l_i-l_j|}^{l_i+l_j} (2l+1) b^l(i;j) \\ & \times \left[\delta_{l0}\left(X_{0ij}X_{4ji} + X_{0ji}X_{4ij} + \tfrac{10}{3}|X_{2ij}|^2\right)\right. \\ & - \frac{4}{3}\delta_{l1}\left(X_{1ij}X_{3ji} + X_{1ji}X_{3ij}\right) \\ & \left. + \frac{8}{15}\delta_{l2}|X_{2ij}|^2\right] \ , \end{aligned} \tag{23}$$

which depends on the full details of the relevant spin-orbitals via the Condon-Shortley parameters $a^l(i;j)$ and $b^l(i;j)$. Unfortunately we cannot derive a general formula like Eq. (21a) for the subshell component $\langle u^4 \rangle_{nl}$. For two-electron moments with odd k or $k < 0$, we could not find any simple and useful relations with one-electron moments.

3 Computational details

For the 53 neutral atoms from He to Xe in their experimental ground LS multiplet states [11], the Hartree-Fock orbitals were numerically generated by using an enhanced version of the MCHF72 code [12, 13]. The spherically averaged one-electron subshell density $\rho_{nl}(r)$ and the associated moments $\langle r^k \rangle_{nl}$ in position space were obtained directly from the numerical radial functions as described in Ref. [14]. The corresponding momentum density $\Pi_{nl}(p)$ and the associated moments $\langle p^k \rangle_{nl}$ were determined by incorporating the numerical Hankel transformation [15] of the Hartree-Fock radial functions into the MCHF72 code, as explained in Ref. [16]. The subshell intracule densities $h_{nl}(u)$ in position space and $\bar{h}_{nl}(v)$ in momentum space as well as their moments $\langle u^k \rangle_{nl}$ and $\langle v^k \rangle_{nl}$ were obtained by the method developed recently [3]. The extracule densities $d_{nl}(R)$ and $\bar{d}_{nl}(P)$ and moments $\langle R^k \rangle_{nl}$ and $\langle P^k \rangle_{nl}$ were determined by the procedure given in Ref. [4]. However, these extracule properties were only used to verify numerically the equalities proved in Sect. 2.4 and are not presented in Sect. 4.

4 Numerical results and discussion

By definition, all the one-electron subshell density functions are normalized to the number of subshell electrons N_{nl}, while all the two-electron subshell density functions are normalized to the number of subshell electron pairs $N_{nl}(N_{nl}-1)/2$. Throughout this Section, however, we will use a modified normalization scheme, which normalizes *all* the one- and two-electron subshell densities to *unity*, in order to avoid large numbers and to facilitate the mutual comparison of the one- and two-electron moments.

We have first confirmed the validity of the 2^k-rule [Eq. (16c) and its momentum-space analog] between the intracule and extracule moments numerically. Thus, only the intracule moments $\langle u^k \rangle_{nl}$ and $\langle v^k \rangle_{nl}$ are discussed below.

In the modified normalization scheme, Eq. (21a) for the second intracule $\langle u^2 \rangle_{nl}$ and one-electron $\langle r^2 \rangle_{nl}$ moments in position space reads

$$\langle u^2 \rangle_{nl} = 2\langle r^2 \rangle_{nl} \ , \tag{24a}$$

and the second subshell moments are strictly proportional. Motivated by the simplicity, yet rigor of this relation, we have examined possible correlations between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ for $k = +1, -1$, and -2, based on the numerical Hartree-Fock data for 357 subshells of 53 atoms. We have found that there is a good linear correlation between the one- and two-electron moments for each value of k, if the subshells are classified according to the n and l values. Table 1 summarizes the correlation coefficients (CCs) between the moments $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ together with the values of a parameter a_{knl} appearing in the least squares linear approximation,

$$\langle u^k \rangle_{nl} \cong a_{knl} \langle r^k \rangle_{nl} \ . \tag{24b}$$

For $k = +1$, we find in Table 1 that excellent correlations with CC > 0.9999 exist for all the subshells with the sole exception for $5p$. Figure 1a depicts the correla-

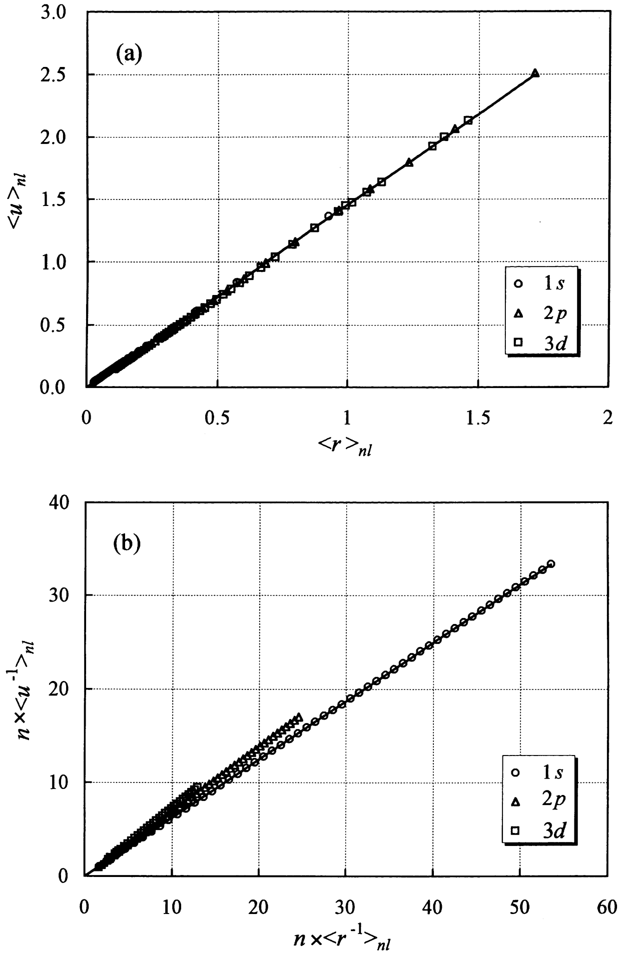

Fig. 1a,b Examples of the linear correlations observed in position space between one- and two-electron subshell moments. Note that all subshell densities are normalized to unity. All values in hartree atomic units. (*a*) $\langle u \rangle_{nl}$ and $\langle r \rangle_{nl}$ (*b*) $\langle u^{-1} \rangle_{nl}$ and $\langle r^{-1} \rangle_{nl}$

Table 1. Linear correlation coefficient (CC) in position space between subshell moments $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$. Normalizations are $\langle u^0 \rangle_{nl} = \langle r^0 \rangle_{nl} = 1$. For $k = +2$, $\langle u^2 \rangle_{nl} = 2\langle r^2 \rangle_{nl}$ holds exactly for any subshell nl. The coefficient a_{knl} is defined in Eq. (24b)

nl	No. of subshells	$k = +1$		$k = -1$		$k = -2$	
		a_{1nl}	CC	a_{-1nl}	CC	a_{-2nl}	CC
$1s$	53	1.465601	0.999998	0.623410	1.000000	0.331315	0.999999
$2s$	51	1.418377	0.999998	0.609413	0.999997	0.152081	1.000000
$3s$	43	1.405515	0.999999	0.629798	0.999977	0.104530	0.999959
$4s$	33	1.402308	0.999993	0.667440	0.999854	0.089914	0.999374
$5s$	11	1.398631	0.999986	0.710404	0.999956	0.098896	0.998568
$2p$	49	1.455512	0.999987	0.689377	0.999999	0.519710	0.999992
$3p$	41	1.428648	0.999979	0.630442	0.999980	0.282467	0.999986
$4p$	23	1.419981	0.999941	0.644366	0.999659	0.212776	0.999648
$5p$	5	1.420583	0.999852	0.666561	0.996537	0.198457	0.989615
$3d$	33	1.446091	0.999976	0.721547	0.999988	0.615637	0.999956
$4d$	15	1.429191	0.999979	0.663355	0.999858	0.359209	0.999482

tion for the $1s, 2p$, and $3d$ subshells. The proportionality constants a_{1nl} distribute around 1.42 and do not differ much from one subshell to another. However, the a_{1nl} values tend to decrease when n and l values increase. It may be interesting to find the presence of an approximate linear relation between the average electron-nucleus distance $\langle r \rangle_{nl}$ and the average electron-electron distance $\langle u \rangle_{nl}$ of an atomic subshell. When the $\langle u \rangle_{nl}$ values are estimated from the $\langle r \rangle_{nl}$ values based on the regression line (24b) with the a_{1nl} values in Table 1, the average relative error for each subshell is largest for $3d$, 1.31%, among the 11 subshells. Linear correlation between $\langle u \rangle_{nl}$ and $\langle r \rangle_{nl}$ is concluded to be highly accurate though not rigorous.

For $k = -1$, the CCs in Table 1 are slightly worse than those for $k = +1$, but still greater than 0.9998 except for the $4p$ and $5p$ subshells. Examples are given in Fig. 1b. The proportionality constants a_{-1nl} are distributed around 0.65, but their dependence on the n and l values is not simple. It is noteworthy that the electron repulsion energy $\langle u^{-1} \rangle_{nl}$ between a pair of electrons in an nl subshell has a good linear relation with the average value $\langle r^{-1} \rangle_{nl}$ of the reciprocal electron-nucleus distance of that subshell. When Eq. (24b) is employed to estimate $\langle u^{-1} \rangle_{nl}$ from $\langle r^{-1} \rangle_{nl}$, the average relative error was largest (3.26%) for the $4s$ subshell. For $k = -2$, the correlation between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ is reduced from that for $k = -1$. The proportionality constants a_{-2nl} change considerably depending on n and l. Nevertheless, we still observe sufficiently accurate linear correlations for inner subshells such as $1s$–$3s$, $2p, 3p$, and $3d$.

The linearity observed above depends on the power k and the principal n and azimuthal l quantum numbers of atomic (radial) orbitals. To explain this fact, we have considered a hydrogenic radial function with an exponent ζ,

$$R_{nl}(r) = (-1)^{n-l-1} 2\zeta^{3/2} \left[\frac{(n-l-1)!}{n(n+l)!} \right]^{1/2} \times (2\zeta r)^l \, L_{n-l-1}^{2l+1}(2\zeta r) \exp(-\zeta r) \ , \tag{25}$$

where $L_n^k(x)$ is the associated Laguerre polynomial and the phase factor $(-1)^{n-l-1}$ is included for consistency through Eq. (4c) with the momentum-space counterpart that will be introduced later. The hydrogenic function (25) predicts that the moments $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ are proportional, and the proportionality constant is independent of ζ but dependent on k, n, l, electronic configuration, and LS coupling of the subshell. For closed $ns(2), np(6)$, and $nd(10)$ subshells with ${}^1S$ coupling, we have evaluated the hydrogenic proportionality constants and tabulated them in Table 2. Comparison of the values in Tables 1 and 2 shows that the hydrogenic constants are not far from the Hartree-Fock ones, and our hydrogenic model with the correct nodal structure of atomic subshells appears to explain semi-quantitatively the observed linear correlations between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$. However, the differences between the hydrogenic and Hartree-Fock constants are generally larger for outer subshells than for inner subshells, as anticipated.

Table 2. Hydrogenic proportionality constants $\langle u^k \rangle_{nl} / \langle r^k \rangle_{nl}$ for subshells in position space. Normalizations are $\langle u^0 \rangle_{nl} = \langle r^0 \rangle_{nl} = 1$. For $k = +2, \langle u^2 \rangle_{nl} / \langle r^2 \rangle_{nl} = 2$ exactly for any subshell nl

nl	$k = +1$	$k = -1$	$k = -2$
$1s$	1.458 333	0.622 500	0.333 333
$2s$	1.410 807	0.601 563	0.152 381
$3s$	1.402 247	0.597 656	0.099 375
$4s$	1.399 266	0.596 344	0.073 882
$5s$	1.397 888	0.595 749	0.058 847
$2p$	1.428 281	0.698 438	0.537 143
$3p$	1.420 102	0.620 898	0.296 623
$4p$	1.415 020	0.597 455	0.207 233
$5p$	1.412 383	0.587 122	0.159 969
$3d$	1.403 179	0.752 973	0.681 685
$4d$	1.411 583	0.664 305	0.416 793
$5d$	1.409 854	0.630 566	0.304 921

In momentum space, the rigorous relation of (21b) between the second intracule $\langle v^2 \rangle_{nl}$ and one-electron $\langle p^2 \rangle_{nl}$ moments reads

$$\langle v^2 \rangle_{nl} = 2 \langle p^2 \rangle_{nl} \ , \tag{26a}$$

when the modified normalization scheme is applied. The proportionality is thus exact for $k = +2$ between $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$. For $k = +1, -1$, and -2, we have examined correlations between $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ for the 357 subshells of the 53 neutral atoms. The results are

Table 3. Linear correlation coefficient (CC) in momentum space between subshell moments $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$. Normalizations are $\langle v^0 \rangle_{nl} = \langle p^0 \rangle_{nl} = 1$. For $k = +2$, $\langle v^2 \rangle_{nl} = 2 \langle p^2 \rangle_{nl}$ holds exactly for any subshell nl. The coefficient b_{knl} is defined by Eq. (26b)

nl	No. of subshells	$k = +1$		$k = -1$		$k = -2$	
		b_{1nl}	CC	b_{-1nl}	CC	b_{-2nl}	CC
$1s$	53	1.459791	1.000000	0.646575	0.999985	0.398035	0.999973
$2s$	51	1.559090	1.000000	0.653098	0.999963	0.438708	0.999941
$3s$	43	1.587224	0.999997	0.634094	0.999781	0.433559	0.999792
$4s$	33	1.603397	0.999998	0.638655	0.999927	0.432529	0.999970
$5s$	11	1.608559	0.999999	0.630928	0.999835	0.424518	0.999956
$2p$	49	1.434626	1.000000	0.665294	0.999536	0.428764	0.992649
$3p$	41	1.516092	0.999999	0.679695	0.999421	0.479898	0.988800
$4p$	23	1.540707	0.999998	0.679708	0.998789	0.497200	0.982301
$5p$	5	1.535947	0.999979	0.673404	0.993029	0.487975	0.883961
$3d$	33	1.422632	0.999995	0.685015	0.999481	0.473280	0.993814
$4d$	15	1.488385	0.999994	0.697565	0.999414	0.527757	0.990074

summarized in Table 3, where b_{knl} is the parameter appearing in the least square linear fitting,

$$\langle v^k \rangle_{nl} \cong b_{knl} \langle p^k \rangle_{nl} \ . \tag{26b}$$

For $k = +1$, an excellent linear correlation is seen in Table 3, as was the case in position space. All the CCs between $\langle v \rangle_{nl}$ and $\langle p \rangle_{nl}$ are larger than 0.99999 except for the $5p$ subshell. Thus, the two-electron $\langle v \rangle_{nl}$ and one-electron and $\langle p \rangle_{nl}$ moments are essentially proportional. The proportionality constants b_{1nl} in Table 3 range from 1.42 to 1.61, and show a tendency to increase with increasing n but decrease with increasing l. When Eq. (26b) is employed to approximate $\langle v \rangle_{nl}$ based on $\langle p \rangle_{nl}$, the average relative error does not exceed 1% for any subshell and is largest (0.93%) for the $3d$ subshell. For $k = -1$ and -2, the momentum-space correlation between $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ is generally worse than the position-space one between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$. In particular, the poorest correlation in momentum space is found for the $5p$ subshell with CC = 0.993 when $k = -1$ and CC = 0.884 when $k = -2$. This observation may be explained by the position-momentum reciprocity. Outer subshells, which are most sensitive to the atomic circumstances, have electronic distributions mainly around the origin in momentum space, and the moments $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ with $k < 0$ are largely influenced by the differences. Figure 2 illustrates the linear correlations observed in momentum space for $k = +1$ and -1.

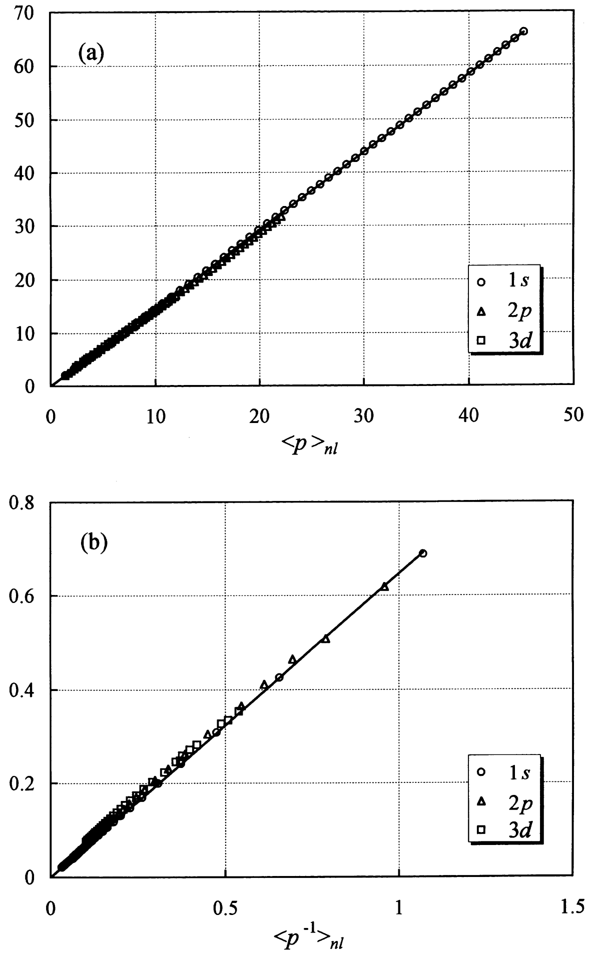

Fig. 2a,b Examples of the linear correlations observed in momentum space between one- and two-electron subshell moments. Note that all subshell densities are normalized to unity. All values in hartree atomic units. (*a*) $\langle v \rangle_{nl}$ and $\langle p \rangle_{nl}$ (*b*) $\langle v^{-1} \rangle_{nl}$ and $\langle p^{-1} \rangle_{nl}$

When a momentum-space hydrogenic radial function,

$$P_{nl}(p) = (-i)^l \, 2^{l+2} \zeta^{5/2} \, l! \left[\frac{2n(n-l-1)!}{\pi(n+l)!} \right]^{1/2} \times \frac{(2\zeta p)^l}{(p^2+\zeta^2)^{l+2}} C_{n-l-1}^{l+1}\left(\frac{\zeta^2 - p^2}{\zeta^2 + p^2} \right), \tag{27}$$

with $C_n^k(x)$ being the Gegenbauer polynomial, is assumed for a closed nl subshell, we find that the moments $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ are precisely proportional, independent of the exponent value ζ. The hydrogenic constants of proportion b_{knl} are summarized in Table 4. When the proportionality constants in Tables 3 and 4 are compared, we find that the Hartree-Fock results are approximately explained by the hydrogenic model. However, the difference between the corresponding two values increases when the k value decreases. For $k = -2$, the hydrogenic constants are far from the Hartree-Fock values particularly for p and d subshells.

5 Summary

The two-electron intracule $\langle u^k \rangle_{nl}$ and extracule $\langle R^k \rangle_{nl}$ subshell moments in position space have been studied as well as their counterparts $\langle v^k \rangle_{nl}$ and $\langle P^k \rangle_{nl}$ in momentum space, when n and l are the principal and azimuthal quantum numbers of the atomic subshell, respectively. We have proved that equalities $\langle u^k \rangle_{nl} = 2^k \langle R^k \rangle_{nl}$ and $\langle v^k \rangle_{nl} = 2^k \langle P^k \rangle_{nl}$ hold between the intracule and extracule moments for any nl subshell, where k is a real number for which the relevant moments are well defined. We have also shown that for a particular case of $k = +2$, relations $\langle u^2 \rangle_{nl} = (N_{nl} - 1)\langle r^2 \rangle_{nl}$ and $\langle v^2 \rangle_{nl} = (N_{nl} - 1)\langle p^2 \rangle_{nl}$ are strictly valid, where N_{nl} (≥ 2) is the number of electrons in the subshell nl, and $\langle r^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$ are the one-electron subshell moments in position

Table 4. Hydrogenic proportionality constants $\langle v^k \rangle_{nl} / \langle p^k \rangle_{nl}$ for subshells in momentum space. Normalizations are $\langle v^0 \rangle_{nl} = \langle p^0 \rangle_{nl} = 1$. For $k = +2$, $\langle v^2 \rangle_{nl} / \langle p^2 \rangle_{nl} = 2$ exactly for any subshell nl

nl	$k = +1$	$k = -1$	$k = -2$
$1s$	1.458 333	0.656 250	0.416 667
$2s$	1.557 292	0.632 813	0.425 641
$3s$	1.575 617	0.570 429	0.351 020
$4s$	1.582 162	0.528 809	0.297 222
$5s$	1.585 238	0.499 072	0.258 578
$2p$	1.428 281	0.715 000	0.595 000
$3p$	1.510 882	0.673 391	0.573 143
$4p$	1.541 432	0.635 091	0.511 606
$5p$	1.557 306	0.604 108	0.458 726
$3d$	1.403 179	0.764 100	0.726 455
$4d$	1.475 697	0.712 252	0.676 142
$5d$	1.509 565	0.680 002	0.620 401

and momentum spaces, respectively. The latter equality yields a new and rigorous relation between the second electron-pair moments in momentum space and the total energy of an atom through the virial theorem. For $k = +1, -1$, and -2, the numerical Hartree-Fock results for the 357 subshells of the 53 neutral atoms from He to Xe show that there are approximate but accurate linear relations between $\langle u^k \rangle_{nl}$ and $\langle r^k \rangle_{nl}$ and between $\langle v^k \rangle_{nl}$ and $\langle p^k \rangle_{nl}$, in which the proportionality constant in each space is common to all the atoms and depends on n, l, and k.

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