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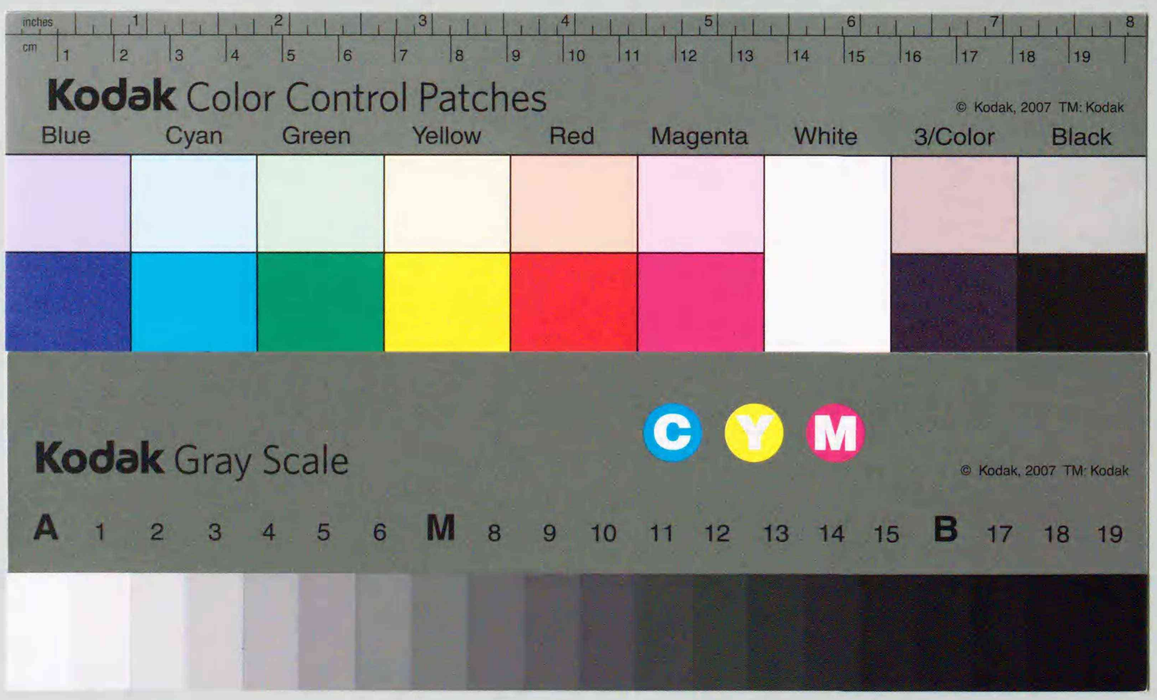
THEORETICAL STUDIES

OF

ELECTROMAGNETIC DEVICES

IN POSITION AND VELOCITY SENSING

ELIAS MATSIUKA



THEORETICAL STUDIES

ON

ELECTRON-PAIR DENSITIES

IN POSITION AND MOMENTUM SPACES

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GENERAL INTRODUCTION

In experimental and theoretical quantum chemistry, many studies on one- and two-electron densities in position and momentum spaces have been carried out [see, Refs. 1-6 for comprehensive reviews], where position-space coordinates are a distance from some fixed spatial origin, and momentum-space coordinates are components of the momentum of an electron. It is important to examine the one- and two-electron densities in detail, because knowledge obtained from the densities give information about the electron-nuclear and electron-electron interactions which make the major contribution to the chemical and physical properties of atoms and molecules. The nonrelativistic total energy of electrons in an atom, for example, consists of the kinetic, electron-nucleus attraction, and electron repulsion energies, which are obtained from the one- and two-electron densities. Both of these densities are closely related to some properties measured by an x-ray scattering experiment. Benesch and Smith showed [7] that within the Waller-Hartree approximation [8], the total $I_t(\mathbf{K})$ and coherent $I_c(\mathbf{K})$ intensities of radiation scattered by an N-electron atom are given by

$$I_t(\mathbf{K})/I_{cl} \equiv |F(\mathbf{K})|^2 + S(\mathbf{K}) = N + 2\int d\mathbf{r}_1 d\mathbf{r}_2 \exp[i\mathbf{K}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\Gamma(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{1}$$

$$I_c(\mathbf{K})/I_{cl} = |F(\mathbf{K})|^2 = |\int d\mathbf{r}\exp(i\mathbf{K}\cdot\mathbf{r})\rho(\mathbf{r})|^2\ , \tag{2}$$

where $\mathbf{K}$ is the momentum transfer vector, $\mathbf{r}$ the position-space vector of an electron, I_{cl} the Thomson factor, and $F(\mathbf{K})$ the atomic form factor. The function $S(\mathbf{K})$ is the incoherent scattering factor, which is defined as the difference between the total and coherent intensities. The two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ in position space is defined by

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

where the density is normalized to the number of electron pairs, $\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ represents a normalized N-electron wave function for an atomic state, and $\mathbf{x}_i \equiv (\mathbf{r}_i,\sigma_i)$ denotes the combined space and spin coordinates of electron i. The position-space one-electron density is defined by

$$\rho(\mathbf{r}) \equiv N\int d\sigma d\mathbf{x}_2\cdots d\mathbf{x}_N |\Psi(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2\ . \tag{4}$$

The incoherent scattering factor $S(\mathbf{K})$ is also equal [9] to the integration of the dynamical structure factor $S(\mathbf{K},\omega)$,

$$S(\mathbf{K}) = \int_{|E_b|}^{\omega_1} \omega_2/\omega_1 S(\mathbf{K},\omega)d\omega\ , \tag{5}$$

where the limits of integration are taken between the electron binding energy $|E_b|$, the energy of the incident x-ray photon ω_1, and $\omega = \omega_1 - \omega_2$ is the energy transfer. The superscripts 1 and 2 refer to incoming and outgoing photons, respectively. The dynamical structure factor $S(\mathbf{K},\omega)$ is [2,9,10] given by

$$S(\mathbf{K},\omega) = \sum_f |<\Psi_f|\sum_{j=1}^{N}\exp(i\mathbf{K}\cdot\mathbf{r}_j)|\Psi_i>|^2\,\delta(E_f - E_i - \omega)\ . \tag{6}$$

Here, δ means the delta function, and the functions Ψ_i and Ψ_f represent initial and final state, respectively. Moreover, $S(\mathbf{K},\omega)$ is related [11] to the generalized oscillator strength and stopping power. Benesch and Smith employed [2] a density-matrix

formalism, and showed that within the impulse approximation, Eq.(6) reduces to

$$S(\mathbf{K},\omega) = S_1(\mathbf{K},\omega) + S_2(\mathbf{K},\omega) \ , \tag{7}$$

where

$$S_1(\mathbf{K},\omega) = \int d\mathbf{p}_1 \delta(\omega - \tfrac{1}{2}K^2 - \mathbf{K}\cdot\mathbf{p}_1)\gamma(\mathbf{p}_1'|\mathbf{p}_1) \ , \tag{8}$$

and

$$S_2(\mathbf{K},\omega) = 2\int d\mathbf{p}_1 d\mathbf{p}_2 \delta(\omega - \tfrac{1}{2}K^2 - \mathbf{K}\cdot\mathbf{p}_1)\Gamma(\mathbf{p}_1+\mathbf{K},\mathbf{p}_2-\mathbf{K}|\mathbf{p}_1,\mathbf{p}_2) \ , \tag{9}$$

where $K \equiv |\mathbf{K}|$, and the densities $\gamma(\mathbf{p}_1'|\mathbf{p}_1)$ and $\Gamma(\mathbf{p}_1',\mathbf{p}_2'|\mathbf{p}_1,\mathbf{p}_2)$ are the momentum space analogues of the one- and two-electron densities in position space.

It is not easy to study the two-electron density in detail, because the density is a complicated function of six variables. One way to solve the difficulty is to separate the motion of any two electrons into relative (intracule) and center-of-mass (extracule) motions of an electron pair. Thus, we have two electron-pair densities, that is, intracule and extracule densities. A merit of using the electron-pair densities is that the densities are visualized readily. Coleman introduced [12] intracule coordinate, $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$, and extracule coordinate, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ in position space. The intracule density $I(\mathbf{u})$ is [5,6,12] given by

$$I(\mathbf{u}) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma(\mathbf{r}_1,\mathbf{r}_2)\delta[\mathbf{u} - (\mathbf{r}_1 - \mathbf{r}_2)] \ , \tag{10}$$

and the extracule density [5,6,12] by

$$E(\mathbf{R}) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma(\mathbf{r}_1,\mathbf{r}_2)\delta[\mathbf{R} - (\mathbf{r}_1 + \mathbf{r}_2)/2] \ , \tag{11}$$

When the intracule $\mathbf{u}$ and extracule $\mathbf{R}$ vectors can be expressed by spherical coordinates $\mathbf{u} \equiv (u,\Omega_u)$ and $\mathbf{R} \equiv (R,\Omega_R)$, integrating over the angle variables Ω_u and Ω_R yields [5] the spherically averaged intracule density

$$h(u) \equiv \frac{1}{4\pi}\int d\Omega_u I(\mathbf{u}) \ , \tag{12}$$

and the spherically averaged extracule density

$$d(R) \equiv \frac{1}{4\pi}\int d\Omega_R E(\mathbf{R}) \ . \tag{13}$$

The intracule density $I(\mathbf{u})$ and its spherical average $h(u)$ represent, respectively, the probability density functions for the relative vector $\mathbf{u}$ and distance u. On the other hand, the extracule density $E(\mathbf{R})$ and its spherical average $d(R)$ are the probability density functions for the center-of-mass vector $\mathbf{R}$ and distance R, respectively. The intracule $<u^k>$ and extracule $<R^k>$ moments can be given by

$$<u^k> \equiv \int d\mathbf{u} u^k I(\mathbf{u}) = 4\pi\int du u^{k+2} h(u) \ , \tag{14}$$

$$<R^k> \equiv \int d\mathbf{R} R^k E(\mathbf{R}) = 4\pi\int dR R^{k+2} d(R) \ , \tag{15}$$

where the superscript k is a real number, and both of these densities are normalized to the number of electron pairs; $<u^0> = <R^0> = N(N-1)/2$. The moment $<u^{-1}>$ is equal to the electron-electron repulsion energy, and $<u>$ denotes the average interelectronic distance. The moment $<R>$ means the average center-of-mass distance. The first explicit calculation of the intracule density has been carried out [13] by Coulson and Neilson in their study of the electron correlation in the He ground state. They have

defined the Coulomb hole as the difference between the exact or best radial intracule density and the Hartree-Fock radial intracule density. The Coulomb hole allows us to visualize the electron correlation, although the hole is not an observable. A number of the studies on the intracule densities have been inspired by their work. Since then the Coulomb hole has been examined on light atoms [14-32] and small molecules [33-37]. Moreover, many articles have been devoted to investigations on the behaviors of the intracule densities for atoms [38-46] and molecules [47-59]. The intracule density $I(\mathbf{u})$ at $\mathbf{u} = \mathbf{0}$ or electron-electron coalescence density has recently received attention [60-65]. This quantity is directly related to the relativistic [66] and radiative [67] corrections to the ground state of atoms, and appears in the electron-electron cusp condition [68]. The exact eigenfunction of a non-relativistic hamiltonian must satisfy the condition for an atom. The Fourier transform of intracule density $I(\mathbf{u})$ is, within Waller-Hartree theory [8], to x-ray scattering intensity [7], and within the first Born approximation, to high energy electron scattering intensity [7]. In fact, several scattering intensities were obtained [69-80] by the Fourier transformation of the intracule density. On the other hand, the first calculation of the extracule densities for atomic and molecular systems was done [81] by Thakkar and Moore. After the appearance of their pioneering paper, several researchers have examined [51,52,55-59,82] the behaviors of the extracule densities for analyzing chemical bonds of molecules, and only four studies on the extracule densities for atoms [43,54,55,82] have reported to date.

The momentum-space intracule density $\bar{I}(\mathbf{v})$, its spherical average $\bar{h}(v)$, and their moments $<v^k>$ are [5] defined by

$$\bar{I}(\mathbf{v}) \equiv \int d\mathbf{p}_1 d\mathbf{p}_2 \bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)\delta[\mathbf{v} - (\mathbf{p}_1 - \mathbf{p}_2)] \ , \tag{16}$$

$$\bar{h}(v) \equiv \frac{1}{4\pi}\int d\Omega_v \bar{I}(\mathbf{v}) \ , \tag{17}$$

$$<v^k> \equiv \int d\mathbf{v} v^k \bar{I}(\mathbf{v}) = 4\pi\int dv v^{k+2}\bar{h}(v) \ , \tag{18}$$

where $\mathbf{v} \equiv (v,\Omega_v)$, $\mathbf{p}$ means the momentum vector of an electron, and the densities are normalized to the number of electron pairs; $<v^0> = N(N-1)/2$. The intracule density $\bar{I}(\mathbf{v})$ and its spherical average $\bar{h}(v)$ are, respectively, the probability density functions for the relative momentum vector $\mathbf{v}$ and its magnitude v. For an N-electron system, the function $\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)$ is [5] the momentum-space two-electron density defined by

$$\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2) = \frac{N(N-1)}{2}\int d\sigma_1 d\sigma_2 d\mathbf{y}_3 \cdots d\mathbf{y}_N |\Phi(\mathbf{y}_1,\mathbf{y}_2,\ldots,\mathbf{y}_N)|^2 \ , \tag{19}$$

where $\mathbf{y}_i \equiv (\mathbf{p}_i,\sigma_i)$, and $\Phi(\mathbf{y}_1,\mathbf{y}_2,\ldots,\mathbf{y}_N)$ is an electronic wave function in momentum space. The extracule density $\bar{E}(\mathbf{P})$, its spherical average $\bar{d}(P)$, and their moments $<P^k>$ are [5] defined by

$$\bar{E}(\mathbf{P}) \equiv \int d\mathbf{p}_1 d\mathbf{p}_2 \bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)\delta[\mathbf{P} - (\mathbf{p}_1 + \mathbf{p}_2)/2] \ , \tag{20}$$

$$\bar{d}(P) \equiv \frac{1}{4\pi}\int d\Omega_P \bar{E}(\mathbf{P}) \ , \tag{21}$$

$$<P^k> \equiv \int d\mathbf{P} P^k \bar{E}(\mathbf{P}) = 4\pi\int_0^\infty dP P^{k+2}\bar{d}(P) \ , \tag{22}$$

where $\mathbf{P} \equiv (P, \Omega_P)$ and $< P^0 > = N(N-1)/2$. The extracule density $\bar{E}(\mathbf{P})$ and its spherical average $\bar{d}(P)$ represent the probability density functions for the center-of-mass vector $\mathbf{P}$ and its magnitude P. By analogy with the work of Coulson and Neilson [13] in position space, Banyard and co-researchers [83-90], Doggett [91], Ugalde [92], and Wang and Smith [93] have investigated the effects of electron correlation for atoms and molecules based on the Coulomb hole defined by the intracule density in momentum space. There is only one study [93] of the extracule density for the first-row hydrides.

There are several problems about previous studies on the intracule and extracule densities in position and momentum spaces for atomic systems within the Hartree-Fock framework. First, a method for the evaluation of two electron-pair densities in position space have not yet developed for open-shell systems. In momentum space, there is no a method of calculating the intracule and extracule densities for both closed- and open-shell systems. Second, almost all studies are limited to light atoms and atomic ions. Third, the intracule and extracule densities were constructed from basis-set-expansion Hartree-Fock wave functions, some of which are not sufficiently accurate. Fourth, we do not know a detailed discussion about a relation between the intracule and extracule densities, and between their moments. The present thesis is written with the aim of developing a theory for constructing the intracule and extracule densities, as well as their moments, in position and momentum spaces for the atomic systems. The wave functions are given by a single Slater determinant or a linear combination of Slater determinants. We apply the theory to neutral atoms and atomic ions with $2 \le N \le 54$ based on the numerical Hartree-Fock calculations. The obtained densities are systematically examined to clarify a relation between the two electron-pair densities, and between their moments. Since the electron correlation is defined as the difference in the electronic motions in the Hartree-Fock and exact solutions within the non-relativistic framework, the present results on the densities and moments are expected to be useful as reference data in the study of electronic correlation. To consider the electron correlation, we develop a theory of constructing the position-space extracule density and the moments for two-electron atomic systems for the wave function containing an interelectronic distance r_{12}.

The text is divided into three parts. The first part presents the values of intracule and extracule densities at the origin, and the average values of one-electron densities for neutral atoms in position and momentum spaces based on the numerical Hartree-Fock calculations. In Chapter 2, we define [94] the electron-electron coalescence $I(0) = h(0)$ and counterbalance $E(0) = d(0)$ densities in position space for the atoms He through Ne in their ground state when the wave function is expressed by a single Slater determinant. The electron-electron coalescence and counterbalance densities are probability densities of finding any two electrons at the same position and at the reflection points, respectively. We show that these densities are exactly expressible by the one-electron density $\rho(\mathbf{r})$. It is found that the electron-electron coalescence $I(0)$ and counterbalance $E(0)$ densities are well approximated by the average one-electron density $<\rho>$. This means that the coalescence and counterbalance densities can be estimated by the value of $<\rho>$. In Chapter 3, we examine [95] the electron-electron coalescence $\bar{I}(0) = \bar{h}(0)$ and counterbalance $\bar{E}(0) = \bar{d}(0)$ densities, together with their counterparts in position space, of the atoms He through Xe in their ground state in momentum space for a single Slater determinant wave function. The momentum-space

$\bar{h}(0)$ and $\bar{d}(0)$ densities represent the probability densities for any pair of electrons to have exactly the same and opposite momenta, respectively. The both of densities are exactly expressible by the momentum-space one-electron density $\gamma(\mathbf{p})$. The coalescence, counterbalance, and one-electron densities in both position and momentum spaces are calculated by the numerical Hartree-Fock method. In position space, the electron-electron coalescence density $h(0)$ is found to be sufficiently approximated by the average one-electron density $<\rho>$ even for larger atoms. The $h(0)$ and $d(0)$ densities are monotonically increasing functions against atomic number Z, while the values of $\bar{h}(0)$ and $\bar{d}(0)$ show a periodic behavior as a function of Z. The contributions of subshell pairs to the total intracule density are analyzed in both spaces. The intracule and extracule densities are found to be very sensitive probe of the behaviors of wave functions at small values of u and R in position space, and υ and P in momentum space.

In the second part, we develop a theory of constructing the intracule and extracule densities, as well as their moments, in position and momentum spaces for atoms when the wave function is expressed by a single Slater determinant or a linear combination of Slater determinants. The theory is applied to the neutral atoms with $2 \le N \le 54$. In Chapter 2, we present [96] the spherically averaged intracule densities $h(u)$ in position space and $\bar{h}(\upsilon)$ in momentum space for the atoms from He to Xe in their ground state. The numerical Hartree-Fock method is used to calculate these densities. The position-space intracule density $h(u)$ is a monotonically decreasing function for all the atoms. On the other hand, the intracule densities $\bar{h}(\upsilon)$ in momentum space are found to be classified into three types according to the number of local maxima and their locations, and depend explicitly on the valence configuration of atoms under consideration. The behaviors of the densities $h(u)$ and $\bar{h}(\upsilon)$ are studied in detail based on a decomposition of the intracule density into subshell-pair and spin-orbital-pair contributions. In Chapter 3, we report [97] two methods of calculating interelectronic moments $<u^k>$ in position space and $<\upsilon^k>$ in momentum space of atomic systems for a single Slater determinant. The first method uses the spherically averaged intracule densities $h(u)$ and $\bar{h}(\upsilon)$, while the second method uses their characteristic functions. The two methods are applied to the neutral atoms from He to Xe in their ground state, and the moments $<u^k>$ with $k = -2$ to $+4$ and $<\upsilon^k>$ with $k = -2$ to $+3$ are calculated by the numerical Hartree-Fock method. Some trends of these interelectronic moments are also discussed as a function of Z. In Chapter 4, a theory for calculating spherically averaged extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space are reported [98] when the wave function is expressed by a Slater determinant. We show that the individual spin-orbital-pair component of the extracule density has a definite relation with the corresponding one of the intracule density, but the total extracule and intracule densities are not related in a simple manner. The extracule densities $d(R)$ and $\bar{d}(P)$ are constructed and examined systematically for the atoms from He to Xe in their ground state. In position space, the extracule density $d(R)$ is a monotonically decreasing function for all the atoms. The momentum-space extracule densities $\bar{d}(P)$ are found to be classified into two types according to the location of a

maximum. These different behaviors of the densities $d(R)$ and $\bar{d}(P)$ are studied based on the contributions of electrons in a pair of atomic subshells and spin orbitals. In Chapter 5, we present [99] a theory for constructing the extracule moments $< R^k >$ in position space and $< P^k >$ in momentum space of atomic systems for a single-Slater-determinant wave function. For the atoms from He to Xe in their ground state, we also report the moments $< R^k >$ with $k = -2$ to $+4$ and $< P^k >$ with $k = -2$ to $+3$, and use the numerical Hartree-Fock method. These extracule moments are pointed out to have intimate relations with their partner intracule moments. In Chapter 6, we present [100] a unified theory which is applied for the evaluation of the intracule and extracule densities in both position and momentum spaces for wave functions expressed as a linear combination of Slater determinants. Detailed expressions are developed for atomic systems where angular integrations can be performed analytically. Interesting relations between atomic intracule and extracule densities and between their moments are discussed. An illustrative application of the result is given for the $1s2p$ ^1P and ^3P states of the helium atom. We report the singlet-triplet differences in the extracule densities and in the intracule densities for both spaces.

The purpose of the last part is to examine systematically the intracule and extracule densities, as well as their moments, in both position and momentum spaces of atomic ions with $2 \le N \le 54$. We develop a theory for calculating the extracule density of the wavefunction containing an interelectronic distance. In Chapter 2, spherically averaged intracule density $h(u)$, extracule density $d(R)$, and their moments $< u^k >$ and $< R^k >$ are examined [101] for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground state. The intracule and extracule densities of all the 96 ions are found to be monotonically decreasing functions in the same manner as neutral atoms. A few approximate relations between the intracule and extracule densities, and their moments are confirmed to be valid for the charged atoms as well. In Chapter 3, momentum-space spherically averaged intracule and extracule densities are constructed and examined [102] systematically for the singly charged 53 cations from Li^+ to Cs^+ and 43 stable anions from H^- to I^- in their ground state based on numerical Hartree-Fock calculations. The intracule and extracule densities are found to be classified into three and two types, respectively, according to the number of extrema and their locations. The modalities of the electron-pair densities for all the 96 ions are governed by a few outermost electron pairs as reported for neutral atoms. The intracule and extracule moments as well as the electron-electron coalescence and counterbalance densities are computed for the 96 ions and are compared with the corresponding values for the isoelectronic neutral atoms. In Chapter 4, a method is presented [103] to obtain the extracule density $d(R)$ for a particular class of correlated wave functions which explicitly include an r_{12} term. The method is applied to the ground state helium atom and its isoelectronic analogs described by highly accurate Kinoshita wave functions. Near exact extracule densities $d(R)$, their moments $< R^k >$ with $k = -2$ to $+4$, and electron-electron counterbalance densities $d(0)$ are determined. A comparison of the correlated results with the corresponding Hartree-Fock values shows that the electron correlation shifts the extracule density $d(R)$ from a small to a large R region. Different

roles of the radial and angular correlation contributions are also clarified in the electron correlation.

Finally, general conclusion of the present thesis is given at the end of this thesis.

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PART 1.
CHAPTER 1.

INTRODUCTION

The intracule (relative motion) and extracule (center-of-mass motion) densities are a couple of electron-pair densities useful to analyze the motion of a pair of electrons in atoms and molecules. The position-space intracule $I(\mathbf{u})$ and its spherically averaged $h(u)$ densities are [1] the probability density functions for the relative vector $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ and its magnitude $u = |\mathbf{r}_1 - \mathbf{r}_2|$. On the other hand, the extracule $E(\mathbf{R})$ and its spherically averaged $d(R)$ densities in position space represent [1] the probability density functions for the center-of-mass vector $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and its magnitude $R = |\mathbf{r}_1 + \mathbf{r}_2|/2$. Analogously, the intracule $\bar{I}(\mathbf{v})$ and its spherical-average $\bar{h}(v)$ densities, and extracule $\bar{E}(\mathbf{P})$ densities and its spherical-average $\bar{d}(P)$ densities are also [2] introduced in momentum space.

A special case of the intracule $I(\mathbf{u})$ at $\mathbf{u} = \mathbf{0}$ or $h(u)$ at $u = 0$ defines the electron-electron coalescence density $I(\mathbf{0}) = h(0)$, which is the probability density of finding any two electrons at the same position in space. The density appears in the calculation of the relativistic [3] and radiative [4] corrections to the ground-state energy of atoms and ions as well as in the realization of the electron-electron or correlation cusp condition [5] of many-electron systems. Within the Hartree-Fock framework, an equality $h(0) = <\rho>/4$ holds [6] for closed-shell atoms and atomic ions, where $<\rho> \equiv \int d\mathbf{r}[\rho(\mathbf{r})]^2$ is the average electron density, and $\rho(\mathbf{r})$ is the one-electron density. A special case of $E(\mathbf{R})$ at $\mathbf{R} = \mathbf{0}$ or $d(R)$ at $R = 0$ yields the electron-electron counterbalance density $E(\mathbf{0}) = d(0)$, which is the probability density of finding any two electrons at opposite positions with respect to the origin (i.e., the nucleus in an atom). No numerical results for the electron-electron counterbalance density are reported from both Hartree-Fock and correlated calculations. In momentum space, we can also define the electron-electron coalescence $\bar{I}(\mathbf{0}) = \bar{h}(0)$ and counterbalance $\bar{E}(\mathbf{0}) = \bar{d}(0)$ densities, and represent the probability densities for a pair of electrons to have exactly the same and opposite momenta, respectively. The momentum-space electron-electron coalescence and counterbalance densities have never been examined. The purpose of this part is to report Hartree-Fock-limit values of the position- and momentum-space electron-electron coalescence and counterbalance densities for atoms, and is to study relations among these densities and the average electron density in both spaces.

In Chapter 2, we present [7] the electron-electron coalescence $I(\mathbf{0})$ and counterbalance $E(\mathbf{0})$ densities, and the average electron density $<\rho>$ obtained from the numerical Hartree-Fock calculations for the atoms He through Ne in their experimental ground state. For a single Slater determinant wave function, these electron-pair properties are shown to be exactly expressible in terms of the one-electron density $\rho(\mathbf{r})$. We examine the relations $I(\mathbf{0}) = (<\rho> - \Delta_I)/4$ and $E(\mathbf{0}) = 2(<\rho> - \Delta_E)$, where Δ_I and Δ_E are linear combinations of overlaps between two orbital densities, that depend on the electronic configuration and the *LS* multiplet state of the atom under

consideration. For the atoms He through Ne, the explicit forms of Δ_I and Δ_E are derived.

In Chapter 3, we study [8] the electron-electron coalescence and counterbalance densities, as well as the average electron density, of the atoms He through Xe in position and momentum spaces. These electron-pair densities and the average one-electron densities are computed by using the numerical Hartree-Fock method. The results are discussed in terms of the atomic number, electronic configuration and subshell-pair contributions.

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PART 1.
CHAPTER 2.

RELATIONSHIP AMONG ONE-ELECTRON, COALESCENCE AND COUNTERBALANCE DENSITIES

1-2-1. INTRODUCTION

The intracule $I(\vec{u})$ and extracule $E(\vec{R})$ densities are two important electron-pair densities which provide us with profound understanding of the interaction among electrons in atoms and molecules (see, *e.g.*, [1] for a review). For an N-electron system $(N \geq 2)$, the intracule density $I(\vec{u})$ is defined by

$$I(\vec{u}) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta[\vec{u} - (\vec{r}_i - \vec{r}_j)] \right\rangle , \tag{1}$$

where $\delta(\vec{x})$ is the three-dimensional Dirac delta function. The intracule density $I(\vec{u})$ represents the probability density function for an interelectronic vector $\vec{u}$. On the other hand, the extracule density $E(\vec{R})$, defined by

$$E(\vec{R}) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta[\vec{R} - (\vec{r}_i + \vec{r}_j)/2] \right\rangle , \tag{2}$$

represents the probability density function for the center of mass $\vec{R}$. In recent years, there has been increasing interest in studies of the electron-pair densities, particularly of the intracule density, for applications to various chemical and physical problems. These studies include Hund's rules [2,3], chemical bondings [4-6], Coulomb holes [7-12], and correlation density functionals [13,14], for example. Efficient algorithms for the calculation of $I(\vec{u})$ and $E(\vec{R})$ have also been developed [4,8,15-18].

A special case of the intracule density $I(\vec{u})$ for $\vec{u} = \vec{0}$ gives the electron-electron coalescence density $I(\vec{0})$, which is the probability density of finding any two electrons i and j at the same position in space or $\vec{r}_i = \vec{r}_j$. Very recently, the electron-electron coalescence density $I(\vec{0})$ has received considerable attention for the analysis of interelectronic interactions and several rigorous inequalities have been found [19-21] among $I(\vec{0})$ and the interelectronic moments $<u^k>$ and $<u^k \ln u>$. Analogously, a special case of the extracule density $E(\vec{R})$ for $\vec{R} = \vec{0}$ defines the electron-electron counterbalance density $E(\vec{0})$, which represents the probability density of finding any two electrons i and j exactly at the opposite (mirror) positions with respect to the origin (*i.e.*, the nucleus in atoms) or $\vec{r}_i = -\vec{r}_j$. To our knowledge, however, no studies have been reported in the literature on the electron-electron counterbalance density $E(\vec{0})$.

In Chapter 2, we report theoretical structures of the electron-electron coalescence $I(\vec{0})$ and counterbalance $E(\vec{0})$ densities for atoms in the Hartree-Fock approximation. Both the *two*-electron properties $I(\vec{0})$ and $E(\vec{0})$ are shown to be exactly expressible in terms of the familiar *one*-electron density function $\rho(\vec{r})$ and its orbital components $\rho_i(\vec{r})$. Some general inequalities are also derived. The explicit forms of $I(\vec{0})$ and $E(\vec{0})$

depend on the electronic configuration and the *LS* multiplet state of the atom under consideration. For the atoms from He to Ne in their experimental ground state, the expressions for $I(\vec{0})$ and $E(\vec{0})$ are derived and their values are determined by the numerical Hartree-Fock method. The numerical results add approximate and empirical relations among $I(\vec{0})$, $E(\vec{0})$, and the average electron density $<\rho>$. Hartree atomic units are used throughout this chapter.

1-2-2. ELECTRON-ELECTRON COALESCENCE DENSITY

If an *N*-electron wave function is expressed by a single Slater determinant of *N* spinorbitals $\psi_i(\vec{r})\eta_i(\sigma)$, the electron intracule density $I(\vec{u})$ defined by Eq. (1) is rewritten, due to the Condon-Slater rules, as

$$I(\vec{u}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \{f_{ii,jj}(\vec{u}) - \delta_{m_{si}m_{sj}} f_{ij,ji}(\vec{u})\} , \tag{3}$$

$$f_{ij,kl}(\vec{u}) \equiv \int \psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1)\delta[\vec{u} - (\vec{r}_1 - \vec{r}_2)]\psi_k^*(\vec{r}_2)\psi_l(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 , \tag{4}$$

where the Kronecker delta $\delta_{m_{si}m_{sj}}$ is unity if the two spinorbitals *i* and *j* have the same spin and zero if *i* and *j* have different spins.

Setting $\vec{u} = \vec{0}$ in Eqs. (3) and (4), we obtain the electron-electron coalescence density $I(\vec{0})$ as

$$I(\vec{0}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} [1 - \delta_{m_{si}m_{sj}}](i,j) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} [1 - \delta_{m_{si}m_{sj}}](i,j) , \tag{5}$$

where

$$(i,j) \equiv \int [\rho_i(\vec{r})][\rho_j(\vec{r})]d\vec{r} = (j,i) , \tag{6a}$$

and

$$\rho_i(\vec{r}) \equiv \psi_i^*(\vec{r})\psi_i(\vec{r}) \tag{6b}$$

is the electron density of orbital *i*. Equation (5) shows that the electron-electron coalescence density is the sum of overlaps between orbital densities with different spins. The contributions from electrons with the same spin vanish corresponding to the Fermi hole in the Hartree-Fock theory. Using the total electron density

$$\rho(\vec{r}) \equiv \sum_{i=1}^{N} \rho_i(\vec{r}) , \tag{7}$$

we can rearrange Eq. (5) as

$$I(\vec{0}) = \frac{1}{4}\{<\rho> - \Delta_I\} , \tag{8}$$

in which

$$<\rho> \equiv \int [\rho(\vec{r})]^2 d\vec{r} = \sum_{i=1}^{N}\sum_{j=1}^{N}(i,j) , \tag{9a}$$

$$\Delta_I \equiv \sum_{i=1}^{N}\sum_{j=1}^{N} [-1 + 2\delta_{m_{si}m_{sj}}](i,j) . \tag{9b}$$

As shown by Ugalde and Sarasola [21], the term Δ_I in Eq. (8) is identically zero for closed-shell systems. For open-shell systems, Δ_I depends explicitly on the electron configuration and on the orbital and spin angular momenta, but is always positive since only the contributions from open-shell orbitals remain. In the Hartree-Fock approximation, we thus have

$$I(\vec{0}) \leq \frac{1}{4}<\rho> , \tag{10}$$

where the equality holds for closed-shell systems and the inequality holds for open-shell systems. The relation (10) has been mentioned also by Wang *et al.* [22] in their analysis of intracule densities for a few ten-electron molecules. The detailed expressions for Δ_I will be presented in Section 1-2-4 for selected atoms.

Beyond the orbital approximation, the electron correlation works to separate electrons each other, which would result in a reduction of the Hartree-Fock $I(\vec{0})$ value. On the other hand, the Hartree-Fock one-electron density $\rho(\vec{r})$ is known to be identical to the exact correlated density to first order in the perturbation theory. Thus, we expect that only the inequality in Eq. (10) holds for correlated wave functions. For two-electron atomic systems in their ground ^{1}S state, this conjecture is numerically verified using the data given in Ref. [21].

In the case of atoms and atomic ions, the angular part of the integral (i,j) is analytically carried out, since we can generally assume

$$\psi_i(\vec{r}) = R_i(r)Y_{l_i m_i}(\theta,\phi) , \tag{11}$$

where $Y_{lm}(\theta,\phi)$ is a spherical harmonic. After some manipulation, we obtain

$$(i,j) = A_{ij}(R_i,R_j) , \tag{12}$$

where

$$(R_i,R_j) \equiv \int_0^\infty dr\, r^2 |R_i(r)|^2 |R_j(r)|^2 , \tag{13a}$$

$$\begin{aligned} A_{ij} &\equiv \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, |Y_{l_i m_i}(\theta,\phi)|^2 |Y_{l_j m_j}(\theta,\phi)|^2 \\ &= (-1)^{m_i+m_j} \frac{(2l_i+1)(2l_j+1)}{4\pi} \sum_{L=0}^{\min(2l_i,2l_j)} (2L+1) \\ &\times \begin{pmatrix} l_i & l_i & L \\ m_i & -m_i & 0 \end{pmatrix} \begin{pmatrix} l_i & l_i & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & l_j & L \\ m_j & -m_j & 0 \end{pmatrix} \begin{pmatrix} l_j & l_j & L \\ 0 & 0 & 0 \end{pmatrix} , \end{aligned} \tag{13b}$$

in which $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denotes a 3*j* symbol. We note that the summation in Eq. (13b) runs only over even values of *L*.

1-2-3. ELECTRON-ELECTRON COUNTERBALANCE DENSITY

For an *N*-electron single determinant wave function, the extracule density $E(\vec{R})$ defined by Eq. (2) can be rewritten as

$$E(\vec{R}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \{g_{ii,jj}(\vec{R}) - \delta_{m_{si}m_{sj}} g_{ij,ji}(\vec{R})\} , \tag{14}$$

where

$$g_{ij,kl}(\vec{R}) \equiv \int \psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1)\delta[\vec{R}-(\vec{r}_1+\vec{r}_2)/2]\psi_k^*(\vec{r}_2)\psi_l(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \ . \tag{15}$$

The electron-electron counterbalance density $E(\vec{0})$ is a special value of $E(\vec{R})$ for $\vec{R}=\vec{0}$, and includes two basic integrals,

$$g_{ii,jj}(\vec{0}) = 8\int |\psi_i(\vec{r})|^2 |\psi_j(-\vec{r})|^2 d\vec{r} \ , \tag{16a}$$

$$g_{ij,ji}(\vec{0}) = 8\int [\psi_i^*(\vec{r})\psi_i(-\vec{r})][\psi_j^*(-\vec{r})\psi_j(\vec{r})]d\vec{r} \ . \tag{16b}$$

For atomic systems with the spatial orbital (11), we obtain

$$\psi_i(-\vec{r}) = R_i(r)Y_{l_i m_i}(\pi-\theta,\phi+\pi) = (-1)^{l_i}\psi_i(\vec{r}) \ , \tag{17}$$

and hence

$$g_{ii,jj}(\vec{0}) = 8(i,j) \ , \quad g_{ij,ji}(\vec{0}) = 8(-1)^{l_i+l_j}(i,j) \ . \tag{18}$$

The electron-electron counterbalance density for atoms is finally obtained to be

$$\begin{aligned} E(\vec{0}) &= 8\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}[1-(-1)^{l_i+l_j}\delta_{m_{si}m_{sj}}](i,j) \\ &= 4\sum_{i=1}^{N}\sum_{j=1}^{N}[1-(-1)^{l_i+l_j}\delta_{m_{si}m_{sj}}](i,j) \ , \end{aligned} \tag{19}$$

within the Hartree-Fock approximation. It is interesting to find in Eq. (19) that $E(\vec{0})$ has a structure similar to $I(\vec{0})$ [Eq. (5)] and is again expressed by the overlaps (i,j) of two orbital densities. However, $E(\vec{0})$ includes an additional factor $(-1)^{l_i+l_j}$ and depends on the azimuthal quantum numbers l_i as well as the spin quantum numbers m_{si}.

Analogous to Eq. (8), we can rewrite Eq. (19) as

$$E(\vec{0}) = 2\{<\rho> - \Delta_E\} \ , \tag{20}$$

where

$$\Delta_E \equiv \sum_{i=1}^{N}\sum_{j=1}^{N}[-1+2(-1)^{l_i+l_j}\delta_{m_{si}m_{sj}}](i,j) \ . \tag{21}$$

The value of Δ_E is either negative, zero, or positive, depending on the electron configuration and *LS* term of the atom under consideration. Even for closed shells, Δ_E is not always zero. However, we find that the constant factor in front of the integral (i,j) in Eq. (21) is -1 for different spins, -3 for the same spin with odd l_i+l_j, and $+1$ for the same spin with even l_i+l_j. We therefore expect that Δ_E would be negative except for few-electron cases, as will be numerically confirmed in Section 1-2-4. Comparison of the expressions for Δ_I and Δ_E gives

$$\Delta_I - \Delta_E = 2\sum_{i=1}^{N}\sum_{j=1}^{N}[1-(-1)^{l_i+l_j}]\delta_{m_{si}m_{sj}}(i,j) \ \geq \ 0 \ . \tag{22}$$

We thus obtain a general inequality relation,

$$E(\vec{0}) \geq 8I(\vec{0}) \ . \tag{23}$$

1-2-4. NUMERICAL RESULTS

Within the nonrelativistic framework and in the absence of an external field, the *LS* multiplet states of an atom with a given electronic configuration are $(2L+1)(2S+1)$-fold degenerate with respect to the total energy, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively. In general, each of these multiplets is expressed by a linear combination of a finite number of Slater determinants in the Hartree-Fock theory. For the neutral atoms He through Ne in their experimental ground state [23], we have examined the structure of the corresponding Hartree-Fock wave functions and confirmed that there exists at least one set of specific z-component M_L and M_S values of L and S which results in a single determinant wave function. Based on such single determinants, the detailed expressions for Δ_I are derived and summarized in Table 1. The simplified expressions of Δ_I in terms of (R_i,R_j) are also given in the table. We there observe that a particle-hole relationship holds for Δ_I. Similarly, Table 2 summarizes the explicit forms of Δ_E for the atoms He through Ne. Comparison of the results in Tables 1 and 2 exemplifies the validity of the inequality (22).

A special case is found for He, Be, and their isoelectronic analogs, where only s orbitals constitute a closed ${}^1S$ shell. For these species, we have a peculiar relation,

$$\Delta_E = \Delta_I = 0 \quad \text{and} \quad \frac{1}{2}E(\vec{0}) = 4I(\vec{0}) = <\rho> \ . \tag{24}$$

The Li atom and its isoelectronic analogs constitute another special case. For these species, we obtain

$$\Delta_E = \Delta_I = (2s,2s) \quad \text{and} \quad \frac{1}{2}E(\vec{0}) = 4I(\vec{0}) = <\rho> - (2s,2s) \ . \tag{25}$$

We have performed the numerical Hartree-Fock calculations of the quantities $<\rho>$, Δ_I, Δ_E, $I(\vec{0})$, and $E(\vec{0})$ by using a modified version of the program MCHF72 [24]. The results are summarized in Table 3 for the above-mentioned atoms. In the table, we find examples of the equalities and inequalities discussed in Sections 1-2-2 and 1-2-3 and in the second paragraph of this Section. The $(1s,1s)$ term gives a predominant contribution to the average electron density $<\rho>$. Since $(1s,1s) = Z^3/(8\pi)$ for a hydrogenic $1s$ function with nuclear charge Z, $<\rho>$ is also proportional to Z^3 approximately. We find Δ_I is very small compared to $<\rho>$. Then

$$I(\vec{0}) \cong \frac{1}{4}<\rho> \tag{26}$$

is a good approximation within the Hartree-Fock theory. The accuracy of Eq. (26) is more than 99% for all the first-row atoms. Except for the fewer-electron atoms He-Be, the Δ_E value is negative as anticipated. However, its magnitude is considerably larger than Δ_I, and therefore an approximation,

$$E(\vec{0}) \cong 2<\rho> \ , \tag{27}$$

is no more than an estimate of $E(\vec{0})$. The error of Eq. (27) increases with increasing Z, and amounts to 11% for the Ne atom. Nevertheless, the combination of Eqs. (26) and (27),

$$2<\rho> \cong 8I(\vec{0}) \cong E(\vec{0}) \ , \tag{28}$$

may be important, not only because it connects the one- and two-electron properties in a

very simple manner but also because $\rho(\vec{r})$ is an experimentally measurable quantity. Figure 1 illustrates the relation (28), where the slopes of the three lines are seen to be close to +3, reflecting the Z^3 dependence. However, remind the rigorous relations (10) and (23).

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Table 1. The explicit formulas of Δ_1 for the atoms He through Ne.

Z	Atom	State	Δ_1
2	He	$1s(2)$, ^1S	0
3	Li	$2s(1)$, ^2S	$(2s,2s) = \frac{1}{4\pi}(R_{2s},R_{2s})$
4	Be	$2s(2)$, ^1S	0
5	B	$2p(1)$, ^2P	$(2p_0,2p_0) = \frac{9}{20\pi}(R_{2p},R_{2p})$
6	C	$2p(2)$, ^3P	$(2p_{+1},2p_{+1}) + 2(2p_{+1},2p_{-1}) + (2p_{-1},2p_{-1}) = \frac{6}{5\pi}(R_{2p},R_{2p})$
7	N	$2p(3)$, ^4S	$(2p_{+1},2p_{+1}) + (2p_0,2p_0) + (2p_{-1},2p_{-1}) = \frac{9}{4\pi}(R_{2p},R_{2p})$
			$+ 2\{(2p_{+1},2p_0) + (2p_0,2p_{-1}) + (2p_{-1},2p_{+1})\}$
8	O	$2p(4)$, ^3P	$(2p_{+1},2p_{+1}) + 2(2p_{+1},2p_{-1}) + (2p_{-1},2p_{-1}) = \frac{6}{5\pi}(R_{2p},R_{2p})$
9	F	$2p(5)$, ^2P	$(2p_0,2p_0) = \frac{9}{20\pi}(R_{2p},R_{2p})$
10	Ne	$2p(6)$, ^1S	0

Table 2. The explicit formulas of Δ_E for the atoms He through Ne.

Z	Atom	State	Δ_E
2	He	$1s(2)$, ^1S	0
3	Li	$2s(1)$, ^2S	$(2s,2s)=\frac{1}{4\pi}(R_{2s},R_{2s})$
4	Be	$2s(2)$, ^1S	0
5	B	$2p(1)$, ^2P	$-8\{(1s,2p_0)+(2s,2p_0)\}+(2p_0,2p_0)=-\frac{2}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}+\frac{9}{20\pi}(R_{2p},R_{2p})$
6	C	$2p(2)$, ^3P	$-8\{(1s,2p_{+1})+(1s,2p_{-1})+(2s,2p_{+1})+(2s,2p_{-1})\}+(2p_{+1},2p_{+1})+2(2p_{+1},2p_{-1})+(2p_{-1},2p_{-1})$ $=-\frac{4}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}+\frac{6}{5\pi}(R_{2p},R_{2p})$
7	N	$2p(3)$, ^4S	$-8\{(1s,2p_{+1})+(1s,2p_0)+(1s,2p_{-1})+(2s,2p_{+1})+(2s,2p_0)+(2s,2p_{-1})\}$ $+(2p_{+1},2p_{+1})+(2p_0,2p_0)+(2p_{-1},2p_{-1})+2\{(2p_{+1},2p_0)+(2p_0,2p_{-1})+(2p_{-1},2p_{+1})\}$ $=-\frac{6}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}+\frac{9}{4\pi}(R_{2p},R_{2p})$
8	O	$2p(4)$, ^3P	$-8\{(1s,2p_{+1})+2(1s,2p_0)+(1s,2p_{-1})+(2s,2p_{+1})+2(2s,2p_0)+(2s,2p_{-1})\}$ $+(2p_{+1},2p_{+1})+2(2p_{+1},2p_{-1})+(2p_{-1},2p_{-1})$ $=-\frac{8}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}+\frac{6}{5\pi}(R_{2p},R_{2p})$
9	F	$2p(5)$, ^2P	$-8\{2(1s,2p_{+1})+(1s,2p_0)+2(1s,2p_{-1})+2(2s,2p_{+1})+(2s,2p_0)+2(2s,2p_{-1})\}+(2p_0,2p_0)$ $=-\frac{10}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}+\frac{9}{20\pi}(R_{2p},R_{2p})$
10	Ne	$2p(6)$, ^1S	$-16\{(1s,2p_{+1})+(1s,2p_0)+(1s,2p_{-1})+(2s,2p_{+1})+(2s,2p_0)+(2s,2p_{-1})\}$ $=-\frac{12}{\pi}\{(R_{1s},R_{2p})+(R_{2s},R_{2p})\}$

Table 3. Numerical Hartree-Fock results for $2<\rho>$, $8I(\vec{0})$, and $E(\vec{0})$.

Atom	$2<\rho>$	Δ_I	Δ_E	$8I(\vec{0})$	$E(\vec{0})$
He	1.524832	0	0	1.524832	1.524832
Li	6.278230	0.001960	0.001960	6.274309	6.274309
Be	16.792516	0	0	16.792516	16.792516
B	35.069991	0.018395	-0.218991	35.033202	35.507972
C	63.644983	0.106509	-0.931900	63.431965	65.508782
N	105.215506	0.364736	-2.494066	104.486033	110.203638
O	162.997836	0.302746	-5.836315	162.392345	174.670465
F	240.155756	0.170085	-11.493190	239.815585	263.142136
Ne	340.337803	0	-20.254378	340.337803	380.846559

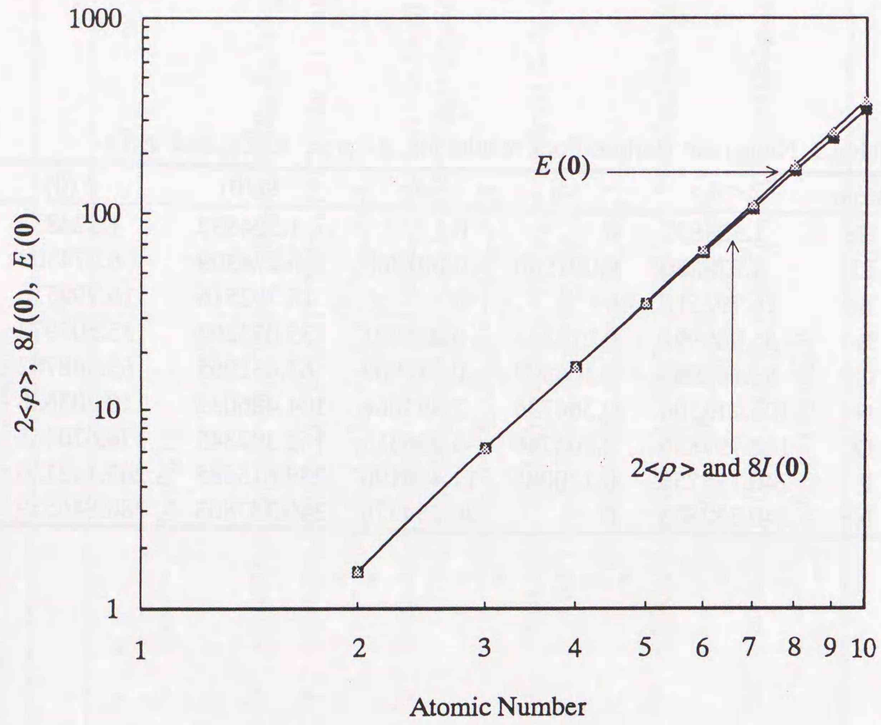


Fig. 1. Logarithmic plots of $2<\rho>$, $8I(\vec{0})$, and $E(\vec{0})$ as a function of Z.

PART 1.
CHAPTER 3.

COALESCENCE AND COUNTERBALANCE DENSITIES IN POSITION AND MOMENTUM SPACES

1-3-1. INTRODUCTION

The intracule $I(\mathbf{u})$ and extracule $E(\mathbf{R})$ densities, as well as their spherical averages $h(u)$ and $d(R)$, are electron-pair densities useful to analyze and characterize the motion of a pair of electrons in atoms and molecules [1-7]. For an N-electron system $(N \geq 2)$, the intracule densities $I(\mathbf{u})$ and $h(u)$ are defined by

$$I(\mathbf{u}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{u} - (\mathbf{r}_j - \mathbf{r}_k)] \right\rangle , \quad h(u) \equiv \frac{1}{4\pi} \int d\Omega_u \, I(\mathbf{u}) , \tag{1}$$

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 the angular brackets $\langle\ \rangle$ stand for the expectation value. The intracule densities $I(\mathbf{u})$ and $h(u)$ are the probability density functions for an interelectronic vector $\mathbf{u}$ and its magnitude u, respectively. On the other hand, the extracule densities $E(\mathbf{R})$ and $d(R)$ are defined by

$$E(\mathbf{R}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{R} - (\mathbf{r}_j + \mathbf{r}_k)/2] \right\rangle , \quad d(R) \equiv \frac{1}{4\pi} \int d\Omega_R \, E(\mathbf{R}) , \tag{2}$$

and represent the probability density functions for the center-of-mass vector $\mathbf{R}$ and its magnitude R, respectively, where $\mathbf{R} \equiv (R, \Omega_R)$ and $\Omega_R \equiv (\theta_R, \phi_R)$.

A special case of $I(\mathbf{u})$ at $\mathbf{u}=\mathbf{0}$ or $h(u)$ at $u=0$ defines the electron-electron coalescence density $I(\mathbf{0})=h(0)$, which is the probability density of finding any two electrons at the same position. Analogously, a special case of $E(\mathbf{R})$ at $\mathbf{R}=\mathbf{0}$ or $d(R)$ at $R=0$ yields the electron-electron counterbalance density $E(\mathbf{0})=d(0)$, which is the probability density of finding any two electrons at the opposite positions with respect to the origin (*i.e.*, the nucleus in atoms). The electron-electron coalescence density $h(0)$ appears in the evaluation of the relativistic [8] and radiative [9] corrections for atoms and molecules. Recently, the properties of the electron-electron coalescence density $h(0)$ have been received increasing attention. Dehesa *et al* [10] have analytically derived upper and lower bounds to $h(0)$ in terms of interelectronic moments $<u^k>$ and $u_{\max}$, where $u_{\max}$ denotes the location of the maximum of the spherically-averaged intracule density $h(u)$. Improved lower bounds have also been reported by Koga *et al* [11] by using logarithmic moments $<u^k \ln u>$. Ugalde and Sarasola [12] have shown that for closed-shell systems, an equality

$$h(0) = \frac{1}{4} <\rho> , \tag{3}$$

holds within the Hartree-Fock approximation, where $<\rho>$ is the average electron density defined by $<\rho> \equiv \int d\mathbf{r}[\rho(\mathbf{r})]^2$ and $\rho(\mathbf{r})$ represents one-electron density function. In a previous paper [13], we have shown that both for closed- and open-shell

systems described by a single Slater determinant wave function, the electron-pair densities $h(0)$ and $d(0)$ are exactly expressible in terms of the one-electron density function $\rho(\mathbf{r})$ and its orbital components $\rho_j(\mathbf{r})$. Moreover, we have proved that inequalities

$$h(0) \le \frac{1}{4} < \rho > \quad \text{and} \quad h(0) \le \frac{1}{8} d(0) \ , \tag{4}$$

have general validity in the Hartree-Fock framework.

In spite of these increasing interests, neither accurate nor systematic values are known for $h(0)$, $d(0)$, and $<\rho>$, except for some two-electron atomic systems. In the chapter, we first point out that the momentum space electron-electron coalescence $\bar{I}(\mathbf{0}) = \bar{h}(0)$ and counterbalance $\bar{E}(\mathbf{0}) = \bar{d}(0)$ densities can also be expressed exactly by the one-electron momentum density $\gamma(\mathbf{p})$ and its orbital components $\gamma_j(\mathbf{p})$ in a manner similar to their counterparts in position space. For the 53 neutral atoms He through Xe in their ground state, we then report Hartree-Fock-limit values of the electron-electron coalescence and counterbalance densities, in both position and momentum spaces. Since the electron correlation is defined as the difference in the electronic motions in the Hartree-Fock and exact solutions within the nonrelativistic framework, the present results on the electron-pair densities are expected to be useful as reference data in the study of electron correlations. The dependence of these densities on atomic number is analyzed and the contributions from different pairs of atomic subshells are discussed. Hartree atomic units are used throughout the chapter.

1-3-2. ELECTRON-ELECTRON COALESCENCE AND COUNTERBALANCE DENSITIES IN HARTREE-FOCK THEORY

We assume that a wave function of an N-electron atom is expressed by a single Slater determinant of N spinorbitals $\psi_j(\mathbf{r})\eta_j(\sigma)$. Integrating Eq. (1) over the spin variables and setting $\mathbf{u}=\mathbf{0}$ give [13] the electron-electron coalescence density

$$I(\mathbf{0}) = h(0) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} [1 - \delta_{m_{sj} m_{sk}}](j,k) \ , \tag{5}$$

in position space, where m_{sj} and m_{sk} are the spin quantum numbers, $\delta_{m_{sj} m_{sk}}$ is the Kronecker delta, and

$$(j,k) \equiv \int d\mathbf{r} \, [\rho_j(\mathbf{r})][\rho_k(\mathbf{r})] = (k,j) \ , \tag{6}$$

in which $\rho_j(\mathbf{r}) \equiv \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})$. Similarly, integrating Eq. (2) over the spin variables and setting $\mathbf{R}=\mathbf{0}$ give [13] the electron-electron counterbalance density

$$E(\mathbf{0}) = d(0) = 8 \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} [1 - (-1)^{l_j + l_k} \delta_{m_{sj} m_{sk}}](j,k) \ , \tag{7}$$

where l_j and l_k are the orbital azimuthal quantum numbers. The average electron density $<\rho>$ can also be expressed by (j,k):

$$< \rho > \equiv \int d\mathbf{r} [\rho(\mathbf{r})]^2 = \sum_{j=1}^{N} \sum_{k=1}^{N} (j,k) \ . \tag{8}$$

For atoms and atomic ions, we can generally assume that a spatial function $\psi_j(\mathbf{r})$ is a product of radial $R_j(r)$ and spherical harmonic $Y_{l_j m_j}(\theta,\phi)$ functions. Then, the angular part of the integral (j,k) is analytically integrated to obtain

$$(j,k) = A_{jk}(R_j, R_k) \ , \tag{9}$$

where

$$(R_j, R_k) \equiv \int_0^\infty dr \, r^2 |R_j(r)|^2 |R_k(r)|^2 \ , \tag{10a}$$

$$\begin{aligned} A_{jk} &\equiv \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \, |Y_{l_j m_j}(\theta,\phi)|^2 |Y_{l_k m_k}(\theta,\phi)|^2 \\ &= \frac{1}{4\pi} \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1) \, a^l(l_j m_j; l_k m_k) \ , \end{aligned} \tag{10b}$$

in which $a^k(lm;l'm')$ is the Condon-Shortley parameter [14].

A momentum-space N-electron wave function is given by the $3N$-dimensional Fourier transformation of the corresponding position-space wave function. Then the Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, provided that a position orbital $\psi_k(\mathbf{r})$ is replaced with the corresponding momentum orbital

$$\phi_k(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp(-i\mathbf{p}\cdot\mathbf{r}) \, \psi_k(\mathbf{r}) \ . \tag{11}$$

Expanding $\exp(-i\mathbf{p}\cdot\mathbf{r})$ in Eq. (11) by means of plane waves [15] and integrating over the angular variable Ω_r, we find

$$\phi_k(\mathbf{p}) = P_k(p) Y_{l_k m_k}(\Omega_p) \ , \tag{12}$$

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

$$P_k(p) = (-i)^{l_k} \sqrt{\frac{2}{\pi}} \int_0^\infty dr \, r^2 j_{l_k}(pr) \, R_k(r) \ , \tag{13}$$

in which $j_l(pr)$ is the spherical Bessel function of the first kind. As a result, theoretical structures of the electron-electron coalescence and counterbalance densities in the Hartree-Fock approximation are essentially the same in position and momentum spaces. Then all the position-space results [Eqs.(5)-(10)] hold in momentum space as well, if we replace $h(0)$ with $\bar{h}(0)$, $d(0)$ with $\bar{d}(0)$, $\rho(\mathbf{r})$ with $\gamma(\mathbf{p})$, $\rho_j(\mathbf{r})$ with $\gamma_j(\mathbf{p})$, $<\rho>$ with $<\gamma>$, and $R_j(r)$ with $P_j(p)$.

1-3-3. COMPUTATIONAL METHOD

Within the nonrelativistic framework and in the absence of an external field, the LS multiplet states of an atom with a given electronic configuration are $(2L+1)(2S+1)$-fold degenerate with respect to the total energy, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively. Each of these multiplets is expressed in general by a linear combination of a finite number of Slater determinants in the Hartree-Fock theory. For the neutral atoms He through Xe in their experimental ground state [16], we have first examined the structure of the corresponding Hartree-Fock wave functions and confirmed that there exists at least one set of specific z-component M_L and M_S values of L and S that results in a single determinant wave

function, to which our method described in Section 1-3-2 can be applied.

For these ground *LS* terms of the 53 atoms, the Hartree-Fock radial functions $R_j(r)$ in position space have been generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [17]. A table of the ground electronic configurations and *LS* terms examined in this study is found in a recent work [18]. Then the radial integrals (R_j, R_k) have been computed numerically according to Eq. (10a), and the coefficients A_{jk} have been calculated by the use of the parameters $a^k(lm;l'm')$ given in the Slater's book [19]. The values of A_{jk} appeared in the present study are summarized in Table 1. Calculations of $h(0)$, $d(0)$, and $<\rho>$ have been carried out based on Eqs. (5), (7), and (8).

In momentum space, the radial position functions $R_j(r)$, generated by numerical Hartree-Fock calculations, have been numerically Hankel-transformed [20] to obtain the radial momentum functions $P_j(p)$ according to Eq. (13). Then $\bar{h}(0)$, $\bar{d}(0)$, and $<\gamma>$ have been calculated in the same manner as in position space.

1-3-4. RESULTS AND DISCUSSION

Table 2 shows the electron-electron coalescence $h(0)$ and counterbalance $d(0)$ densities and the average one-electron density $<\rho>$ in position space for the atoms He to Xe in their ground state. The values of $h(0)$, $d(0)$, and $<\rho>$ increase monotonically with increasing atomic number *Z*. Figure 1 depicts $8h(0)$, $d(0)$, and $2<\rho>$ as a function of *Z*. The validity of the inequalities (4) is confirmed in the table and figure. An equality $h(0) = <\rho>/4$ holds for closed-shell atoms, *i.e.*, the group 2 (Be, Mg, Ca, Sr), group 12 (Zn, Cd), and group 18 (He, Ne, Ar, Kr, Xe) atoms. Among 42 open-shell atoms, the largest difference between $h(0)$ and $<\rho>/4$ is found for the N atom (*Z*=7), but the relative error is only 0.69%. Thus, an approximation $h(0) \cong <\rho>/4$ is [13] found to be very accurate for all the atoms He through Xe. On the other hand, the difference between $8h(0)$ and $d(0)$ increases with increasing *Z*, and the relative error amounts to 27% for Xe. Thus, another approximation $h(0) \cong d(0)/8$ is [13] poor for a large *Z*.

Beyond the Hartree-Fock approximation, the effect of the electron correlation in atomic systems may be classified into radial and angular contributions. The radial correlation means that when one electron is close to the nucleus, the other electron tends to be distant from the nucleus. Thus, the radial correlation is expected to reduce both $h(0)$ and $d(0)$ from the Hartree-Fock values. The angular correlation implies that two electrons have a tendency to be on opposite sides of the nucleus. Then the angular correlation will also decrease $h(0)$, but may slightly increase $d(0)$, compared to their Hartree-Fock values. Our anticipation on the electron-electron coalescence density $h(0)$ is verified, if the present Hartree-Fock values in Table 2 are compared with the correlated values for He [10,12], Li [21], and Be [22] atoms. To our knowledge, however, no numerical results for the electron-electron counterbalance density $d(0)$ are reported from correlated calculations.

For an *N*-electron atom, there are $N(N-1)/2$ different spinorbital-pair contributions to $h(0)$, $d(0)$, and $<\rho>$, but they can be grouped into subshell-pair

contributions based on different (R_j, R_k). Such a grouping into subshell pairs greatly reduces the number of different pairs and facilitates the analysis of the origin of the electron-pair densities. For example, the Xe atom (*Z*=54) contains 1431 spinorbital pairs, but there are only 66 subshell pairs. The subshell-pair contributions depend not only on the number of electrons and their spins in the two subshells, but also on the values of (R_j, R_k) and A_{jk}. Figure 2 shows main subshell-pair contributions to $h(0)$ for the atoms He to Xe. It can be seen from Fig. 2 that for all the 53 atoms the majority of $h(0)$ comes from a few pairs of inner subshells, 1*s*1*s*, 1*s*2*s*, 1*s*2*p*, and 2*p*2*p*, regardless of their electronic configurations, where the magnitude of each contribution to $h(0)$ decreases in the order given above. Though the 1*s*1*s* subshell-pair contribution decreases gradually with increasing *Z*, it amounts to about 56% even for Xe atom. Thus, the 1*s*1*s* subshell pair is found to give the largest contribution to $h(0)$ for all the 53 atoms, from which it follows that $h(0)$ is proportional to Z^3 approximately [13]. The main reason for the predominant 1*s*1*s* contribution is that the electrons in the 1*s*1*s* subshell pair are confined in a very small space around the nucleus compared with the electrons in other subshell pairs, and hence the probability of finding two electrons at the same position is largest for the 1*s*1*s* subshell pair.

The electron-electron coalescence $\bar{h}(0)$ and counterbalance $\bar{d}(0)$ densities and the average one-electron density $<\gamma>$ in momentum space are given in Table 3 for the atoms He to Xe in their ground state. Since the Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, the counterparts of Eq. (4),

$$\bar{h}(0) \le \frac{1}{4}<\gamma> \quad \text{and} \quad \bar{h}(0) \le \frac{1}{8}\bar{d}(0) , \tag{14}$$

hold in momentum space. The inequalities (14) are verified numerically in Table 3. Figure 3 shows $8\bar{h}(0)$, $\bar{d}(0)$, and $2<\gamma>$ as a function of *Z*. In contrast to a smooth *Z*-dependence of the position-space counterparts, the behaviors of $\bar{h}(0)$, $\bar{d}(0)$, and $<\gamma>$ in momentum space are not simple against *Z*. However, the behaviors of these three densities have a few common features. First, there is a steep rise when we move from the group 1 atom to the group 2 atom for the second- through fifth-period. Second, within the second- and third-periods, the $8\bar{h}(0)$, $\bar{d}(0)$, and $2<\gamma>$ values have a trend to decrease from the group 2 atom to the group 18 atom, although it is subject to exceptions. Third, the density values of the fourth- and fifth-period atoms with a singly-occupied *s* orbital are smaller than those of other atoms with a doubly-occupied *s* orbital in the same period. The Pd atom (*Z*=46) with $5s^0 4d^{10}$ configuration also belongs to this group.

Figure 4 depicts main subshell-pair contributions to $\bar{h}(0)$, where we have selected contributions having more than 10% of the total value. The symbols *s*, *p*, and *d* stand respectively for the outermost subshell (*i.e.*, the occupied subshell with the largest principal quantum number) of each symmetry, and *s'* means the second outermost *s* subshell. We can see from Fig. 4 that the electron-electron coalescence density $\bar{h}(0)$ in momentum space is governed by a few pairs of outermost subshells, and depends largely on the electronic configuration of each atom. In momentum space, the electrons in an

outermost subshell pair are confined in a small *momentum* space around the origin **p=0**, and therefore the probability of finding two electrons at the same momentum is largest for an outermost subshell pair compared with an inner subshell pair. On the basis of dominant subshell-pair contributions to $\bar{h}(0)$, the atoms He to Xe can be classified into five types:

(i) For the group 1 atoms with a singly-occupied *s* orbital, $\bar{h}(0)$ comes mainly from *ss'*, *s'p*, and *pp* subshell pairs. The last two contributions do not exist for the Li atom.

(ii) For the group 13-18 atoms with an s^2p^n configuration (n=1-6), the *ss*, *sp*, and *pp* subshell pairs give predominant contributions. The relative contribution of the *ss* pair decreases with increasing n. The *pp* contribution appears only for n=4-6, since for n=1-3, the electrons have parallel spins in the ground *LS* term and $\delta_{m_{sj}m_{sk}}=1$ in Eq. (5). The *sp* contribution keeps almost the same relative significance for n=1-6.

(iii) For the group 2-12 atoms with an s^2d^n configuration (n=0-10), only the *ss* subshell pair gives a major contribution to $\bar{h}(0)$.

(iv) The density $\bar{h}(0)$ of the four transition atoms Cu, Ru, Rh, and Ag with s^1d^n configuration contains *pd*, *dd*, and *s'd* subshell-pairs, arising from the 3*d* or 4*d* subshell, as main contributions. The Pd atom with $5s^04d^{10}$ configuration belongs to this group, if *s'd* is replaced with *sd*.

(v) The three transition atoms Cr, Nb, and Mo with the same electronic configuration s^1d^n as the type (iv) atoms, however, do not have any *dd* contributions. Since the *d* electrons in these atoms have parallel spins, it results that $\delta_{m_{sj}m_{sk}}=1$ in Eq. (5) as seen for some of the type (ii) atoms. Thus, the contributions from the *pd* and *pp* subshell pairs are important.

In a marked contrast to the electron-electron coalescence density $h(0)$ in position space, the momentum-space counterpart $\bar{h}(0)$ has an intimate relation to the detailed electronic structure of valence subshells. We therefore expect the applicability of the quantity $\bar{h}(0)$ to chemical problems where valence electrons receive more interest than core electrons, but we have to await further examinations.

1-3-5. CONCLUSION

Within the Hartree-Fock framework, we have shown that the electron-electron coalescence and counterbalance densities have the same theoretical structure in both position and momentum spaces. For the atoms He through Xe in their ground state, we have evaluated these densities as the sum of subshell-pair contributions using the numerical Hartree-Fock method. In position space, the electron-electron coalescence and counterbalance densities increase gradually with increasing *Z*. The position-space coalescence density is strongly sensitive to electron pairs in inner subshells, particularly in the 1*s* subshell, for all the 53 atoms. In momentum space, however, the electron-electron coalescence and counterbalance densities are not simple functions of *Z* but reflect sensitively the electronic configuration of an atom. The momentum-space electron-electron coalescence density has been found to be sensitive mainly to electron pairs in outermost subshells.

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Table 1. Values of A_{jk} for s, p, and d orbitals. The values of l_j and l_k are given by the symbols s, p, and d of the orbitals. In cases with two $\pm$ signs, the signs can be combined in any of the four possible ways.

$l_j\, l_k$	m_j	m_k	A_{jk}
ss	0	0	$1/(4\pi)$
sp	0	± 1	$1/(4\pi)$
	0	0	$1/(4\pi)$
pp	± 1	± 1	$3/(10\pi)$
	± 1	0	$3/(20\pi)$
	0	0	$9/(20\pi)$
sd	0	± 2	$1/(4\pi)$
	0	± 1	$1/(4\pi)$
	0	0	$1/(4\pi)$
pd	± 1	± 2	$9/(28\pi)$
	± 1	± 1	$3/(14\pi)$
	± 1	0	$5/(28\pi)$
	0	± 2	$3/(28\pi)$
	0	± 1	$9/(28\pi)$
	0	0	$11/(28\pi)$
dd	± 2	± 2	$5/(14\pi)$
	± 2	± 1	$5/(28\pi)$
	± 2	0	$5/(28\pi)$
	± 1	± 1	$5/(14\pi)$
	± 1	0	$5/(28\pi)$
	0	0	$15/(28\pi)$

Table 2. Numerical Hartree-Fock values for $h(0)$, $d(0)$, and $<\rho>$ in position space. A(±n) means $A\times 10^{\pm n}$.

Z	Atom	$h(0)$	$d(0)$	$<\rho>$
2	He	1.906040(-1)	1.524832	7.624160(-1)
3	Li	7.842886(-1)	6.274309	3.139115
4	Be	2.099065	1.679252(+1)	8.396258
5	B	4.379150	3.550797(+1)	1.753500(+1)
6	C	7.928996	6.550878(+1)	3.182249(+1)
7	N	1.306075(+1)	1.102036(+2)	5.260775(+1)
8	O	2.029904(+1)	1.746705(+2)	8.149892(+1)
9	F	2.997695(+1)	2.631421(+2)	1.200779(+2)
10	Ne	4.254223(+1)	3.808466(+2)	1.701689(+2)
11	Na	5.849903(+1)	5.319756(+2)	2.339975(+2)
12	Mg	7.830212(+1)	7.215920(+2)	3.132085(+2)
13	Al	1.022808(+2)	9.538015(+2)	4.091282(+2)
14	Si	1.309020(+2)	1.233823(+3)	5.236336(+2)
15	P	1.646285(+2)	1.566934(+3)	6.585954(+2)
16	S	2.039659(+2)	1.958636(+3)	8.159280(+2)
17	Cl	2.493911(+2)	2.414632(+3)	9.975990(+2)
18	Ar	3.014123(+2)	2.940831(+3)	1.205649(+3)
19	K	3.606117(+2)	3.542482(+3)	1.442448(+3)
20	Ca	4.274574(+2)	4.225141(+3)	1.709829(+3)
21	Sc	5.015596(+2)	4.984803(+3)	2.006292(+3)
22	Ti	5.838141(+2)	5.831902(+3)	2.335441(+3)
23	V	6.747441(+2)	6.772562(+3)	2.699470(+3)
24	Cr	7.740348(+2)	7.803559(+3)	3.097413(+3)
25	Mn	8.845149(+2)	8.956925(+3)	3.540041(+3)
26	Fe	1.004904(+3)	1.021703(+4)	4.021167(+3)
27	Co	1.136048(+3)	1.159483(+4)	4.545314(+3)
28	Ni	1.278494(+3)	1.309678(+4)	5.114638(+3)
29	Cu	1.431672(+3)	1.471603(+4)	5.726691(+3)
30	Zn	1.599404(+3)	1.649831(+4)	6.397615(+3)
31	Ga	1.780268(+3)	1.842805(+4)	7.121076(+3)
32	Ge	1.975039(+3)	2.051416(+4)	7.900179(+3)
33	As	2.184289(+3)	2.276356(+4)	8.737219(+3)
34	Se	2.408589(+3)	2.518277(+4)	9.634402(+3)
35	Br	2.648530(+3)	2.777946(+4)	1.059414(+4)
36	Kr	2.904710(+3)	3.056102(+4)	1.161884(+4)
37	Rb	3.177814(+3)	3.353258(+4)	1.271126(+4)
38	Sr	3.468357(+3)	3.670120(+4)	1.387343(+4)
39	Y	3.775873(+3)	4.006201(+4)	1.510351(+4)
40	Zr	4.101403(+3)	4.362747(+4)	1.640567(+4)
41	Nb	4.444712(+3)	4.739536(+4)	1.777909(+4)
42	Mo	4.808056(+3)	5.139192(+4)	1.923270(+4)
43	Tc	5.192318(+3)	5.562779(+4)	2.076995(+4)
44	Ru	5.595136(+3)	6.007543(+4)	2.238084(+4)
45	Rh	6.019956(+3)	6.477571(+4)	2.408001(+4)
46	Pd	6.465405(+3)	6.971255(+4)	2.586162(+4)
47	Ag	6.935153(+3)	7.492982(+4)	2.774061(+4)
48	Cd	7.428463(+3)	8.041807(+4)	2.971385(+4)
49	In	7.945231(+3)	8.617976(+4)	3.178093(+4)
50	Sn	8.486431(+3)	9.222563(+4)	3.394574(+4)
51	Sb	9.052684(+3)	9.856325(+4)	3.621078(+4)
52	Te	9.644584(+3)	1.051994(+5)	3.857836(+4)
53	I	1.026278(+4)	1.121427(+5)	4.105112(+4)
54	Xe	1.090790(+4)	1.194011(+5)	4.363159(+4)

Table 3. Numerical Hartree-Fock values for $\bar{h}(0)$, $\bar{d}(0)$, and $<\gamma>$ in momentum space. A(±n) means $A \times 10^{\pm n}$.

Z	Atom	$\bar{h}(0)$	$\bar{d}(0)$	$<\gamma>$
2	He	5.227634(-2)	4.182107(-1)	2.091054(-1)
3	Li	5.621598(-2)	4.497279(-1)	2.817850
4	Be	9.017376(-1)	7.213901	3.606950
5	B	5.341718(-1)	6.777763	2.311092
6	C	3.505749(-1)	5.253693	1.621304
7	N	2.477194(-1)	4.074051	1.219273
8	O	2.422993(-1)	3.817125	1.050851
9	F	2.206360(-1)	3.381470	9.034653(-1)
10	Ne	1.952452(-1)	2.940108	7.809809(-1)
11	Na	1.915248(-1)	2.468803	3.943123
12	Mg	1.623668	1.369023(+1)	6.494672
13	Al	1.281588	1.799804(+1)	5.743769
14	Si	9.982960(-1)	1.613866(+1)	4.831834
15	P	7.973418(-1)	1.385073(+1)	4.127132
16	S	8.923539(-1)	1.415341(+1)	3.919121
17	Cl	8.826776(-1)	1.338274(+1)	3.624188
18	Ar	8.304774(-1)	1.226868(+1)	3.321910
19	K	8.117963(-1)	1.093112(+1)	8.710898
20	Ca	3.507666	3.179204(+1)	1.403067(+1)
21	Sc	2.981726	2.738318(+1)	1.195402(+1)
22	Ti	2.635225	2.434077(+1)	1.058272(+1)
23	V	2.360882	2.188685(+1)	9.505687
24	Cr	4.396369(-1)	6.653380	3.965136
25	Mn	1.955329	1.818473(+1)	7.917729
26	Fe	1.788039	1.666828(+1)	7.206050
27	Co	1.650423	1.539979(+1)	6.629462
28	Ni	1.530472	1.428766(+1)	6.133733
29	Cu	3.442297(-1)	4.848305	2.980463
30	Zn	1.334066	1.245074(+1)	5.336262
31	Ga	1.293751	1.874983(+1)	5.783383
32	Ge	1.158621	1.897282(+1)	5.565788
33	As	1.032628	1.800833(+1)	5.284922
34	Se	1.245516	1.981538(+1)	5.451668
35	Br	1.320446	2.006055(+1)	5.416957
36	Kr	1.321922	1.955142(+1)	5.287687
37	Rb	1.345485	1.852499(+1)	1.184885(+1)
38	Sr	4.748083	4.501780(+1)	1.899233(+1)
39	Y	3.994346	3.908635(+1)	1.606095(+1)
40	Zr	3.543539	3.528058(+1)	1.430012(+1)
41	Nb	9.914573(-1)	1.536436(+1)	6.766255
42	Mo	9.114829(-1)	1.431043(+1)	6.251337
43	Tc	2.723067	2.778212(+1)	1.117906(+1)
44	Ru	9.161103(-1)	1.358399(+1)	5.796848
45	Rh	8.920211(-1)	1.303959(+1)	5.604157
46	Pd	9.068429(-1)	1.334449(+1)	3.627372
47	Ag	8.260112(-1)	1.187813(+1)	5.272984
48	Cd	2.078395	2.128471(+1)	8.313579
49	In	2.061967	2.978349(+1)	9.037582
50	Sn	1.920834	3.095423(+1)	8.982102
51	Sb	1.775089	3.031117(+1)	8.792788
52	Te	2.128698	3.367295(+1)	9.229066
53	I	2.286972	3.473581(+1)	9.360271
54	Xe	2.331602	3.456309(+1)	9.326408

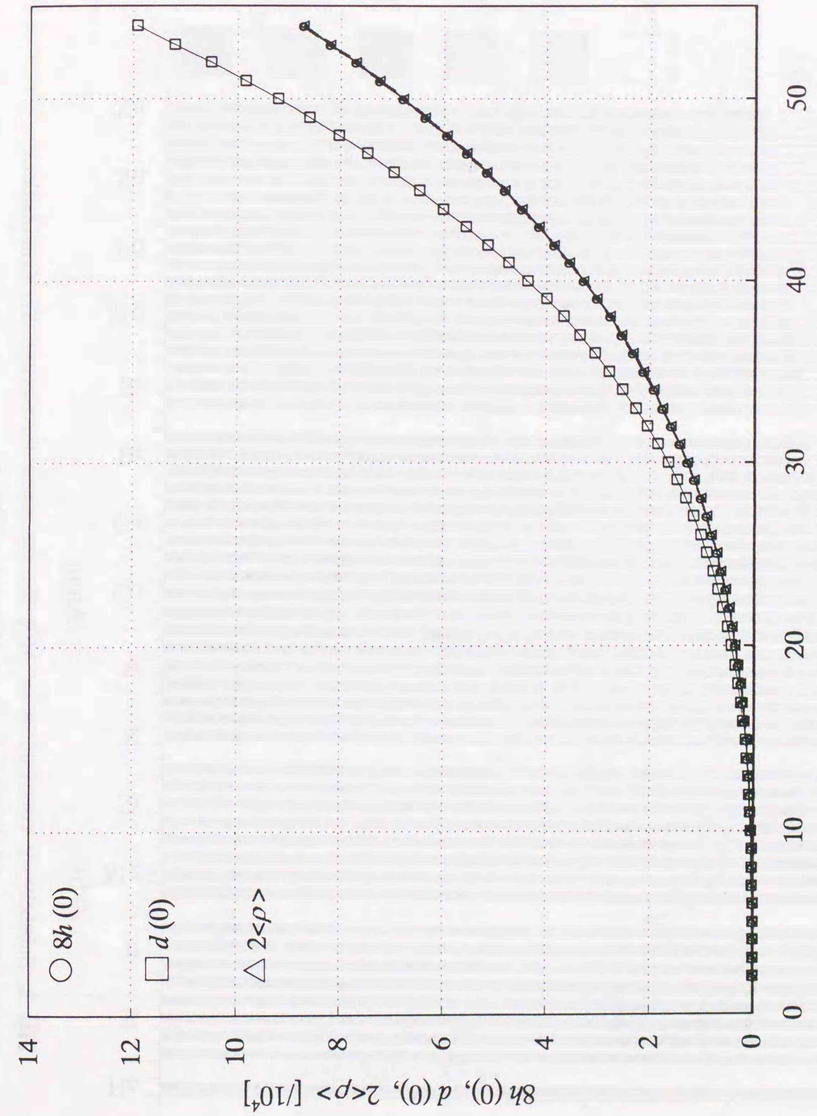


Fig. 1. Behavior of $8\bar{h}(0)$, $\bar{d}(0)$, and $2<\rho>$ as a function of atomic number.

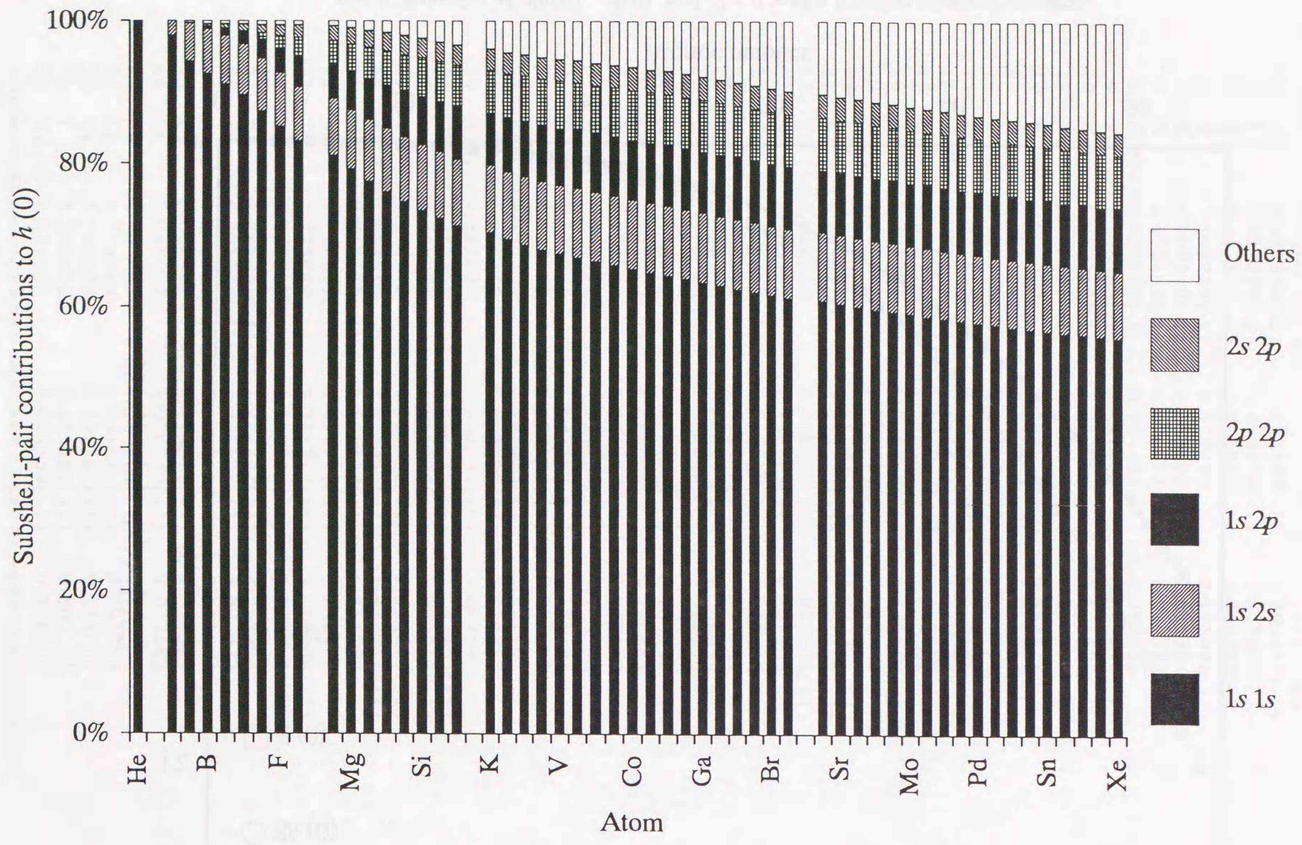


Fig. 2. Subshell-pair contributions to $h(0)$ for the atoms He through Xe. Contributions smaller than that of $2s2p$ subshell pair are collected as 'Others'.

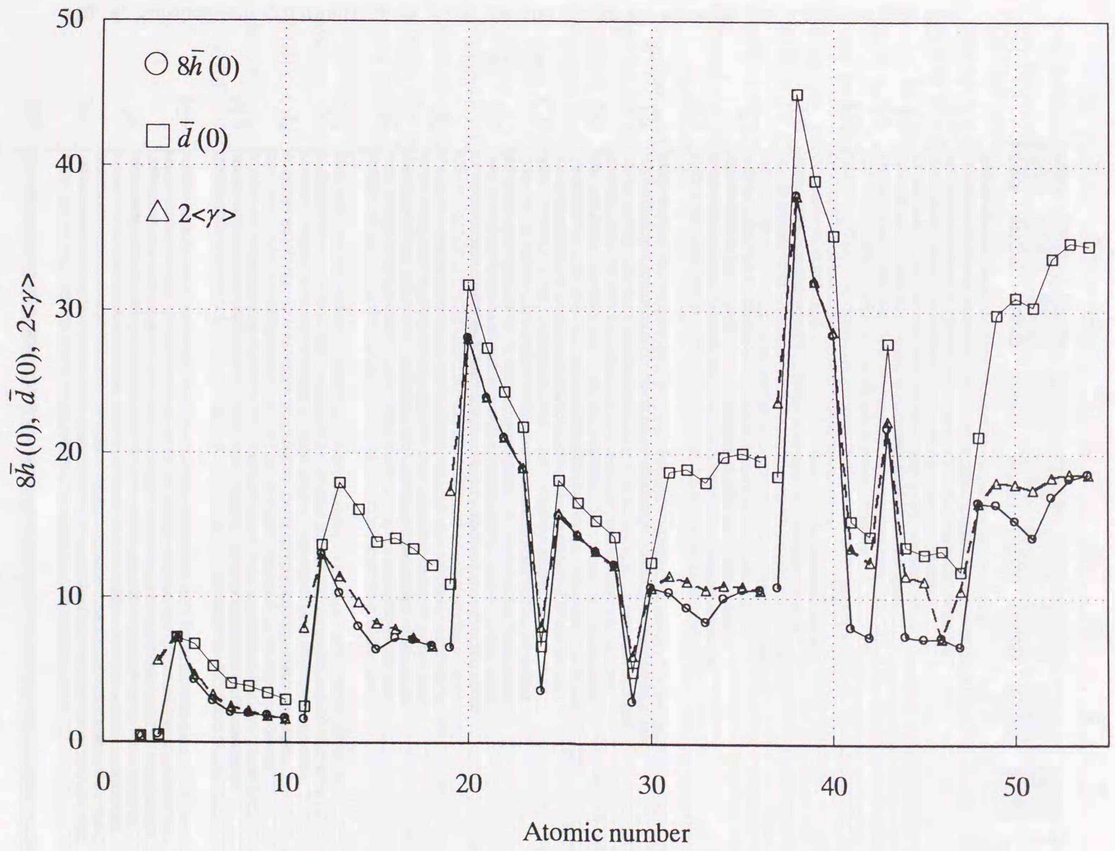


Fig. 3. Behavior of $8\bar{h}(0)$, $\bar{d}(0)$, and $2<\gamma>$ as a function of atomic number.

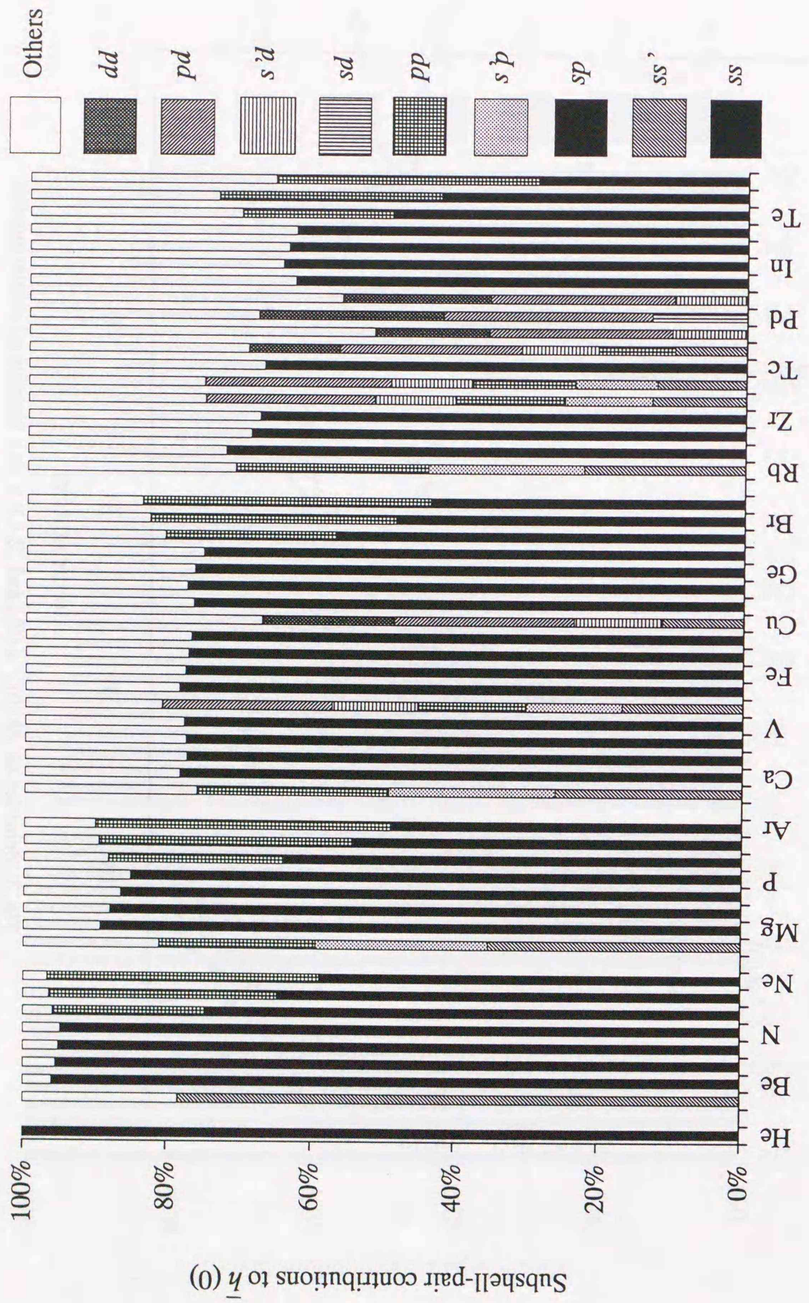


Fig. 4. Subshell-pair contributions to $\bar{h}(0)$ for the atoms He through Xe. Contributions less than 10% of the total $\bar{h}(0)$ value are collected as 'Others'.

PART 1.
CHAPTER 4.

SUMMARY

The purpose of Part 1 is to examine the electron-electron coalescence and counterbalance densities, as well as the average electron density, for atoms in position and momentum spaces based on the numerical Hartree-Fock calculations. We have also clarified several relations among these densities in both spaces, and analyzed the dependence of these densities on atomic number Z based on the decomposition of total density into subshell-pair contributions.

In Chapter 2, the electron-electron coalescence $I(\mathbf{0}) = h(0)$ and counterbalance $E(\mathbf{0}) = d(0)$ densities, as well as the average electron density $<\rho>$, in position space have been derived for the atoms He through Ne in their experimental ground state, by using the numerical Hartree-Fock calculations. We have found $I(\mathbf{0}) \cong <\rho>/4$ and $E(\mathbf{0}) \cong 2<\rho>$ are good approximations within the Hartree-Fock theory. The equality holds only for He, Be, and their isoelectronic species, where only s orbitals constitute a closed ^1S shell.

In Chapter 3, the electron-electron coalescence and counterbalance densities, together with the average electron densities, are reported in position and momentum spaces for the atoms He through Xe in their ground state. The numerical Hartree-Fock method has been used to calculate these densities. In position space, the electron-electron coalescence $h(0)$ and counterbalance $d(0)$ densities, and the average electron density $<\rho>$ increase monotonically with increasing Z. An approximation $h(0) \cong <\rho>/4$ is found to be very accurate for all the atoms He through Xe within the Hartree-Fock framework. Thus, the approximate relation allows us to estimate an electron-electron coalescence density from an average electron density even for larger atoms. The position-space coalescence density is strongly influenced by electron pairs in inner subshells, particularly in the 1s subshell, for all the 53 atoms. In momentum space, the electron-electron coalescence $\bar{h}(0)$ and counterbalance $\bar{d}(0)$ densities, and the average electron density $<\gamma>$ show periodic behaviors as a function of Z. The relations $\bar{h}(0) \le <\gamma>/4$ and $\bar{h}(0) \le \bar{d}(0)/8$ hold for all the atoms in momentum space. A decomposition of total density into subshell-pair contributions shows that the electron-electron coalescence density $\bar{h}(0)$ is governed by a few pairs of outermost subshells.

PART 2.
CHAPTER 1.

INTRODUCTION

For an N-electron system, P.-O. Löwdin defined [1] the two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ to calculate the expectation value of a two-electron operator. The two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is the probability density that electron 1 lies at $\mathbf{r}_1$ and electron 2 lies at $\mathbf{r}_2$, at the same time. It is difficult to visualize the two-electron density, because $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is a complicated function of six variables. One way to solve the problem is to separate the motion of two electrons into the relative (intracule) and center-of-mass (extracule) motions. The intracule $I(\mathbf{u})$ and extracule $E(\mathbf{R})$, introduced by Coleman [2], are the probability density functions for the relative $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$ and center-of-mass $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$ vectors, respectively. The pioneering work on the intracule density was done by Coulson and Neilson [3] who studied the Coulomb hole in the helium ground state. Since then the intracule and extracule densities of many atomic and molecular systems have been studied for the chemical and physical problems [see, for example, Refs. 4 and 5]. In momentum space, the corresponding intracule $\bar{I}(\mathbf{v})$ and extracule $\bar{E}(\mathbf{P})$ densities are also introduced [4], and represent the probability density functions for the relative $\mathbf{v}$ and center-of-mass $\mathbf{P}$ momentum vectors, respectively. The momentum-space intracule and extracule densities have also been used [4] for the investigations on the same problems as in position space, but almost all the studies are limited to light atoms and a few simple molecules.

The purpose of this part is to present a theory of constructing the intracule and extracule densities for atoms and atomic ions in position and momentum spaces. The wave function is given by a Slater determinant or a linear combination of Slater determinants. We apply the theory to neutral atoms, and examine the intracule and extracule densities in position and momentum spaces based on the Hartree-Fock calculations.

In Chapter 2, we present [6] the spherically averaged intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space for the atoms from He to Xe in their ground state. The variables u and v are the interelectronic position and momentum distances of any pair of electrons, respectively. The numerical Hartree-Fock method is used to calculate these densities. The spherical averages $h(u)$ and $\bar{h}(v)$ represent probability densities of finding interelectronic position u and momentum v of an electron pair, respectively. In position space, the intracule density $h(u)$ is a monotonically decreasing function for all the atoms. The momentum-space intracule densities $\bar{h}(v)$ are found to be classified into three types according to the number of local maxima and their locations. These different behaviors of the densities $h(u)$ and $\bar{h}(v)$ are studied in detail based on the contributions of electrons in a pair of atomic spinorbitals and subshells.

In Chapter 3, two methods are presented [7] for the examination of interelectronic moments $<u^k>$ in position space and $<v^k>$ in momentum space of atomic systems, where $<>$ stand for the expectation value. The first method uses the spherically averaged intracule density, while the second method uses their characteristic functions. The two methods are applied to the neutral atoms from He to Xe in their ground state. The moments $<u^k>$ with $k=-2$ to $+4$ and $<v^k>$ with $k=-2$ to $+3$ are calculated based on the numerical Hartree-Fock calculations. Some trends of these interelectronic moments are also discussed as a function of atomic number Z.

In Chapter 4, spherically averaged extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space are [8] constructed and examined systematically for the atoms from He to Xe in their ground state within the Hartree-Fock framework. The $d(R)$ and $\bar{d}(P)$ represent probability densities of finding center-of-mass radii R and P in position and momentum spaces of an electron pair, respectively. In the Hartree-Fock approximation, the individual spin-orbital-pair component of the extracule density has a definite relation with the corresponding one of the intracule density, although the total extracule and intracule densities are not related in a simple manner. The position-space extracule density $d(R)$ is a monotonically decreasing function for all the atoms. In momentum space, however, the extracule densities $\bar{d}(P)$ are found to be classified into two types according to the location of a maximum. These different behaviors of the densities $d(R)$ and $\bar{d}(P)$ are studied in detail based on the contributions of electrons in a pair of atomic subshells and spin orbitals.

In Chapter 5, we report [9] the extracule moments $<R^k>$ in position space and $<P^k>$ in momentum space of atomic systems. The variables R and P are, respectively, the position and momentum distances between the center-of-mass of any pair of electrons and the coordinate origin. For the neutral atoms from He to Xe in their ground state, the moments $<R^k>$ with $k=-2$ to $+4$ and $<P^k>$ with $k=-2$ to $+3$ are computed based on the numerical Hartree-Fock calculations. These extracule moments are pointed out to have intimate relations with their partner intracule moments.

In Chapter 6, we present [10] a unified method which is presented for the evaluation of the intracule and extracule densities in both position and momentum spaces for wave functions expressed as a linear combination of Slater determinants. Detailed expressions are developed for atomic systems where angular integrations can be performed analytically. Interesting relations between atomic intracule and extracule densities and between their moments are discussed. An illustrative application of the result is given for the $1s2p$ ^1P and ^3P states of the helium atom. We report the singlet-triplet differences in the extracule densities and in the momentum-space intracule density.

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PART 2.
CHAPTER 2.

HARTREE-FOCK INTRACULE DENSITIES

2-2-1. INTRODUCTION

The intracule (relative motion) and extracule (center-of-mass motion) densities are a couple of particle-pair densities. For atoms and molecules, the elucidation of the relative motion between a pair of electrons is a keystone in profound understanding of their electronic structures. Therefore, the intracule density, in either its three-dimensional or spherically-averaged form, is a convenient and powerful tool for such purpose. In position space, the three-dimensional intracule density $I(\vec{u})$ and its spherical average $h(u)$ of an N-electron system $(N \geq 2)$ are defined [1] by

$$I(\vec{u}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{u} - (\vec{r}_j - \vec{r}_k)] \right\rangle , \tag{1a}$$

$$h(u) \equiv \frac{1}{4\pi} \int d\Omega_u I(\vec{u}) , \tag{1b}$$

where $\vec{u} \equiv (u, \Omega_u)$, $\delta(\vec{r})$ is the three-dimensional Dirac delta function, and the angular brackets $\langle\ \rangle$ stand for the expectation value. The intracule densities $I(\vec{u})$ and $h(u)$ represent the probability density functions for the relative *position* vector $\vec{u}$ and its magnitude u, respectively. The two densities are normalized to the number of electron pairs:

$$\int d\vec{u}\, I(\vec{u}) = 4\pi \int_0^\infty du\, u^2\, h(u) = N(N-1)/2 . \tag{1c}$$

The momentum-space counterparts are defined, analogously to Eq.(1a-c), by

$$\bar{I}(\vec{v}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{v} - (\vec{p}_j - \vec{p}_k)] \right\rangle , \tag{2a}$$

$$\bar{h}(v) \equiv \frac{1}{4\pi} \int d\Omega_v I(\vec{v}) , \tag{2b}$$

$$\int d\vec{v}\, \bar{I}(\vec{v}) = 4\pi \int_0^\infty dv\, v^2\, \bar{h}(v) = N(N-1)/2 . \tag{2c}$$

where $\vec{v} \equiv (v, \Omega_v)$. The intracule densities $\bar{I}(\vec{v})$ and $\bar{h}(v)$ are the probability density functions for the relative *momentum* vector $\vec{v}$ and its magnitude v, respectively.

The intracule densities in position space have been used for the analysis of several physical and chemical problems such as Hund's rules [2,3], chemical bonds [4-9], Coulomb holes [10-16], and correlation density functionals [17,18]. The intracule densities in momentum space have been applied [19-26] to the Coulomb correlation problem. However, these studies were carried out only on a limited number of light atoms and diatomic molecules based on basis-set-expansion wave functions, some of which may not be sufficiently accurate.

In Chapter 2, we report accurate Hartree-Fock intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space for a series of 53 atoms from He (Z=2) to Xe

(Z=54) in their ground state, where Z stands for atomic number. The numerical Hartree-Fock method is used instead of the conventional Roothaan-Hartree-Fock or basis-set-expansion method. Systematic analysis of the resultant intracule densities shows that in position space, the intracule density $h(u)$ is a unimodal function with a maximum at $u = 0$ for all the 53 atoms. In momentum space, on the other hand, the intracule densities $\bar{h}(v)$ are found to be classified into three types; (i) 18 atoms have a unimodal density with a maximum at $v = 0$, (ii) 32 atoms have a unimodal density with a local minimum at $v = 0$ and a maximum at $v > 0$, and (iii) 3 atoms have a bimodal density with a primary maximum at $v = 0$ and a secondary maximum at $v > 0$. These different features of the densities $h(u)$ and $\bar{h}(v)$ are discussed in detail based on the contributions of electrons in a pair of atomic subshells and of atomic spinorbitals. Hartree atomic units are used throughout this chapter.

2-2-2. COMPUTATIONAL METHOD

2-2-2-1. THEORETICAL GROUND

We consider the case where a Hartree-Fock wave function of an N-electron atom or atomic ion is expressed by a single Slater determinant of N spinorbitals $\psi_j(\vec{r})\eta_j(\sigma)$ and where the spatial orbital $\psi_j(\vec{r})$ has a form,

$$\psi_j(\vec{r}) = R_j(r) Y_{l_j m_j}(\Omega_r), \tag{3}$$

in which $Y_{lm}(\Omega)$ is a spherical harmonic and $\vec{r} = (r, \Omega_r)$. Then, the Condon-Slater rule (see, *e.g.*, [27]) rewrites the spherically-averaged intracule density $h(u)$, defined by Eq. (1b), as a sum of contributions $h_{jk}(u)$ from pairs of atomic spinorbitals j and k:

$$h(u) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} h_{jk}(u), \tag{4}$$

$$h_{jk}(u) = (2\pi^2)^{-1} \int_0^\infty ds\, s^2 j_0(us) H_{jk}(s), \tag{5}$$

where $j_l(x)$ is the l-th order spherical Bessel function of the first kind and

$$H_{jk}(s) = H_{jj,kk}(s) - \delta_{m_{sj} m_{sk}} H_{kj,kj}(s), \tag{6}$$

in which the Kronecker delta $\delta_{m_{sj} m_{sk}}$ is unity if the two spinorbitals j and k have the same spin and zero if j and k have different spins. The explicit forms of $H_{jj,kk}$ and $H_{kj,kj}$ appeared in Eq. (6) are obtained [28] as

$$H_{jj,kk}(s) = \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1) a^l(l_j m_j; l_k m_k) W^*_{ljj}(s) W_{lkk}(s), \tag{7a}$$

$$H_{kj,kj}(s) = \sum_{l=|l_j - l_k|}^{l_j + l_k} (2l+1) b^l(l_j m_j; l_k m_k) W^*_{lkj}(s) W_{lkj}(s), \tag{7b}$$

where the summations run over every other integers between the specified values, the symbols $a^k(lm;l'm')$ and $b^k(lm;l'm')$ are Condon-Shortley parameters [29], and

$$W_{ljk}(s) \equiv \int_0^\infty dr\, r^2 j_l(sr)\, R^*_j(r) R_k(r) = W^*_{lkj}(s). \tag{8}$$

A momentum-space N-electron wave function is given by the $3N$-dimensional Fourier transformation of the corresponding position-space wave function. Then the Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, provided that a position orbital $\psi_k(\vec{r})$ is replaced with the corresponding momentum orbital

$$\phi_k(\vec{p}) = (2\pi)^{-3/2} \int d\vec{r}\, \exp(-i\vec{p}\cdot\vec{r})\, \psi_k(\vec{r}). \tag{9}$$

Expanding $\exp(-i\vec{p}\cdot\vec{r})$ in Eq. (9) by means of plane waves [30] and integrating over the angular variable Ω_r, we find the momentum orbital corresponding to Eq. (3) to be

$$\phi_k(\vec{p}) = P_k(p) Y_{l_k m_k}(\Omega_p), \tag{10}$$

where $\vec{p} = (p, \Omega_p)$ and

$$P_k(p) = (-i)^{l_k} \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2 j_{l_k}(pr)\, R_k(r). \tag{11}$$

Consequently, theoretical structures of the spherically-averaged intracule density are the same in position and momentum spaces, and all the position-space results hold in momentum space as well, if we replace $h(u)$ with $\bar{h}(v)$ and $R_k(r)$ with $P_k(p)$.

2-2-2-2. NUMERICAL PROCEDURE

Each of atomic LS multiplets is expressed in general by a linear combination of a finite number of Slater determinants in the Hartree-Fock theory, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively. For the neutral atoms He (Z=2) through Xe (Z=54) in their experimental ground state [31], we have first examined the structure of the corresponding Hartree-Fock wave functions and confirmed that among $(2L+1)(2S+1)$ multiplets there exists at least one state with a set of specific z-component M_L and M_S values of L and S that results in a single determinant wave function, to which our method described in Subsection 2-2-2-1 can be applied.

For these ground LS terms of the 53 atoms, the radial functions $R_j(r)$ in position space have been generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [32]. A table of the ground electronic configurations and LS terms examined in this study is found in Ref. [33]. Then the products $r^2 R_j(r) R_k(r)$ of two radial functions have been numerically Hankel-transformed to obtain $W_{ljk}(s)$, by using the algorithm of Talman [34]. Following Eqs.(6), (7a), and (7b), we obtain the function $H_{jk}(s)$ as the sum of products of two $W_{ljk}(s)$ with appropriate coefficients. The parameters a^k and b^k have been taken from the Slater's book [35]. An additional Hankel transformation [Eq.(5)] of the function $H_{jk}(s)$ gives the spherically-averaged intracule density $h_{jk}(u)$.

In momentum space, the position-space radial functions $R_j(r)$, generated by numerical Hartree-Fock calculations, have been first Hankel-transformed to obtain the momentum-space radial functions $P_j(p)$ according to Eq. (11). Then the same procedure as in position space has been applied to derive $\bar{h}_{jk}(v)$.

2-2-3. RESULTS AND DISCUSSION

2-2-3-1. INTRACULE DENSITY IN POSITION SPACE

Figure 1 exemplifies the position-space intracule density $h(u)$ for several atoms in their ground state. Note that in this Section the densities are normalized to unity instead of $N(N-1)/2$ for all the 53 atoms, in order to avoid large numbers and to facilitate mutual comparison. The intracule densities of F and Al atoms decrease smoothly as u increases. The densities of Mn, Kr, and Cd atoms are also monotonically decreasing functions, but have shoulders. In the case of Kr atom, for example, a shoulder is observed in the region $0.05 \le u \le 0.15$. Analogous and systematic examinations show that the intracule density $h(u)$ in position space is a unimodal function with a maximum at $u = 0$ for all the 53 atoms considered in this study.

Table 1 summarizes the maximum height $h_{\max} = h(0)$ of $h(u)$. The maxima $h_{\max}$ increase gradually with increasing Z, and a formula $h(0) \cong 0.0424Z^{2.3}/(Z-1)$ is found to be an excellent approximation. The intracule density $h(u)$ at $u = 0$ is called [36] the electron-electron coalescence density and represents the probability density of finding any two electrons at the same position. Detailed discussion on the property of the electron-electron coalescence density $h(0)$ is found in Refs.[36-39]. The exact intracule density $h(u)$ must satisfy [13] the cusp condition $h'(0) = h(0)$, where $h'(u) = dh(u)/du$. However, we find from Eq.(5) that $h'(0) = 0$ within the Hartree-Fock framework, and hence the Hartree-Fock intracule density does not satisfy the correct electron-electron cusp condition.

A decomposition of the intracule density into subshell-pair contributions shows that for all the atoms, the largest contributions to $h(u)$ come from the four innermost subshell-pairs $1s1s$, $1s2p$, $2p2p$, and $1s2s$, which consist of 1, 12, 15, and 4 spinorbital-pair contributions, respectively, when fully occupied. For the Kr atom (Z=36), Fig. 2 illustrates these four contributions out of the total 36 subshell-pair contributions. The $1s1s$ contribution is a unimodal function with a maximum at $u = 0$, and decreases rapidly compared with the other main subshell-pair contributions. The value of the $1s1s$ contribution at $u = 0$ is about six times larger than those of the remaining three contributions, and the $1s1s$ subshell-pair is seen to give a significant contribution in a small u region. On the other hand, the $1s2p$ and $2p2p$ contributions are unimodal functions with a maximum at $u = 0.0672$ and 0.0810, respectively, and these subshell-pairs contribute to $h(u)$ in the region where the $1s1s$ contribution is small. The smallest $1s2s$ contribution is a bimodal function with a primary maximum at $u = 0$ and a secondary maximum at $u = 0.1103$. Thus, the subshell-pair decomposition clarifies that a shoulder in $h(u)$ appears mainly when the $1s2p$ contribution is enough large as seen for Cd, Mn, and Kr atoms in Fig.1, whereas it does not appear when the contribution is small as seen for F and Al atoms.

Figure 3 depicts typical spinorbital-pair contributions $h_{jk}(u)$ to $h(u)$ in Kr atom, where a total of 630 spinorbital-pairs exists. Figure 3(a) shows the contributions from five spinorbital-pairs with *different* spins; $1s\alpha 1s\beta$, $1s\alpha 2s\beta$, $1s\alpha 2p_0\beta$, $2p_{-1}\alpha 2p_{+1}\beta$, and $2s\alpha 2p_0\beta$. The $1s\alpha 1s\beta$ pair gives a unimodal distribution with a maximum at $u = 0$, and its contribution is more than ten times larger than the other four contributions. The $1s\alpha 2s\beta$ contribution is a bimodal function with maxima at $u = 0$ and 0.1171. The

$1s\alpha 2p_0\beta$ contribution is unimodal with a maximum at u=0.0527. The last two spinorbital-pair contributions are small compared with the first three spinorbital-pairs. Figure 3(b) shows the contributions from four spinorbital-pairs with the *same* spin; $1s\alpha 2p_0\alpha$, $1s\alpha 2s\alpha$, $2p_{-1}\alpha 2p_{+1}\alpha$, and $2s\alpha 2p_0\alpha$. Note the different scales of the ordinates in Figs.3(a) and 3(b). All these four contributions have unimodal distributions with zero at $u = 0$ and with a maximum away from $u = 0$. The property $h_{jk}(0) = 0$ is valid for any contribution from spinorbitals j and k with the same spin, because a Hartree-Fock wave function properly takes into account the correlation motion between electrons with the same spin (Fermi hole). The Fermi hole in Hartree-Fock intracule densities is proved by the use of Eqs. (5)-(8) together with an identity,

$$\sum_{l=0}^{\min(2l_j,2l_k)} (2l+1)a^l(l_jm_j;l_km_k) = \sum_{l=|l_j-l_k|}^{l_j+l_k} (2l+1)b^l(l_jm_j;l_km_k) \ , \qquad (12)$$

for any l_j, m_j, l_k, m_k and the property [40] of the kernel of Hankel transformations

$$\int_0^\infty ds\, s^2 j_l(rs) j_l(r's) = \frac{\pi}{2r^2}\delta(r-r') \ . \qquad (13)$$

Since the essential feature of spinorbital-pair contributions shown in Fig. 3 for the Kr atom is the same for all the 53 atoms, we conclude that the position-space intracule density $h(u)$ is a unimodal function with a maximum at $u = 0$ due to the predominant $1s\alpha 1s\beta$ spinorbital-pair or $1s1s$ subshell-pair contribution.

2-2-3-2. INTRACULE DENSITY IN MOMENTUM SPACE

Figure 4 exemplifies the momentum-space intracule density $\bar{h}(v)$ for the same atoms examined in Fig.1 in position space. All the momentum-space densities are also normalized to unity. In contrast with a single common modality observed for the position-space densities, Fig.4 shows that in momentum space there are at least three different types of modality in the intracule densities depending on atoms. The intracule densities $\bar{h}(v)$ of Al and Mn atoms are unimodal functions with a maximum at $v = 0$. The intracule densities of F and Kr atoms are unimodal with a maximum at $v = 0.7892$ and at $v = 0.6395$, respectively. The intracule density for the Cd atom is bimodal with two maxima at $v = 0$ and 1.2081.

A systematic examination of all the 53 atoms concludes that the momentum-space intracule densities are classified into the following three types based on the number of local maxima and their locations:

Type A. Unimodal intracule density with a maximum at $v = 0$. The next 18 atoms have densities of this type: He, group 2 atoms, transition atoms (Sc-V, Mn-Ni, Y, and Zr) with a doubly-occupied s orbital, and group 13 atoms.

Type B. Unimodal intracule density with a local minimum at $v = 0$ and a maximum at $v > 0$. The next 32 atoms have Type B densities: group 1 atoms, transition atoms (Cr, Cu, Nb, Mo, Ru, Rh, and Ag) with a singly-occupied s orbital, Pd, group 14-17 atoms, and group 18 atoms except for He.

Type C. Bimodal intracule density with a primary maximum at $v = 0$ and a secondary maximum at $v > 0$. It also has a local minimum between the two maxima. Three atoms Tc, Zn, and Cd have Type C densities.

Table 2 summarizes the above classification of the momentum-space intracule density $\bar{h}(v)$ together with the maximal subshell-pair contribution to it. If the subshell-pairs in the table are grouped, five different subshell-pairs *SS*, *SS'*, *SP*, *PP*, and *PD* appear as maximal contributions, where the symbols *S*, *P*, and *D* denote the outermost subshells of the respective symmetries, and the symbol *S'* the second outermost *s* subshell. Thus, it is immediately seen that the momentum-space intracule density $\bar{h}(v)$ is governed by a few outermost subshell-pairs and depends explicitly on the valence configuration of an atom, in marked contrast to the position-space intracule density.

Table 3 tabulates the maximum value $\bar{h}_{\max} \equiv \bar{h}(v_{\max})$ of $\bar{h}(v)$ and its location $v_{\max}$ which characterize the distribution of the momentum-space intracule density. When atomic number increases within a period, there is a trend that $\bar{h}_{\max}$ decreases while $v_{\max}$ increases, although it is subject to several exceptions. A special case of $\bar{h}(v)$ at $v=0$, $\bar{h}(0)$, represents [39] the electron-electron coalescence density in momentum space, which is the probability density for the momenta $\vec{p}_j$ and $\vec{p}_k$ of any pair of electrons j and k to be exactly the same. Some discussion on the momentum-space electron-electron coalescence density is found in Ref.[39]. In the Hartree-Fock approximation, a property $\bar{h}'(0)=0$ is derived from the momentum-space counterpart of Eq. (5).

For the Kr atom, Fig.5 illustrates five major subshell-pair contributions, $4p4p$, $4s4p$, $4s4s$, $3d4p$, and $3s4s$ out of the total 36 subshell-pair contributions which constitute $\bar{h}(v)$. These subshell-pairs consist respectively of 15, 12, 1, 60, and 4 spinorbital-pair contributions, when the subshells are fully occupied. The $4p4p$, $4s4p$, $3d4p$, and $3s4s$ contributions have unimodal distributions with a maximum at $v=0.6356$, 0.6534, 2.9009, and 1.0316, respectively. However, the $3d4p$ and $3s4s$ contributions are small compared to the others. The $4s4s$ contribution is a unimodal function with a maximum at $v=0$. The above behaviors of $4p4p$, $4s4p$, $4s4s$, $3d4p$, and $3s4s$ contributions represent those of the outermost subshell-pairs *PP*, *SP*, *SS*, *PD*, and *SS'* appeared in Table 2. Therefore, the analysis of these subshell-pair contributions clarifies the relationship between the behaviors of the total intracule density and its maximal subshell-pair contribution given in Table 2: When the *SS* subshell-pair contribution is large, the intracule density belongs to Type A. When one of the subshell-pair contributions *SS'*, *SP*, *PP*, and *PD* is large, the density has the Type B behavior. The Type C behavior of the intracule densities originates from a mixture of Type A and B contributions from *SS* and *SP* subshell-pairs (Tc atom) or from *SS* and *PD* subshell-pairs (Zn and Cd atoms).

Figure 6 exemplifies some spinorbital-pair contributions $\bar{h}_{jk}(v)$ to $\bar{h}(v)$ for the Kr atom. Figure 6(a) shows the contributions from seven spinorbital-pairs with *different* spins; $3s\alpha 4s\beta$, $3d_{-1}\alpha 3d_{+1}\beta$, $4s\alpha 4s\beta$, $4s\alpha 4p_0\beta$, $4p_{-1}\alpha 4p_{+1}\beta$, $3d_0\alpha 4s\beta$, and $3d_0\alpha 4p_0\beta$. The first five spinorbital-pairs have Type A distributions, whereas the last two spinorbital-pairs have Type B distributions. Note that when $3d$ orbitals participate, the contribution of the spinorbital-pair is about 1/100 times smaller than that of the $4s\alpha 4s\beta$ spinorbital-pair. Figure 6(b) shows the contributions from six spinorbital-pairs with the *same* spin; $3s\alpha 4s\alpha$, $3d_0\alpha 4s\alpha$, $3d_0\alpha 4p_0\alpha$, $3d_{-1}\alpha 3d_{+1}\alpha$, $4s\alpha 4p_0\alpha$, and

$4p_{-1}\alpha 4p_{+1}\alpha$. As discussed in the Subsection 2-2-3-1, the spinorbital-pair contributions with the same spin have zero value at $v=0$ due to the Fermi hole in the Hartree-Fock theory, and hence such spinorbital-pairs have Type B distributions necessarily. The three contributions containing $3d$ orbitals are about 1/50 times smaller than the $4s\alpha 4p_0\alpha$ and $4p_{-1}\alpha 4p_{+1}\alpha$ contributions.

The behaviors of spinorbital-pair contributions analyzed in Fig. 6 lead us to a conclusion that in momentum space, spinorbital-pairs with different spins in the *SS*, *SP*, *PP*, *SS'*, and *DD* subshell-pairs have contributions to Type A distribution, while all the spinorbital-pairs with the same spin and spinorbital-pairs with different spins in the *PD* and *SD* subshell-pairs have contributions to Type B distribution. A sum of these contributions of constituent spinorbital-pairs, which explicitly depend on the electronic configuration and the *LS* term, gives the subshell-pair contribution discussed before.

2-2-4. CONCLUSION

Within the Hartree-Fock framework, we have systematically examined the structure of spherically-averaged intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space for the atoms He through Xe in their ground state. The numerical Hartree-Fock method has been used to construct these intracule densities. The contributions of subshell-pairs and spinorbital-pairs to the total intracule density have been analyzed in both spaces. For all the 53 atoms, the position-space intracule density has been found to be a unimodal function with a maximum at $u=0$ due to the predominant $1s1s$ subshell-pair contribution. In momentum space, however, the intracule densities have been classified into three types based on their modalities. We have further found that the different modalities in the momentum-space intracule densities originate from a few outermost subshell-pairs. Thus, the momentum-space intracule densities give us information about outer or valence electrons, whereas the position-space intracule densities mainly reflect the character of innermost $1s$ electrons.

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Table 1. The maximum value $h_{\max} \equiv h(0)$ of the position-space intracule density $h(u)$. Note that $h(u)$ is normalized to unity instead of $N(N-1)/2$. A(n) means $A \times 10^{n}$. All values in Hartree atomic units.

Z	Atom	$h_{\max}$	Z	Atom	$h_{\max}$
2	He	1.9060(-1)	29	Cu	3.5263
3	Li	2.6143(-1)	30	Zn	3.6768
4	Be	3.4984(-1)	31	Ga	3.8285
5	B	4.3792(-1)	32	Ge	3.9819
6	C	5.2860(-1)	33	As	4.1369
7	N	6.2194(-1)	34	Se	4.2934
8	O	7.2497(-1)	35	Br	4.4513
9	F	8.3269(-1)	36	Kr	4.6107
10	Ne	9.4538(-1)	37	Rb	4.7715
11	Na	1.0636	38	Sr	4.9337
12	Mg	1.1864	39	Y	5.0956
13	Al	1.3113	40	Zr	5.2582
14	Si	1.4385	41	Nb	5.4204
15	P	1.5679	42	Mo	5.5843
16	S	1.6997	43	Tc	5.7501
17	Cl	1.8338	44	Ru	5.9145
18	Ar	1.9700	45	Rh	6.0808
19	K	2.1088	46	Pd	6.2468
20	Ca	2.2498	47	Ag	6.4155
21	Sc	2.3884	48	Cd	6.5855
22	Ti	2.5273	49	In	6.7561
23	V	2.6670	50	Sn	6.9277
24	Cr	2.8045	51	Sb	7.1001
25	Mn	2.9484	52	Te	7.2734
26	Fe	3.0920	53	I	7.4476
27	Co	3.2366	54	Xe	7.6226
28	Ni	3.3823			

Table 2. Classification of the momentum-space intracule density $\bar{h}(v)$ and the maximal subshell-pair contribution to it.

Z	Atom	Type	Subshell-pair	Z	Atom	Type	Subshell-pair
2	He	A	1*s*1*s*	29	Cu	B	3*p*3*d*
3	Li	B	1*s*2*s*	30	Zn	C	4*s*4*s*
4	Be	A	2*s*2*s*	31	Ga	A	4*s*4*s*
5	B	A	2*s*2*s*	32	Ge	B	4*s*4*p*
6	C	B	2*s*2*p*	33	As	B	4*s*4*p*
7	N	B	2*s*2*p*	34	Se	B	4*s*4*p*
8	O	B	2*s*2*p*	35	Br	B	4*p*4*p*
9	F	B	2*p*2*p*	36	Kr	B	4*p*4*p*
10	Ne	B	2*p*2*p*	37	Rb	B	4*p*4*p*
11	Na	B	2*s*3*s*	38	Sr	A	5*s*5*s*
12	Mg	A	3*s*3*s*	39	Y	A	5*s*5*s*
13	Al	A	3*s*3*s*	40	Zr	A	5*s*5*s*
14	Si	B	3*s*3*p*	41	Nb	B	4*p*4*d*
15	P	B	3*s*3*p*	42	Mo	B	4*p*4*d*
16	S	B	3*s*3*p*	43	Tc	C	5*s*5*s*
17	Cl	B	3*p*3*p*	44	Ru	B	4*p*4*d*
18	Ar	B	3*p*3*p*	45	Rh	B	4*p*4*d*
19	K	B	3*p*3*p*	46	Pd	B	4*p*4*d*
20	Ca	A	4*s*4*s*	47	Ag	B	4*p*4*d*
21	Sc	A	4*s*4*s*	48	Cd	C	5*s*5*s*
22	Ti	A	4*s*4*s*	49	In	A	5*s*5*s*
23	V	A	4*s*4*s*	50	Sn	B	5*s*5*p*
24	Cr	B	3*p*3*d*	51	Sb	B	5*s*5*p*
25	Mn	A	4*s*4*s*	52	Te	B	5*s*5*p*
26	Fe	A	4*s*4*s*	53	I	B	5*p*5*p*
27	Co	A	4*s*4*s*	54	Xe	B	5*p*5*p*
28	Ni	A	4*s*4*s*				

Table 3. Characteristics v_{max} and $\bar{h}_{max} \equiv \bar{h}(v_{max})$ of the maximum of the momentum-space intracule density $\bar{h}(v)$. Note that $\bar{h}(v)$ is normalized to unity instead of $N(N-1)/2$. A(n) means $A \times 10^{n}$. All values in Hartree atomic units.

Z	Atom	v_{max}	$\bar{h}_{max}$	Z	Atom	v_{max}	$\bar{h}_{max}$
2	He	0	5.2276(-2)	29	Cu	1.2700	1.2871(-3)
3	Li	0.6169	2.2831(-2)	30[a]	Zn	0	3.0668(-3)
4	Be	0	1.5029(-1)	31	Ga	0	2.7823(-3)
5	B	0	5.3417(-2)	32	Ge	0.4000	2.4957(-3)
6	C	0.2887	2.3508(-2)	33	As	0.5651	2.3772(-3)
7	N	0.6593	1.2921(-2)	34	Se	0.5466	2.4614(-3)
8	O	0.6934	9.1906(-3)	35	Br	0.5764	2.4227(-3)
9	F	0.7892	6.5112(-3)	36	Kr	0.6395	2.3184(-3)
10	Ne	0.9307	4.6838(-3)	37	Rb	0.5808	2.7381(-3)
11	Na	0.8246	4.8568(-3)	38	Sr	0	6.7540(-3)
12	Mg	0	2.4601(-2)	39	Y	0	5.3905(-3)
13	Al	0	1.6431(-2)	40	Zr	0	4.5430(-3)
14	Si	0.3637	1.1523(-2)	41	Nb	0.8152	1.9564(-3)
15	P	0.5593	9.0608(-3)	42	Mo	0.8946	1.7502(-3)
16	S	0.5542	8.1491(-3)	43[b]	Tc	0	3.0156(-3)
17	Cl	0.6010	7.0225(-3)	44	Ru	0.9851	1.4710(-3)
18	Ar	0.6856	5.9494(-3)	45	Rh	1.0374	1.3487(-3)
19	K	0.6337	6.4968(-3)	46	Pd	1.1505	1.1469(-3)
20	Ca	0	1.8461(-2)	47	Ag	1.1509	1.1384(-3)
21	Sc	0	1.4199(-2)	48[c]	Cd	0	1.8425(-3)
22	Ti	0	1.1408(-2)	49	In	0	1.7534(-3)
23	V	0	9.3316(-3)	50	Sn	0.4033	1.6970(-3)
24	Cr	0.9919	2.6028(-3)	51	Sb	0.5382	1.7090(-3)
25	Mn	0	6.5178(-3)	52	Te	0.5210	1.8089(-3)
26	Fe	0	5.5017(-3)	53	I	0.5429	1.8408(-3)
27	Co	0	4.7021(-3)	54	Xe	0.5903	1.8277(-3)
28	Ni	0	4.0489(-3)				

a. The Zn atom has a local minimum $\bar{h}_{min} = 1.1683(-3)$ at $v_{min} = 1.1059$ and a secondary maximum $\bar{h}_{max} = 1.1741(-3)$ at $v_{max} = 1.3507$.

b. The Tc atom has a local minimum $\bar{h}_{min} = 1.6760(-3)$ at $v_{min} = 0.8252$ and a secondary maximum $\bar{h}_{max} = 1.6763(-3)$ at $v_{max} = 0.8796$.

c. The Cd atom has a local minimum $\bar{h}_{min} = 1.0680(-3)$ at $v_{min} = 0.8300$ and a secondary maximum $\bar{h}_{max} = 1.0948(-3)$ at $v_{max} = 1.2081$.

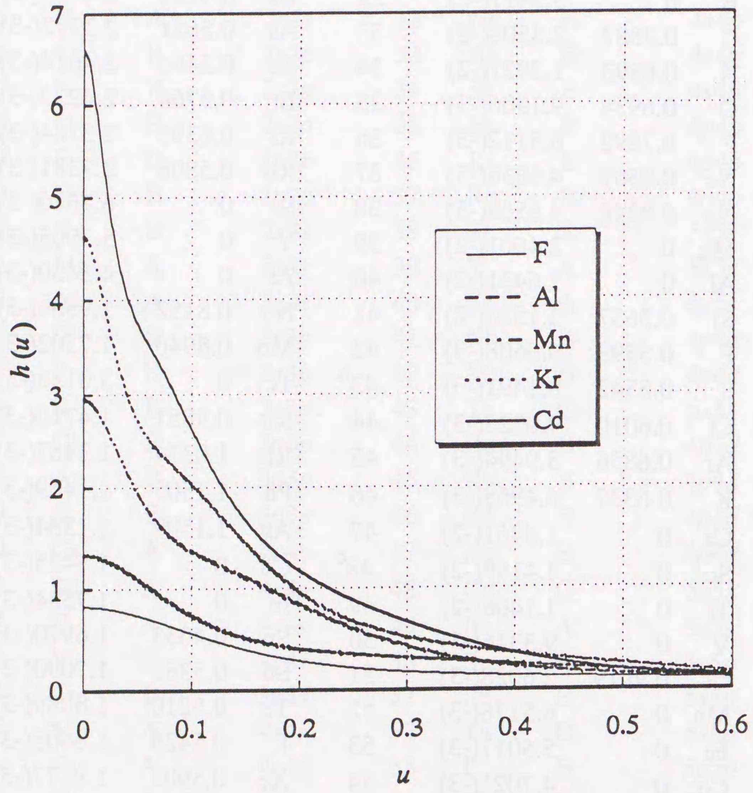


Fig. 1. Examples of the position-space intracule density $h(u)$.

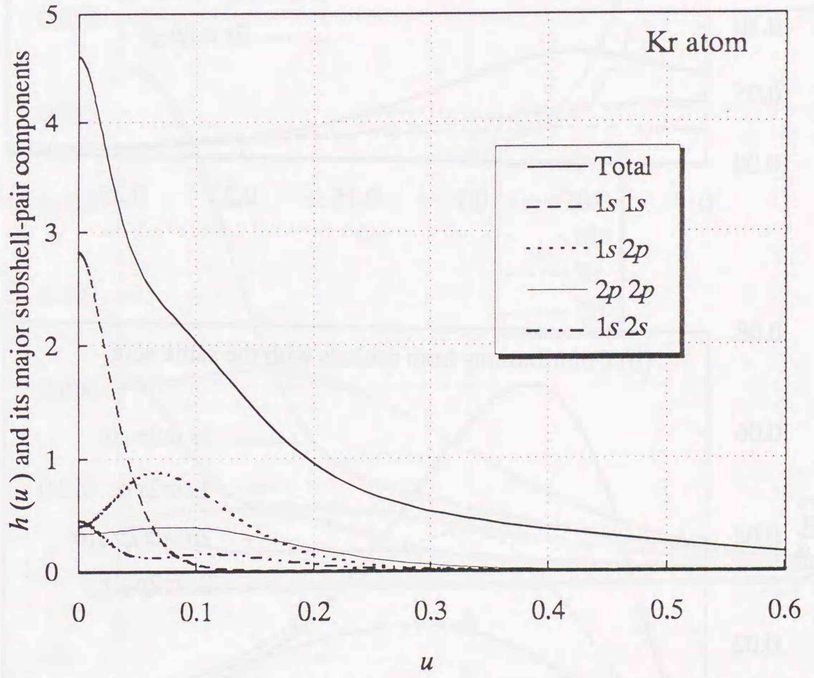


Fig. 2. Major subshell-pair contributions to the position-space intracule density $h(u)$ of the Kr atom (Z=36).

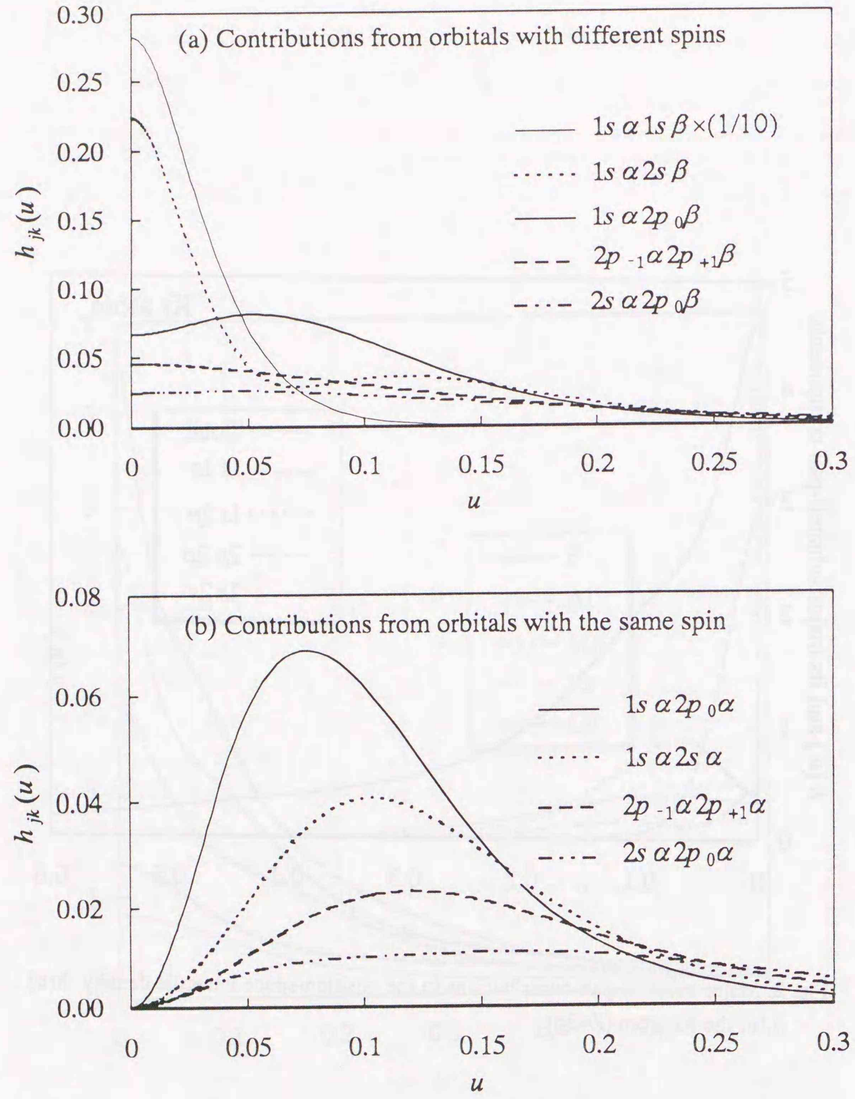


Fig. 3. Major spinorbital-pair contributions to the position-space intracule density $h(u)$ of the Kr atom (Z=36). (a) Pairs with different spins. (b) Pairs with the same spin.

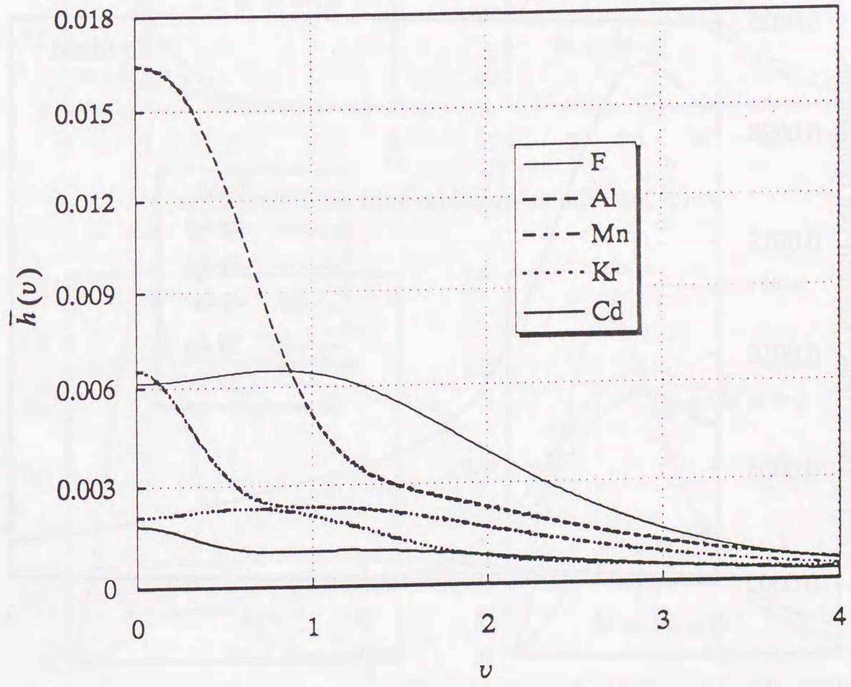


Fig. 4. Examples of the momentum-space intracule density $\bar{h}(v)$.

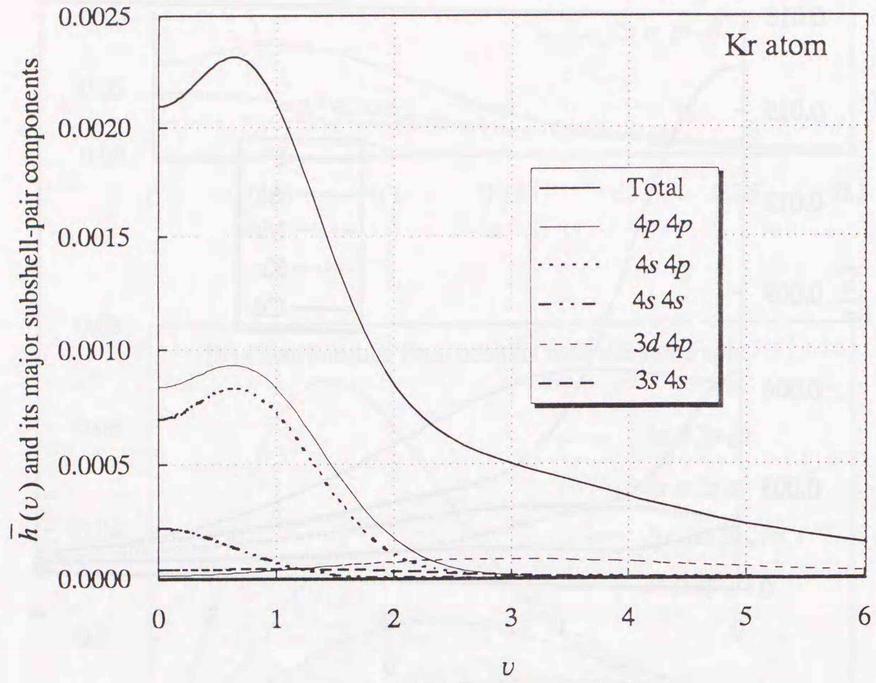
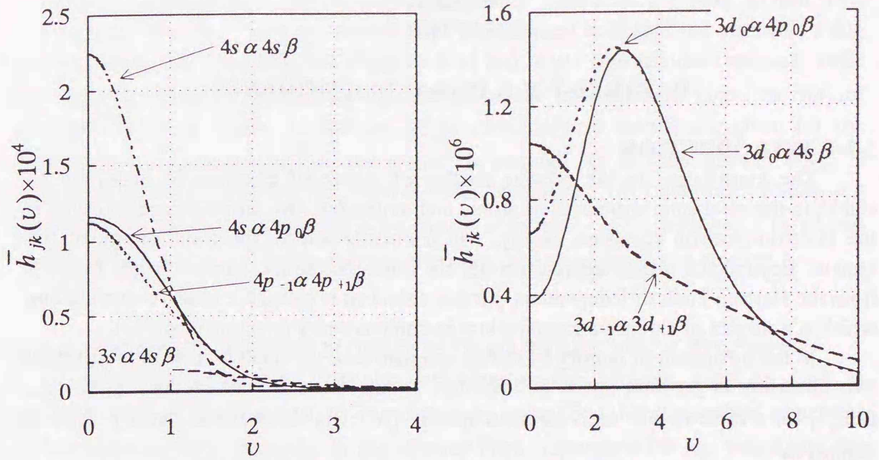
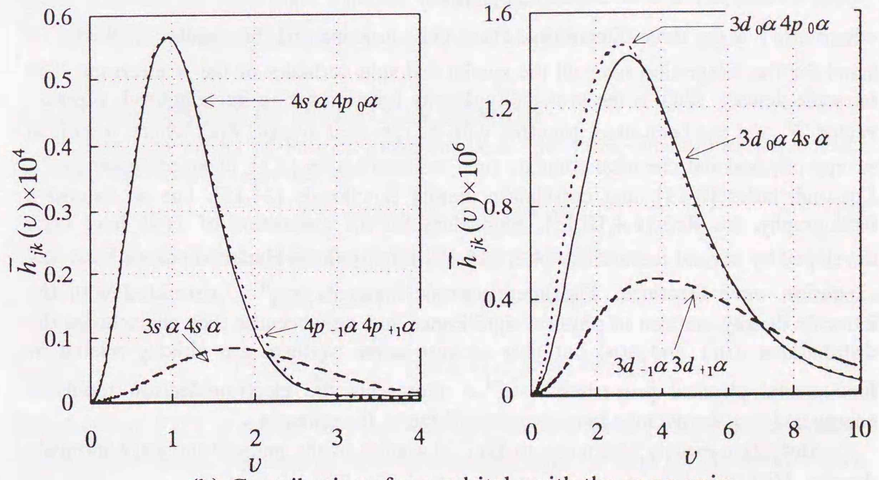


Fig. 5. Major subshell-pair contributions to the momentum-space intracule density $\bar{h}(\upsilon)$ of the Kr atom (Z=36).



(a) Contributions from orbitals with different spins



(b) Contributions from orbitals with the same spin

Fig. 6. Major spinorbital-pair contributions to the momentum-space intracule density $\bar{h}(\upsilon)$ of the Kr atom (Z=36). (a) Pairs with different spins. (b) Pairs with the same spin.

PART 2.
CHAPTER 3.

HARTREE-FOCK INTRACULE MOMENTS

2-3-1. INTRODUCTION

The knowledge on the relative motion of a pair of electrons is important to elucidate the electronic structures of atoms and molecules. One of its concrete results is the electron-electron repulsion energy, which directly affects the total energy of the system. Beyond the orbital approximation, the difference in the interelectronic motions from the Hartree-Fock or independent-particle solutions is called the electron correlation, which is a subject of extensive examinations in contemporary quantum chemistry.

In the formalism of density functions and matrices, the relative motion of arbitrary two electrons in position space is embodied by the intracule density $I(\vec{u})$ (see, *e.g.*, Ref.[1] for a review). For an N-electron system $(N \geq 2)$, the intracule density $I(\vec{u})$ is defined by

$$I(\vec{u}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{u} - (\vec{r}_j - \vec{r}_k)] \right\rangle , \tag{1a}$$

where $\delta(\vec{r})$ is the three-dimensional Dirac delta function and the angular brackets $\langle\ \rangle$ stand for the integration over all the spatial and spin variables of the N electrons. The intracule density $I(\vec{u})$ is the probability density function for an interelectronic *position* vector $\vec{u}$, and has been used, together with its spherical average $h(u)$ where $u = |\vec{u}|$, in several physical and chemical contexts such as Hund's rules [2,3], chemical bonds [4-7], Coulomb holes [8-13], and correlation density functionals [14,15]. For an extensive bibliography, see Refs.[1,4,10,13]. Algorithms for the calculation of $I(\vec{u})$ have been developed by several researchers [4,5,9,16-19] for Roothaan-Hartree-Fock or basis-set-expansion wave functions. The interelectronic moments $<u^n>$ associated with the intracule density are also of physical significance, not only because they characterize the distributions $I(\vec{u})$ and $h(u)$ but also because some of them are directly related to fundamental physical properties; $<u^{-1}>$ represents the electron-electron repulsion energy and $<u>$ the average interelectronic distance, for example.

Definition exactly analogous to Eq.(1a) applies to the momentum-space intracule density $\bar{I}(\vec{v})$,

$$\bar{I}(\vec{v}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{v} - (\vec{p}_j - \vec{p}_k)] \right\rangle , \tag{1b}$$

which is the probability density function for an interelectronic *momentum* vector $\vec{v}$. The spherical average $\bar{h}(v)$ and the interelectronic momentum moments $<v^n>$ follow accordingly where $v = |\vec{v}|$. Intracule studies of the Coulomb correlation from the momentum space viewpoint have also been reported [20-25].

The purpose of Chapter 3 is to determine accurate Hartree-Fock values of interelectronic moments $<u^n>$ in position space and $<v^n>$ in momentum space for atoms. These data are expected to be highly useful for the studies on the electron correlation which always refer to the Hartree-Fock values. In the next section, two methods are developed for this purpose: The first method evaluates the moments using the spherically-averaged intracule densities $h(u)$ and $\bar{h}(v)$ in a standard manner, while the second method determines the moments from the characteristic functions $H(s)$ of $h(u)$ and $\bar{H}(t)$ of $\bar{h}(v)$. In Section 2-3-3, computational details are given for the application of these methods to the atoms He through Xe in their ground state, in combination with the numerical Hartree-Fock technique. The numerical results are presented and discussed in Section 2-3-4 for the moments $<u^n>$ with n=−2 to +4 and $<v^n>$ with n=−2 to +3. Hartree atomic units are used throughout this chapter.

2-3-2. INTERELECTRONIC MOMENTS IN HARTREE-FOCK THEORY

As can be anticipated from the definitions of the intracule densities $I(\vec{u})$ in position space [Eq.(1a)] and $\bar{I}(\vec{v})$ in momentum space [Eq.(1b)], theoretical structures of the interelectronic moments in the Hartree-Fock approximation are essentially the same in position and momentum spaces. Thus the following three subsections describe two alternative methods for the evaluation of interelectronic position moments in some detail, and the last subsection explains the correspondence to the momentum-space counterparts.

2-3-2-1. STRUCTURE OF INTRACULE DENSITY

Using the kernel of Fourier transformations, the three-dimensional Dirac delta function $\delta(\vec{r})$ can be expressed as

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

Then the intracule density $I(\vec{u})$ defined by Eq.(1a) is rewritten as

$$I(\vec{u}) = (2\pi)^{-3} \int d\vec{s}\, \exp(i\vec{s}\cdot\vec{u}) F(\vec{s}) , \tag{3a}$$

$$F(\vec{s}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\langle \exp(-i\vec{s}\cdot\vec{r}_j) \exp(+i\vec{s}\cdot\vec{r}_k) \right\rangle . \tag{3b}$$

The function $F(\vec{s})$ is related to x-ray scattering cross-sections [26,27] in the Waller-Hartree theory and to high energy electron scattering cross-sections [27] in the first Born and binary encounter approximations.

For a single Slater determinant wave function composed of N spinorbitals $\psi_j(\vec{r})\eta_j(\sigma)$, the function $F(\vec{s})$ is rearranged, by the Condon-Slater rules (see, *e.g.*, Ref.[28]), as

$$F(\vec{s}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\{ f_{jj}^{*}(\vec{s}) f_{kk}(\vec{s}) - \delta_{m_{sj} m_{sk}} f_{kj}^{*}(\vec{s}) f_{kj}(\vec{s}) \right\} , \tag{4a}$$

where

$$f_{jk}(\vec{s}) \equiv \int d\vec{r}\, \exp(+i\vec{s}\cdot\vec{r}) \psi_j^{*}(\vec{r}) \psi_k(\vec{r}) , \tag{4b}$$

and m_{sj} $(= +1/2 \text{ or } -1/2)$ denotes the spin quantum number of the spinorbital j.

Equation (3a) with (4a) is essentially identical to that derived by Wang and Smith [19], but the spin contribution is missing in their result.

For atoms and atomic ions, we can generally assume that the spatial orbital $\psi_j(\vec{r})$ has a form,

$$\psi_j(\vec{r}) = R_j(r) Y_{l_j m_j}(\Omega_r), \tag{5}$$

where $Y_{lm}(\Omega)$ is a spherical harmonic and $\vec{r} = (r, \Omega_r)$. Then, using an expansion [29]

$$\exp(+i\vec{s}\cdot\vec{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} i^l j_l(sr) Y_{lm}^*(\Omega_s) Y_{lm}(\Omega_r), \tag{6}$$

with $j_l(x)$ being the l-th order spherical Bessel function of the first kind, we find that

$$f_{jk}(\vec{s}) = \sqrt{4\pi} \sum_{l=0}^{\infty} i^l \sqrt{2l+1}\, c^l(l_j m_j; l_k m_k) Y_{l,m_j - m_k}^*(\Omega_s) W_{2ljk}(s), \tag{7a}$$

where

$$W_{nljk}(s) \equiv \int_0^\infty dr\, r^n j_l(sr)\, R_j^*(r) R_k(r), \tag{7b}$$

and c^l is the Condon-Shortley parameter [30].

2-3-2-2. MOMENTS FROM SPHERICALLY-AVERAGED INTRACULE DENSITY

The spherically-averaged intracule density $h(u)$, defined by

$$h(u) \equiv (4\pi)^{-1} \int d\Omega_u\, I(\vec{u}), \tag{8}$$

can be expressed as a Hankel transform of a function $H(s)$,

$$h(u) = (2\pi^2)^{-1} \int_0^\infty ds\, s^2 j_0(us) H(s), \tag{9a}$$

where

$$H(s) \equiv (4\pi)^{-1} \int d\Omega_s\, F(\vec{s}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\{ H_{jj,kk}(s) - \delta_{m_{sj} m_{sk}} H_{kj,kj}(s) \right\}, \tag{9b}$$

in which

$$H_{ij,kl}(s) \equiv (4\pi)^{-1} \int d\Omega_s\, f_{ij}^*(\vec{s}) f_{kl}(\vec{s}). \tag{9c}$$

From Eq.(7a), the explicit forms of $H_{jj,kk}$ and $H_{kj,kj}$ appeared in Eq.(9b) are obtained as

$$H_{jj,kk}(s) = \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1) a^l(l_j m_j; l_k m_k) W_{2ljj}^*(s) W_{2lkk}(s), \tag{10a}$$

$$H_{kj,kj}(s) = \sum_{l=|l_j - l_k|}^{l_j + l_k} (2l+1) b^l(l_j m_j; l_k m_k) W_{2lkj}^*(s) W_{2lkj}(s), \tag{10b}$$

where the summations run over every other integers between the specified values. The

symbols a^l and b^l are Condon-Shortley parameters [30] defined by

$$a^l(l_j m_j; l_k m_k) \equiv c^l(l_j m_j; l_j m_j) c^l(l_k m_k; l_k m_k), \tag{11a}$$

$$b^l(l_j m_j; l_k m_k) \equiv [c^l(l_j m_j; l_k m_k)]^2, \tag{11b}$$

and the function $W_{nljk}(s)$ is given by Eq.(7b).

The interelectronic moments $< u^n >$ are then obtained by

$$\langle u^n \rangle \equiv \int d\vec{u}\, u^n I(\vec{u}) = 4\pi \int_0^\infty du\, u^{n+2} h(u), \tag{12}$$

where $n > -3$ and $< u^0 >$ is equal to $N(N-1)/2$, the number of electron pairs.

2-3-2-3. MOMENTS FROM CHARACTERISTIC FUNCTION

Equation (9a) implies that the function $H(s)$ is the characteristic function of the spherically-averaged intracule density $h(u)$. Then the interelectronic moments $< u^n >$ can be directly obtained from the characteristic function $H(s)$ for an integer value of n.

Combining Eqs. (9a) and (12), and interchanging the order of integrations with respect to u and s, we find

$$\langle u^n \rangle = (2/\pi) \int_0^\infty ds\, s^2 H(s) \left[\int_0^\infty du\, u^{n+2} j_0(su) \right]. \tag{13}$$

As shown previously [31-33], the integration with respect to u can be performed by using techniques of generalized functions. The results are :

For $n = -2$:

$$\langle u^{-2} \rangle = \int_0^\infty ds\, s\, H(s). \tag{14a}$$

For $n = -1$:

$$\langle u^{-1} \rangle = (2/\pi) \int_0^\infty ds\, H(s). \tag{14b}$$

For a nonnegative *even* integer n:

$$\langle u^n \rangle = (-1)^{\frac{n}{2}} (n+1) H^{(n)}(0). \tag{14c}$$

For a positive *odd* integer n:

$$\langle u^n \rangle = (-1)^{\frac{n+1}{2}} \left(\frac{2}{\pi} \right) (n+1) \int_0^\infty ds\, s^{-1} H^{(n)}(s), \tag{14d}$$

where $H^{(n)}(s)$ is the n-th derivative of the function $H(s)$. The above results show that the calculation of the moments $< u^n >$ with a nonnegative even n is particularly simple, since they are proportional to the value of $H^{(n)}(s)$ at $s = 0$. Especially, $H(0) = < u^0 > = N(N-1)/2$.

A derivative of $H(s)$ reduces to a combination of derivatives of the functions $W_{nljk}(s)$ through Eqs. (9b), (10a), and (10b). Then the relation

$$\frac{d}{ds} W_{nljk}(s) = \frac{1}{2l+1} [l\, W_{n+1,l-1,jk}(s) - (l+1) W_{n+1,l+1,jk}(s)], \tag{15a}$$

is useful, which can be applied recursively. We also note that

$$W_{nljk}(0) = \delta_{l0} \int_0^\infty dr\, r^n\, R_j^*(r) R_k(r), \tag{15b}$$

where δ_{ij} is the Kronecker delta.

2-3-2-4. INTERELECTRONIC MOMENTS IN MOMENTUM SPACE

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 $\psi_k(\vec{r})$ is replaced with

$$\phi_k(\vec{p}) = (2\pi)^{-3/2} \int d\vec{r}\, \exp(-i\vec{p}\cdot\vec{r})\, \psi_k(\vec{r}). \tag{16a}$$

For the position-space atomic orbital given by Eq.(5), the corresponding momentum-space orbital is

$$\phi_k(\vec{p}) = P_k(p) Y_{l_k m_k}(\Omega_p), \tag{16b}$$

where $\vec{p} = (p, \Omega_p)$ and

$$P_k(p) = (-i)^{l_k} \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2 j_{l_k}(pr)\, R_k(r). \tag{16c}$$

Then all the position-space results in the previous subsections hold in momentum space as well, if we replace $W_{nljk}(s)$ with

$$\overline{W}_{nljk}(t) \equiv \int_0^\infty dp\, p^n j_l(tp)\, P_j^*(p) P_k(p), \tag{17}$$

$I(\vec{u})$ with $\bar{I}(\vec{v})$, $F(\vec{s})$ with $\overline{F}(\vec{t})$, $f_{jk}(\vec{s})$ with $\bar{f}_{jk}(\vec{t})$, $h(u)$ with $\bar{h}(v)$, $H(s)$ with $\overline{H}(t)$, and $<u^n>$ with $<v^n>$.

2-3-3. COMPUTATIONAL METHOD

Within the nonrelativistic framework and in the absence of an external field, the *LS* multiplet states of an atom with a given electronic configuration are $(2L+1)(2S+1)$-fold degenerate with respect to the total energy, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively. Each of these multiplets is expressed in general by a linear combination of a finite number of Slater determinants in the Hartree-Fock theory. For the neutral atoms He (Z=2) through Xe (Z=54) in their experimental ground state [34], we have first examined the structure of the corresponding Hartree-Fock wave functions and confirmed that there exists at least one set of specific z-component M_L and M_S values of L and S that results in a single determinant wave function, to which our methods described in Section 2-3-2 can be applied.

For these ground *LS* terms of the 53 atoms, the radial functions $R_j(r)$ in position space have been generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [35]. A table of the ground electronic configurations and *LS* terms examined in this study is found in Ref.[36]. Then the products $r^n R_j(r) R_k(r)$ of two radial functions and a power of r have been numerically Hankel-transformed to obtain $W_{nljk}(s)$, by using the algorithm of Talman [37].

Following Eqs.(9b), (10a), and (10b), we obtain the characteristic function $H(s)$ as the sum of products of two $W_{nljk}(s)$ with appropriate coefficients. The parameters a^l and b^l have been taken from the Slater's book [38]. An additional Hankel transformation [Eq.(9a)] of the function $H(s)$ gives the spherically-averaged intracule density $h(u)$.

For the interelectronic moments in momentum space, the position-space radial functions $R_j(r)$, generated by numerical Hartree-Fock calculations, have been first Hankel-transformed to obtain the momentum-space radial functions $P_j(p)$ according to Eq.(16c). Then the same procedure has been applied as in position space to derive the functions $\overline{W}_{nljk}(t)$, $\overline{H}(t)$, and $\bar{h}(v)$.

2-3-4. RESULTS AND DISCUSSION

Table 1 summarizes the interelectronic moments $<u^n>$ in position space for the atoms He through Xe in their ground state. Note that to avoid large numbers, the moments have been divided by $N(N-1)/2$ and they show average values for a *single* pair of electrons. For all the 53 atoms, we have used the first method described in Section 2-3-2-2 for the moments with n=−2 to +4, and the second method described in Section 2-3-2-3 for the moments with n=−2, −1, +2, and +4. Based on the comparison of the two sets of moment values, we have judged that the present results have the accuracy of 7 significant figures as given in Table 1.

An interelectronic moment $<u^n>$ with a positive n generally decreases with an increasing atomic number Z, but the behavior is quite irregular except for the second period atoms. Figure 1(a) exemplifies the Z-dependence of the average interelectronic distance $<u>$. Within a period, the $<u>$ value has a trend to decrease from the group 1 atom to the group 18 atom, and there is a jump when we move from the group 18 atom to the group 1 atom of the next period. This behavior can be roughly understood by the distance of electrons in the innermost 1*s* and outermost orbitals. The maxima in the second through fifth periods are found for the Li, Al, Ca, and Sr atoms, respectively, and the Li atom has the largest $<u>$ among the 53 atoms. On the other hand, the minima in the four periods are observed for the Ne, Ar, Cu, and Pd atoms, respectively, and the Pd atom has the smallest $<u>$ among the 53 atoms.

A moment $<u^n>$ with a negative n generally increases with an increasing Z. Figure 1(b) shows the behavior of $<1/u>$, which is equal to the electron repulsion energy when multiplied by $N(N-1)/2$. The moment $<1/u>$ is smallest for Be and largest for Xe among the 53 atoms studied. It may be interesting to note that in Fig. 1(b), $<1/u>$ for the atoms Li through O is smaller than that of He, though the electron repulsion energy monotonically increases with Z. The corresponding situation is also seen for $<u>$ depicted in Fig. 1(a).

In some cases, the knowledge on the contribution of a pair of electrons in the innermost 1*s* orbital is useful. For this purpose, we have examined the helium-like atoms with nuclear charge Z in the Kellner approximation [39] which uses $R_{1s}(r) = 2\zeta^{3/2} \exp(-\zeta r)$ with $\zeta = Z - (5/16)$. We find

$$h(u) = \frac{\zeta^3}{24\pi}(4\zeta^2u^2 + 6\zeta u + 3)\exp(-2\zeta u) \ , \tag{18a}$$

and

$$< u > = \frac{35}{16\zeta} \ , \qquad < 1/u > = \frac{5}{8}\zeta \ , \tag{18b}$$

for example. Thus, it is clear that the Z-dependence of the interelectronic moments $< u^n >$ cannot be estimated only from the 1s electron pair, particularly for a positive n.

The interelectronic moments $< v^n >$ in momentum space are summarized in Table 2, with our normalization scheme $< v^0 > = 1$, based on the duplicate calculations by the two methods. In contrast to the position moments $< u^n >$, however, we could not determine sufficiently accurate values for the higher moments $< v^3 >$ and $< v^4 >$, due to a slow decay of $\bar{h}(v)$ for a large v as will be explained below for the He atom with the Kellner approximation.

A moment $< v^n >$ with a positive n increases monotonically as Z increases. As Fig. 2(a) exemplifies the results for $< v >$, the Z-dependence is very smooth in marked contrast with $< u >$ or $< 1/u >$. In fact, $\ln < v >$ and $\ln Z$ have a correlation coefficient 0.999813 and $< v > = 1.2724 Z^{0.6408}$ is found to be a good approximation for $2 \le Z \le 54$. An analogous fitting is also possible for $< v^2 >$. A moment $< v^n >$ with a negative n generally decreases with increasing Z. However, the Z-dependence is less regular compared to the moments with positive n. Figure 2(b) shows the results for $< 1/v >$.

Though we expect some reciprocal nature between the position $< u^n >$ and momentum $< v^n >$ moments as seen in Figs. 1 and 2, the physical interpretation of the interelectronic momentum moments is not very clear. We need more accumulation of the momentum-space knowledge on the electronic structure of atoms.

The Kellner approximation $P_{1s}(p) = (2^5\zeta^5/\pi)^{1/2}(p^2 + \zeta^2)^{-2}$ for helium-like atoms gives,

$$\bar{h}(v) = \frac{16\zeta^5}{3\pi^2}\frac{3v^4 + 88\zeta^2v^2 + 1584\zeta^4}{(v^2 + 4\zeta^2)^6} \ , \tag{19a}$$

and

$$< v > = \frac{35}{9\pi}\zeta \ , \qquad < 1/v > = \frac{7}{2\pi\zeta} \ , \tag{19b}$$

for example. Equation (19a) suggests v^{-8} decay of $\bar{h}(v)$ for a large v, which should be compared with an exponential decay of $h(u)$ given by Eq. (18a). This makes accurate determination of higher moments $< v^n >$ difficult. Equation (19a) also shows that $< v^n >$ with $n \ge 5$ does not exist at least for the Kellner approximation of helium-like atoms. As has been the case of position moments, Eq. (19b) shows that the contribution of a pair of 1s electrons is not sufficient to explain the Z-dependence of the momentum moments.

Few interelectronic moments $< u^n >$ and $< v^n >$ are known from beyond-Hartree-Fock calculations. For the He, Li, and Be atoms, Table 3 collects the

interelectronic moments from explicitly-correlated near-exact wave functions and compares them with the Hartree-Fock values obtained in this study. For the He and Be atoms, the electron correlation decreases $< u^n >$ with negative n and increases $< u^n >$ with positive n in position space. As shown by Coulson and Neilson [8] in their pioneering work, this is consistent with the observation that the electron correlation shifts the density in $h(u)$ from a small u to a large u region. For the Li atom, however, all the moments $< u^n >$ are larger in the Hartree-Fock approximation, and the above simple interpretation dose not apply. Though the number of available data is very limited, the interelectronic moments $< v^n >$ in momentum space show a similar trend; all the Hartree-Fock moments $< v^n >$ shown in Table 3 are larger than the corresponding near-exact values. Using the radial function $4\pi v^2\bar{h}(v)$, Banyard and coworkers [20,21,23] have shown that in momentum space, the electron correlation in He and Li accumulates the density in an intermediate v region with the corresponding reduction of the density in small and large v regions. This observation in $\bar{h}(v)$ is consistent with the correlation effects on $< v^n >$ and suggests that there is some noninteger value of n for which $< v^n >$ is larger in the correlated calculations.

2-3-5. CONCLUSION

Within the Hartree-Fock framework of atoms, we have developed two alternative methods for the calculation of interelectronic moments $< u^n >$ in position space and $< v^n >$ in momentum space. The first method uses the spherically-averaged intracule densities $h(u)$ and $\bar{h}(v)$, while the second method uses their characteristic functions $H(s)$ and $\bar{H}(t)$.

The two methods have been applied to the atoms from He to Xe in their ground state, and the moments $< u^n >$ with n=−2 to +4 and $< v^n >$ with n=−2 to +3 have been reported based on numerical Hartree-Fock calculations. The present results are expected to be useful as reference data in the study of electron correlations.

Our examination of these moments as a function of atomic number Z has shown that many moments do not reveal a simple Z-dependence, and a decomposition of the moments into the contributions from orbital pairs is needed for better understanding. Such a study is planned in our laboratory.

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Table 1. Interelectronic moments in position space. Note that the normalization is $\langle u^0\rangle=1$ instead of $N(N-1)/2$. A(±n) means $A\times10^{\pm n}$.

Z	Atom	$N(N-1)/2$	$\langle 1/u^2\rangle$	$\langle 1/u\rangle$	$\langle u\rangle$	$\langle u^2\rangle$	$\langle u^3\rangle$	$\langle u^4\rangle$
2	He	1	1.842045	1.025769	1.362124	2.369657	5.008953	1.245529(+1)
3	Li	3	1.677431	7.603070(-1)	2.896363	1.242138(+1)	6.527813(+1)	3.956954(+2)
4	Be	6	1.756103	7.481907(-1)	2.520086	8.659386	3.635297(+1)	1.791377(+2)
5	B	10	1.886959	7.839123(-1)	2.222331	6.619682	2.421727(+1)	1.046183(+2)
6	C	15	2.073204	8.506431(-1)	1.917449	4.932279	1.484951(+1)	5.361594(+1)
7	N	21	2.301207	9.309238(-1)	1.672125	3.626246	9.542776	2.942971(+1)
8	O	28	2.582897	1.016280	1.500203	2.921076	6.935719	1.940480(+1)
9	F	36	2.899849	1.106908	1.352630	2.370463	5.074617	1.283455(+1)
10	Ne	45	3.250292	1.200866	1.227692	1.947525	3.775010	8.655417
11	Na	55	3.484627	1.200308	1.617740	4.983532	2.400595(+1)	1.477092(+2)
12	Mg	66	3.706840	1.209337	1.679690	4.966032	2.077471(+1)	1.069504(+2)
13	Al	78	3.912255	1.214701	1.744749	5.237130	2.169535(+1)	1.106213(+2)
14	Si	91	4.113106	1.227540	1.703145	4.704018	1.722239(+1)	7.611725(+1)
15	P	105	4.311845	1.245557	1.633726	4.126810	1.345636(+1)	5.234538(+1)
16	S	120	4.509004	1.265699	1.573801	3.726412	1.127381(+1)	4.065517(+1)
17	Cl	136	4.707637	1.289611	1.505104	3.322547	9.274726	3.076283(+1)
18	Ar	153	4.908583	1.316490	1.435486	2.955539	7.622386	2.327061(+1)
19	K	171	5.079045	1.313635	1.690053	5.440157	2.820908(+1)	1.957289(+2)
20	Ca	190	5.242334	1.314124	1.758986	5.693502	2.716466(+1)	1.638068(+2)
21	Sc	210	5.414971	1.335330	1.685094	5.097587	2.261870(+1)	1.274922(+2)
22	Ti	231	5.592152	1.361157	1.610374	4.591169	1.926061(+1)	1.034019(+2)
23	V	253	5.773076	1.389418	1.540508	4.160791	1.661452(+1)	8.550843(+1)
24	Cr	276	5.971771	1.436084	1.377699	3.167549	1.096611(+1)	5.126964(+1)
25	Mn	300	6.147662	1.451678	1.414733	3.469950	1.274136(+1)	6.115030(+1)
26	Fe	325	6.342561	1.483550	1.360541	3.186487	1.120104(+1)	5.173117(+1)
27	Co	351	6.542860	1.517028	1.309418	2.937770	9.934065	4.438193(+1)
28	Ni	378	6.748277	1.551579	1.261639	2.717684	8.864034	3.840928(+1)
29	Cu	406	6.978952	1.603223	1.158092	2.236620	6.792330	2.908350(+1)
30	Zn	435	7.175190	1.623550	1.174917	2.347317	7.176526	2.947599(+1)
31	Ga	465	7.364096	1.637953	1.219690	2.667298	8.083768	4.149951(+1)
32	Ge	496	7.549997	1.652764	1.224340	2.627737	8.357384	3.426721(+1)
33	As	528	7.733514	1.667754	1.215478	2.516394	7.432553	2.761716(+1)
34	Se	561	7.914248	1.681936	1.209029	2.448204	6.946141	2.456146(+1)
35	Br	595	8.093607	1.696655	1.194537	2.341782	6.305502	2.096704(+1)
36	Kr	630	8.271891	1.711854	1.175738	2.221338	5.665336	1.768659(+1)
37	Rb	666	8.437482	1.713732	1.326144	3.710426	1.847075(+1)	1.299861(+2)
38	Sr	703	8.598882	1.716328	1.386402	4.021955	1.897786(+1)	1.178820(+2)
39	Y	741	8.760641	1.724901	1.371603	3.781681	1.645510(+1)	9.380832(+1)
40	Zr	780	8.922300	1.735538	1.347403	3.539872	1.447457(+1)	7.779878(+1)
41	Nb	820	9.087856	1.753305	1.265347	2.895209	1.006280(+1)	4.687806(+1)
42	Mo	861	9.249890	1.766745	1.236891	2.702857	8.893270	3.943142(+1)
43	Tc	903	9.405778	1.773516	1.268071	2.954222	1.056335(+1)	5.046334(+1)
44	Ru	946	9.572881	1.794050	1.194871	2.472531	7.736331	3.322735(+1)
45	Rh	990	9.734873	1.808819	1.172853	2.364154	7.244773	3.082659(+1)
46	Pd	1035	9.903434	1.831262	1.095987	1.868412	4.331056	1.281934(+1)
47	Ag	1081	1.006040(+1)	1.840178	1.129076	2.166649	6.417279	2.705045(+1)
48	Cd	1128	1.021478(+1)	1.848491	1.145822	2.277425	6.920346	2.876561(+1)
49	In	1176	1.036549(+1)	1.854409	1.179295	2.526898	8.495899	3.912141(+1)
50	Sn	1225	1.051428(+1)	1.860813	1.188644	2.540301	8.196630	3.480232(+1)
51	Sb	1275	1.066131(+1)	1.867480	1.188703	2.492538	7.631739	2.993517(+1)
52	Te	1326	1.080631(+1)	1.873803	1.190065	2.471834	7.369206	2.783022(+1)
53	I	1378	1.094992(+1)	1.880471	1.185399	2.413998	6.925701	2.487876(+1)
54	Xe	1431	1.109227(+1)	1.887438	1.177090	2.339506	6.437069	2.194182(+1)

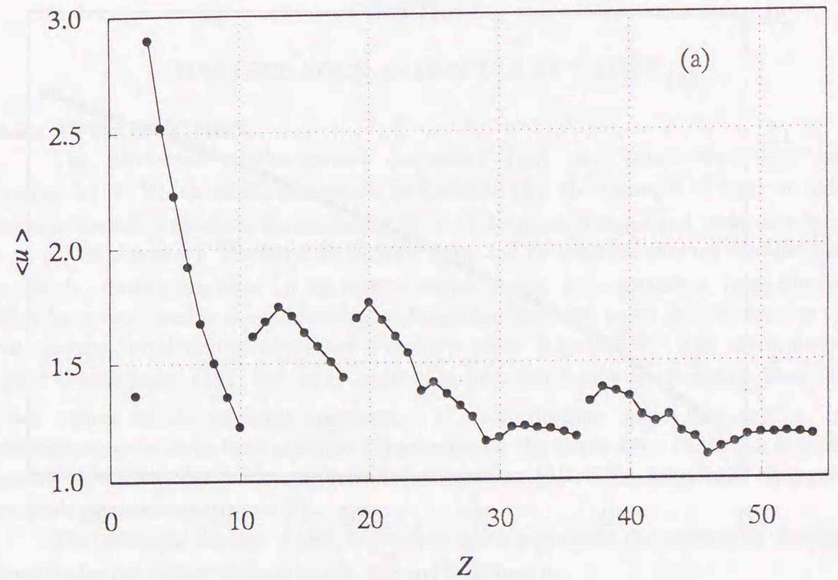
Table 2. Interelectronic moments in momentum space. Note that the normalization is $\langle v^0\rangle=1$ instead of $N(N-1)/2$. A(± n) means $A\times10^{\pm n}$.

Z	Atom	$N(N-1)/2$	$\langle 1/v^2\rangle$	$\langle 1/v\rangle$	$\langle v\rangle$	$\langle v^2\rangle$	$\langle v^3\rangle$
2	He	1	8.11757(-1)	6.880270(-1)	2.058629	5.72336	2.19(+1)
3	Li	3	4.89428(-1)	5.448338(-1)	2.654390	9.91030	5.32(+1)
4	Be	6	1.12593	6.349007(-1)	3.076185	1.45730(+1)	1.0(+2)
5	B	10	6.80074(-1)	5.428971(-1)	3.502470	1.97042(+1)	1.7(+2)
6	C	15	4.46725(-1)	4.655211(-1)	3.930083	2.53116(+1)	2.5(+2)
7	N	21	3.14163(-1)	4.051750(-1)	4.358588	3.13890(+1)	3.5(+2)
8	O	28	2.54249(-1)	3.669606(-1)	4.764455	3.78225(+1)	4.8(+2)
9	F	36	2.04701(-1)	3.324492(-1)	5.175853	4.47215(+1)	6.2(+2)
10	Ne	45	1.66091(-1)	3.024839(-1)	5.591020	5.20845(+1)	7.9(+2)
11	Na	55	1.56621(-1)	2.904599(-1)	5.949760	5.96143(+1)	9.8(+2)
12	Mg	66	2.48110(-1)	2.985992(-1)	6.281870	6.73749(+1)	1.2(+3)
13	Al	78	2.36444(-1)	2.955793(-1)	6.598586	7.53362(+1)	1.4(+3)
14	Si	91	2.14708(-1)	2.888695(-1)	6.905206	8.35151(+1)	1.7(+3)
15	P	105	1.92588(-1)	2.804014(-1)	7.204451	9.19140(+1)	2.0(+3)
16	S	120	1.85670(-1)	2.746793(-1)	7.492908	1.00500(+2)	2.3(+3)
17	Cl	136	1.73119(-1)	2.672862(-1)	7.777184	1.09304(+2)	2.6(+3)
18	Ar	153	1.59016(-1)	2.591136(-1)	8.058183	1.18327(+2)	2.9(+3)
19	K	171	1.59153(-1)	2.573741(-1)	8.318801	1.27455(+2)	3.3(+3)
20	Ca	190	2.07519(-1)	2.620869(-1)	8.568891	1.36723(+2)	3.7(+3)
21	Sc	210	1.80745(-1)	2.505815(-1)	8.837108	1.46146(+2)	4.1(+3)
22	Ti	231	1.58457(-1)	2.390504(-1)	9.108698	1.55756(+2)	4.6(+3)
23	V	253	1.40064(-1)	2.283651(-1)	9.380721	1.65546(+2)	5.1(+3)
24	Cr	276	9.32157(-2)	2.102821(-1)	9.669730	1.75533(+2)	5.6(+3)
25	Mn	300	1.11572(-1)	2.092247(-1)	9.926301	1.85679(+2)	6.1(+3)
26	Fe	325	1.01143(-1)	2.013694(-1)	1.019459(+1)	1.95990(+2)	6.6(+3)
27	Co	351	9.19662(-2)	1.938604(-1)	1.046428(+1)	2.06489(+2)	7.2(+3)
28	Ni	378	8.39420(-2)	1.868410(-1)	1.073403(+1)	2.17170(+2)	7.8(+3)
29	Cu	406	6.13158(-2)	1.755296(-1)	1.101858(+1)	2.28042(+2)	8.4(+3)
30	Zn	435	7.06160(-2)	1.740471(-1)	1.127457(+1)	2.39086(+2)	9.1(+3)
31	Ga	465	7.21934(-2)	1.724152(-1)	1.152480(+1)	2.50262(+2)	9.7(+3)
32	Ge	496	7.18047(-2)	1.707729(-1)	1.176971(+1)	2.61578(+2)	1.0(+4)
33	As	528	7.05587(-2)	1.690674(-1)	1.201017(+1)	2.73032(+2)	1.1(+4)
34	Se	561	7.23095(-2)	1.681144(-1)	1.224547(+1)	2.84608(+2)	1.2(+4)
35	Br	595	7.23224(-2)	1.668631(-1)	1.247738(+1)	2.96319(+2)	1.3(+4)
36	Kr	630	7.12922(-2)	1.653839(-1)	1.270629(+1)	3.08164(+2)	1.4(+4)
37	Rb	666	7.42286(-2)	1.656897(-1)	1.292749(+1)	3.20092(+2)	1.4(+4)
38	Sr	703	9.17265(-2)	1.678158(-1)	1.314375(+1)	3.32118(+2)	1.5(+4)
39	Y	741	8.62049(-2)	1.657413(-1)	1.336159(+1)	3.44244(+2)	1.6(+4)
40	Zr	780	8.08975(-2)	1.631950(-1)	1.357887(+1)	3.56483(+2)	1.7(+4)
41	Nb	820	6.35997(-2)	1.576847(-1)	1.380004(+1)	3.68839(+2)	1.8(+4)
42	Mo	861	6.02736(-2)	1.550798(-1)	1.401571(+1)	3.81308(+2)	1.9(+4)
43	Tc	903	6.77618(-2)	1.552335(-1)	1.422404(+1)	3.93875(+2)	2.0(+4)
44	Ru	946	5.57826(-2)	1.505541(-1)	1.444112(+1)	4.06558(+2)	2.1(+4)
45	Rh	990	5.34669(-2)	1.482287(-1)	1.465249(+1)	4.19353(+2)	2.2(+4)
46	Pd	1035	5.02487(-2)	1.450399(-1)	1.486732(+1)	4.32264(+2)	2.3(+4)
47	Ag	1081	4.90038(-2)	1.435891(-1)	1.507284(+1)	4.45283(+2)	2.4(+4)
48	Cd	1128	5.34280(-2)	1.433184(-1)	1.527471(+1)	4.58398(+2)	2.5(+4)
49	In	1176	5.45969(-2)	1.429003(-1)	1.547397(+1)	4.71600(+2)	2.7(+4)
50	Sn	1225	5.49226(-2)	1.424330(-1)	1.567063(+1)	4.84894(+2)	2.8(+4)
51	Sb	1275	5.47969(-2)	1.418995(-1)	1.586497(+1)	4.98278(+2)	2.9(+4)
52	Te	1326	5.63092(-2)	1.417073(-1)	1.605654(+1)	5.11743(+2)	3.0(+4)
53	I	1378	5.69248(-2)	1.413619(-1)	1.624612(+1)	5.25298(+2)	3.2(+4)
54	Xe	1431	5.69349(-2)	1.408873(-1)	1.643387(+1)	5.38942(+2)	3.3(+4)

Table 3. Comparison of interelectronic moments from Hartree-Fock and near-exact wave functions.

Atom	Moment	Hartree-Fock	Near-Exact
	Position Space		
He	$\langle 1/u^2 \rangle$	1.842045	1.464771[a]
	$\langle 1/u \rangle$	1.025769	0.945818[a]
	$\langle u \rangle$	1.362124	1.422070[a]
	$\langle u^2 \rangle$	2.369657	2.516439[a]
	$\langle u^3 \rangle$	5.008953	5.30801[b]
	$\langle u^4 \rangle$	12.45529	12.9813[b]
Li	$\langle 1/u^2 \rangle$	1.677431	1.460692[c]
	$\langle 1/u \rangle$	0.760307	0.732737[d]
	$\langle u \rangle$	2.896363	2.889476[d]
	$\langle u^2 \rangle$	12.42138	12.28270[d]
	$\langle u^3 \rangle$	65.27813	64.27[e]
	$\langle u^4 \rangle$	395.6954	387.0[e]
Be	$\langle 1/u^2 \rangle$	1.756103	1.589487[f]
	$\langle 1/u \rangle$	0.748191	0.729116[f]
	$\langle u \rangle$	2.520086	2.545279[f]
	$\langle u^2 \rangle$	8.659386	8.80816[f]
	$\langle u^3 \rangle$	36.35297	37.0718[f]
	$\langle u^4 \rangle$	179.1377	181.685[f]
	Momentum Space		
He	$\langle 1/v^2 \rangle$	0.811757	0.79550[g]
	$\langle 1/v \rangle$	0.688027	0.68666[g]
	$\langle v \rangle$	2.058629	2.0291[g]
	$\langle v^2 \rangle$	5.72336	5.4892[g]
Li	$\langle v \rangle$	2.654390	2.6344[h]
	$\langle v^2 \rangle$	9.91030	9.7062[h]

a. Ref. [40] b. Ref. [41] c. Ref. [42] d. Ref. [43]
e. Ref. [44] f. Ref. [45] g. Ref. [46]
h. Ref. [21,23]



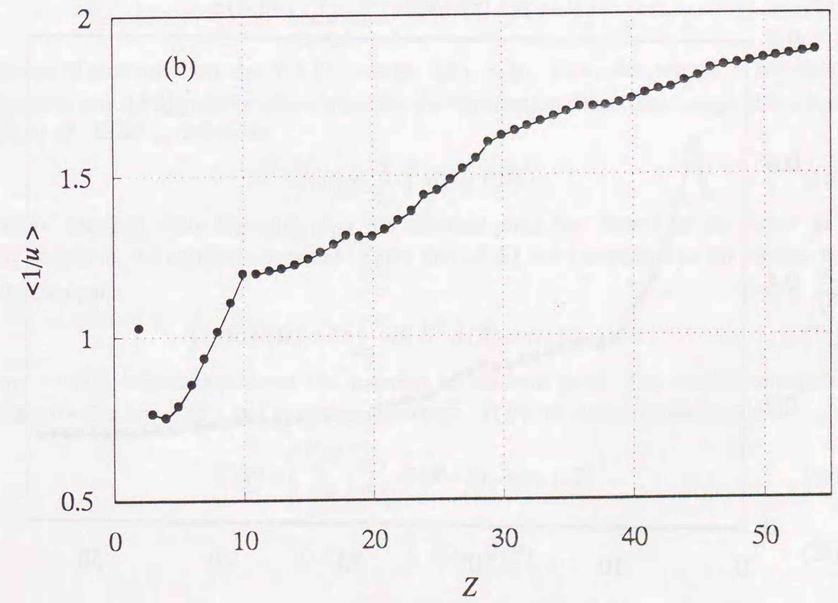
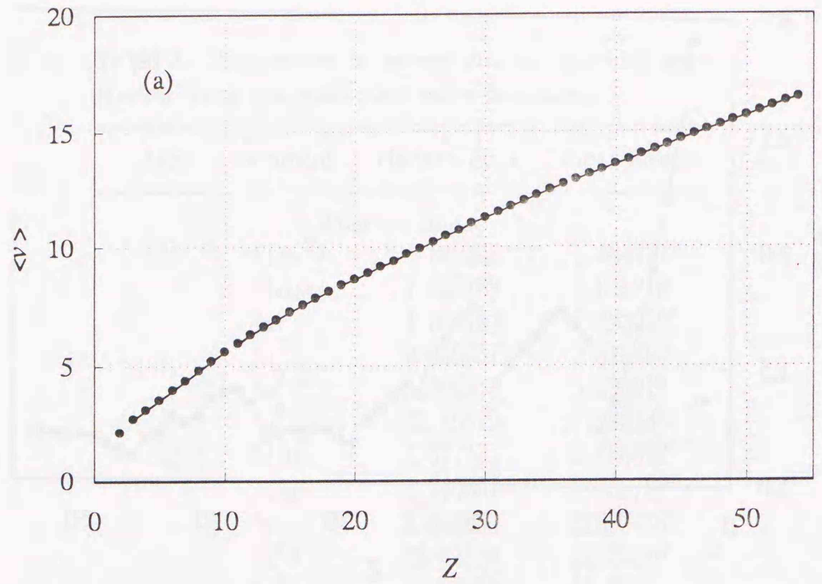


Fig. 1. Interelectronic position moments $\langle u \rangle$ and $\langle 1/u \rangle$ as a function of atomic number Z. Note that the normalization $\langle u^0 \rangle = 1$ is used.



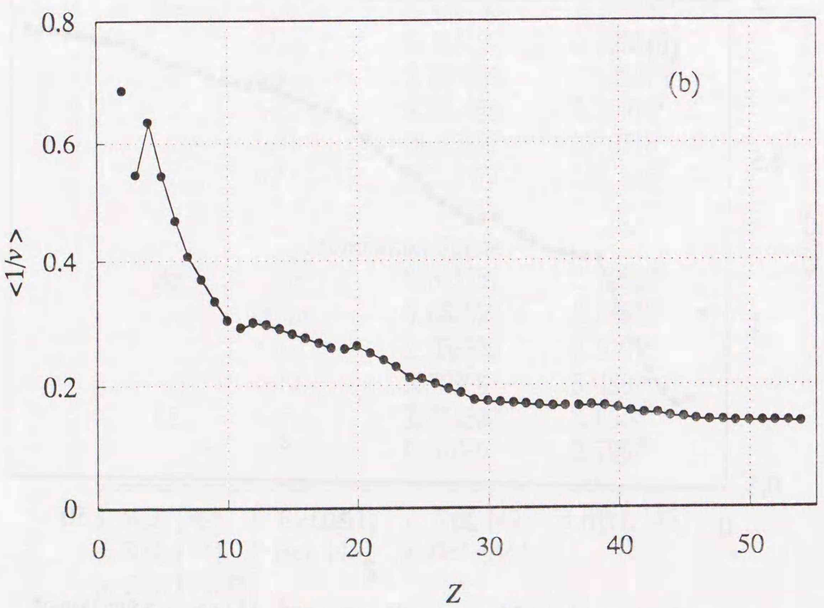


Fig. 2. Interelectronic momentum moments $<v>$ and $<1/v>$ as a function of atomic number Z. Note that the normalization $<v^0>=1$ is used.

PART 2.
CHAPTER 4.

HARTREE-FOCK EXTRACULE DENSITIES

2-4-1. INTRODUCTION

The electronic relative-motion (intracule) $I(\mathbf{u})$ and center-of-mass-motion (extracule) $E(\mathbf{R})$ densities, introduced by Coleman [1], are a couple of electron-pair densities useful to elucidate the motion of a pair of electrons in atoms and molecules (see, *e.g.*, [2] for a review). The intracule density $I(\mathbf{u})$ and its spherical average $h(u)$ are the probability density functions for the relative vector $\mathbf{u}$ and its magnitude u, respectively. They have been used in several physical and chemical contexts, particularly in relation to the electron correlation problem (see references given in Refs.[2-4]). The momentum-space counterparts $\bar{I}(\mathbf{v})$ and $\bar{h}(v)$ have been introduced as well. Accurate Hartree-Fock values of the intracule moments $<u^n>$ in position space and $<v^n>$ in momentum space have been reported [3] recently for the atoms from He to Xe in their ground state, together with a systematic examination [4] of the spherically-averaged intracule densities $h(u)$ and $\bar{h}(v)$.

The extracule density $E(\mathbf{R})$ in position space represents the probability density function for the center-of-mass vector $\mathbf{R}$, and is defined by

$$E(\mathbf{R}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{R} - (\mathbf{r}_j + \mathbf{r}_k)/2] \right\rangle , \tag{1a}$$

for an N-electron system $(N \geq 2)$, where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function and the angular brackets stand for the expectation value. The spherical average $d(R)$ of $E(\mathbf{R})$ is defined by

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

where (R,Ω_R) with $\Omega_R \equiv (\theta_R,\phi_R)$ are spherical polar coordinates of the vector $\mathbf{R}$. By definition, the extracule densities $E(\mathbf{R})$ and $d(R)$ are normalized to the number of electron pairs,

$$\int d\mathbf{R} \, E(\mathbf{R}) = 4\pi \int_0^\infty dR \, R^2 \, d(R) = N(N-1)/2 , \tag{1c}$$

and contain information about the location of electron pairs. The momentum-space extracule density $\bar{E}(\mathbf{P})$ and its spherical average $\bar{d}(P)$ are defined analogously by

$$\bar{E}(\mathbf{P}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta\,[\mathbf{P} - (\mathbf{p}_j + \mathbf{p}_k)/2] \right\rangle , \tag{2a}$$

$$\bar{d}(P) \equiv \frac{1}{4\pi} \int d\Omega_P \, \bar{E}(\mathbf{P}) , \tag{2b}$$

$$\int d\mathbf{P} \, \bar{E}(\mathbf{P}) = 4\pi \int_0^\infty dP \, P^2 \, \bar{d}(P) = N(N-1)/2 , \tag{2c}$$

where $\mathbf{P} \equiv (P,\Omega_P)$ and $\Omega_P \equiv (\theta_P,\phi_P)$. The functions $\bar{E}(\mathbf{P})$ and $\bar{d}(P)$ are probability densities for the center-of-mass momentum vector $\mathbf{P}$ and its magnitude P,

respectively.

Evaluation of accurate Hartree-Fock values of the electronic extracule moments $< R^n >$ and $< P^n >$ has been performed [5] very recently for the atoms He through Xe in their ground state. However, only a few studies are reported on the extracule densities of specific atoms and molecules (see references given in Ref.[5]). Moreover, all these studies are based on basis-set-expansion wave functions, and no accurate and/or systematic results concerning the distribution of extracule densities are known even for atoms.

In Chapter 4, we report accurate Hartree-Fock extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space for a series of 53 atoms from He (Z=2) to Xe (Z=54) in their ground state, where Z stands for atomic number. The numerical Hartree-Fock method is used instead of the conventional Roothaan-Hartree-Fock or basis-set-expansion method. The next section explains the theoretical structure of the extracule densities in position and momentum spaces. It will be also clarified that a spin-orbital-pair component of the extracule density has a definite relation with the corresponding component of the intracule density in the Hartree-Fock framework. In Section 2-4-3, the computational details are described and in Section 2-4-4 the results are presented and discussed. A systematic analysis shows that in position space, the extracule density $d(R)$ is a unimodal function with a maximum at $R = 0$ for all the 53 atoms. In momentum space, on the other hand, the extracule densities $\bar{d}(P)$ are found to be classified into two types; (i) 42 atoms have a unimodal density with a maximum at $P = 0$, and (ii) 11 atoms have a unimodal density with a local minimum at $P = 0$ and a maximum at $P > 0$. These different features of the densities $d(R)$ and $\bar{d}(P)$ are discussed in detail based on the contributions of electrons in a pair of atomic subshells and of atomic orbitals. Hartree atomic units are used throughout this chapter.

2-4-2. THERETICAL STRUCTURE OF EXTRACULE DENSITY

2-4-2-1. EXTRACULE DENSITY IN POSITION SPACE

We consider the case where a Hartree-Fock wave function of an N-electron system is expressed by a single Slater determinant of N spin-orbitals $\psi_j(\mathbf{r})\eta_j(\sigma)$. Then, using the Condon-Slater rule (see, *e.g.*, [6]), we can rewrite the spherically-averaged extracule density $d(R)$, defined by Eq. (1b), as a sum of contributions $d_{jk}(R)$ from pairs of spin-orbitals j and k:

$$d(R) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} d_{jk}(R) \ , \tag{3}$$

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

where $j_l(x)$ is the l-th order spherical Bessel function of the first kind and

$$D_{jk}(s) = D_{jj,kk}(s) - \delta_{m_{sj} m_{sk}} D_{jk,kj}(s) \ , \tag{5a}$$

is the characteristic function of $d_{jk}(R)$, in which

$$D_{ij,kl}(s) \equiv (4\pi)^{-1} \int d\Omega_s \, f_{ij}^*(\mathbf{s}) f_{kl}^*(\mathbf{s}) \ , \tag{5b}$$

$$f_{jk}(\mathbf{s}) \equiv \int d\mathbf{r} \exp(+i\mathbf{s}\cdot\mathbf{r}) \psi_j^*(\mathbf{r}) \psi_k(\mathbf{r}) = f_{kj}^*(-\mathbf{s}) \ . \tag{5c}$$

In Eq.(5a), the Kronecker delta $\delta_{m_{sj} m_{sk}}$ is unity if the two spin-orbitals j and k have the same spin and zero if j and k have different spins. If we further restrict ourselves to atomic systems where the spatial function $\psi_j(\mathbf{r})$ has a form,

$$\psi_j(\mathbf{r}) = R_j(r) Y_{l_j m_j}(\Omega_r) \ , \tag{6}$$

with $Y_{lm}(\Omega)$ being a spherical harmonic and $\mathbf{r} = (r, \Omega_r)$, the explicit forms of $D_{jj,kk}$ and $D_{jk,kj}$ appeared in Eq. (5a) are obtained [5] as

$$D_{jj,kk}(s) = \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1) a^l(l_j m_j; l_k m_k) W_{ljj}(s) W_{lkk}(s) \ , \tag{7a}$$

$$D_{jk,kj}(s) = (-1)^{l_j + l_k} \sum_{l=|l_j - l_k|}^{l_j + l_k} (2l+1) b^l(l_j m_j; l_k m_k) W_{ljk}(s) W_{lkj}(s) \ , \tag{7b}$$

where the summations run over every other integers between the specified values, the symbols $a^k(lm;l'm')$ and $b^k(lm;l'm')$ are Condon-Shortley parameters [7], and

$$W_{ljk}(s) \equiv \int_0^\infty dr\, r^2 j_l(sr) R_j^*(r) R_k(r) = W_{lkj}^*(s) \ . \tag{8}$$

2-4-2-2. EXTRACULE DENSITY IN MOMENTUM SPACE

A momentum-space N-electron wave function is given by the $3N$-dimensional Fourier transformation of the corresponding position-space wave function. Then the Hartree-Fock wave function in momentum space has exactly the same determinantal structure as that in position space, provided that a position orbital $\psi_k(\mathbf{r})$ is replaced with the corresponding momentum orbital

$$\phi_k(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp(-i\mathbf{p}\cdot\mathbf{r}) \psi_k(\mathbf{r}) \ . \tag{9}$$

Expanding $\exp(-i\mathbf{p}\cdot\mathbf{r})$ in Eq. (9) by means of plane waves [8] and integrating over the angular variable Ω_r, we find the momentum orbital corresponding to Eq. (6) to be

$$\phi_k(\mathbf{p}) = P_k(p) Y_{l_k m_k}(\Omega_p) \ , \tag{10}$$

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

$$P_k(p) = (-i)^{l_k} \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2 j_{l_k}(pr) R_k(r) \ . \tag{11}$$

Consequently, theoretical structures of the spherically-averaged extracule density are the same in position and momentum spaces, and all the position-space results explained in Subsection 2-4-2-1 hold in momentum space as well, if we replace $d(R)$ with $\bar{d}(P)$ and $R_k(r)$ with $P_k(p)$.

2-4-2-3. RELATION BETWEEN EXTRACULE AND INTRACULE DENSITIES

There are some general relations between the extracule $d_{jk}(R)$ and intracule $h_{jk}(u)$ density components arising from two spin-orbitals j and k. Comparison of the structure of extracule densities given in Subsection 2-4-2-1 with that [4] of intracule

densities shows that the two components of their characteristic functions satisfy

$$D_{jj,kk}(s) = H_{jj,kk}(s) \ , \quad D_{jk,kj}(s) = (-1)^{l_j + l_k} H_{kj,kj}(s) \ . \tag{12}$$

We immediately obtain

$$d_{jk}(R) = 8h_{jk}(2R) \ , \tag{13a}$$

if $m_{sj} \neq m_{sk}$ or if $m_{sj} = m_{sk}$ and $l_j + l_k$ = even, and

$$d_{jk}(R) = 8h_{jk}(2R) + (8/\pi^2)\int_0^\infty ds\, s^2 j_0(2Rs) H_{kj,kj}(s) \ , \tag{13b}$$

if $m_{sj} = m_{sk}$ and $l_j + l_k$ = odd. Thus the intracule and extracule densities are not completely independent as suggested previously [5,9]. A special case of Eq.(13a) for $m_{sj} = m_{sk}$, $l_j + l_k$ = even, and R=0 gives the electron-electron counterbalance and coalescence (or Fermi) holes [10] $d_{jk}(0) = h_{jk}(0) = 0$ simultaneously. The same discussion holds in momentum space.

If the second term on the right-hand side of Eq. (13b) is small or if the spin-orbital-pair contributions in the form of Eq. (13b) are small by themselves, we obtain an approximation $d(R) \cong 8h(2R)$ between the total extracule and intracule densities. Our previous study [4] on the intracule density has clarified that in position space, the $1s\alpha 1s\beta$ spin-orbital-pair gives a predominant contribution to the total density $h(u)$. Since Eq. (13a) is valid for the $1s\alpha 1s\beta$ pair, we anticipate that the behavior of the extracule density $d(R)$ will be similar to that of the intracule density $h(u)$ in position space. In momentum space, however, it has been shown [4] that major contributions to the intracule density $\bar{h}(v)$ come from pairs of valence spin-orbitals. Equation (13b) appears more often for these spin-orbital-pairs, and therefore we expect that in momentum space the behaviors of the extracule $\bar{d}(P)$ and intracule $\bar{h}(v)$ densities may show some differences. These anticipations will be actually confirmed in Section 2-4-4.

2-4-3. COMPUTATIONAL METHOD

For the neutral atoms He (Z=2) through Xe (Z=54) in their experimental ground LS term [11], we have previously confirmed [3] that among $(2L+1)(2S+1)$ degenerate states, there exists at least one state with specific z-component M_L and M_S values of L and S that results in a single determinant wave function, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively.

For these ground LS states of the 53 atoms, the radial functions $R_j(r)$ in position space have been generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [12]. Then the products $r^2 R_j(r) R_k(r)$ of two radial functions have been numerically Hankel-transformed to obtain $W_{ljk}(s)$, by using the algorithm of Talman [13]. Following Eqs.(5a), (7a), and (7b), we obtain the function $D_{jk}(s)$ as the sum of products of two $W_{ljk}(s)$ with appropriate coefficients. The parameters a^k and b^k have been taken from the Slater's book [14]. An additional Hankel transformation [Eq.(4)] of the function $D_{jk}(s)$ gives the spherically-averaged extracule density $d_{jk}(R)$.

In momentum space, the position-space radial functions $R_j(r)$, generated by

numerical Hartree-Fock calculations, have been first Hankel-transformed to obtain the momentum-space radial functions $P_j(p)$ according to Eq. (11). Then the same procedure as in position space has been applied to derive $\bar{d}_{jk}(P)$.

2-4-4. RESULTS AND DISCUSSION

Throughout this Section, total extracule densities are normalized to unity instead of $N(N\text{-}1)/2$ for all the 53 atoms in order to avoid large numbers and to facilitate mutual comparison. Accordingly, all the spin-orbital-pair components are normalized to $2/N(N\text{-}1)$ and the subshell-pair contributions are obtained as their partial sum.

2-4-4-1. EXTRACULE DENSITY IN POSITION SPACE

Position-space extracule densities $d(R)$ are exemplified in Fig.1 for a few selected atoms in their ground state. All the extracule densities shown in Fig.1 are monotonically decreasing functions, when R increases. However, the densities for the Zn and Mo atoms have a shoulder around R=0.05. Analogous and systematic examinations show that the extracule density $d(R)$ in position space is a unimodal function with a maximum at $R = 0$ for all the 53 atoms, as is [4] the intracule density $h(u)$. Table 1 summarizes the maximum height $d_{\max} = d(0)$. The maxima $d_{\max}$ increase with increasing Z, and we find an approximate relation $d(0) \cong 0.2942 Z^{2.4169}/(Z-1)$ for $2 \le Z \le 54$. We also find $d(0)/h(0)$=8 exactly for Z=2-4 as proved in Ref.[9], but for the remaining atoms the ratio increases monotonically from 8.108 for Z=5 to 10.946 for Z=54. The extracule density $d(R)$ at $R = 0$ is called [9] the electron-electron counterbalance density and represents the probability density of finding any two electrons precisely at the opposite positions with respect to the nucleus. Some discussion on the property of the electron-electron counterbalance density $d(0)$ is found in Refs.[9,10,15].

A decomposition of the extracule density into subshell-pair contributions shows that for all the atoms, the five largest contributions to $d(R)$ come from the inner subshell-pairs $1s1s$, $1s2s$, $1s2p$, $2s2p$, and $2p2p$, which consist of 1, 4, 12, 12, and 15 spin-orbital-pair contributions, respectively, when fully occupied. For the Zn atom (Z=30), Fig. 2 illustrates these five contributions out of the total 28 subshell-pair contributions. Clearly, the $1s1s$ subshell-pair is seen to give a significant contribution for the region R<0.02, and the $1s2p$ subshell-pair is largest for 0.02<R<0.10. These two contributions are unimodal with a maximum at R=0 and form the monotonically decreasing behavior of the extracule density $d(R)$. Due to Eq. (13b), the contribution of the $1s2p$ subshell-pair is slightly different in $d(R)$ and $h(u)$; in a small R or u region, the pair has a larger density in $d(R)$ than in $h(u)$.

Figure 3 depicts typical spin-orbital-pair contributions $d_{jk}(R)$ to $d(R)$ in Zn atom, where there is a total of 435 spin-orbital-pairs. Figure 3(a) shows the contributions from five spin-orbital-pairs with *different* spins; $1s\alpha 1s\beta$, $1s\alpha 2s\beta$, $1s\alpha 2p_0\beta$, $2p_{-1}\alpha 2p_{+1}\beta$, and $2s\alpha 2p_0\beta$. Because of Eq. (13a), all these contributions have essentially the same behavior as that we have already discussed [4] for the intracule density. We here simply note that the $1s\alpha 1s\beta$ pair gives a unimodal distribution with a maximum at R=0, and its contribution is more than ten times larger than the other four contributions. Figure 3(b) shows the contributions from four spin-orbital-pairs with the

same spin; $1s\alpha 2p_0\alpha$, $2s\alpha 2p_0\alpha$, $1s\alpha 2s\alpha$, and $2p_{-1}\alpha 2p_{+1}\alpha$. The first two contributions are unimodal with a maximum at R=0, while the last two are unimodal with zero at R=0 and a maximum away from R=0. The property $d_{jk}(0)=0$ is known [10] as the electron-electron counterbalance hole and valid for any contribution from spin-orbitals j and k with the same spin and with the same inversion symmetry. The counterbalance hole implies that these electrons cannot be at the opposite positions with respect to the inversion center and is a consequence of the antisymmetry of electronic wave functions as the electron-electron coalescence or Fermi hole. Since the essential feature of spin-orbital-pair contributions shown in Fig. 3 for the Zn atom is the same for all the 53 atoms, we conclude that the position-space extracule density $d(R)$ is a unimodal function with a maximum at R=0 due to the predominant $1s\alpha 1s\beta$ spin-orbital-pair or $1s1s$ subshell-pair contribution, and has a behavior similar to the corresponding intracule density $h(u)$ apart from two constant factors appearing in Eq. (13a).

2-4-4-2. EXTRACULE DENSITY IN MOMENTUM SPACE

Figure 4 exemplifies the momentum-space extracule density $\bar{d}(P)$ for the same atoms examined in Fig.1 in position space. In contrast with a single common modality observed for the position-space densities, Fig.4 shows that there are at least two different types of modality in the momentum-space extracule densities. The extracule densities $\bar{d}(P)$ of F and Zn atoms are unimodal functions with a maximum at P=0. The extracule densities of K and Mo atoms are unimodal with a maximum at P=0.2266 and at P=0.3018, respectively.

A systematic examination of all the 53 atoms concludes that the momentum-space extracule densities are classified into two types based on the location of the maximum:

Type A. Unimodal extracule density with a maximum at P=0. The next 42 atoms have densities of this type; group 2 atoms, transition atoms Sc-V, Mn-Ni, Zn, Y, Zr, Tc, Pd, and Cd, and group 13-18 atoms. All these atoms have two electrons in the outermost s orbital.

Type B. Unimodal extracule density with a local minimum at P=0 and a maximum at P>0. The next 11 atoms have Type B densities; group 1 atoms and transition atoms Cr, Cu, Nb, Mo, Ru, Rh, and Ag. All these atoms have single electron in the outermost s orbital.

Table 2 summarizes the above classification of the momentum-space extracule density $\bar{d}(P)$ together with the maximal subshell-pair contribution to it. If we introduce symbols S, P, and D for the outermost s, p, and d subshells, respectively, and a symbol S' for the second outermost s subshell, the subshell-pairs appeared in Table 2 are grouped into only four types SS, SS', SP, and PD. Thus, it is immediately seen that the momentum-space extracule density $\bar{d}(P)$ is governed by a few outermost subshell-pairs and depends explicitly on the valence electronic configuration of an atom, in marked contrast to the position-space extracule density. In general, two neighboring atomic subshells have different spatial inversion symmetries to which Eq. (13b) applies. As a result, the extracule $\bar{d}(P)$ and intracule $\bar{h}(v)$ densities in momentum space show different behaviors. For the intracule density $\bar{h}(v)$, we have observed [4] three types of the modality and five types of major subshell-pair contributions.

Table 2 also tabulates the maximum value $\bar{d}_{max} \equiv \bar{d}(P_{max})$ of $\bar{d}(P)$ and its location P_{max} which characterize the distribution of the momentum-space extracule density. When atomic number increases within a period, there is a trend that $\bar{d}_{max}$ decreases, although it is subject to some exceptions. A special case of $\bar{d}(P)$ at P=0, $\bar{d}(0)$, represents [15] the electron-electron counterbalance density in momentum space, which is the probability density for a pair of electrons to have exactly opposite momenta. For Z=2-4, the ratio $\bar{d}(0)/\bar{h}(0)$ is 8 exactly, but for Z=5-54, it irregularly distributes between 8.432 and 17.439, reflecting the difference in the extracule and intracule densities for these atoms in momentum space.

For the Zn atom having Type A density, Fig. 5 depicts four major subshell-pair contributions, $4s4s$, $3p3d$, $3d4s$, and $3s4s$. These subshell-pairs consist respectively of 1, 60, 20, and 4 spin-orbital-pairs, when the subshells are fully occupied. The first two subshell-pair contributions are unimodal with a maximum at P=0, while the last two are unimodal with a maximum away from P=0. The modality of $\bar{d}(P)$ of the Zn atom is attributed to the largest $4s4s$ or SS contribution. The Type A modality of atoms with an outermost $s(2)$ configuration is explained analogously except that for the group 13-18 atoms, the SP contribution is larger than the SS one. Figure 5 also shows that the Type B modality appears if we remove the SS contribution as in the case of atoms with an outermost $s(1)$ configuration. We note that the Type A modality of $\bar{d}(P)$ is explained based only on the largest subshell-pair contribution given in Table 2, but the Type B modality comes from secondary subshell-pair contributions with a maximum at P>0.

Figure 6 shows some spin-orbital-pair contributions $\bar{d}_{jk}(P)$ to $\bar{d}(P)$ for the Zn atom. Figure 6(a) compares the contributions from five spin-orbital-pairs with *different* spins; $4s\alpha 4s\beta$, $3s\alpha 4s\beta$, $3p_0\alpha 3d_0\beta$, $3d_{-1}\alpha 3d_{+1}\beta$, and $3d_0\alpha 4s\beta$. Due to Eq. (13a), the behavior of these contributions is essentially same as those examined [4] for the intracule density. The first four spin-orbital-pairs have Type A distributions, whereas the last spin-orbital-pairs have Type B distributions. When $3d$ orbitals participate, the contribution of the spin-orbital-pair is about 1/100 times smaller than that of the $4s\alpha 4s\beta$ spin-orbital-pair. Figure 6(b) shows the contributions from four spin-orbital-pairs with the *same* spin; $3s\alpha 4s\alpha$, $3d_0\alpha 4s\alpha$, $3d_{-1}\alpha 3d_{+1}\alpha$, and $3p_0\alpha 3d_0\alpha$. As discussed in the Subsection 2-4-4-1, the spin-orbital-pair contributions with the same spin and even l_j+l_k have zero value at P=0 due to the counterbalance hole in the Hartree-Fock theory, and hence such spin-orbital-pairs always contribute to Type B distributions. The first three pairs belong to this group. On the other hand, the $3p_0\alpha 3d_0\alpha$ pair with $l_j+l_k=3$ is unimodal with a maximum at P=0.

The analysis of spin-orbital-pair contributions leads us to the conclusion that in momentum space, the Type A modality of the extracule density is mainly due to electrons with different spins in SS and SP subshell-pairs. On the other hand, the Type B modality comes mainly from electrons in SD subshell-pair and from electrons with the same spin in SS', PP, and DD subshell-pairs.

2-4-5. CONCLUSION

Within the Hartree-Fock framework, the theoretical structure of the spherically-averaged extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space has been clarified in relation to the corresponding intracule densities $h(u)$ and $\bar{h}(v)$. Using the numerical Hartree-Fock method, we have systematically constructed these extracule densities for the atoms He through Xe in their ground state. The contributions of subshell-pairs and spin-orbital-pairs to the total extracule density have been analyzed in both spaces. For all the 53 atoms, the position-space extracule density has been found to be a unimodal function with a maximum at R=0 due to the predominant $1s1s$ subshell-pair contribution. In momentum space, however, the extracule densities have been classified into two types based on their modalities. We have further found that the different modalities in the momentum-space extracule densities originate from a few outermost subshell-pairs.

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Table 1. The maximum value $d_{max} \equiv d(0)$ of the position-space extracule density $d(R)$. Note that $d(R)$ is normalized to unity instead of $N(N-1)/2$. A(n) means A$\times 10^{n}$.

Z	Atom	d_{max}	Z	Atom	d_{max}
2	He	1.5248	29	Cu	3.6246(1)
3	Li	2.0914	30	Zn	3.7927(1)
4	Be	2.7988	31	Ga	3.9630(1)
5	B	3.5508	32	Ge	4.1359(1)
6	C	4.3673	33	As	4.3113(1)
7	N	5.2478	34	Se	4.4889(1)
8	O	6.2382	35	Br	4.6688(1)
9	F	7.3095	36	Kr	4.8510(1)
10	Ne	8.4633	37	Rb	5.0349(1)
11	Na	9.6723	38	Sr	5.2207(1)
12	Mg	1.0933(1)	39	Y	5.4065(1)
13	Al	1.2228(1)	40	Zr	5.5933(1)
14	Si	1.3558(1)	41	Nb	5.7799(1)
15	P	1.4923(1)	42	Mo	5.9689(1)
16	S	1.6322(1)	43	Tc	6.1603(1)
17	Cl	1.7755(1)	44	Ru	6.3505(1)
18	Ar	1.9221(1)	45	Rh	6.5430(1)
19	K	2.0716(1)	46	Pd	6.7355(1)
20	Ca	2.2238(1)	47	Ag	6.9315(1)
21	Sc	2.3737(1)	48	Cd	7.1293(1)
22	Ti	2.5246(1)	49	In	7.3282(1)
23	V	2.6769(1)	50	Sn	7.5286(1)
24	Cr	2.8274(1)	51	Sb	7.7305(1)
25	Mn	2.9856(1)	52	Te	7.9336(1)
26	Fe	3.1437(1)	53	I	8.1381(1)
27	Co	3.3034(1)	54	Xe	8.3439(1)
28	Ni	3.4648(1)			

Table 2. Classification of the momentum-space extracule density $\bar{d}(P)$ and the maximal subshell-pair contribution to it. Characteristics P_{max} and $\bar{d}_{max} \equiv \bar{d}(P_{max})$ of the maximum of the momentum-space extracule density $\bar{d}(P)$ are also given. Note that $\bar{d}(P)$ is normalized to unity instead of $N(N-1)/2$. A(n) means A$\times 10^n$.

Z	Atom	Type	Subshell-pair	P_{max}	$\bar{d}_{max}$
2	He	A	1*s*1*s*	0	4.1821(-1)
3	Li	B	1*s*2*s*	0.3085	1.8265(-1)
4	Be	A	2*s*2*s*	0	1.2023
5	B	A	2*s*2*p*	0	6.7778(-1)
6	C	A	2*s*2*p*	0	3.5025(-1)
7	N	A	2*s*2*p*	0	1.9400(-1)
8	O	A	2*s*2*p*	0	1.3633(-1)
9	F	A	2*s*2*p*	0	9.3930(-2)
10	Ne	A	2*s*2*p*	0	6.5336(-2)
11	Na	B	2*s*2*p*	0.3316	4.9862(-2)
12	Mg	A	3*s*3*s*	0	2.0743(-1)
13	Al	A	3*s*3*p*	0	2.3074(-1)
14	Si	A	3*s*3*p*	0	1.7735(-1)
15	P	A	3*s*3*p*	0	1.3191(-1)
16	S	A	3*s*3*p*	0	1.1795(-1)
17	Cl	A	3*s*3*p*	0	9.8403(-2)
18	Ar	A	3*s*3*p*	0	8.0187(-2)
19	K	B	3*s*3*p*	0.2266	6.7492(-2)
20	Ca	A	4*s*4*s*	0	1.6733(-1)
21	Sc	A	4*s*4*s*	0	1.3040(-1)
22	Ti	A	4*s*4*s*	0	1.0537(-1)
23	V	A	4*s*4*s*	0	8.6509(-2)
24	Cr	B	3*p*3*d*	0.3528	2.7148(-2)
25	Mn	A	4*s*4*s*	0	6.0616(-2)
26	Fe	A	4*s*4*s*	0	5.1287(-2)
27	Co	A	4*s*4*s*	0	4.3874(-2)
28	Ni	A	4*s*4*s*	0	3.7798(-2)
29	Cu	B	3*p*3*d*	0.4471	1.3259(-2)
30	Zn	A	4*s*4*s*	0	2.8622(-2)
31	Ga	A	4*s*4*p*	0	4.0322(-2)
32	Ge	A	4*s*4*p*	0	3.8252(-2)
33	As	A	4*s*4*p*	0	3.4107(-2)
34	Se	A	4*s*4*p*	0	3.5322(-2)
35	Br	A	4*s*4*p*	0	3.3715(-2)
36	Kr	A	4*s*4*p*	0	3.1034(-2)

Table 2. (continued)

Z	Atom	Type	Subshell-pair	P_{max}	$\bar{d}_{max}$
37	Rb	B	4*s*4*p*	0.1949	2.8894(-2)
38	Sr	A	5*s*5*s*	0	6.4037(-2)
39	Y	A	5*s*5*s*	0	5.2748(-2)
40	Zr	A	5*s*5*s*	0	4.5232(-2)
41	Nb	B	4*p*4*d*	0.2754	2.0497(-2)
42	Mo	B	4*p*4*d*	0.3018	1.8214(-2)
43	Tc	A	5*s*5*s*	0	3.0766(-2)
44	Ru	B	4*p*4*d*	0.3157	1.5290(-2)
45	Rh	B	4*p*4*d*	0.3299	1.3964(-2)
46	Pd	A	4*p*4*d*	0	1.2893(-2)
47	Ag	B	4*p*4*d*	0.3686	1.1653(-2)
48	Cd	A	5*s*5*s*	0	1.8869(-2)
49	In	A	5*s*5*p*	0	2.5326(-2)
50	Sn	A	5*s*5*p*	0	2.5269(-2)
51	Sb	A	5*s*5*p*	0	2.3773(-2)
52	Te	A	5*s*5*p*	0	2.5394(-2)
53	I	A	5*s*5*p*	0	2.5207(-2)
54	Xe	A	5*s*5*p*	0	2.4153(-2)

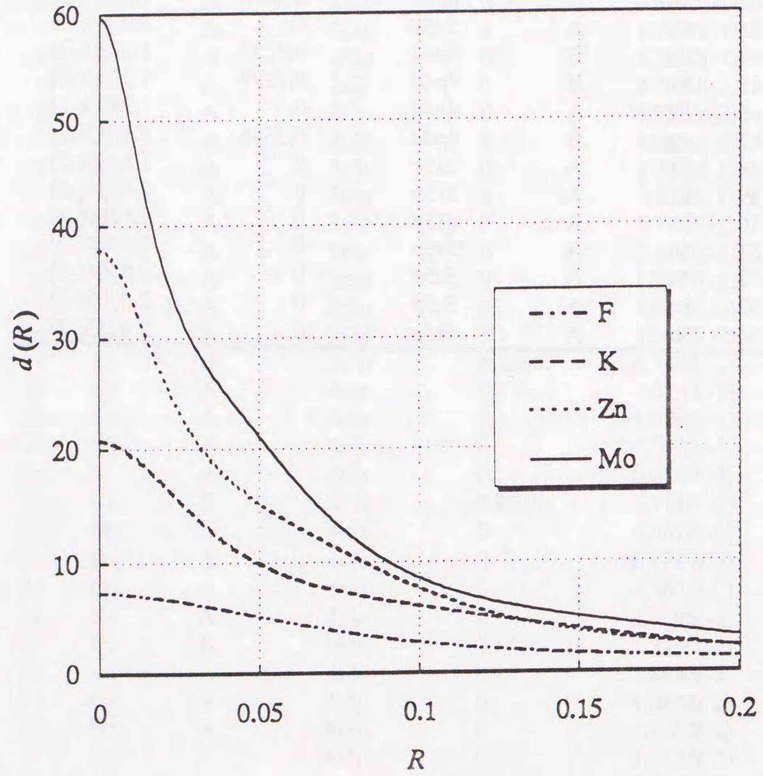


Fig. 1. Examples of the position-space extracule density $d(R)$.

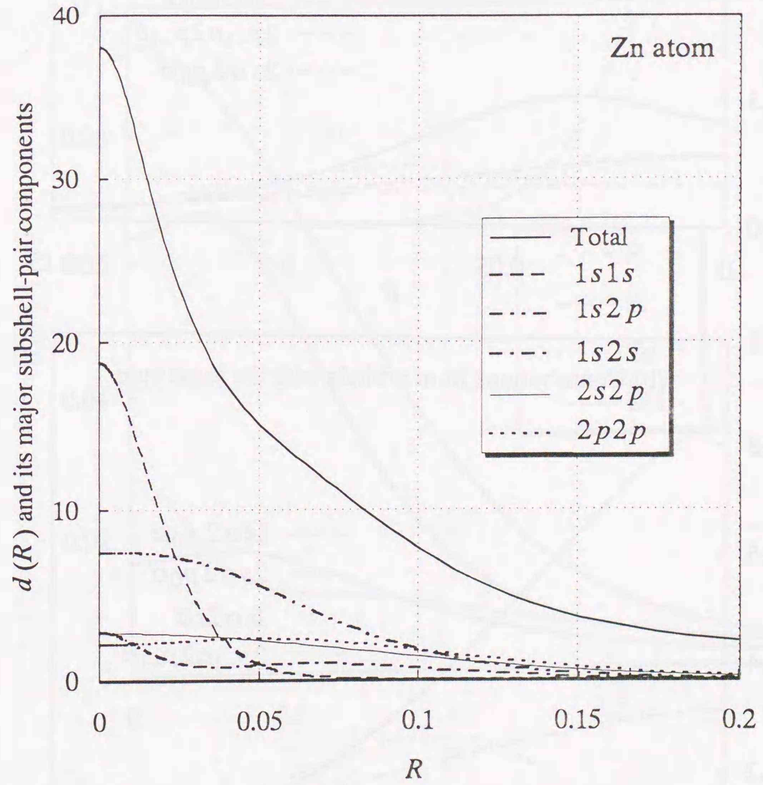


Fig. 2. Major subshell-pair contributions to the position-space extracule density $d(R)$ of the Zn atom (Z=30).

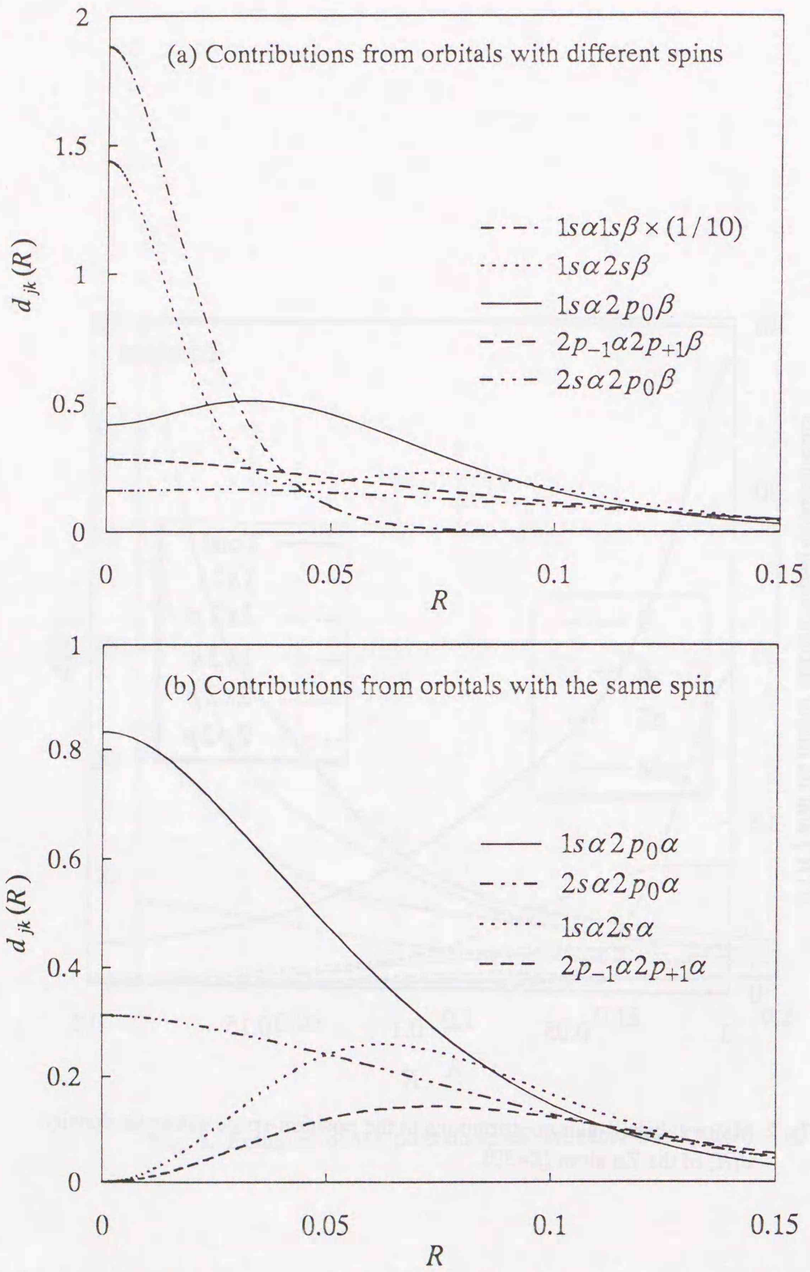


Fig. 3. Major spin-orbital-pair contributions to the position-space extracule density $d(R)$ of the Zn atom (Z=30). (a) Pairs with different spins. (b) Pairs with the same spin.

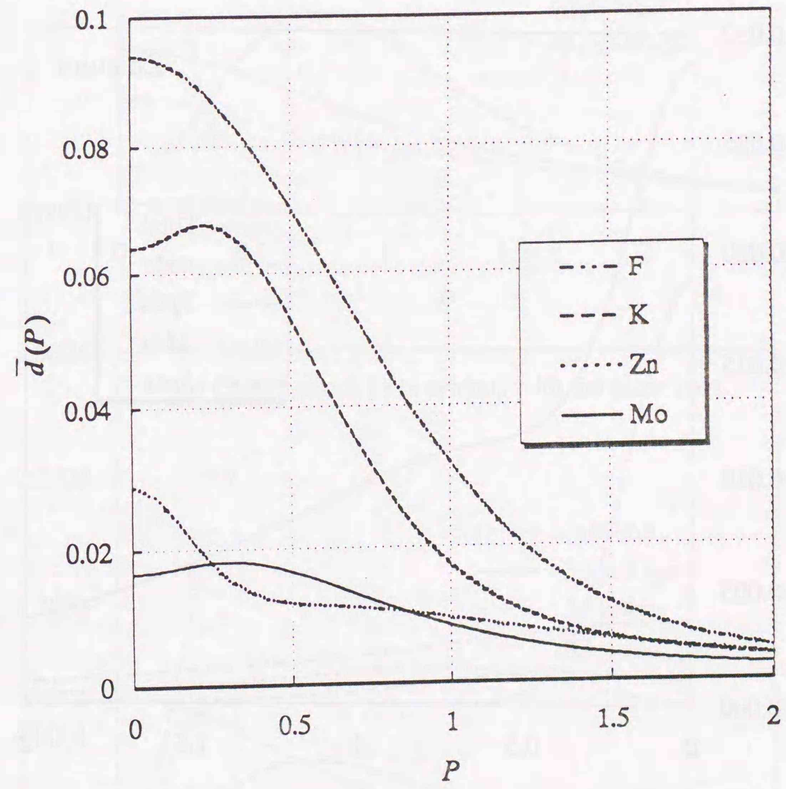


Fig. 4. Examples of the momentum-space extracule density $\bar{d}(P)$.

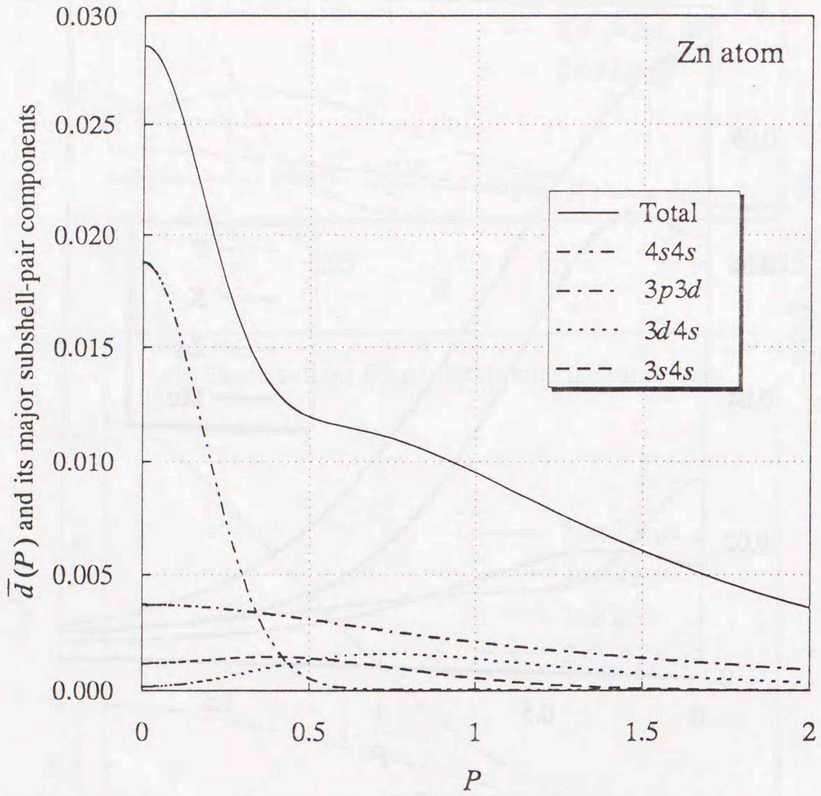


Fig. 5. Major subshell-pair contributions to the momentum-space extracule density $\bar{d}(P)$ of the Zn atom (Z=30).

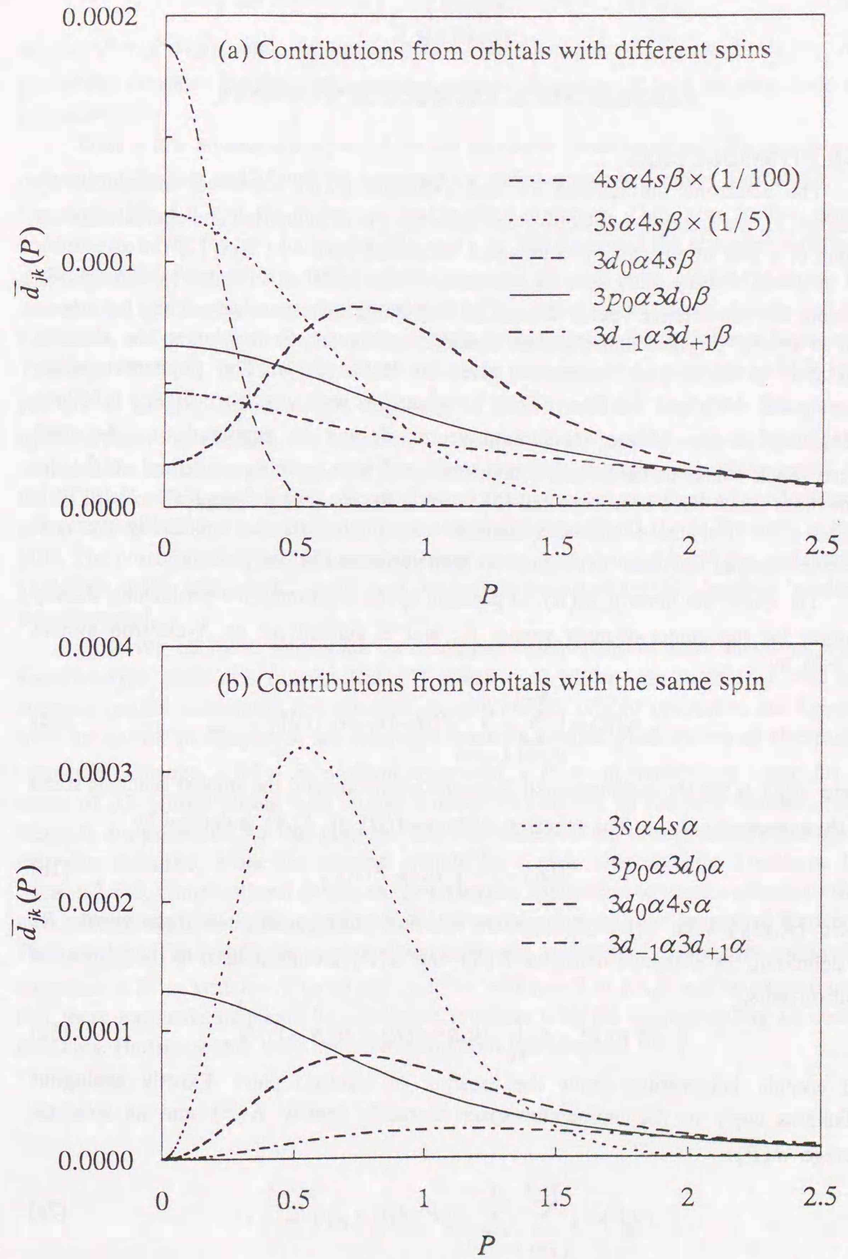


Fig. 6. Major spin-orbital-pair contributions to the momentum-space extracule density $\bar{d}(P)$ of the Zn atom (Z=30). (a) Pairs with different spins. (b) Pairs with the same spin.

PART 2.
CHAPTER 5.

HARTREE-FOCK EXTRACULE MOMENTS

2-5-1. INTRODUCTION

The electronic intracule $I(\vec{u})$ and extracule $E(\vec{R})$ densities, introduced by Coleman [1], are a couple of electron-pair densities useful to analyze and characterize the motion of a pair of electrons in atoms and molecules (see, *e.g.*, Ref. [2] for a review). The intracule density $I(\vec{u})$ and its spherical average $h(u)$ are the probability density functions for the relative vector $\vec{u}$ and its magnitude u, respectively. They have been used in several physical and chemical contexts particularly in relation to the electron correlation problem (see references given in Refs. [2,3]). The momentum-space counterparts $\bar{I}(\vec{v})$ and $\bar{h}(v)$ have been introduced as well, which are density functions respectively of the relative momentum vector $\vec{v}$ and its magnitude v. Accurate Hartree-Fock values of the intracule moments $<u^n>$ in position space and $<v^n>$ in momentum space have been reported [3] recently for the atoms from He to Xe in their ground state. For these atoms, systematic examination of the spherically-averaged intracule densities $h(u)$ and $\bar{h}(v)$ has also been performed [4] very recently.

The extracule density $E(\vec{R})$ in position space represents the probability density function for the center-of-mass vector $\vec{R}$, and is defined for an N-electron system $(N \geq 2)$ by

$$E(\vec{R}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{R} - (\vec{r}_j + \vec{r}_k)/2] \right\rangle , \tag{1a}$$

where $\delta(\vec{r})$ is the three-dimensional Dirac delta function and the angular brackets stand for the expectation value. The spherical average $d(R)$ of $E(\vec{R})$ is defined by

$$d(R) \equiv \frac{1}{4\pi} \int d\Omega_R \, E(\vec{R}) , \tag{1b}$$

where (R,Ω_R) with $\Omega_R \equiv (\theta_R, \phi_R)$ are spherical polar coordinates of the vector $\vec{R}$. By definition, the extracule densities $E(\vec{R})$ and $d(R)$ are normalized to the number of electron pairs,

$$\int d\vec{R} \, E(\vec{R}) = 4\pi \int_0^\infty dR \, R^2 \, d(R) = N(N-1)/2 , \tag{1c}$$

and contain information about the location of electron pairs. Exactly analogous definitions apply to the momentum-space extracule density $\bar{E}(\vec{P})$ and its spherical average $\bar{d}(P)$:

$$\bar{E}(\vec{P}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\vec{P} - (\vec{p}_j + \vec{p}_k)/2] \right\rangle , \tag{2a}$$

$$\bar{d}(P) \equiv \frac{1}{4\pi} \int d\Omega_P \, \bar{E}(\vec{P}) , \tag{2b}$$

$$\int d\vec{P} \, \bar{E}(\vec{P}) = 4\pi \int_0^\infty dP \, P^2 \, \bar{d}(P) = N(N-1)/2 , \tag{2c}$$

where $\vec{P} \equiv (P,\Omega_P)$ and $\Omega_P \equiv (\theta_P, \phi_P)$. The functions $\bar{E}(\vec{P})$ and $\bar{d}(P)$ are probability densities for the center-of-mass *momentum* vector $\vec{P}$ and its magnitude P, respectively.

Only a few studies are reported on the extracule densities of specific atoms and molecules. Thakkar and Moore [5] examined the radial extracule density $4\pi R^2 d(R)$ for the atoms He, Li, and Be in relation to the shell structure. They also studied cross sections of $E(\vec{R})$ for two molecules H_2 and LiH and discussed the chemical bonding. The Laplacian of extracule densities was discussed by Sarasola *et al.* [6] for the atoms Li through Ar. For the Ne atom, Wang and Smith [7] studied the extracule density and its Laplacian, and pointed out discrepancies in their characteristics due to different basis sets. Topology of $E(\vec{R})$ in a few planar molecules was examined by Cioslowski and Liu [8]. Fradera *et al.* [9] examined the topology of $E(\vec{R})$ and its Laplacian for simple hydrocarbons. For the first-row hydrides, Sarasola *et al.* [10] and Wang and Smith [11] analyzed the radial, longitudinal, and transverse extracule densities in position space at the SCF level. Wang *et al.* [12] also performed analogous examinations of the hydrides at the SCF and CI levels and found a few essential differences with the SCF results in Ref. [10]. The corresponding analysis in momentum space was reported by Wang and Smith [13] both at the SCF and CI levels, and the correlation effect on the chemical bonding was discussed.

However, all these studies are based on basis-set-expansion wave functions with Gaussian-type basis sets (except Ref. [7] which used Slater-type functions), and no accurate results concerning the extracule density and its related properties are known even for atoms. In Chapter 5, we determine accurate Hartree-Fock values of electronic extracule moments $<R^n>$ in position space and $<P^n>$ in momentum space for a series of 53 neutral atoms with atomic number Z=2 to 54. In the next section, two methods are presented for this purpose: The first method uses the spherically-averaged extracule densities, while the second method uses their characteristic functions. In Section 2-5-3, computational details are given for the application of these methods to the atoms He through Xe in their ground state, in combination with the numerical Hartree-Fock method. The results are presented and discussed in Section 2-5-4 for the extracule moments $<R^n>$ with n=−2 to +4 and $<P^n>$ with n=−2 to +3. It will be pointed out that these extracule moments have intimate relations with the corresponding intracule moments. Hartree atomic units are used throughout this chapter.

2-5-2. EXTRACULE MOMENTS IN HARTREE-FOCK THEORY

2-5-2-1. MOMENTS IN POSITION SPACE

Using the kernel of three-dimensional Fourier transformations for the Dirac delta function $\delta(\vec{r})$ (see, *e.g.*, Ref. [14]), the extracule density $E(\vec{R})$ defined by Eq.(1a) is rewritten as

$$E(\vec{R}) = \pi^{-3} \int d\vec{s} \exp(+2i\vec{s}\cdot\vec{R})\, G(\vec{s}) \ , \tag{3a}$$

$$G(\vec{s}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\langle \exp(-i\vec{s}\cdot\vec{r}_j) \exp(-i\vec{s}\cdot\vec{r}_k) \right\rangle \ . \tag{3b}$$

For a single Slater determinant wave function composed of N spinorbitals $\psi_j(\vec{r})\eta_j(\sigma)$, the Condon-Slater rules (see, *e.g.*, Ref. [15]) rearrange the function $G(\vec{s})$ as

$$G(\vec{s}) = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\{ f_{jj}^{*}(\vec{s}) f_{kk}^{*}(\vec{s}) - \delta_{m_{sj} m_{sk}} f_{jk}^{*}(\vec{s}) f_{kj}^{*}(\vec{s}) \right\}, \tag{4a}$$

where m_{sj} denotes the spin quantum number of the spinorbital j and

$$f_{jk}(\vec{s}) \equiv \int d\vec{r} \exp(+i\vec{s}\cdot\vec{r}) \psi_j^{*}(\vec{r}) \psi_k(\vec{r}) \ . \tag{4b}$$

For atoms and atomic ions, we can generally assume that the spatial orbital $\psi_j(\vec{r})$ has a form,

$$\psi_j(\vec{r}) = R_j(r) Y_{l_j m_j}(\Omega_r) \, , \tag{5}$$

where $Y_{lm}(\Omega)$ is a spherical harmonic and $\vec{r} = (r, \Omega_r)$. Then, we find [3] that

$$f_{jk}(\vec{s}) = \sqrt{4\pi} \sum_{l=0}^{\infty} i^l \sqrt{2l+1}\, c^l(l_j m_j; l_k m_k) Y_{l, m_j - m_k}^{*}(\Omega_s) W_{2ljk}(s) \, , \tag{6a}$$

where $c^k(lm;l'm')$ is the Condon-Shortley parameter [16] and

$$W_{nljk}(s) \equiv \int_0^{\infty} dr\, r^n j_l(sr)\, R_j^{*}(r) R_k(r) = W_{nlkj}^{*}(s) \ , \tag{6b}$$

in which $j_l(x)$ is a spherical Bessel function of the first kind.

The spherically-averaged intracule density $d(R)$, defined by Eq.(1b), can be expressed as a Hankel transform of a function $D(s)$,

$$d(R) = (4/\pi^2) \int_0^{\infty} ds\, s^2 j_0(2Rs) D(s) \, , \tag{7a}$$

where

$$D(s) \equiv (4\pi)^{-1} \int d\Omega_s\, G(\vec{s})$$

$$= \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \left\{ D_{jj,kk}(s) - \delta_{m_{sj} m_{sk}} D_{jk,kj}(s) \right\}, \tag{7b}$$

in which

$$D_{ij,kl}(s) \equiv (4\pi)^{-1} \int d\Omega_s\, f_{ij}^{*}(\vec{s}) f_{kl}^{*}(\vec{s}) \, . \tag{7c}$$

From Eq.(6a), $D_{jj,kk}$ and $D_{jk,kj}$ are explicitly obtained as

$$D_{jj,kk}(s) = \sum_{l=0}^{\min(2l_j, 2l_k)} (2l+1)\, a^l(l_j m_j; l_k m_k)\, W_{2ljj}(s) W_{2lkk}(s) \, , \tag{8a}$$

$$D_{jk,kj}(s) = \sum_{l=|l_j - l_k|}^{l_j + l_k} (-1)^l (2l+1)\, b^l(l_j m_j; l_k m_k)\, W_{2ljk}(s)\, W_{2lkj}(s) \, , \tag{8b}$$

where the summations run over every other integers between the specified values, and the symbols $a^k(lm;l'm')$ and $b^k(lm;l'm')$ are Condon-Shortley parameters [16]. The above restriction on the summations means that in Eq.(8b) we can omit the factor $(-1)^l$ in the summation, if an alternative factor $(-1)^{l_j + l_k}$ is simply added in front of the summation. The extracule moments $< R^n >$ are then obtained by

$$\left\langle R^n \right\rangle \equiv \int d\vec{R}\, R^n E(\vec{R}) = 4\pi \int_0^{\infty} dR\, R^{n+2} d(R) \, , \tag{9}$$

where n is a *real* number greater than -3. Particularly, $< R^0 >$ is equal to $N(N-1)/2$, the number of electron pairs.

Equation (7a) implies that the function $D(s)$ is the characteristic function of the spherically-averaged extracule density $d(R)$. Then the extracule moments $< R^n >$ can be directly obtained from the characteristic function $D(s)$ for an *integer* value of n. As was the case [3] of the intracule moments $< u^n >$, we combine Eqs. (7a) and (9) and interchange the order of integrations with respect to R and s. We finally find

For $n = -2$:

$$\left\langle R^{-2} \right\rangle = 4 \int_0^{\infty} ds\, s\, D(s) \ . \tag{10a}$$

For $n = -1$:

$$\left\langle R^{-1} \right\rangle = (4/\pi) \int_0^{\infty} ds\, D(s) \ . \tag{10b}$$

For a nonnegative *even* integer n:

$$\left\langle R^n \right\rangle = (-1)^{\frac{n}{2}} 2^{-n} (n+1) D^{(n)}(0) \ . \tag{10c}$$

For a positive *odd* integer n:

$$\left\langle R^n \right\rangle = (-1)^{\frac{n+1}{2}} \pi^{-1} 2^{1-n} (n+1) \int_0^{\infty} ds\, s^{-1} D^{(n)}(s) \ , \tag{10d}$$

where $D^{(n)}(s)$ is the n-th derivative of the function $D(s)$ with respect to s. A special case of Eq.(10c) reads $D(0) =< R^0 >= N(N-1)/2$. A derivative of $D(s)$ reduces to a combination of derivatives of the function $W_{nljk}(s)$. Then a recursive relation given in Ref.[3] is useful for its evaluation.

2-5-2-2. MOMENTS IN MOMENTUM SPACE

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 $\psi_k(\vec{r})$ is replaced with its momentum-space counterpart,

$$\phi_k(\vec{p}) = (2\pi)^{-3/2} \int d\vec{r}\, \exp(-i\vec{p}\cdot\vec{r})\, \psi_k(\vec{r})\,. \tag{11a}$$

For the position-space atomic orbital given by Eq.(5), the corresponding momentum-space orbital is given by

$$\phi_k(\vec{p}) = P_k(p) Y_{l_k m_k}(\Omega_p)\,, \tag{11b}$$

$$P_k(p) = (-i)^{l_k} \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2 j_{l_k}(pr)\, R_k(r)\,. \tag{11c}$$

where $\vec{p} = (p, \Omega_p)$. Then the extracule moments $< P^n >$ in momentum space, associated with the densities $\bar{E}(\vec{P})$ and $\bar{d}(P)$, are obtained by exactly the same procedures as in position space.

2-5-2-3. CHARACTERISTIC FUNCTIONS OF EXTRACULE AND INTRACULE DENSITIES

It may be interesting to note that the structure of the characteristic function $D(s)$ of the extracule density, defined by Eq.(7b), is very similar to that of the corresponding function $H(s)$ appeared [3] in the evaluation of the intracule moments $< u^n >$. We immediately find that the 'direct' term $D_{jj,kk}(s)$ [Eq.(8a)] is identical to $H_{jj,kk}(s)$. On the other hand, the 'exchange' term $D_{jk,kj}(s)$ [Eq.(8b)] includes an additional factor $(-1)^l$ in the summation, or a factor $(-1)^{l_j + l_k}$ in front of the summation, compared to $H_{kj,kj}(s)$. The factor generates a difference between the two exchange terms only when the sum $l_j + l_k$ of the azimuthal quantum numbers of the relevant orbitals j and k is an odd integer. Remind also that in Eq.(7b) the exchange term $D_{jk,kj}(s)$ contributes only when the spinorbitals j and k have the same spin. For the three atoms He, Li, and Be, we therefore have $D(s)=H(s)$ exactly, since in He there is no exchange term and in Li and Be only the s orbitals are occupied and the factor $(-1)^{l_j + l_k}$ gives no contribution in $D_{jk,kj}(s)$.

These similarities in the extracule $D(s)$ and intracule $H(s)$ characteristic functions suggest that there may be some relations between the extracule $< R^n >$ and intracule $< u^n >$ moments in position space. The same is true for the characteristic functions in momentum space, and hence for the electron-pair moments $< P^n >$ and $< v^n >$ in momentum space. Such anticipation will be discussed in Section 2-5-4.

2-5-3. COMPUTATIONAL METHOD

Each of atomic LS multiplet states is expressed in general by a linear combination of a finite number of Slater determinants in the Hartree-Fock theory, where L and S represent the total orbital and spin angular momentum quantum numbers, respectively. For the neutral atoms He (Z=2) through Xe (Z=54) in their experimental ground state [17], we have examined the structure of the Hartree-Fock wave functions. The results

show that among (2L+1)(2S+1) multiplet states, there exists at least one state with specific z-component M_L and M_S values of L and S that results in a single determinant wave function, to which our methods described in Section 2-5-2 can be applied.

For these ground states of the 53 atoms with single determinant wave functions, radial functions $R_j(r)$ in position space have been generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [18]. Then products $r^2 R_j(r) R_k(r)$ have been numerically Hankel-transformed to obtain $W_{2ljk}(s)$, by using the algorithm of Talman [19]. Following Eqs.(7b), (8a), and (8b), we obtain the characteristic function $D(s)$ as the sum of products of two $W_{2ljk}(s)$ with appropriate coefficients. The parameters $a^k(lm;l'm')$ and $b^k(lm;l'm')$ have been taken from the Slater's book [20]. An additional Hankel transformation [Eq.(7a)] of the function $D(s)$ gives the spherically-averaged extracule density $d(R)$.

For the extracule moments in momentum space, the position-space radial functions $R_j(r)$, generated by numerical Hartree-Fock calculations, have been first Hankel-transformed to obtain the momentum-space radial functions $P_j(p)$ according to Eq.(11c). Then the same procedure has been applied as in position space to derive the functions $\bar{D}(t)$ and $\bar{d}(P)$.

2-5-4. RESULTS AND DISCUSSION

Table 1 summarizes the extracule moments $< R^n >$ in position space for the atoms He through Xe in their ground state. Note that to avoid large numbers and to facilitate comparison, the moments have been divided by $N(N-1)/2$ and they show average values for a *single* pair of electrons. For all the 53 atoms, we have used the first method for the moments with n=−2 to +4, and the second method for the moments with n=−2, −1, +2, and +4. Based on the comparison of the two sets of moment values, we have judged that the present results have the accuracy of 7 significant figures as shown in Table 1.

An extracule moment $< R^n >$ with a positive n generally decreases with an increasing atomic number Z, but the behavior is not regular except for the second period atoms. Figure 1(a) exemplifies the Z-dependence of the average extracule distance $< R >$. Also plotted there for comparison is the average intracule distance divided by two, $< u > /2$. A surprisingly good resemblance is observed for the two results, and the analysis and discussion given [3] for $< u >$ apply to $< R >$ as well. A moment $< R^n >$ with a negative n generally increases with an increasing Z. Figure 1(b) shows the behavior of $< 1/R >$ and compares it with $2 < 1/u >$. Similarity between $< 1/R >$ and $2 < 1/u >$ is again good.

Analogous examinations of the extracule moments $< R^n >$ and intracule moments $< u^n >$ for n=−2 to +4 show

$$< u^n > / < R^n > \;\cong\; 2^n \tag{12}$$

is a good approximation for all the n values and for all the 53 atoms examined. The

equality is trivially correct for a special case of n=0. Table 2 demonstrates the relation (12) based on the statistical analysis of the results for atoms in each period. The approximation is seen to be better for a small $|n|$ than for a large $|n|$. Equation (12) can be explained theoretically: Comparison of the definition [Eq.(7a)] of the spherically-averaged extracule density $d(R)$ with that [3] of the spherically-averaged intracule density $h(u)$ shows that

$$d(R) \cong 8h(2R) \ , \tag{13}$$

if $D(s) \cong H(s)$ *holds* between their characteristic functions. Equation (12) follows immediately from Eq.(13). It is evident that the moments $< R^n >$ and $< u^n >$ differ exactly by a factor 2^n, if the two characteristic functions $D(s)$ and $H(s)$ are identical. As we have discussed in Subsection 2-5-2-3, however, the functions $D(s)$ and $H(s)$ are slightly different in their exchange parts, and this difference causes a deviation from a simple constant factor 2^n. Nevertheless, the deviation is not very large as shown in Fig.1 and Table 2, suggesting that the overall behaviors of the functions $D(s)$ and $H(s)$ are rather similar. Note that for the three atoms He, Li, and Be, we have $< u^n > / < R^n > = 2^n$ exactly in the Hartree-Fock theory, since $D(s)$=$H(s)$ for these atoms as shown in Subsection 2-5-2-3. It should be also mentioned that a particular case of Eq.(13) for R=0 reduces to a relation $d(0) \cong 8h(0)$, which was previously derived [21] in the study of the electron-electron coalescence $h(0)\,[= I(\vec{0})]$ and counterbalance $d(0)\,[= E(\vec{0})]$ densities.

The extracule moments $< P^n >$ in momentum space are summarized in Table 3, with our normalization scheme $< P^0 > = 1$, based on the duplicate calculations by the two methods. As was the case [3] for the intracule moments $< v^n >$, however, we could not determine sufficiently accurate values for the higher moments $< P^3 >$ and $< P^4 >$, due to a slow decay of the momentum-space extracule density $\bar{d}(P)$ for a large P, which is estimated (see Ref. [3]) to be P^{-8} for the He atom with the Kellner approximation [22].

As Z increases, an extracule moment $< P^n >$ in momentum space increases monotonically when n is positive, whereas it generally decreases when n is negative. Figure 2 depicts the Z-dependence of the moments $< P >$ and $< 1/P >$, and compares them with the intracule moments $< v > /2$ and $2 < 1/v >$. As this figure shows two examples and Table 4 tabulates the statistical results, an approximate relation,

$$< v^n > / < P^n > \cong 2^n \ , \tag{14}$$

is valid in momentum space, which is the partner with Eq.(12). Theoretical ground for Eq.(14) is analogous to that for Eq.(12) as discussed above. Comparison of the results given in Table 2 for position space and in Table 4 for momentum space shows that the accuracy of the relations (12) and (14) is more or less the same. We expect that the approximate relations (12) and (13) in position space and their counterparts in momentum space are of some practical use, since they straightforwardly allow us to obtain extracule information from intracule one in a semiquantitative manner, and *vice versa*.

2-5-5. CONCLUSION

Within the Hartree-Fock framework of atoms, two alternative methods for the calculation of extracule moments $< R^n >$ in position space and $< P^n >$ in momentum space have been presented. The first method uses the spherically-averaged extracule densities, while the second method uses their characteristic functions. The two methods have been applied to the atoms from He to Xe in their ground state, and the moments $< R^n >$ with n = −2 to +4 and $< P^n >$ with n = −2 to +3 have been reported based on numerical Hartree-Fock calculations. The present results are expected to be useful as reference data in the study of electron correlations, since they are defined as the differences in electronic motion from the Hartree-Fock solution.

We have found that the characteristic functions $D(s)$ and $H(s)$ of the spherically-averaged extracule $d(R)$ and intracule $h(u)$ densities are similar in the Hartree-Fock approximation. This fact results in approximate but useful relations $d(R) \cong 8h(2R)$ and $< u^n > / < R^n > \cong 2^n$ between the two densities and the associated moments. Especially, the equalities in the above relations hold for the three atoms He, Li, and Be. Exactly the same is true for the corresponding momentum-space quantities. Then it may be interesting to examine how these relations are valid or should be modified beyond the orbital approximation.

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Table 1. Extracule moments in position space. Note that the normalization is $\langle R^0 \rangle = 1$ instead of $N(N\text{-}1)/2$. A(n) means $A \times 10^n$.

Z	Atom	$N(N\text{-}1)/2$	$\langle 1/R^2 \rangle$	$\langle 1/R \rangle$	$\langle R \rangle$	$\langle R^2 \rangle$	$\langle R^3 \rangle$	$\langle R^4 \rangle$
2	He	1	7.368179	2.051538	6.810622(-1)	5.924142(-1)	6.261191(-1)	7.784555(-1)
3	Li	3	6.709724	1.520614	1.448181	3.105345	8.159766	2.473096(1)
4	Be	6	7.024411	1.496381	1.260043	2.164846	4.544121	1.119611(1)
5	B	10	7.737292	1.610020	1.066007	1.515296	2.642386	5.451563
6	C	15	8.717182	1.773941	9.108569(-1)	1.090618	1.598356	2.768985
7	N	21	9.885256	1.956784	7.934240(-1)	8.194924(-1)	1.033333	1.538178
8	O	28	1.126043(1)	2.142592	7.136487(-1)	6.658112(-1)	7.643069(-1)	1.043697
9	F	36	1.278990(1)	2.336141	6.453527(-1)	5.444917(-1)	5.667880(-1)	7.039006(-1)
10	Ne	45	1.446175(1)	2.534190	5.874372(-1)	4.503033(-1)	4.260501(-1)	4.813547(-1)
11	Na	55	1.560010(1)	2.530795	7.897491(-1)	1.222820	2.974639	9.198634
12	Mg	66	1.666963(1)	2.545705	8.255219(-1)	1.226122	2.580893	6.665189
13	Al	78	1.765942(1)	2.555618	8.537715(-1)	1.265834	2.579189	6.441829
14	Si	91	1.862109(1)	2.580819	8.316909(-1)	1.128313	2.022480	4.367341
15	P	105	1.956646(1)	2.616491	7.970708(-1)	9.866167(-1)	1.572778	2.988506
16	S	120	2.049719(1)	2.656198	7.679280(-1)	8.910486(-1)	1.320357	2.335091
17	Cl	136	2.142884(1)	2.703564	7.345986(-1)	7.948232(-1)	1.087982	1.773546
18	Ar	153	2.236563(1)	2.756942	7.008747(-1)	7.074701(-1)	8.954714(-1)	1.345319
19	K	171	2.316795(1)	2.748800	8.310172(-1)	1.336353	3.485643	1.215605(1)
20	Ca	190	2.393500(1)	2.747306	8.676716(-1)	1.404916	3.365757	1.018277(1)
21	Sc	210	2.474790(1)	2.790560	8.310763(-1)	1.257258	2.801272	7.923651
22	Ti	231	2.558099(1)	2.843566	7.940638(-1)	1.131962	2.384964	6.426712
23	V	253	2.642936(1)	2.901537	7.595355(-1)	1.025678	2.057280	5.315303
24	Cr	276	2.735606(1)	2.998219	6.777603(-1)	7.771608(-1)	1.351627	3.177384
25	Mn	300	2.817801(1)	3.029066	6.975186(-1)	8.553683(-1)	1.578067	3.802711
26	Fe	325	2.908057(1)	3.094025	6.708973(-1)	7.855931(-1)	1.387477	3.217418
27	Co	351	3.000551(1)	3.162254	6.457831(-1)	7.243886(-1)	1.230754	2.760814
28	Ni	378	3.095108(1)	3.232603	6.223219(-1)	6.702434(-1)	1.098401	2.389709
29	Cu	406	3.200321(1)	3.338504	5.705304(-1)	5.501347(-1)	8.398323(-1)	1.807611
30	Zn	435	3.290725(1)	3.378970	5.797497(-1)	5.791409(-1)	8.896713(-1)	1.834579
31	Ga	465	3.378007(1)	3.407836	6.016156(-1)	6.550486(-1)	1.110762	2.519957
32	Ge	496	3.463851(1)	3.437401	6.037122(-1)	6.435681(-1)	1.015765	2.062181
33	As	528	3.548524(1)	3.467215	5.992452(-1)	6.152988(-1)	9.002495(-1)	1.653634
34	Se	561	3.631825(1)	3.495266	5.961345(-1)	5.986724(-1)	8.409732(-1)	1.471269
35	Br	595	3.714392(1)	3.524352	5.890543(-1)	5.722570(-1)	7.630303(-1)	1.255633
36	Kr	630	3.796359(1)	3.554367	5.798542(-1)	5.427226(-1)	6.852769(-1)	1.058757
37	Rb	666	3.872781(1)	3.557173	6.557973(-1)	9.168609(-1)	2.290062	8.084863
38	Sr	703	3.947220(1)	3.561321	6.865566(-1)	9.961538(-1)	2.356427	7.334795
39	Y	741	4.021632(1)	3.577886	6.793193(-1)	9.363824(-1)	2.041999	5.833639
40	Zr	780	4.095855(1)	3.598722	6.673256(-1)	8.761765(-1)	1.795330	4.836319
41	Nb	820	4.171576(1)	3.634298	6.261008(-1)	7.146089(-1)	1.243505	2.904450
42	Mo	861	4.245677(1)	3.660882	6.119906(-1)	6.668700(-1)	1.098368	2.442033
43	Tc	903	4.317062(1)	3.673687	6.279983(-1)	7.306942(-1)	1.309250	3.136113
44	Ru	946	4.392986(1)	3.714864	5.912818(-1)	6.101080(-1)	9.558633(-1)	2.059491
45	Rh	990	4.466664(1)	3.744133	5.804210(-1)	5.834027(-1)	8.953406(-1)	1.911523
46	Pd	1035	4.542936(1)	3.789119	5.419349(-1)	4.594249(-1)	5.312473(-1)	7.866394(-1)
47	Ag	1081	4.614326(1)	3.806375	5.588263(-1)	5.347590(-1)	7.935091(-1)	1.678860
48	Cd	1128	4.684497(1)	3.822303	5.675561(-1)	5.631667(-1)	8.576381(-1)	1.788189
49	In	1176	4.753103(1)	3.833608	5.840412(-1)	6.234641(-1)	1.044874	2.394294
50	Sn	1225	4.820821(1)	3.845888	5.885758(-1)	6.258223(-1)	1.004172	2.116390
51	Sb	1275	4.887723(1)	3.858689	5.885456(-1)	6.134469(-1)	9.327414(-1)	1.813427
52	Te	1326	4.953669(1)	3.870767	5.892380(-1)	6.081668(-1)	9.001270(-1)	1.685296
53	I	1378	5.018951(1)	3.883541	5.869449(-1)	5.937786(-1)	8.454667(-1)	1.505589
54	Xe	1431	5.083622(1)	3.896916	5.828521(-1)	5.753342(-1)	7.854264(-1)	1.326968

Table 2. Average of the ratios $<u^n>/<R^n>$ of the extracule and intracule moments in position space.

Period		$n=-2$	$n=-1$	$n=2$	$n=3$	$n=4$
First	(1 atom)	0.25	0.5	4	8	16
Second	(8 atoms)	0.24 ± 0.02	0.48 ± 0.02	4.3 ± 0.3	8.8 ± 0.8	18.±2.
Third	(8 atoms)	0.221 ± 0.003	0.476 ± 0.002	4.14 ± 0.09	8.4 ± 0.4	17.±1.
Fourth	(18 atoms)	0.218 ± 0.002	0.480 ± 0.003	4.07 ± 0.03	8.1 ± 0.2	16.3 ± 0.5
Fifth	(18 atoms)	0.2180 ± 0.0002	0.483 ± 0.002	4.05 ± 0.02	8.11 ± 0.09	16.2 ± 0.4
All	(53 atoms)	0.222	0.481	4.11	8.27	16.6

Table 3. Extracule moments in momentum space. Note that the normalization is $<P^0>=1$ instead of $N(N-1)/2$. A(n) means $A \times 10^n$.

Z	Atom	$N(N-1)/2$	$<1/P^2>$	$<1/P>$	$<P>$	$<P^2>$	$<P^3>$
2	He	1	3.24703	1.376054	1.029314	1.43084	2.74
3	Li	3	1.95771	1.089668	1.327195	2.47758	6.65
4	Be	6	4.50371	1.269801	1.538092	3.64326	1.27(1)
5	B	10	3.44032	1.169360	1.730677	4.88556	2.08(1)
6	C	15	2.37679	1.017672	1.929345	6.23496	3.11(1)
7	N	21	1.68816	8.866875(-1)	2.132283	7.69586	4.37(1)
8	O	28	1.34868	8.011802(-1)	2.326795	9.24672	5.87(1)
9	F	36	1.06974	7.226189(-1)	2.525761	1.09106(1)	7.63(1)
10	Ne	45	8.55767(-1)	6.543288(-1)	2.727855	1.26883(1)	9.65(1)
11	Na	55	7.40875(-1)	6.151946(-1)	2.908822	1.45253(1)	1.20(2)
12	Mg	66	1.06840	6.227498(-1)	3.076266	1.64254(1)	1.45(2)
13	Al	78	1.19475	6.270008(-1)	3.234936	1.83777(1)	1.74(2)
14	Si	91	1.11677	6.153637(-1)	3.388511	2.03861(1)	2.05(2)
15	P	105	1.00398	5.974287(-1)	3.538361	2.24507(1)	2.40(2)
16	S	120	9.54226(-1)	5.846667(-1)	3.682769	2.45632(1)	2.77(2)
17	Cl	136	8.77628(-1)	5.678136(-1)	3.825060	2.67308(1)	3.17(2)
18	Ar	153	7.96304(-1)	5.491900(-1)	3.965686	2.89536(1)	3.60(2)
19	K	171	7.53180(-1)	5.398013(-1)	4.097079	3.12062(1)	4.06(2)
20	Ca	190	9.21255(-1)	5.453688(-1)	4.223003	3.34951(1)	4.56(2)
21	Sc	210	8.07740(-1)	5.220668(-1)	4.355889	3.58191(1)	5.08(2)
22	Ti	231	7.10974(-1)	4.983966(-1)	4.490307	3.81887(1)	5.63(2)
23	V	253	6.30028(-1)	4.762592(-1)	4.624947	4.06032(1)	6.20(2)
24	Cr	276	4.44206(-1)	4.411725(-1)	4.766606	4.30631(1)	6.81(2)
25	Mn	300	5.03074(-1)	4.362785(-1)	4.895076	4.55692(1)	7.46(2)
26	Fe	325	4.56084(-1)	4.197437(-1)	5.028036	4.81139(1)	8.13(2)
27	Co	351	4.14580(-1)	4.039118(-1)	5.161719	5.07050(1)	8.83(2)
28	Ni	378	3.78199(-1)	3.890889(-1)	5.295478	5.33414(1)	9.57(2)
29	Cu	406	2.87422(-1)	3.667324(-1)	5.435456	5.60216(1)	1.03(3)
30	Zn	435	3.17656(-1)	3.620402(-1)	5.563631	5.87521(1)	1.11(3)
31	Ga	465	3.50547(-1)	3.599804(-1)	5.688910	6.15159(1)	1.20(3)
32	Ge	496	3.55427(-1)	3.569276(-1)	5.811602	6.43157(1)	1.28(3)
33	As	528	3.50589(-1)	3.533617(-1)	5.932105	6.71506(1)	1.37(3)
34	Se	561	3.57126(-1)	3.512624(-1)	6.050047	7.00169(1)	1.47(3)
35	Br	595	3.54488(-1)	3.484018(-1)	6.166296	7.29172(1)	1.57(3)
36	Kr	630	3.46777(-1)	3.450027(-1)	6.281050	7.58506(1)	1.67(3)
37	Rb	666	3.47802(-1)	3.440913(-1)	6.392166	7.88075(1)	1.77(3)
38	Sr	703	4.11154(-1)	3.472579(-1)	6.500770	8.17882(1)	1.88(3)
39	Y	741	3.89099(-1)	3.431248(-1)	6.609822	8.47940(1)	1.99(3)
40	Zr	780	3.66763(-1)	3.379651(-1)	6.718541	8.78297(1)	2.10(3)
41	Nb	820	3.00572(-1)	3.276085(-1)	6.828868	9.08930(1)	2.22(3)
42	Mo	861	2.84851(-1)	3.221516(-1)	6.936733	9.39853(1)	2.34(3)
43	Tc	903	3.08663(-1)	3.214602(-1)	7.041281	9.71033(1)	2.47(3)
44	Ru	946	2.62032(-1)	3.124914(-1)	7.149541	1.00249(2)	2.60(3)
45	Rh	990	2.50496(-1)	3.075274(-1)	7.255264	1.03424(2)	2.73(3)
46	Pd	1035	2.38186(-1)	3.013868(-1)	7.362406	1.06626(2)	2.86(3)
47	Ag	1081	2.28475(-1)	2.976231(-1)	7.465499	1.09858(2)	3.00(3)
48	Cd	1128	2.42312(-1)	2.963043(-1)	7.566807	1.13115(2)	3.14(3)
49	In	1176	2.59111(-1)	2.959340(-1)	7.666775	1.16392(2)	3.29(3)
50	Sn	1225	2.64283(-1)	2.951144(-1)	7.765442	1.19694(2)	3.44(3)
51	Sb	1275	2.64699(-1)	2.940103(-1)	7.862939	1.23018(2)	3.59(3)
52	Te	1326	2.71329(-1)	2.935757(-1)	7.959048	1.26364(2)	3.75(3)
53	I	1378	2.73098(-1)	2.927578(-1)	8.054155	1.29732(2)	3.91(3)
54	Xe	1431	2.71806(-1)	2.916370(-1)	8.148335	1.33122(2)	4.07(3)

Table 4. Average of the ratios $<v^n>/<P^n>$ of the extracule and intracule moments in momentum space.

Period		$n=-2$	$n=-1$	$n=1$	$n=2$	$n=3$
First	(1 atom)	0.25	0.5	2	4	8
Second	(8 atoms)	0.21 ± 0.04	0.47 ± 0.03	2.03 ± 0.03	4.06 ± 0.06	8.1 ± 0.1
Third	(8 atoms)	0.20 ± 0.04	0.472 ± 0.008	2.038 ± 0.008	4.10 ± 0.02	8.2 ± 0.2
Fourth	(18 atoms)	0.21 ± 0.02	0.479 ± 0.003	2.027 ± 0.005	4.07 ± 0.02	8.2 ± 0.5
Fifth	(18 atoms)	0.21 ± 0.02	0.482 ± 0.002	2.019 ± 0.004	4.055 ± 0.007	8.1 ± 0.2
All	(53 atoms)	0.21	0.478	2.026	4.066	8.1

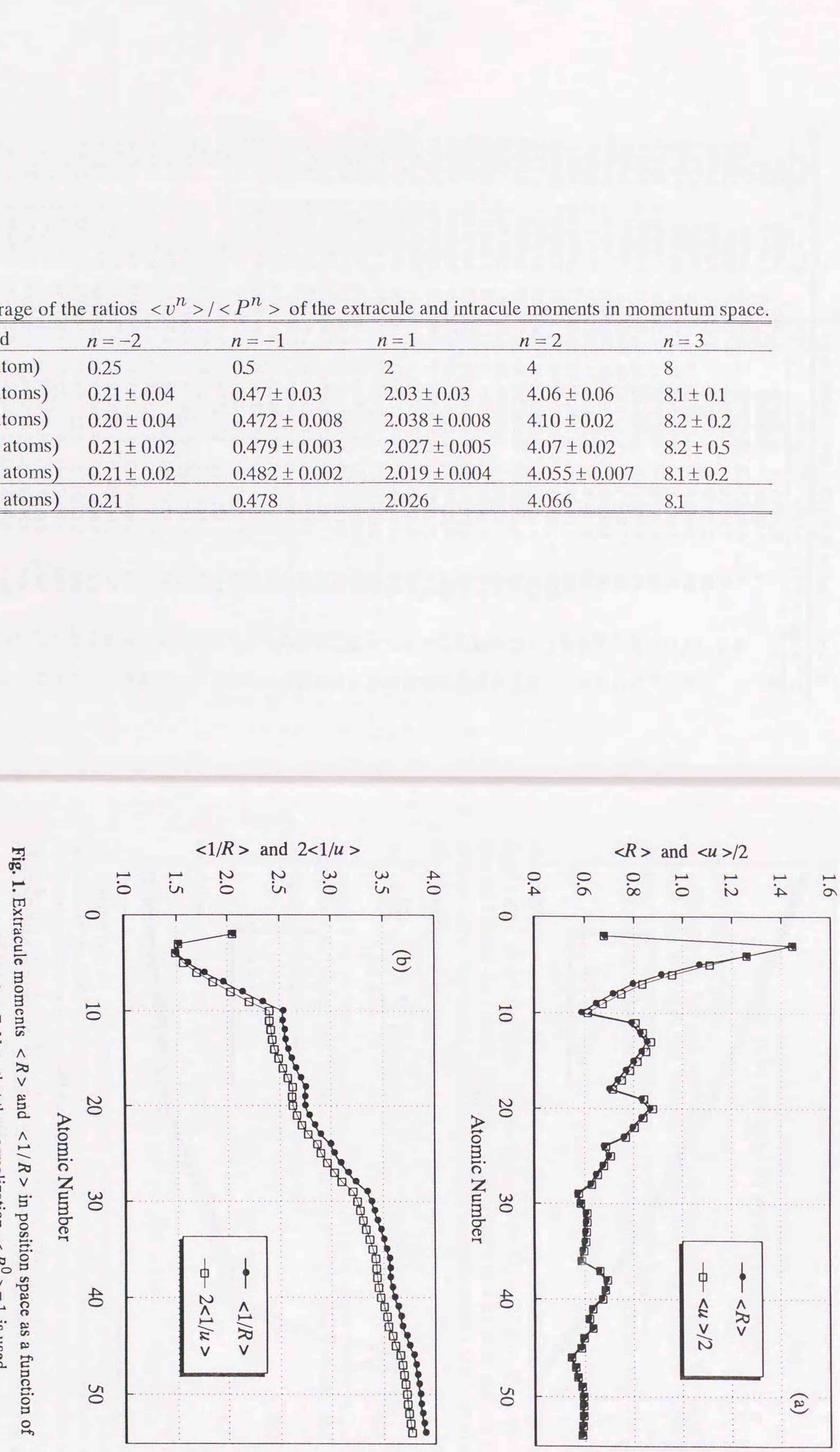
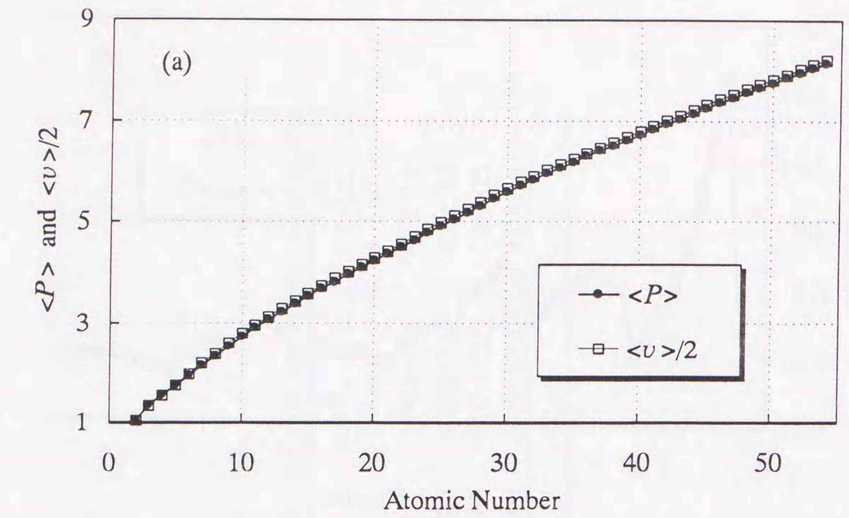


Fig. 1. Extracule moments $<R>$ and $<1/R>$ in position space as a function of atomic number Z. Note that the normalization $<R^0>=1$ is used. Intracule moments $<u>/2$ and $2<1/u>$ are also plotted for comparison.



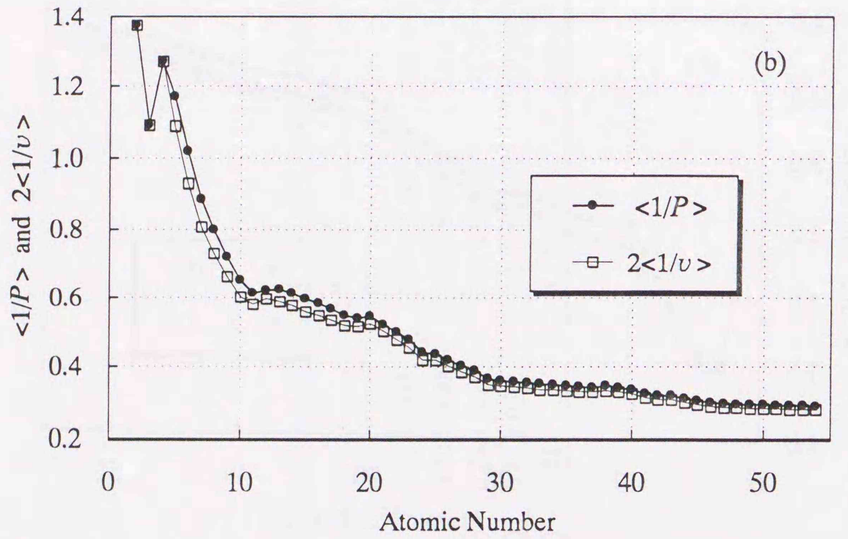


Fig. 2. Extracule moments $<P>$ and $<1/P>$ in momentum space as a function of atomic number Z. Note that the normalization $<P^0>=1$ is used. Intracule moments $<\upsilon>/2$ and $2<1/\upsilon>$ are also plotted for comparison.

PART 2.
CHAPTER 6.

ELECREON-PAIR DENSITIES FOR MULTI-DETERMINANT WAVE FUNCTIONS

2-6-1. INTRODUCTION

The intracule $I(\mathbf{u})$ and extracule $E(\mathbf{R})$ 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, *e.g.*, Ref. [2] for a review). For an N-electron system ($N\geq 2$), the intracule densities $I(\mathbf{u})$ and $h(u)$ are defined by

$$I(\mathbf{u}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{u} - (\mathbf{r}_j - \mathbf{r}_k)] \right\rangle , \qquad h(u) \equiv (4\pi)^{-1} \int d\Omega_u \, I(\mathbf{u}) , \tag{1}$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function, the angular brackets $\langle\ \rangle$ stand for the expectation value, and $\mathbf{u} = (u, \Omega_u)$ with $\Omega_u = (\theta_u, \phi_u)$. The intracule densities $I(\mathbf{u})$ and $h(u)$ are the probability density functions for the *relative* vector $\mathbf{u}$ and its magnitude u, respectively. On the other hand, the extracule densities $E(\mathbf{R})$ and $d(R)$ are defined by

$$E(\mathbf{R}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{R} - (\mathbf{r}_j + \mathbf{r}_k)/2] \right\rangle , \qquad d(R) \equiv (4\pi)^{-1} \int d\Omega_R \, E(\mathbf{R}) , \tag{2}$$

and represent the probability density functions for the *center-of-mass* vector $\mathbf{R}$ and its magnitude R, respectively, where $\mathbf{R} = (R, \Omega_R)$ with $\Omega_R = (\theta_R, \phi_R)$. The corresponding intracule $\bar{I}(\mathbf{v})$ and $\bar{h}(\upsilon)$ densities,

$$\bar{I}(\mathbf{v}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{v} - (\mathbf{p}_j - \mathbf{p}_k)] \right\rangle , \qquad \bar{h}(\upsilon) \equiv (4\pi)^{-1} \int d\Omega_\upsilon \, \bar{I}(\mathbf{v}) , \tag{3}$$

and extracule $\bar{E}(\mathbf{P})$ and $\bar{d}(P)$ densities,

$$\bar{E}(\mathbf{P}) \equiv \left\langle \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \delta[\mathbf{P} - (\mathbf{p}_j + \mathbf{p}_k)/2] \right\rangle , \qquad \bar{d}(P) \equiv (4\pi)^{-1} \int d\Omega_P \, \bar{E}(\mathbf{P}) , \tag{4}$$

are also introduced in momentum space, which represent the probability density functions for the relative and center-of-mass momentum vectors and their magnitudes of an electron pair. As reviewed in Refs. [2-4], for example, studies on the two-electron intracule and extracule densities are limited compared with those on the familiar one-electron position $\rho(\mathbf{r})$ and momentum $\Pi(\mathbf{p})$ densities or their spherical averages.

We have recently developed [3,4] a method for the evaluation of the above four electron-pair densities and their spherical averages, when the wave function of the system under consideration is expressed by a single Slater determinant. The results have been applied [5,6] to systematic examinations of the spherically-averaged intracule $h(u)$ and extracule $d(R)$ densities, as well as their momentum-space counterparts $\bar{h}(\upsilon)$ and $\bar{d}(P)$, for the neutral atoms from He to Xe in their ground states within the Hartree-

Fock framework. Accurate Hartree-Fock values of the intracule moments $<u^n>$ and $<v^n>$ and the extracule moments $<R^n>$ and $<P^n>$ have been also published [3,4] for the atoms He through Xe, based on numerical Hartree-Fock calculations.

In Chapter 6, we generalize our method for evaluating the four kinds of electron-pair densities to the cases where an N-electron wave function is given by a linear combination of Slater determinants. The results are useful not only for the configuration-interaction approximation but also for the Hartree-Fock approximation of some systems, where a linear combination of two or more Slater determinants is needed for symmetry requirements. In the next section, we describe our method based on rewriting the electron-pair densities, defined by Eqs. (1)-(4), as the Fourier or Hankel transforms of their characteristic functions. As an illustrative application of the present results, we discuss in Section 2-6-3 the difference of the electron-pair motion in the ${}^1P$ and ${}^3P$ multiplet states of the helium atom. Hartree atomic units are used throughout this chapter.

2-6-2. ELECTRON-PAIR DENSITIES IN POSITION AND MOMENTUM SPACES

2-6-2-1. WAVE FUNCTIONS

We consider an N-electron wave function Ψ in position space expressed by a linear combination of M Slater determinants $\{S_J\}$,

$$\Psi(\mathbf{x}_1,...,\mathbf{x}_N) = \sum_{J=1}^{M} C_J\, S_J(\mathbf{x}_1,...,\mathbf{x}_N)\ , \tag{5a}$$

$$S_J(\mathbf{x}_1,...,\mathbf{x}_N) \equiv \det\{\psi_{J1}(\mathbf{r}_1)\eta_{J1}(\sigma_1)\ \ ...\ \ \psi_{JN}(\mathbf{r}_N)\eta_{JN}(\sigma_N)\}, \tag{5b}$$

where $\mathbf{x}_k \equiv (\mathbf{r}_k, \sigma_k)$ is the combined position-spin coordinates of the electron k, and $\psi_{Jk}(\mathbf{r})$ and $\eta_{Jk}(\sigma)$ are respectively the spatial and spin parts of the kth spin-orbital of the Jth Slater determinant. The spatial functions are assumed to be orthonormal, and the symbol $\det\{...\}$ implicitly includes the normalization constant $(N!)^{-1/2}$.

The corresponding wave function $\Phi(\mathbf{y}_1,...,\mathbf{y}_N)$ in momentum space, with $\mathbf{y}_k \equiv (\mathbf{p}_k, \sigma_k)$ being the combined momentum-spin coordinates of the electron k, is given by the $3N$-dimensional Fourier transformation of $\Psi(\mathbf{x}_1,...,\mathbf{x}_N)$ with respect to the position coordinates $\{\mathbf{r}_k\}$,

$$\Phi(\mathbf{y}_1,...,\mathbf{y}_N) = (2\pi)^{-3N/2}\int d\mathbf{r}_1...d\mathbf{r}_N\ \exp(-i\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k)\,\Psi(\mathbf{x}_1,...,\mathbf{x}_N)\ . \tag{6a}$$

Then the momentum-space wave function Φ is found [7] to have exactly the same linear-combination-of-determinant structure as that in position space [Eqs. (5a) and (5b)], provided that the one-electron spatial function $\psi_{Jk}(\mathbf{r})$ is replaced with its momentum-space counterpart,

$$\phi_{Jk}(\mathbf{p}) = (2\pi)^{-3/2}\int d\mathbf{r}\,\exp(-i\mathbf{p}\cdot\mathbf{r})\,\psi_{Jk}(\mathbf{r})\ . \tag{6b}$$

For atoms and atomic ions, we can generally assume that the one-electron spatial function $\psi_{Jk}(\mathbf{r})$ has a form,

$$\psi_{Jk}(\mathbf{r}) = R_{Jk}(r)\,Y_{l_{Jk}m_{Jk}}(\Omega_r)\ , \tag{7a}$$

where $Y_{lm}(\Omega)$ is a spherical harmonic and $\mathbf{r} = (r, \Omega_r)$. For the spatial function given by Eq. (7a), Eq. (6b) reduces to

$$\phi_{Jk}(\mathbf{p}) = P_{Jk}(p)\,Y_{l_{Jk}m_{Jk}}(\Omega_p)\ , \tag{7b}$$

$$P_{Jk}(p) = (-i)^{l_{Jk}}\sqrt{\frac{2}{\pi}}\int_0^\infty dr\, r^2\, j_{l_{Jk}}(pr)\,R_{Jk}(r)\ , \tag{7c}$$

where $\mathbf{p} = (p, \Omega_p)$ and $j_l(x)$ is a spherical Bessel function of the first kind.

2-6-2-2. INTRACULE DENSITIES

Using the kernel of three-dimensional Fourier transformations for the Dirac delta function,

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

the intracule densities $I(\mathbf{u})$ and $h(u)$ defined by Eq. (1) are rewritten as

$$I(\mathbf{u}) = (2\pi)^{-3}\int ds \exp(+i\mathbf{u}\cdot\mathbf{s})\,F(\mathbf{s})\ , \tag{9a}$$

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

where $\mathbf{s} = (s, \Omega_s)$,

$$F(\mathbf{s}) \equiv \sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\left\langle \exp(-i\mathbf{s}\cdot\mathbf{r}_j)\exp(+i\mathbf{s}\cdot\mathbf{r}_k)\right\rangle\ , \tag{10a}$$

$$H(s) \equiv (4\pi)^{-1}\int d\Omega_s F(\mathbf{s})\ . \tag{10b}$$

For the wave function given by Eqs. (5a) and (5b), the Condon-Slater rules (see, *e.g.*, Ref. [8]) rearrange the characteristic function $F(\mathbf{s})$ of $I(\mathbf{u})$ as

$$F(\mathbf{s}) = F_0(\mathbf{s}) + F_1(\mathbf{s}) + F_2(\mathbf{s})\ , \tag{11a}$$

$$F_0(\mathbf{s}) = \sum_{J=1}^{M}|C_J|^2\left\{\sum_{j=1}^{n'}\sum_{k=j+1}^{n}\left[F_{JkJk}^{JjJj}(\mathbf{s}) - \delta_s(Jj,Jk)\,F_{JkJj}^{JkJj}(\mathbf{s})\right]\right\}\ , \tag{11b}$$

$$F_1(\mathbf{s}) = \sum_{J=1}^{M-1}\sum_{K=J+1}^{M}\Delta_1(J,K)\left\{C_J^* C_K\sum_{j=1}^{n'}\left[\delta_s(Jn,Kn)F_{KjKj}^{KnJn}(\mathbf{s}) - \delta_s(Jn,Kj)\delta_s(Kj,Kn)F_{KjKn}^{KjJn}(\mathbf{s})\right]\right.$$
$$\left. + C_K^* C_J\sum_{j=1}^{n'}\left[\delta_s(Jn,Kn)F_{JjJj}^{JnKn}(\mathbf{s}) - \delta_s(Jj,Kn)\delta_s(Jj,Jn)F_{JjJn}^{JjKn}(\mathbf{s})\right]\right\}\ , \tag{11c}$$

$$F_2(\mathbf{s}) = \sum_{J=1}^{M-1}\sum_{K=J+1}^{M}\Delta_2(J,K)$$
$$\times\left\{C_J^* C_K\left[\delta_s(Jn,Kn)\delta_s(Jn',Kn')F_{Jn'Kn'}^{KnJn}(\mathbf{s}) - \delta_s(Jn,Kn')\delta_s(Jn',Kn)F_{Jn'Kn}^{Kn'Jn}(\mathbf{s})\right]\right.$$
$$\left. + C_K^* C_J\left[\delta_s(Jn,Kn)\delta_s(Jn',Kn')F_{Kn'Jn'}^{JnKn}(\mathbf{s}) - \delta_s(Jn,Kn')\delta_s(Jn',Kn)F_{Kn'Jn}^{Jn'Kn}(\mathbf{s})\right]\right\}\ , \tag{11d}$$

where $n = N$, $n' = N-1$,

$$F_{\mu\nu}^{\kappa\lambda}(\mathbf{s}) \equiv f_{\kappa\lambda}^*(\mathbf{s})\,f_{\mu\nu}(\mathbf{s}) = [F_{\kappa\lambda}^{\mu\nu}(\mathbf{s})]^*\ , \tag{12a}$$

$$f_{\kappa\lambda}(\mathbf{s}) \equiv \int d\mathbf{r} \exp(+i\mathbf{s}\cdot\mathbf{r})\psi^*_\kappa(\mathbf{r})\psi_\lambda(\mathbf{r}) = f^*_{\lambda\kappa}(-\mathbf{s}) \ , \tag{12b}$$

$$\Delta_1(J,K) \equiv \begin{cases} 1, & \text{if one spin - orbital is different between } S_J \text{ and } S_K, \\ 0, & \text{otherwise,} \end{cases} \tag{12c}$$

$$\Delta_2(J,K) \equiv \begin{cases} 1, & \text{if two spin - orbitals are different between } S_J \text{ and } S_K, \\ 0, & \text{otherwise,} \end{cases} \tag{12d}$$

$$\delta_s(\kappa,\lambda) \equiv \begin{cases} 1, & \text{if spin - orbitals } \kappa \text{ and } \lambda \text{ have the same spin,} \\ 0, & \text{if spin - orbitals } \kappa \text{ and } \lambda \text{ have different spins,} \end{cases} \tag{12e}$$

in which Greek letters κ, λ, μ, and ν are used to enumerate spin-orbitals and Slater determinants in a combined manner. Since the intracule density operator is a two-electron operator, there is no contribution in Eq. (11a) from a pair of Slater determinants which differ in three or more spin-orbitals. When $\Delta_1(J,K)=1$, it has been assumed in Eq. (11c) that by an appropriate permutation of columns in determinants (with the associated permutation parity -1 or $+1$), the first $N-1$ spin-orbitals of the Slater determinants S_J and S_K are completely identical and the difference appears only in the last spin-orbitals. Similarly, Eq. (11d) assumes that when $\Delta_2(J,K)=1$, the first $N-2$ spin-orbitals of the Slater determinants S_J and S_K are arranged to coincide with each other and the difference appears only in the (N-1)th and Nth spin-orbitals.

The characteristic function $H(s)$ [Eq. (10b)] of the spherically-averaged intracule density $h(u)$ has exactly the same mathematical structure as $F(\mathbf{s})$,

$$H(s) = H_0(s) + H_1(s) + H_2(s) \ , \tag{13a}$$

and all the constituent terms are immediately obtained from Eqs. (11a)-(11d), if we replace $F^{\kappa\lambda}_{\mu\nu}(\mathbf{s})$ with

$$H^{\kappa\lambda}_{\mu\nu}(s) \equiv (4\pi)^{-1}\int d\Omega_s \, F^{\kappa\lambda}_{\mu\nu}(\mathbf{s}) \ . \tag{13b}$$

For atomic systems with the spatial function (7a), Eq. (12b) is simplified [3] to

$$f_{\kappa\lambda}(\mathbf{s}) = \sqrt{4\pi} \sum_{l=|l_\kappa - l_\lambda|}^{l_\kappa + l_\lambda} i^l \sqrt{2l+1}\, c^l(\kappa;\lambda)\, Y^*_{l,m_\kappa - m_\lambda}(\Omega_s)\, W_{l\kappa\lambda}(s) \ , \tag{14a}$$

where

$$W_{l\kappa\lambda}(s) \equiv \int_0^\infty dr\, r^2\, j_l(sr)\, R^*_\kappa(r)\, R_\lambda(r) = W^*_{l\lambda\kappa}(s) \ , \tag{14b}$$

and $c^l(\kappa;\lambda) \equiv c^l(l_\kappa m_\kappa ; l_\lambda m_\lambda)$ is the Condon-Shortley parameter [9]. Note that due to the property of $c^l(\kappa;\lambda)$, the summation in Eq. (14a) runs over every other integers between the specified values. Based on the expression (14a), the angular integrations in the function $H(s)$ are analytically performed. We have

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

if $l_\kappa + l_\lambda + l_\mu + l_\nu = even$ *and* $m_\kappa - m_\lambda = m_\mu - m_\nu$. When either or both of these conditions are not satisfied, $H^{\kappa\lambda}_{\mu\nu}(s)$ vanishes. Two special cases of Eq. (15a) are

$$H^{\kappa\kappa}_{\mu\mu}(s) = \sum_{l=0}^{\min(2l_\kappa, 2l_\mu)} (2l+1)\, a^l(\kappa;\mu)\, W^*_{l\kappa\kappa}(s)\, W_{l\mu\mu}(s) \ , \tag{15b}$$

$$H^{\kappa\mu}_{\kappa\mu}(s) = \sum_{l=|l_\kappa - l_\mu|}^{l_\kappa + l_\mu} (2l+1)\, b^l(\kappa;\mu) \left| W_{l\kappa\mu}(s) \right|^2 \ , \tag{15c}$$

which appear in $H_0(s)$, 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 [9]. The summations in Eqs. (15a)-(15c) run over every other integers between the specified values.

As explained in Section 2-6-2-1, the wave function $\Phi(\mathbf{y}_1,\ldots,\mathbf{y}_N)$ in momentum space is isomorphic [7] with the wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ in position space. Then the formalism for the momentum-space intracule densities $\bar{I}(\mathbf{v})$ and $\bar{h}(v)$ defined by Eq. (3) is exactly analogous to that for the position-space intracule densities presented above,

$$\bar{I}(\mathbf{v}) = (2\pi)^{-3}\int d\mathbf{s} \exp(+i\mathbf{v}\cdot\mathbf{s})\, \bar{F}(\mathbf{s}) \ , \tag{16a}$$

$$\bar{h}(v) = (2\pi^2)^{-1}\int_0^\infty ds\, s^2\, j_0(vs)\, \bar{H}(s) \ . \tag{16b}$$

The explicit forms of the characteristic functions $\bar{F}(\mathbf{s})$ and $\bar{H}(s)$ are obtained respectively by replacing $\psi_\kappa(\mathbf{r})$ with $\phi_\kappa(\mathbf{p})$ and by $R_\kappa(r)$ with $P_\kappa(p)$ in Eqs. (11a)-(15c).

2-6-2-3. EXTRACULE DENSITIES

Since

$$\delta[\mathbf{R} - (\mathbf{r}_j + \mathbf{r}_k)/2] = \pi^{-3}\int d\mathbf{s} \exp(+2i\mathbf{R}\cdot\mathbf{s}) \exp(-i\mathbf{r}_j\cdot\mathbf{s}) \exp(-i\mathbf{r}_k\cdot\mathbf{s}) \ , \tag{17}$$

the position-space extracule densities $E(\mathbf{R})$ and $d(R)$ defined by Eq. (2) are rewritten as

$$E(\mathbf{R}) = \pi^{-3}\int d\mathbf{s} \exp(+2i\mathbf{R}\cdot\mathbf{s})\, G(\mathbf{s}) \ , \tag{18a}$$

$$d(R) = (4/\pi^2)\int_0^\infty ds\, s^2\, j_0(2Rs)\, D(s) \ , \tag{18b}$$

where $\mathbf{R} = (R,\Omega_R)$,

$$G(\mathbf{s}) \equiv \sum_{j=1}^{N-1}\sum_{k=j+1}^{N} \left\langle \exp(-i\mathbf{s}\cdot\mathbf{r}_j) \exp(-i\mathbf{s}\cdot\mathbf{r}_k) \right\rangle \ , \tag{19a}$$

$$D(s) \equiv (4\pi)^{-1}\int d\Omega_s G(\mathbf{s}) \ . \tag{19b}$$

Using the Condon-Slater rules, the characteristic function $G(\mathbf{s})$ for the wave function (5a) is found to have the same mathematical structure as $F(\mathbf{s})$ given in Eqs. (11a)-(11d), provided that the auxiliary function $F^{\kappa\lambda}_{\mu\nu}(\mathbf{s})$ is replaced with

$$G^{\kappa\lambda}_{\mu\nu}(\mathbf{s}) \equiv f^*_{\kappa\lambda}(\mathbf{s}) f_{\mu\nu}(-\mathbf{s}) = f^*_{\kappa\lambda}(\mathbf{s}) f^*_{\nu\mu}(\mathbf{s}) \ , \tag{20a}$$

where $f_{\kappa\lambda}(\mathbf{s})$ is defined by Eq. (12b). Analogously, the characteristic function $D(s)$ is obtained straightforwardly from $H(s)$, if $H^{\kappa\lambda}_{\mu\nu}(s)$ is replaced with

$$D^{\kappa\lambda}_{\mu\nu}(s) \equiv (4\pi)^{-1} \int d\Omega_s \; G^{\kappa\lambda}_{\mu\nu}(\mathbf{s}) \; . \tag{20b}$$

We choose spherical harmonics with the phase:

$$Y^{*}_{lm}(\Omega) = (-1)^{m} Y_{l,-m}(\Omega) \; . \tag{21a}$$

Then the Condon-Shortley parameter $c^{l}(\nu;\mu)$ satisfies a relation,

$$(-1)^{m_\nu - m_\mu} c^{l}(\nu;\mu) = c^{l}(\mu;\nu) \; , \tag{21b}$$

and hence the explicit form of $D^{\kappa\lambda}_{\mu\nu}(s)$ for atomic systems is obtained as

$$D^{\kappa\lambda}_{\mu\nu}(s) = \sum_{l=\max(|l_\kappa - l_\lambda|,|l_\mu - l_\nu|)}^{\min(l_\kappa + l_\lambda, l_\mu + l_\nu)} (-1)^{l} (2l+1)\, c^{l}(\kappa;\lambda)\, c^{l}(\mu;\nu)\, W^{*}_{l\kappa\lambda}(s)\, W_{l\mu\nu}(s) \; , \tag{22a}$$

if $l_\kappa + l_\lambda + l_\mu + l_\nu = even$ *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. (22a) corresponding to Eqs. (15b) and (15c) are

$$D^{\kappa\kappa}_{\mu\mu}(s) = \sum_{l=0}^{\min(2l_\kappa, 2l_\mu)} (2l+1)\, a^{l}(\kappa;\mu)\, W^{*}_{l\kappa\kappa}(s)\, W_{l\mu\mu}(s) \; , \tag{22b}$$

$$D^{\kappa\mu}_{\kappa\mu}(s) = \sum_{l=|l_\kappa - l_\mu|}^{l_\kappa + l_\mu} (-1)^{l} (2l+1)\, b^{l}(\kappa;\mu) \left| W_{l\kappa\mu}(s) \right|^{2} \; , \tag{22c}$$

which have been derived in Ref. [4]. The summations in Eqs. (22a)-(22c) run over every other integers between the specified values.

As has been the case of the intracule densities, the momentum-space extracule densities $\bar{E}(\mathbf{P})$ and $\bar{d}(P)$, defined by Eq. (4), have structures isomorphic with those of the position-space counterparts given by Eqs. (18a) and (18b):

$$\bar{E}(\mathbf{P}) = \pi^{-3} \int d\mathbf{s} \exp(+2i\mathbf{P}\cdot\mathbf{s})\, \bar{G}(\mathbf{s}) \; , \tag{23a}$$

$$\bar{d}(P) = (4/\pi^{2}) \int_0^\infty ds\, s^{2} j_0(2Ps)\, \bar{D}(s) \; , \tag{23b}$$

in which the characteristic functions $\bar{G}(\mathbf{s})$ and $\bar{D}(s)$ are obtained by replacing $\psi_\kappa(\mathbf{r})$ with $\phi_\kappa(\mathbf{p})$ and by $R_\kappa(r)$ with $P_\kappa(p)$, respectively, in the expressions for $G(\mathbf{s})$ and $D(s)$.

2-6-2-4. RELATIONS BETWEEN INTRACULE AND EXTRACULE PROPERTIES

Comparison of the formulas for $H^{\kappa\lambda}_{\mu\nu}(s)$ and $D^{\kappa\lambda}_{\mu\nu}(s)$ shows that they are similar but different by a sign factor $(-1)^{l}$ in the summation of $D^{\kappa\lambda}_{\mu\nu}(s)$ given by Eq. (22a). The l values are all even and odd, if $l_\kappa + l_\lambda$ (or $l_\mu + l_\nu$) is even and odd, respectively. Then interesting relations,

$$D(s) = H(s) \quad \text{and} \quad d(R) = 8h(2R) \; , \tag{24a}$$

follow immediately between the atomic intracule and extracule properties, *if all the relevant* $l_\kappa + l_\lambda$ *values are even*. Equation (24a) further yields a "2^n-rule",

$$< u^{n} > / < R^{n} > = 2^{n} \; , \tag{24b}$$

between the intracule and extracule moments defined by

$$< u^{n} > \equiv \int d\mathbf{u}\, u^{n}\, I(\mathbf{u}) = 4\pi \int_0^\infty du\, u^{n+2}\, h(u) \; , \tag{25a}$$

$$< R^{n} > \equiv \int d\mathbf{R}\, R^{n}\, E(\mathbf{R}) = 4\pi \int_0^\infty dR\, R^{n+2}\, d(R) \; , \tag{25b}$$

where n is a real number greater than -3. The condition that all $l_\kappa + l_\lambda$ are even is not satisfied in general and therefore Eqs. (24a) and (24b) do not hold in general. However, the numerical examinations [4] have shown that the 2^n-rule is approximately valid with satisfactory accuracy, when 53 atoms from He to Xe in their ground states are studied within the Hartree-Fock approximation. In particular, the relations (24a) and (24b) are rigorous for the three atoms He, Li, and Be, where only s orbitals are occupied.

The relations between the intracule and extracule properties discussed above are also valid in momentum space. However, the numerical results [4] for the atoms He through Xe have shown that the 2^n-rule,

$$< v^{n} > / < P^{n} > = 2^{n} \; , \tag{26a}$$

for the momentum-space moments,

$$< v^{n} > \equiv \int d\mathbf{v}\, v^{n}\, \bar{I}(\mathbf{v}) = 4\pi \int_0^\infty dv\, v^{n+2}\, \bar{h}(v) \; , \tag{26b}$$

$$< P^{n} > \equiv \int d\mathbf{P}\, P^{n}\, \bar{E}(\mathbf{P}) = 4\pi \int_0^\infty dP\, P^{n+2}\, \bar{d}(P) \; , \tag{26c}$$

is less accurate than the position-space moments, except for He, Li, and Be.

We note that for integer values of n, the intracule $< u^{n} >$ and $< v^{n} >$ and extracule $< R^{n} >$ and $< P^{n} >$ moments, defined by Eqs. (25a,b) and (26b,c), can be directly obtained from their characteristic functions $H(s)$, $\bar{H}(s)$, $D(s)$ and $\bar{D}(s)$. Explicit formulas are reported in Refs. [3,4].

2-6-3. AN ILLUSTRATIVE APPLICATION

The $2\,{}^{1}P$ and $2\,{}^{3}P$ multiplet states of the helium atom have attracted a large amount of attention since Davidson [10] pointed out (see also [11-15] and references therein) that the interelectronic repulsion $<1/u>$ is greater in the triplet than in the singlet, in contradiction to naïve theoretical models. Older work on interpretation of Hund's rule was summarized by Katiel and Pauncz [16]. Katriel worked [17] with crude radial intracule densities $4\pi u^{2} h(u)$ to show that the Fermi (or electron-electron coalescence) hole in the triplet manifests itself only for $0<u<1$. Colpa *et al.* [18] showed that the radial size $< r >_{2p}$ of the $2p$ orbital is smaller in the triplet than in the singlet. Boyd [19] has also emphasized that high spin states are more compact than low spin states in general. Based on highly-accurate correlated calculations, Regier and Thakkar [20] confirmed that near-exact electron $\rho(r)$ and intracule $h(u)$ densities do not lead to qualitatively different conclusions from those of Colpa *et al.* [18], Boyd [19], and Katriel [17]. Shim and Dahl [21] presented a convincing picture of how Hund's first rule operates: The

electrons in the more compact triplet state repel each other more than in the singlet, Fermi correlation is manifested by an increased tendency for the electrons to be on opposite sides of the nucleus in the triplet, and the increased electron-nucleus attraction results in a lower energy for the triplet.

Despite that there already is a good number of studies on the ^1P-^3P problem, however, it is not reported in the literature how the singlet-triplet difference appears in the momentum-space intracule density $\bar{h}(v)$ and in the extracule $d(R)$ and $\bar{d}(P)$ densities. These densities are examined below as an illustrative application of the present method given in Section 2-6-2.

Within the Hartree-Fock framework, the $1s2p$ ^1P and ^3P wave functions can be expressed by linear combinations of two Slater determinants,

$$^{1,3}\Psi = \frac{1}{\sqrt{2}}\det\{1s\alpha\ \ 2p_m\beta\} \mp \frac{1}{\sqrt{2}}\det\{1s\beta\ \ 2p_m\alpha\}\ , \qquad (27)$$

where m is either -1, 0, or $+1$. The radial functions $R_{1s}(r)$ and $R_{2p}(r)$ in position space were generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [22,23]. The algorithm of Talman [24] was used to perform all the required Hankel-transformations numerically. The values of the Condon-Shortley parameter $c^l(\kappa;\lambda)$ have been taken from the Slater's book [25]. In momentum space, the position-space radial functions $R_\kappa(r)$ have been first Hankel-transformed to obtain the momentum-space radial functions $P_\kappa(p)$ according to Eq. (7c).

In order to check the accuracy of the Hartree-Fock approximation, we have first plotted in Figure 1(a) the singlet-triplet difference of the radial intracule density $4\pi u^2 h(u)$ in position space. We have found that the present Hartree-Fock curve is surprisingly similar to the near-exact one of Regier and Thakkar [20], not only in their behaviors but also in the locations and the values of the three extrema. This observation supports that the present Hartree-Fock results grasp at least the essential feature of the singlet-triplet difference in the four kinds of electron-pair densities $h(u)$, $\bar{h}(v)$, $d(R)$, and $\bar{d}(P)$. Figure 1(a) also confirms Katriel's study [17] at the Hartree-Fock limit level. The singlet-triplet difference corresponding to Fig.1(a) is also seen in the associated intracule moments $<u^n>$ tabulated in the top half of Table 1. Compared to the ^1P values, the ^3P moments $<u^n>$ are larger when $n<0$, and smaller when $n>0$.

The singlet-triplet difference of the radial intracule density $4\pi v^2\bar{h}(v)$ in momentum space is given in Fig.1(b). The ^3P density is smaller for $0<v<0.86$ and larger for $0.86<v$ than the ^1P density. Namely, there is more probability in the ^3P state for the two electrons to have different momenta. Thus the effect of the Fermi hole $\bar{h}(0)=0$ can be considered to appear naively in momentum space. The intracule moments $<v^n>$ in momentum space are compared in the bottom half of Table 1. Corresponding to our observation in Fig.1(b), the moments $<v^n>$ are larger in the singlet when $n<0$ while in the triplet when $n>0$. We note that the average momenta $<p>_{2p}$ of the $2p$ orbitals are 0.439 for ^1P and 0.491 for ^3P, and the difference is

not very large between the two states. The corresponding average $1s$ momenta $<p>_{1s}$ are 1.701 and 1.686, respectively.

Figure 2(a) shows the ^1P-^3P difference of the radial extracule density $4\pi R^2 d(R)$ in position space. The ^3P extracule density is larger than the ^1P density for $0<R<2.17$ and smaller for $2.17<R$. This means that in the triplet state, there is a higher probability for finding the center-of-mass radius R of the two electrons to be small. Such a situation is possible only when the two electrons in ^3P are more probable than in ^1P to be on opposite sides of the nucleus, as suggested by Shim and Dahl [21]. A finer analysis has shown that the electron-electron counterbalance hole [26] $d(0)=0$ appears for the $1s2p$ ^1P state. The Hartree-Fock limit values of the average electron-nucleus distance $<r>_{2p}$ are 5.141 and 4.656 bohrs for the ^1P and ^3P states, respectively, and $<r>_{2p}$ is smaller in the ^3P state as noted before [18]. Then the electrons in the triplet state are interpreted [21] to have tendency to be at the opposite positions with respect to the nucleus (*i.e.*, the position-space origin **r=0**) in order to increase the interelectronic separation and to reduce the electron repulsion energy. The extracule moments $<R^n>$ in position space are summarized in the top half of Table 2. The singlet-triplet differences in the moments $<R^n>$ are consistent with Fig.2(a).

The singlet-triplet difference in the momentum-space radial extracule density $4\pi P^2\bar{d}(P)$ is shown in Fig.2(b). The difference is similar to its position-space counterpart, and the ^3P density is larger for $0<P<0.43$ and smaller for $0.43<P$ than the ^1P density. This implies that the center $(\mathbf{p}_1+\mathbf{p}_2)/2$ of momenta of the two electrons distributes more around the origin **p=0** in the triplet than in the singlet. The moments $<P^n>$ tabulated in the bottom half of Table 2 reflect this difference. In the comparison of the momentum-space intracule densities, we have seen that two electrons have larger probability of having different momenta in the ^3P state. When the extracule result is combined with the intracule result, it is concluded that the probability for the two electrons to have the opposite momenta, with respect to the momentum-space origin **p=0**, is larger in ^3P than ^1P. Indeed, the electron-electron counterbalance hole [26] appears in momentum space as well for the ^1P state. As the similarity of Figs.2(a) and 2(b) suggests, the physical picture in momentum space is analogous to that in position space, when the extracule density is used to elucidate the difference in the electron-pair motion in the ^1P and ^3P states. The present results also suggest that despite few studies on it, the extracule density may be as powerful as the intracule density.

Finally, we have compared the present Hartree-Fock moments $<u^n>$ with the corresponding near-exact values [20,27] reported for $-2\le n\le+2$. The largest relative error of the Hartree-Fock values has been found to be 2.3%. The correlated results are not known for the remaining three kinds of moments, but we expect that the Hartree-Fock values in Tables 1 and 2 for $<v^n>$, $<R^n>$, and $<P^n>$ have similar accuracy.

2-6-4. CONCLUSION

A unified method for the evaluation of the electron-pair intracule and extracule densities has been developed both in position and momentum spaces for wave functions expressed as linear combinations of Slater determinants, with our special interests in atomic systems where all the angular integrations can be performed analytically. Interesting relations between atomic intracule and extracule densities and between their moments have been discussed. An illustrative application of the present results has been given for the $1s2p\ ^1P$ and ^3P states of the helium atom, and new aspects of the singlet-triplet difference in the electron-pair motion have been clarified based on the extracule densities and the momentum-space intracule density.

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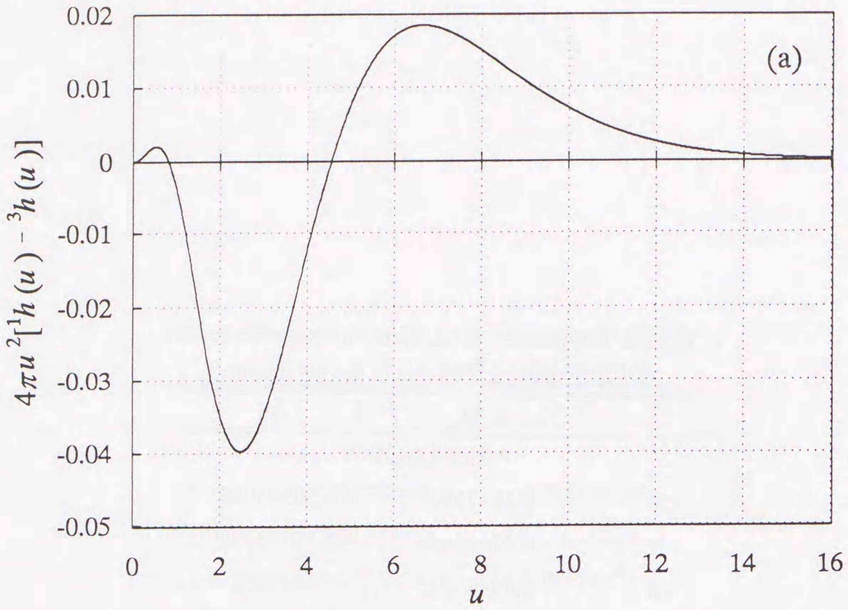
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Table 1. Comparison of the intracule moments for the $2\ ^1P$ and $2\ ^3P$ states of the helium atom.

	$2\ ^1P$	$2\ ^3P$
	Position Space	
$\langle u^{-2} \rangle$	0.087810943	0.095284169
$\langle u^{-1} \rangle$	0.24364468	0.26613201
$\langle u \rangle$	5.1916619	4.7436007
$\langle u^2 \rangle$	32.269925	27.205951
$\langle u^3 \rangle$	233.04368	182.95993
$\langle u^4 \rangle$	1916.3817	1410.7218
	Momentum Space	
$\langle v^{-2} \rangle$	1.449076	0.7153554
$\langle v^{-1} \rangle$	0.8648445	0.7268381
$\langle v \rangle$	1.732860	1.818582
$\langle v^2 \rangle$	4.1746	4.395100
$\langle v^3 \rangle$	14.29	14.8
$\langle v^4 \rangle$	83.0	84.

Table 2. Comparison of the extracule moments for the $2\ ^1P$ and $2\ ^3P$ states of the helium atom.

	$2\ ^1P$	$2\ ^3P$
	Position Space	
$\langle R^{-2} \rangle$	0.29476967	0.50533045
$\langle R^{-1} \rangle$	0.47478894	0.55795890
$\langle R \rangle$	2.6048621	2.3543572
$\langle R^2 \rangle$	8.0890701	6.7588471
$\langle R^3 \rangle$	29.174920	22.774574
$\langle R^4 \rangle$	119.86195	87.942273
	Momentum Space	
$\langle P^{-2} \rangle$	2.979634	5.991698
$\langle P^{-1} \rangle$	1.479459	1.759069
$\langle P \rangle$	0.8983364	0.8589156
$\langle P^2 \rangle$	1.078807	1.0327
$\langle P^3 \rangle$	1.823	1.769
$\langle P^4 \rangle$	5.24	5.14



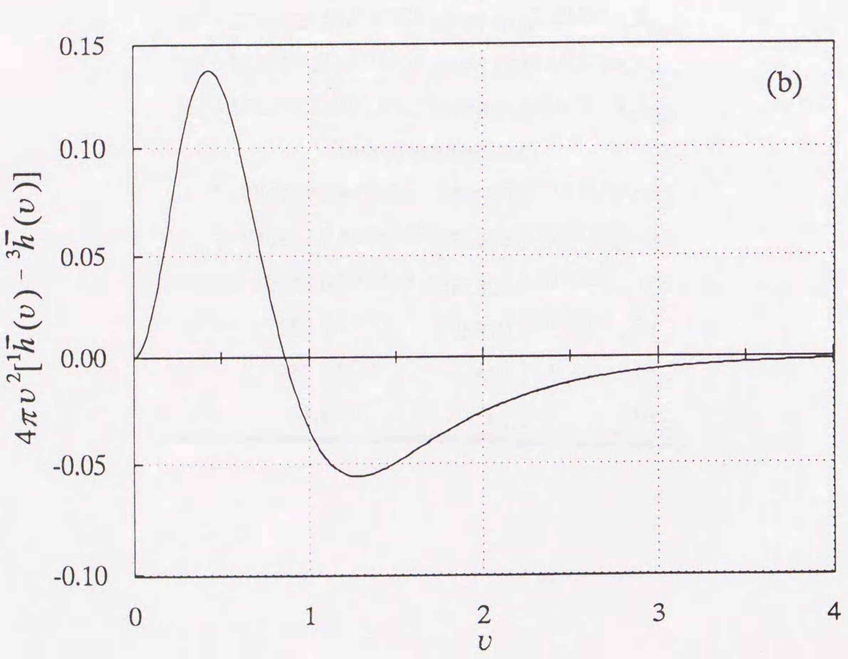
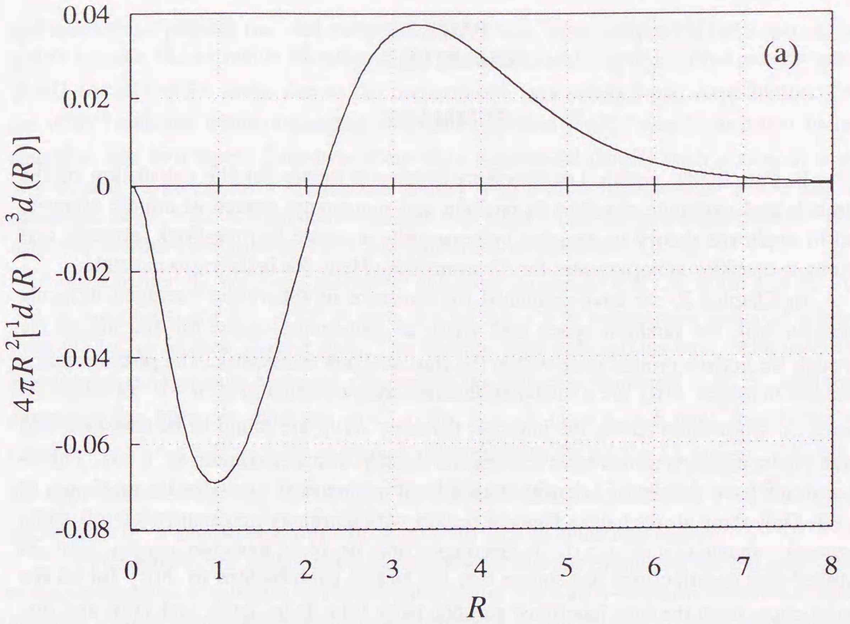


Fig. 1. The difference of the radial intracule densities for the $2\ {}^1P$ and $2\ {}^3P$ states of the helium atom. (a) Position space. (b) Momentum space.



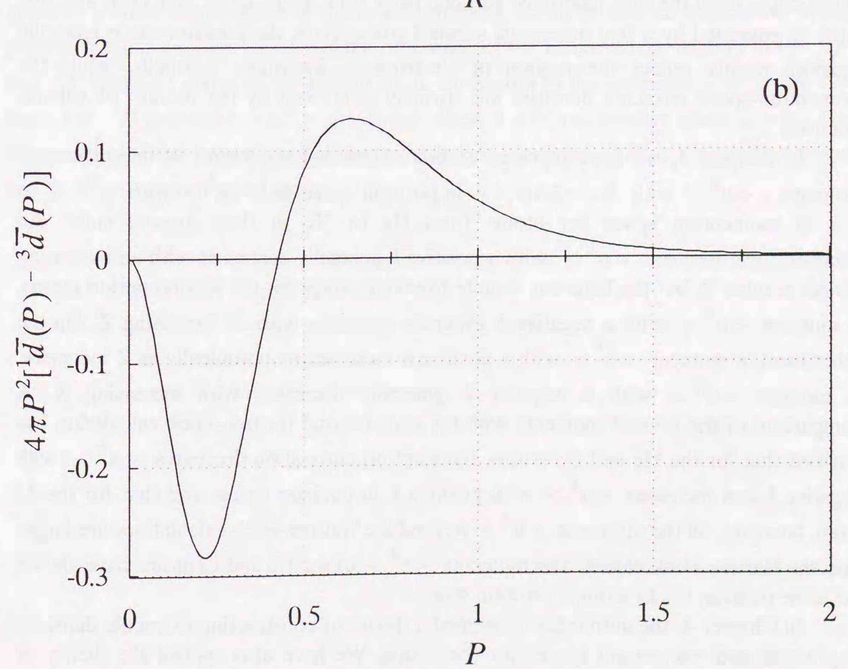


Fig. 2. The difference of the radial extracule densities for the $2\ {}^1P$ and $2\ {}^3P$ states of the helium atom. (a) Position space. (b) Momentum space.

PART 2.
CHAPTER 7.

SUMMARY

In Part 2, the author has aimed to develop a theory for the calculation of the intracule and extracule densities in position and momentum spaces of atomic systems, and to apply the theory to examine systematically accurate Hartree-Fock intracule and extracule densities in both spaces for 53 atoms from He to Xe in their ground state.

In Chapter 2, we have examined the structure of spherically averaged intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space for the atoms He through Xe in their ground state within the Hartree-Fock framework. The position-space intracule densities $h(u)$ are a unimodal function with a maximum at $u=0$ for all the 53 atoms. In momentum space, the intracule densities $\bar{h}(v)$ are found to be classified into three types; eighteen atoms have a unimodal density with a maximum at $v=0$. Thirty-two atoms have a unimodal density with a local minimum at $v=0$ and a maximum at $v>0$. Only three atoms have a bimodal density with a primary maximum at $v=0$ and a secondary maximum at $v>0$. A decomposition of total intracule density into its subshell-pair contributions has shown that the largest contributions to $h(u)$ for all the atoms come from the four innermost subshell pairs 1*s*1*s*, 1*s*2*p*, 2*p*2*p*, and 1*s*2*s*, and that $\bar{h}(v)$ is governed by a few outermost subshell pairs. Thus, the position-space intracule densities mainly reflect the motion of electrons in innermost subshells, while the momentum-space intracule densities are strongly influenced by the motion of valence electrons.

In Chapter 3, we have reported accurate Hartree-Fock values of interelectronic moments $<u^k>$ with $k=-2$ to $+4$ in position space and $<v^k>$ with $k=-2$ to $+3$ in momentum space for atoms from He to Xe in their ground state. An interelectronic moment $<u^k>$ with a positive k generally decreases with an increasing atomic number Z, but the behavior is quite irregular except for the second period atoms. A moment $<u^k>$ with a negative k generally increases with an increasing Z. On the other hand, a moment $<v^k>$ with a positive k increases monotonically as Z increases. A moment $<v^k>$ with a negative k generally decreases with increasing Z. A comparison of the present moments with the ones beyond Hartree-Fock calculation has clarified that for the He and Be atoms, the electron correlation decreases $<u^k>$ with negative k and increases $<u^k>$ with positive k in position space, and that for the Li atom, however, all the moments $<u^k>$ beyond the Hartree-Fock calculations are larger than the Hartree-Fock values. The moments $<v^k>$ of the He and Li atoms have shown the same trend as the Li atom in position space.

In Chapter 4, the author has presented a theory of constructing extracule densities in position and momentum spaces for the atoms. We have also applied the theory to systematically examine spherically averaged extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space for a series of 53 atoms from He to Xe in their ground state based on the numerical Hartree-Fock method. The contributions of subshell pairs

and spin-orbital pairs to the total extracule density have been analyzed in both spaces. In position space, the extracule densities $d(R)$ are a unimodal function with a maximum at $R=0$ for all the 53 atoms due to the predominant 1*s*1*s* subshell-pair contribution. On the other hand, the momentum-space extracule densities $\bar{d}(P)$ have been found to be classified into two types; forty-two atoms have a unimodal density with a maximum at $P=0$, and 11 atoms have a unimodal density with a local minimum at $P=0$ and a maximum at $P>0$. A systematic analysis has shown that in momentum space, the extracule densities are governed by a few outermost subshell pairs.

In Chapter 5, We have presented extracule moments $<R^k>$ with $k=-2$ to $+4$ in position space and $<P^k>$ with $k=-2$ to $+3$ in momentum space of atoms form He to Xe in their ground state. The Hartree-Fock calculations have been used to examined these extracule moments. Comparing the extracule moments $<R^k>$ with the corresponding intracule moments $<u^k>$ for $k=-2$ to $+4$, we have found that a relation $<u^k>/<R^k>\cong 2^k$ is a good approximation for all the 53 atoms. Similarly, an approximate relation $<v^k>/<P^k>\cong 2^k$ between the extracule $<P^k>$ and intracule $<v^k>$ moments is valid for $k=-2$ to $+3$ in momentum space.

In Chapter 6, the author has generalized a method for evaluating the intracule and extracule densities in position and momentum spaces when an *N*-electron wavefunction is given by a linear combination of Slater determinants. As an illustrative application of the present results, we have discussed the difference of the electron-pair motion in the ^1P and ^3P multiplet states of the helium atom. Compared to the moments $<u^k>$ of ^1P state, the ^3P moments $<u^k>$ are larger when $k<0$ and smaller when $k>0$. The similar trends have been observed for the extracule moments $<R^k>$ in position space and $<P^k>$ in momentum space.

PART 3.
CHAPTER 1.

INTRODUCTION

The electronic relative-motion (intracule) and center-of-mass-motion (extracule) densities in position and momentum spaces are very useful quantity [see, Refs. 1 and 2, and GENERAL INTRODUCTION] to analyze the motion of a pair of electrons for atomic and molecular systems. The position intracule density $I(\mathbf{u})$ and its spherical average $h(u)$ are [1-3] the probability density functions for interelectronic vector $\mathbf{u}$ and its magnitude u. The extracule density $E(\mathbf{R})$ and its spherical average $d(R)$ in position space represent [1-3] the probability density functions for center-of-mass vector $\mathbf{R}$ and its magnitude R. 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 [1] in momentum space, and represent the probability density functions for the relative and center-of-mass momentum vectors and their magnitudes. These electron-pair densities have been used [see, Refs. 1 and 2] for neutral atoms and molecules to analyze many chemical and physical problems such as Coulomb hole, x-ray and electron-scattering intensities, Hund's rules, and chemical bonding. Only few attempts, however, have so far been made to study the electron-pair densities of atomic ions.

In the present part, we apply the theory developed in Part 2 to examine systematically the intracule and extracule densities in both position and momentum spaces of atomic ions.

In Chapter 2, spherically averaged electron-pair intracule density $h(u)$, extracule density $d(R)$, and their moments $<u^k>$ and $<R^k>$ are examined [4] for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground state, where u and R are the interelectronic distance and the center-of-mass radius of a pair of electrons, respectively. The intracule and extracule densities of all the 96 ions are found to be monotonically decreasing functions, as shown for neutral atoms. Approximate relations $d(R) \cong 8h(2R)$ and $<u^k>/<R^k> \cong 2^k$ are confirmed to be valid for the charged atoms as well.

In Chapter 3, momentum-space spherically averaged electron-pair intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities are [5] constructed and examined systematically for the singly charged 53 cations from Li^+ to Cs^+ and 43 stable anions from H^- to I^- in their ground state based on numerical Hartree-Fock calculations. The intracule and extracule densities are found to be classified into three and two types, respectively, according to the number of extrema and their locations. The modalities of the electron-pair densities for all the 96 ions are governed by a few outermost electron pairs as reported for neutral atoms. The intracule $<v^k>$ and extracule $<P^k>$ moments are computed for the 96 ions and compared with the corresponding values for the isoelectronic neutral atoms.

In Chapter 4, we construct [6] a method of obtaining the extracule density $d(R)$ for a correlated wave function which explicitly includes an interelectronic distance term.

The method is applied to the ground state helium atom and its isoelectronic analogs described by highly accurate Kinoshita wave functions. Near exact extracule densities $d(R)$, their moments $<R^k>$ with $k=-2$ to $+4$, and electron-electron counterbalance densities $d(0)$ are determined. Comparison of the correlated results with the corresponding Hartree-Fock values shows that the electron correlation shifts the extracule density $d(R)$ from a small R region to a large R region. Different roles of the radial and angular correlation contributions are also clarified in the electron correlation.

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PART 3.
CHAPTER 2.

HARTREE-FOCK ELECTRON-PAIR DENSITIES IN POSITION SPACE

3-2-1. INTRODUCTION

The spherically-averaged intracule (relative-motion) density $h(u)$ and the associated moments $< u^n >$ are defined [1,2] by

$$h(u) \equiv \int d\Omega_u \int d\mathbf{R}\, \tilde{\Gamma}(\mathbf{u},\mathbf{R}) \,, \tag{1a}$$

$$< u^n > \equiv 4\pi \int_0^\infty du\, u^{n+2} h(u) \,, \tag{1b}$$

where $\mathbf{u} \equiv (u, \Omega_u)$ with $\Omega_u \equiv (\theta_u, \phi_u)$ and $\tilde{\Gamma}(\mathbf{u},\mathbf{R})$ is the intracule-extracule representation of the spinless two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$, obtained by the variable transformations $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. The intracule density $h(u)$ represents the probability density function for an interelectronic distance, and directly determines the electron repulsion energy of a system. In the literature (see, *e.g.*, Refs. [2-6] for relevant references), the intracule densities have been used for the analysis of several physical and chemical problems such as Hund's rules, chemical bonds, Coulomb hole, and correlation density functionals. Further, experimental x-ray and fast electron scattering intensities of atoms and molecules are closely related [7] to the intracule density.

On the other hand, the spherically-averaged extracule (center-of-mass-motion) density $d(R)$ and the associated moments $< R^n >$ are defined [1,2] by

$$d(R) \equiv \int d\Omega_R \int d\mathbf{u}\, \tilde{\Gamma}(\mathbf{u},\mathbf{R}) \,, \tag{2a}$$

$$< R^n > \equiv 4\pi \int_0^\infty dR\, R^{n+2} d(R) \,, \tag{2b}$$

where $\mathbf{R} \equiv (R, \Omega_R)$ with $\Omega_R \equiv (\theta_R, \phi_R)$. The extracule density provides useful information about the motion of the center-of-mass of an electron pair, but only a few studies have been reported for light neutral atoms and diatomic molecules [8-10].

All the studies on the intracule and extracule densities in the literature were carried out based on approximate basis-set-expansion wave functions, some of which may not be sufficiently accurate. For the 53 neutral atoms from He to Xe in their ground states, we recently performed [3-6] a systematic examination of $h(u)$ and $d(R)$ as well as their moments $< u^n >$ and $< R^n >$ with $n = -2$ to $+4$ using the numerical Hartree-Fock method. For the neutral atoms, it was clarified [3-6] that (i) both the intracule and extracule densities are monotonically decreasing functions, (ii) the major contributions to the total electron-pair densities $h(u)$ and $d(R)$ come from a few innermost subshell-pairs, and hence the densities strongly reflect the motion of inner electrons, (iii) an approximation $d(R) \cong 8h(2R)$ holds between the two electron-pair densities, (iv) $< u^n > / < R^n > \cong 2^n$ is a good approximation for $n = -2$ to $+4$, and (v) the equalities in (iii) and (iv) hold exactly for He, Li, and Be atoms, where only *s* orbitals are occupied.

In Chapter 2, we report the intracule $h(u)$ and extracule $d(R)$ densities, together with the associated moments $< u^n >$ and $< R^n >$ with $n = -2$ to +2, for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground states based on numerical Hartree-Fock calculations. The electron-electron coalescence $h(0)$ and counterbalance $d(0)$ densities are studied as well. The next section outlines our computational procedures. In Section 3-2-3, the results are presented and discussed. We will find that the above mentioned results (i) to (v) for neutral atoms are also valid for all the 96 singly charged atoms. In addition, several inequalities are obtained for the two-electron properties of isoelectronic species with different nuclear charges. Hartree atomic units are used throughout.

3-2-2. COMPUTATIONAL OUTLINE

A Hartree-Fock wave function is expressed by a linear combination of a finite number of Slater determinants composed of a set of orthonormal spin-orbitals. Then the Condon-Slater rule (see, *e.g.*, Ref. [11]) rewrites the intracule and extracule densities as a sum of spin-orbital-pair contributions. For atomic systems, we assume that the spatial part $\psi_{nlm}(\mathbf{r})$ of a spin-orbital is a product of radial $R_{nl}(r)$ and spherical harmonic $Y_{lm}(\Omega_r)$ functions. This allows us to perform analytically the angular integrations involved in the definitions of the spherically-averaged densities $h(u)$ and $d(R)$. Furthermore, a summation of contributions from one electron with $R_{nl}(r)$ and another electron with $R_{n'l'}(r)$ defines the contribution of a subshell pair $nln'l'$. Details are found in Refs. [3-6, 12].

For the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- with the number of electrons $2 \le N \le 54$, the radial functions $R_{nl}(r)$ were generated by the numerical Hartree-Fock method based on a modified and enhanced version of the MCHF72 code [13]. The experimental ground electronic configurations and terms [14, 15] were considered for all the ions. There are two exceptions, however. For the anions Sc^- and Pd^-, the experimental ground states are reported [15] respectively to be [Ar]4*s*(2)3*d*(1)4*p*(1), ^1D and [Kr]5*s*(1)4*d*(10), ^2S, but we could not obtain meaningful solutions to these states in numerical Hartree-Fock computations. Thus the second lowest states, [Ar]4*s*(2)3*d*(2), ^3F for Sc^- and [Kr]5*s*(2)4*d*(9), ^2D for Pd^-, were examined instead.

3-2-3. RESULTS AND DISCUSSION

By definition, the intracule and extracule densities are normalized to the number of electron pairs $N(N-1)/2$. In this section, however, we use a modified normalization scheme which normalizes all the densities to *unity* to avoid large numbers and to facilitate mutual comparison of species with different numbers of electrons.

Systematic examination of the intracule densities $h(u)$ for the singly charged cations and anions shows that all the densities are monotonically decreasing functions (*i.e.*, unimodal functions with a maximum at $u = 0$), as observed [5] for the neutral atoms with $2 \le N \le 54$. Figure 1(a) exemplifies the intracule densities $h(u)$ of the ions Rb^+ and Br^- with 36 electrons, and compares them with the corresponding result [5] for the isoelectronic neutral atom Kr. We also find in general that an inequality,

$$h^-(u) < h^0(u) < h^+(u) \,, \tag{3}$$

is valid for a small u, where the superscripts -, 0, and + refer to the anionic, neutral, and cationic species, respectively. This means that an increase in the nuclear charge Z among isoelectronic species leads to an increased probability of finding any two electrons at a shorter interelectronic distance.

A decomposition of the total intracule density $h(u)$ into subshell-pair contributions shows that common to all the 96 singly charged ions, the largest contributions to $h(u)$ come from the four innermost subshell pairs $1s1s$, $1s2p$, $2p2p$, and $1s2s$ in the order of decreasing contributions. The relative significance and behaviors of the four subshell pairs are similar to those of neutral atoms [5]; the $1s1s$ contribution is a unimodal function with a maximum at $u = 0$, and is exceptionally large among the four contributions at a small u. The $1s2p$ and $2p2p$ contributions are unimodal functions with a maximum at $u > 0$. The $1s2s$ contribution is a bimodal function with a primary maximum at $u = 0$ and a secondary maximum $u > 0$. Thus intracule density $h(u)$ is a unimodal function with a maximum at $u = 0$ due to the predominant $1s1s$ subshell-pair contribution.

Figure 1(b) plots the electron-electron coalescence densities [16-19] $h(0)$ of the singly charged 53 cations and 43 anions along with the corresponding densities of the neutral atoms [18, 19]. The $h(0)$ values increase monotonically with increasing number N of electrons except for Li^+. For the cations, $N(N-1)h^+(0) = 0.0435Z^{3.29}$ is found to be an excellent approximation. The average relative error is 0.93% for the 53 cations and the largest error is 5.25% for Li^+. For the anions, an approximation $N(N-1)h^-(0) = 0.0365Z^{3.35}$ may be useful to estimate the $h(0)$ values except for light species; the average relative error is 4.15% for the 43 anions and the largest error is 40.7% for H^-. As expected from the discussion on $h(u)$, an inequality $h^-(0) < h^0(0) < h^+(0)$ is true without exception, implying that an increase of Z increases the probability of finding any two electrons at the same position in space.

Table 1 gives the intracule moment $< u^n >$ with $n = -2$ to +2 for the singly charged 53 cations and 43 anions. The results for $< u^3 >$ and $< u^4 >$ are not given, but available upon request to HM. For the 96 singly charged ions, the moment $< u^n >$ with a negative n generally increases with increasing Z. On the other hand, $< u^n >$ with a positive n shows a periodic behavior as a function of N; it decreases as the number of electrons increases towards a rare-gas electronic configuration, and there is a jump-up when additional one or two electrons occupy a new s subshell outside the rare-gas configuration. Comparing the moments $< u^n >$ of the 96 singly charged ions with those of the 53 neutral atoms previously reported [3], we find inequalities,

$$< u^n >^- \; < \; < u^n >^0 \; < \; < u^n >^+, \qquad \text{when } n < 0, \tag{4a}$$

$$< u^n >^+ \; < \; < u^n >^0 \; < \; < u^n >^-, \qquad \text{when } n > 0, \tag{4b}$$

with no exceptions. These relations are consistent with Eq. (3).

For the 53 neutral atoms from He to Xe, the extracule densities were known [6] to be monotonically decreasing functions. For the singly charged 53 cations and 43 anions in their ground states, we have also examined the extracule densities $d(R)$ and again found that all the densities are monotonically decreasing functions. Corresponding to Figure 1(a), the extracule densities of the 36-electrons species are compared in Figure 2(a). A

comparison of $d(R)$ of the 96 ions with those of the neutral atoms clarifies that for a small R region,

$$d^-(R) \; < \; d^0(R) \; < \; d^+(R), \tag{5}$$

holds among all the isoelectronic series with N = 2 to 54. The inequality tells us that an increase in nuclear charge causes an increased probability of finding a pair of electrons with a smaller center-of-mass radius.

By examining subshell-pair contributions, we see that the five largest contributions to the total extracule density $d(R)$ for the ions are $1s1s$, $1s2s$, $1s2p$, $2s2p$, and $2p2p$ subshell pairs as found [6] for the neutral atoms. The $1s1s$, $1s2p$, and $2s2p$ contributions are unimodal functions with a maximum at $R = 0$, and the $1s1s$ contribution is largest at a small R. The $2p2p$ contribution is a unimodal function with a maximum at $R > 0$, and the $1s2s$ contribution is a bimodal function with a primary maximum at $R = 0$ and a secondary maximum $R > 0$. As for the case of $h(u)$, the predominant $1s1s$ contribution is concluded to form the monotonically decreasing behavior of the extracule density $d(R)$ for all the neutral and charged atoms examined.

The N-dependence of electron-electron counterbalance densities [18-20] $d(0)$ is shown in Figure 2(b) for the charged and neutral atoms. The $d(0)$ values for all the three series increase monotonically with increasing N except for Li^+. For the 53 cations, a fitting into an analytical function has given $N(N-1)d^+(0) = 0.294Z^{3.42}$ with the average relative error of 1.49% and the largest error of 3.27% for O^+. Analogously, we have obtained $N(N-1)d^-(0) = 0.263Z^{3.45}$ for the 43 anions, where the average relative error is 3.09% and the largest error is 20.9% for H^-. Among an isoelectronic series, an inequality $d^-(0) < d^0(0) < d^+(0)$ is always valid, indicating that an isoelectronic species with a larger nuclear charge Z has a larger probability of finding any two electrons exactly at the opposite positions with respect to the nucleus. The result works to reduce an increased repulsion among electrons confined in a smaller space around the nucleus due to a larger Z.

Table 2 summarizes the extracule moments $< R^n >$ for the 96 ions, where n ranges from -2 to +2. The results for n = +3 and +4 are available upon request to HM. The dependence of $< R^n >$ on Z and N is analogous to that of the intracule moments $< u^n >$. By comparison of the extracule moments for the ions and neutral atoms, we find among an isoelectronic series that

$$< R^n >^- \; < \; < R^n >^0 \; < \; < R^n >^+, \qquad \text{when } n < 0, \tag{6a}$$

$$< R^n >^+ \; < \; < R^n >^0 \; < \; < R^n >^-, \qquad \text{when } n > 0, \tag{6b}$$

in accord with Eq. (5).

For neutral atoms, an interesting relation,

$$d(R) \cong 8h(2R), \tag{7}$$

was shown [4, 6] between the extracule $d(R)$ and intracule $h(u)$ densities within the Hartree-Fock theory, where the equality holds for the species with N = 2, 3, and 4. We have confirmed that the relation is also valid for the singly charged cations and anions. Examples can be seen in Figures 1(a) and 2(a). The inequalities (3) and (5) are also consistent through Eq. (7). A particular case of Eq. (7) for $R = 0$ reads

$$d(0) \cong 8h(0) \ , \tag{8}$$

which connects [18, 19] the electron-electron coalescence $h(0)$ and counterbalance $d(0)$ densities. The inequalities for $h^x(0)$ and for $d^x(0)$ mentioned above are thus consistent with Eq. (8), where x = -, 0, and +. The approximate analytical expressions for $h^x(0)$ and $d^x(0)$ deviate little from the relation (8). However, the difference between $d(0)$ and $8h(0)$ increases with increasing N, and the relative errors are 27% for the three 54-electron species.

Equation (7) further predicts [4] a relation,

$$< u^n > / < R^n > \cong 2^n \ , \tag{9}$$

between the intracule $< u^n >$ and extracule $< R^n >$ moments. The equality in Eq. (9) is rigorous for the species with N=2 to 4. The inequalities (4) and (6), observed among an isoelectronic series, are consistent with Eq. (9). For the 53 neutral atoms with $2 \le N \le 54$, the average values of $< u^n > / < R^n >$ were reported [4] to be 0.222 (n=-2), 0.481 (n=-1), 2.03 (n=+1), 4.11 (n=+2), 8.27 (n=+3), and 16.6 (n=+4), respectively. For the cations and anions, the corresponding values have been found to be more or less the same when n=-2, -1, and +1. For n=+2, +3, and +4, the values are 4.13 (cations) and 4.08 (anions), 8.34 (cations) and 8.17 (anions), 16.8 (cations) and 16.3 (anions), respectively. In these cases, the deviation from 2^n has been seen to be smaller for a species with a lower Z among an N-electron isoelectronic series for any $2 \le N \le 54$.

3-2-4. CONCLUSION

For the 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^-, both the intracule $h(u)$ and extracule $d(R)$ densities have been found to be monotonically decreasing functions. The approximate but important relations $d(R) \cong 8h(2R)$, $< u^n > / < R^n > \cong 2^n$, and $d(0) \cong 8h(0)$, found previously [4, 6, 18, 19] for neutral atoms, have been confirmed to be valid as well for the singly charged ions. Therefore, the qualitative aspects of the electron-pair properties have been concluded to be essentially common to the neutral and charged atoms. Moreover, a comparison of isoelectronic species has clarified several general inequalities such as $h^-(u) < h^0(u) < h^+(u)$ for a small u. Since the electron-pair properties in position space are strongly influenced by a few innermost subshell pairs, these inequalities for an isoelectronic series can be understood intuitively by the fact that an increased nuclear charge results in an electron distribution more condensed around the nucleus. On the contrary, the electron-pair properties in momentum space are known [3-6] to be most affected by outermost (or valence) subshells. Comparative studies of the momentum-space intracule and extracule densities on the neutral and charged atoms will be interesting.

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Table 1. Intracule moments $<u^n>$ for singly-charged cations and anions. Note that the normalization is $<u^0>=1$ instead of $N(N\text{-}1)/2$.

	Cation					Anion				
Z		n = -2	n = -1	n = 1	n = 2		n = -2	n = -1	n = 1	n = 2
1						H^-	0.29023	0.39548	3.73927	18.8222
3	Li^+	4.72639	1.65169	0.83831	0.89064	Li^-	0.85518	0.45892	5.38580	44.0860
4	Be^+	3.27827	1.11152	1.75339	4.36978					
5	B^+	2.98154	1.01968	1.72580	3.96831	B^-	1.28237	0.60870	3.08049	13.8549
6	C^+	2.94769	1.02834	1.60273	3.36654	C^-	1.51991	0.70568	2.39028	7.83348
7	N^+	3.05526	1.07826	1.45186	2.72090	N^-	1.78225	0.79646	2.05222	5.78535
8	O^+	3.24665	1.14751	1.31391	2.20434	O^-	2.07359	0.89210	1.77881	4.31330
9	F^+	3.53268	1.22796	1.20641	1.85738	F^-	2.39413	0.99033	1.56301	3.29954
10	Ne^+	3.86423	1.31450	1.11011	1.56987					
11	Na^+	4.23613	1.40504	1.02536	1.33640	Na^-	2.90816	1.02462	2.71471	17.5763
12	Mg^+	4.42054	1.38780	1.25495	2.58241					
13	Al^+	4.60185	1.38143	1.34115	2.90441	Al^-	3.35896	1.06830	2.37937	11.0255
14	Si^+	4.77234	1.37539	1.40594	3.15435	Si^-	3.57441	1.09724	2.09677	7.43911
15	P^+	4.94464	1.37841	1.40650	3.04750	P^-	3.78442	1.12435	1.96006	6.22175
16	S^+	5.11977	1.38820	1.37844	2.83120	S^-	3.99364	1.15443	1.82469	5.17342
17	Cl^+	5.29818	1.40206	1.34618	2.64188	Cl^-	4.20327	1.18669	1.70236	4.35017
18	Ar^+	5.48130	1.42050	1.30429	2.42978					
19	K^+	5.66938	1.44259	1.25851	2.22131	K^-	4.57282	1.19426	2.50072	16.2007
20	Ca^+	5.81614	1.43331	1.41445	3.32874					
21	Sc^+	5.97618	1.44945	1.37665	3.08185	Sc^-	4.93248	1.23954	2.15612	10.6029
22	Ti^+	6.14231	1.47107	1.32903	2.82071	Ti^-	5.11766	1.26944	2.05042	9.69605
23	V^+	6.32906	1.51432	1.18171	1.99861	V^-	5.30544	1.30087	1.95128	8.83379
24	Cr^+	6.50775	1.54230	1.14072	1.84181	Cr^-	5.49687	1.33409	1.86265	8.13623
25	Mn^+	6.67252	1.55258	1.19023	2.18475	Mn^-	5.69149	1.36669	1.77224	7.28829
26	Fe^+	6.86144	1.58209	1.15357	2.04298	Fe^-	5.89086	1.40091	1.69293	6.63767
27	Co^+	7.07782	1.63139	1.04461	1.53087	Co^-	6.09464	1.43614	1.62080	6.08617
28	Ni^+	7.27978	1.66428	1.01323	1.43522	Ni^-	6.30300	1.47221	1.55474	5.61070
29	Cu^+	7.48809	1.69863	0.98222	1.34318	Cu^-	6.51648	1.50928	1.49484	5.21615
30	Zn^+	7.67809	1.71527	1.01735	1.57282					
31	Ga^+	7.86456	1.73029	1.03972	1.69613	Ga^-	6.90636	1.54757	1.52867	5.36819
32	Ge^+	8.04433	1.74090	1.07381	1.88050	Ge^-	7.09666	1.56768	1.43182	3.98878
33	As^+	8.22190	1.75205	1.08780	1.92917	As^-	7.28324	1.58511	1.40064	3.65489
34	Se^+	8.39777	1.76373	1.09031	1.91479	Se^-	7.46803	1.60288	1.36201	3.30531
35	Br^+	8.57157	1.77520	1.09071	1.89879	Br^-	7.65138	1.62086	1.32282	2.99880
36	Kr^+	8.74448	1.78738	1.08448	1.85221					
37	Rb^+	8.91674	1.80021	1.07397	1.78988	Rb^-	7.99417	1.62946	1.80021	10.0919
38	Sr^+	9.07315	1.79950	1.17058	2.50051					
39	Y^+	9.22578	1.79925	1.22909	2.83626	Y^-	8.32328	1.64469	1.77822	9.28775
40	Zr^+	9.38820	1.81441	1.16679	2.37828	Zr^-	8.49169	1.66331	1.60489	6.31240
41	Nb^+	9.55100	1.83114	1.10230	1.93958	Nb^-	8.65651	1.67718	1.56522	5.93873
42	Mo^+	9.70930	1.84270	1.08639	1.85062	Mo^-	8.82114	1.69187	1.52875	5.64552
43	Tc^+	9.86040	1.84723	1.11804	2.06190	Tc^-	8.98489	1.70645	1.48856	5.24032
44	Ru^+	10.0253	1.86686	1.05861	1.71997	Ru^-	9.14891	1.72180	1.45241	4.93498
45	Rh^+	10.1841	1.88028	1.04201	1.64781	Rh^-	9.31312	1.73771	1.41844	4.67444
46	Pd^+	10.3434	1.89440	1.02480	1.57689	Pd^-	9.47763	1.75412	1.38627	4.44674
47	Ag^+	10.5037	1.90929	1.00685	1.50608	Ag^-	9.64275	1.77108	1.35617	4.25601
48	Cd^+	10.6544	1.91576	1.03258	1.68055					
49	In^+	10.8030	1.92193	1.05020	1.78364	In^-	9.95238	1.78763	1.38304	4.28552
50	Sn^+	10.9481	1.92620	1.07632	1.93866	Sn^-	10.1043	1.79676	1.33805	3.56178
51	Sb^+	11.0915	1.93087	1.09002	1.99815	Sb^-	10.2537	1.80476	1.32651	3.38943
52	Te^+	11.2334	1.93588	1.09618	2.00879	Te^-	10.4016	1.81306	1.30807	3.17876
53	I^+	11.3735	1.94079	1.10097	2.01689	I^-	10.5481	1.82156	1.28756	2.97966
54	Xe^+	11.5125	1.94608	1.10094	1.99791					
55	Cs^+	11.6503	1.95173	1.09753	1.96288					

Table 2. Extracule moments $<R^n>$ for singly-charged cations and anions. Note that the normalization is $<R^0>=1$ instead of $N(N\text{-}1)/2$.

	Cation					Anion				
Z		n = -2	n = -1	n = 1	n = 2		n = -2	n = -1	n = 1	n = 2
1						H^-	1.16095	0.790970	1.86964	4.70555
3	Li^+	18.9056	3.30337	0.419157	0.222660	Li^-	3.42073	0.917855	2.69290	11.0215
4	Be^+	13.1131	2.22304	0.876695	1.09244					
5	B^+	11.9261	2.03936	0.862900	0.992077	B^-	5.29239	1.25870	1.47931	3.23401
6	C^+	12.1933	2.11941	0.768351	0.770119	C^-	6.42432	1.47590	1.14122	1.80505
7	N^+	12.9866	2.25580	0.688800	0.611864	N^-	7.66389	1.67302	0.982201	1.34435
8	O^+	14.0942	2.41806	0.622528	0.495922	O^-	9.04449	1.87791	0.853085	1.00711
9	F^+	15.5455	2.59405	0.572783	0.420815	F^-	10.5586	2.08605	0.751081	0.773264
10	Ne^+	17.1781	2.77855	0.528600	0.358377					
11	Na^+	18.9708	2.96857	0.489716	0.307216	Na^-	13.0172	2.15773	1.34141	4.37476
12	Mg^+	19.8873	2.92743	0.610523	0.627792					
13	Al^+	20.7737	2.90838	0.657711	0.713866	Al^-	15.1606	2.24604	1.16797	2.68604
14	Si^+	21.6088	2.89398	0.686715	0.759406	Si^-	16.1798	2.30506	1.02606	1.79448
15	P^+	22.4430	2.89816	0.685830	0.728377	P^-	17.1687	2.35977	0.958916	1.49990
16	S^+	23.2820	2.91615	0.671728	0.674798	S^-	18.1490	2.42044	0.892506	1.24602
17	Cl^+	24.1268	2.94227	0.656116	0.629699	Cl^-	19.1263	2.48543	0.832639	1.04710
18	Ar^+	24.9866	2.97778	0.635934	0.579516					
19	K^+	25.8631	3.02079	0.613910	0.530287	K^-	20.8579	2.49789	1.23773	4.02870
20	Ca^+	26.5577	2.99869	0.694311	0.812577					
21	Sc^+	27.3163	3.03131	0.675792	0.752128	Sc^-	22.5430	2.58985	1.06664	2.63306
22	Ti^+	28.1016	3.07542	0.652389	0.688203	Ti^-	23.4099	2.65139	1.01414	2.40772
23	V^+	28.9792	3.16538	0.578150	0.482196	V^-	24.2870	2.71598	0.964988	2.19357
24	Cr^+	29.8162	3.22238	0.558270	0.444614	Cr^-	25.1793	2.78422	0.921112	2.02049
25	Mn^+	30.5885	3.24175	0.584463	0.533194	Mn^-	26.0816	2.85082	0.876423	1.80980
26	Fe^+	31.4646	3.30167	0.566671	0.498938	Fe^-	27.0037	2.92074	0.837241	1.64828
27	Co^+	32.4583	3.40299	0.512103	0.371050	Co^-	27.9434	2.99265	0.801625	1.51142
28	Ni^+	33.3876	3.46963	0.496965	0.348223	Ni^-	28.9016	3.06623	0.769025	1.39345
29	Cu^+	34.3430	3.53923	0.481968	0.326169	Cu^-	29.8806	3.14178	0.739475	1.29561
30	Zn^+	35.2193	3.57188	0.500430	0.385029					
31	Ga^+	36.0778	3.60095	0.512441	0.417080	Ga^-	31.6794	3.21907	0.755687	1.32588
32	Ge^+	36.9092	3.62180	0.529088	0.460464	Ge^-	32.5570	3.25954	0.706966	0.979962
33	As^+	37.7295	3.64363	0.535927	0.471382	As^-	33.4170	3.29448	0.691495	0.897089
34	Se^+	38.5411	3.66646	0.537164	0.467324	Se^-	34.2679	3.32998	0.672347	0.810470
35	Br^+	39.3419	3.68877	0.537457	0.463302	Br^-	35.1112	3.36585	0.652956	0.734720
36	Kr^+	40.1375	3.71248	0.534483	0.451890					
37	Rb^+	40.9291	3.73749	0.529398	0.436681	Rb^-	36.6926	3.38180	0.893200	2.51271
38	Sr^+	41.6510	3.73477	0.578363	0.615688					
39	Y^+	42.3549	3.73290	0.608197	0.700769	Y^-	38.2083	3.41117	0.881724	2.30291
40	Zr^+	43.0993	3.76317	0.576733	0.585551	Zr^-	38.9798	3.44841	0.796076	1.56899
41	Nb^+	43.8435	3.79660	0.544240	0.475378	Nb^-	39.7349	3.47599	0.776338	1.47588
42	Mo^+	44.5674	3.81924	0.536421	0.453500	Mo^-	40.4880	3.50522	0.758211	1.40292
43	Tc^+	45.2595	3.82727	0.552720	0.507354	Tc^-	41.2357	3.53418	0.738259	1.30201
44	Ru^+	46.0082	3.86659	0.522863	0.421678	Ru^-	41.9834	3.56473	0.720321	1.22606
45	Rh^+	46.7299	3.89299	0.514728	0.404041	Rh^-	42.7306	3.59640	0.703472	1.16129
46	Pd^+	47.4530	3.92083	0.506284	0.386699	Pd^-	43.4779	3.62909	0.687528	1.10472
47	Ag^+	48.1787	3.95023	0.497465	0.369365	Ag^-	44.2267	3.66291	0.672609	1.05738
48	Cd^+	48.8637	3.96231	0.510712	0.413733					
49	In^+	49.5382	3.97372	0.519886	0.440166	In^-	45.6361	3.69516	0.685646	1.06051
50	Sn^+	50.1986	3.98158	0.532747	0.477494	Sn^-	46.3273	3.71307	0.662989	0.878891
51	Sb^+	50.8511	3.99025	0.539493	0.491580	Sb^-	47.0074	3.72862	0.657233	0.835866
52	Te^+	51.4964	3.99961	0.542528	0.493844	Te^-	47.6801	3.74477	0.648049	0.783406
53	I^+	52.1333	4.00874	0.544934	0.495710	I^-	48.3460	3.76134	0.637852	0.733935
54	Xe^+	52.7644	4.01865	0.544953	0.490964					
55	Cs^+	53.3901	4.02928	0.543306	0.482306					

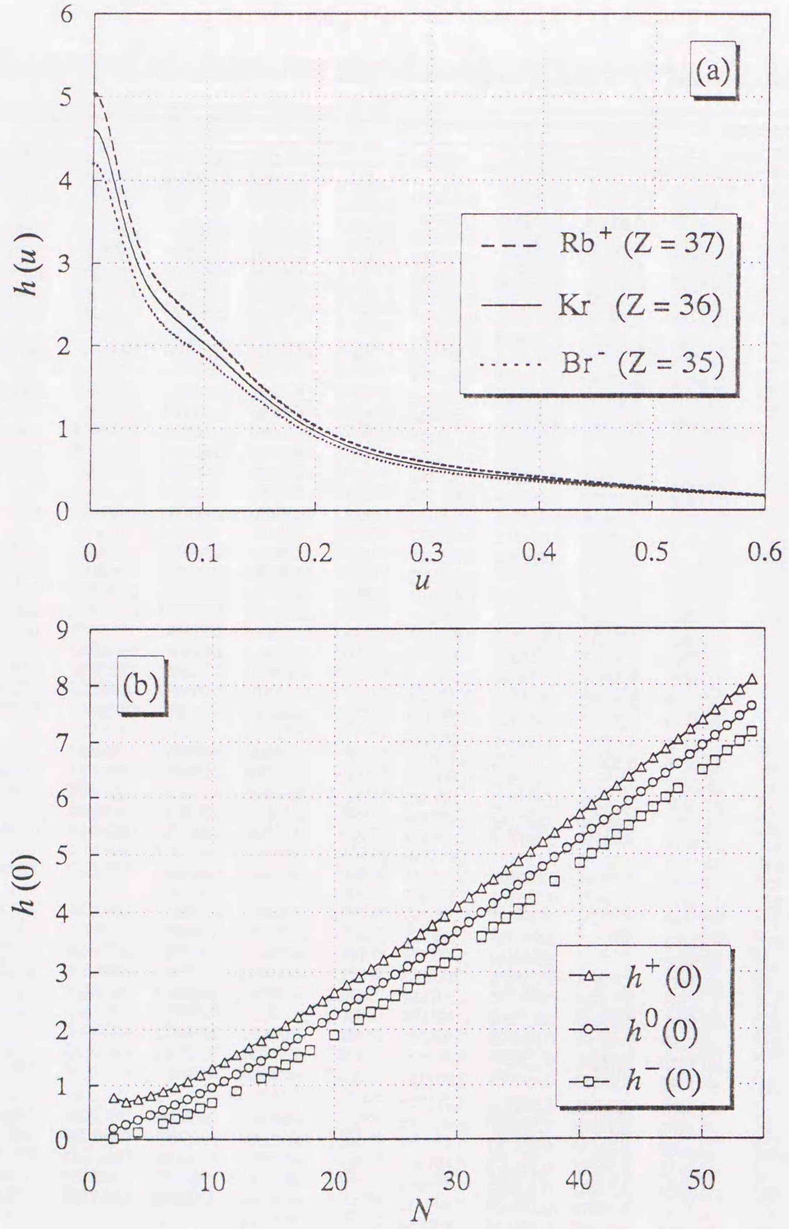


Fig. 1. Comparison of intracule properties of cationic, neutral, and anionic species. (a) Intracule densities $h(u)$ for the 36-electron species Rb^+, Kr, and Br^-. (b) Electron-electron coalescence densities $h(0)$ as a function of the number of electrons N.

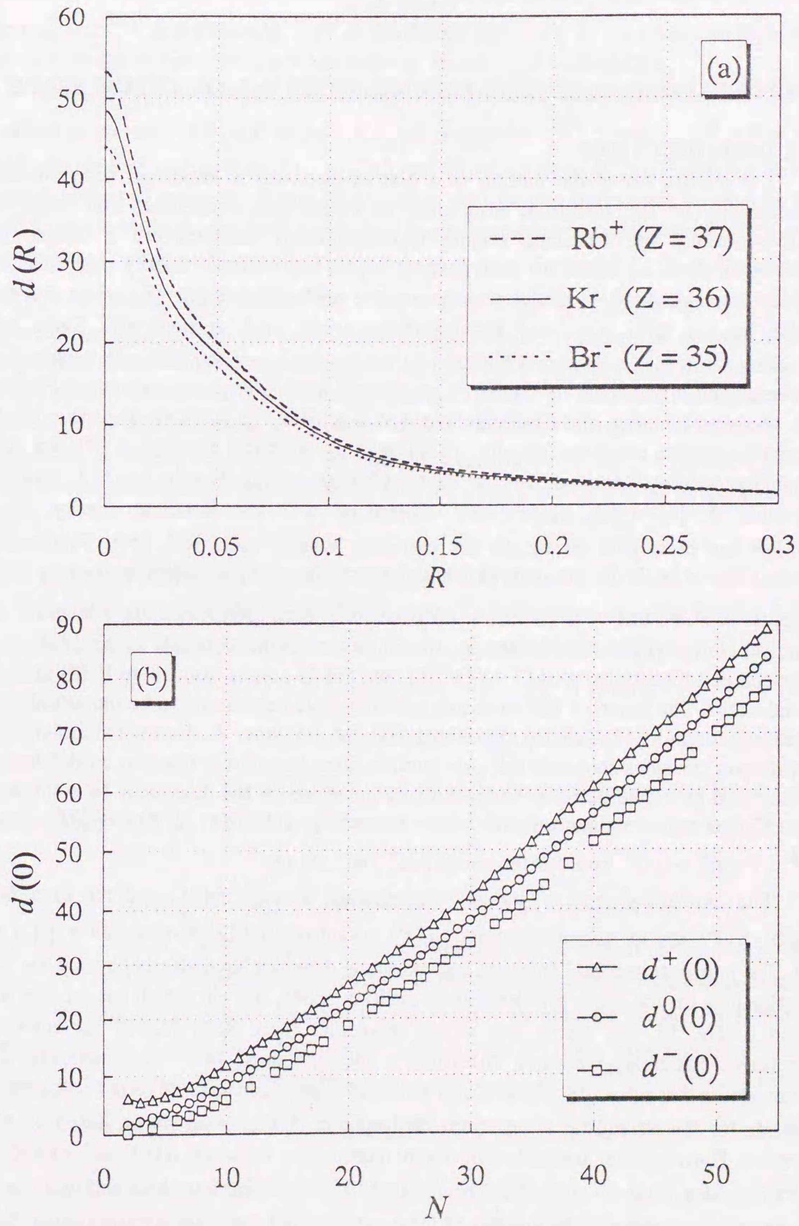


Fig. 2. Comparison of extracule properties of cationic, neutral, and anionic species. (a) Extracule densities $d(R)$ for the 36-electron species Rb^+, Kr, and Br^-. (b) Electron-electron counterbalance densities $d(0)$ as a function of the number of electrons N.

PART 3.
CHAPTER 3.

HARTREE-FOCK ELECTRON-PAIR DENSITIES IN MOMENTUM SPACE

3-3-1. INTRODUCTION

The elucidation of the motion of a pair of electrons is important for profound understanding of the electronic structures of atoms and molecules. The intracule (relative-motion) and extracule (center-of-mass-motion) densities are a couple of electron-pair densities useful for such purpose [1,2]. The intracule density $I(\mathbf{u})$ and its spherical average $h(u)$ in position space are the probability density functions for the relative vector $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$ and its magnitude $u=|\mathbf{r}_1-\mathbf{r}_2|$, respectively. Since the pioneering work by Coulson and Neilson [3] for the He atom, the intracule density has been employed in a number of studies on atomic and molecular problems such as Hund's rules, chemical bonding, and Coulomb hole (see, e.g., Refs. [2,4-7]). On the other hand, the position-space extracule density $E(\mathbf{R})$ and its spherical average $d(R)$ are the probability density functions for the center-of-mass vector $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$ and its magnitude $R=|\mathbf{r}_1+\mathbf{r}_2|/2$, respectively. Compared with the intracule density, little attention has been paid so far to the extracule density (see, Ref. [5]). Systematic examinations of both the intracule $h(u)$ and extracule $d(R)$ densities as well as their moments $<u^k>$ and $<R^k>$ have only recently been performed on the basis of numerical Hartree-Fock calculations for the 53 neutral atoms from He to Xe [4-7], the singly-charged 53 cations from Li^+ to Cs^+ [8], and the 43 anions from H^- to I^- [8] in their ground states. The intracule and extracule densities have been found to be monotonically decreasing functions for all the 53 atoms and the 96 ions. A decomposition of the electron-pair densities into subshell-pair contributions has shown that the modalities of intracule and extracule densities are essentially governed by the innermost 1s1s subshell pair. Moreover, we have found that interesting relations $d(R)\cong 8h(2R)$ and $<u^k>/<R^k>\cong 2^k$ hold for the neutral and ionic atoms.

The intracule density $\bar{I}(\mathbf{v})$ and its spherical average $\bar{h}(v)$, and the extracule density $\bar{E}(\mathbf{P})$ and its spherical average $\bar{d}(P)$ are introduced [2] in momentum space as well. The momentum-space intracule and extracule densities have also been used for the investigations on the same problems as in position space, but almost all the studies are limited to He, Li, Be, and a few simple molecules (see, Refs. [2,4-7] for relevant references). Recently, we have constructed and examined [4-7] systematically the momentum-space intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities together with their moments for the 53 neutral atoms from He to Xe in their ground states, based on the numerical Hartree-Fock method. The momentum-space intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities of the 53 atoms have been found to be classified into three and two types, respectively, according to the number of local extrema and their locations. By separating the electron-pair densities into subshell-pair contributions, we have clarified [6,7] that modalities of the momentum-space electron-pair densities are governed by a few outermost subshell pairs, in marked contrast with those for the position-space electron-

pair densities. A relation $<v^k>/<P^k>\cong 2^k$ is confirmed [5] to be valid between the intracule $<v^k>$ and extracule $<P^k>$ moments. However, no systematic analysis was reported for the momentum-space electron-pair densities of ionic species.

The purpose of Chapter 3 is to study the intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities in momentum space along with their moments $<v^k>$ and $<P^k>$ for the singly-charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- (except for ten unstable anions of group-2, 12, and 18 atoms) in their ground states, and to compare the ionic results with those for neutral atoms. The electron-electron coalescence $\bar{h}(0)$ and counterbalance $\bar{d}(0)$ densities are studied as well. The intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities will be classified into three and two types, respectively, and several important inequalities will be found among isoelectronic species. The present results complement those obtained previously [4-8] for the intracule and extracule densities of the 53 neutral atoms and the 96 singly-charged ions. The next section defines the intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities as well as their moments, and outlines our computational procedures based on the numerical Hartree-Fock method. In Section 3-3-3, the results are presented and discussed. Hartree atomic units are used throughout this chapter.

3-3-2. DEFINITIONS AND COMPUTATIONAL OUTLINE

For an N-electron system $(N\geq 2)$, the spherically-averaged intracule density $\bar{h}(v)$ and the associated moments $<v^k>$ in momentum space are defined [2] by

$$\bar{h}(v)\equiv(4\pi)^{-1}\int d\Omega_v\int d\mathbf{p}_1 d\mathbf{p}_2\,\delta[\mathbf{v}-(\mathbf{p}_1-\mathbf{p}_2)]\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)\ , \tag{1a}$$

$$<v^k>\equiv 4\pi\int_0^\infty dv\,v^{k+2}\,\bar{h}(v)\ , \tag{1b}$$

where $\mathbf{v}\equiv(v,\Omega_v)$ with $\Omega_v\equiv(\theta_v,\phi_v)$, and $\delta(\mathbf{p})$ is the three-dimensional Dirac delta function, and $\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)$ is the spin-reduced two-electron momentum density function [9],

$$\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)\equiv\frac{N(N-1)}{2}\int d\sigma_1 d\sigma_2 d\mathbf{y}_3,\ldots,d\mathbf{y}_N\,|\Phi(\mathbf{y}_1,\ldots,\mathbf{y}_N)|^2\ , \tag{2}$$

in which $\mathbf{y}_i\equiv(\mathbf{p}_i,\sigma_i)$ is the combined momentum-spin coordinate of the electron i and $\Phi(\mathbf{y}_1,\ldots,\mathbf{y}_N)$ is the electronic wave function in momentum space. The intracule density $\bar{h}(v)$ is the probability density function for the relative momentum $v=|\mathbf{p}_1-\mathbf{p}_2|$, and is normalized to the number $N(N-1)/2$ of electron pairs. On the other hand, the spherically-averaged extracule density $\bar{d}(P)$ and the associated moments $<P^k>$ are defined [2] by

$$\bar{d}(P)\equiv(4\pi)^{-1}\int d\Omega_P\int d\mathbf{p}_1 d\mathbf{p}_2\,\delta[\mathbf{P}-(\mathbf{p}_1+\mathbf{p}_2)/2]\bar{\Gamma}(\mathbf{p}_1,\mathbf{p}_2)\ , \tag{3a}$$

$$<P^k>\equiv 4\pi\int_0^\infty dP\,P^{k+2}\,\bar{d}(P)\ , \tag{3b}$$

where $\mathbf{P}\equiv(P,\Omega_P)$ with $\Omega_P\equiv(\theta_P,\phi_P)$. The extracule density $\bar{d}(P)$ is the probability density function for the center-of-mass momentum $P=|\mathbf{p}_1+\mathbf{p}_2|/2$, and is also normalized to the number $N(N-1)/2$ of electron pairs.

For singly-charged 53 cations and 43 anions, the position-space Hartree-Fock

wave function is expressed by a linear combination of a finite number of Slater determinants composed of a set of orthonormal spin-orbitals. The spatial part $\psi_{nlm}(\mathbf{r})$ of a spin-orbital is a product of radial $R_{nl}(r)$ and spherical harmonic $Y_{lm}(\Omega_r)$ functions, where $\mathbf{r} \equiv (r,\Omega_r)$, and n, l, and m stand for the principal, angular momentum, and magnetic quantum numbers, respectively. The momentum-space Hartree-Fock wave function has exactly the same structure as the corresponding wave function in position space, if $\psi_{nlm}(\mathbf{r})$ is replaced [10] with $\phi_{nlm}(\mathbf{p}) = P_{nl}(p)Y_{lm}(\Omega_p)$, where the momentum-space radial function $P_{nl}(p)$ is obtained as the Hankel transform of $R_{nl}(r)$,

$$P_{nl}(p) = (-i)^l \sqrt{\frac{2}{\pi}} \int_0^\infty dr\, r^2\, j_l(pr) R_{nl}(r)\ , \tag{4}$$

with $j_l(x)$ being the lth order spherical Bessel function of the first kind. The position-space radial functions $R_{nl}(r)$ were generated by the numerical Hartree-Fock method based on the MCHF72 code [11]. According to Eq. (4), the functions $R_{nl}(r)$ were then numerically transformed to the functions $P_{nl}(p)$ using Talman's algorithm [12]. The Condon-Slater rule [13] rewrites the intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities as a sum of spin-orbital-pair contributions. The angular integrations in Eqs. (1a) and (3a) were then performed analytically. A summation of contributions from one electron with $P_{nl}(p)$ and another electron with $P_{n'l'}(p)$ defines the contribution of a subshell pair *nln'l'*. The details are found in Refs. [4-7,14]. The experimental ground electronic configurations and terms [15,16] were considered for all the singly-charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^-. An explicit table is found in Ref. [17]. There are two exceptions, however. For the anions Sc^- and Pd^-, meaningful Hartree-Fock solutions were not obtained [17] to their ground states. Thus the second lowest states [17] were examined instead for these ions.

3-3-3. RESULTS AND DISCUSSION

In this section, all the intracule and extracule densities are normalized to *unity*, instead of the number of electron pairs $N(N-1)/2$, to facilitate mutual comparison of species with different numbers of electrons.

Systematic examinations of the intracule densities $\bar{h}(v)$ for the singly-charged 53 cations and 43 anions have shown that the densities $\bar{h}(v)$ are classified into the same three groups as those for neutral atoms [6] according to the number of local extrema and their locations.

Type A. Unimodal density with a maximum at $v = 0$. The next seven cations and nine anions have densities of this type: Li^+, B^+, Al^+, Y^+, and group-1 anions with a valence s^2 configuration, C^+, Si^+, and Ge^+ with a valence p^1 configuration, Sc^-, Ti^-, V^-, and Zr^- with a d^k configuration (k = 2-4). Figure 1(a) shows the intracule density of Si^+ which is of type A.

Type B. Unimodal density with a local minimum at $v = 0$ and a maximum $v > 0$. The 44 cations and 21 anions have densities of this type: Group-1 cations except Li^+, group-15 to group-18 cations, and group-13 to group-17 anions with a p^k configuration (k = 2-6), group-2 cations with an s^1 configuration, transition cations with a valence d^k (k = 4, 5, 7-10) or s^1d^k (k = 1, 2, 5, 6, 10) configuration, Sn^+ with a p^1 configuration, and Y^- with a d^1p^1 configuration. The intracule density of Fe^+ is given in Fig. 1(b).

Type C. Bimodal density with a primary maximum $v = 0$ and a secondary maximum at $v > 0$. There is also a local minimum between the two maxima. The two cations Ga^+ and In^+ with a d^{10} configuration and 13 transition anions with a d^k configuration (k = 4-10) except V^- have densities of this type. An example is shown in Fig. 1(c) for the Ag^- ion.

A decomposition of the total intracule density into subshell-pair contributions has shown that the above modalities of the intracule densities $\bar{h}(v)$ are governed by a few outermost subshell pairs SS, SS', SP, PP, and PD as reported for neutral atoms [6], where the symbols S, P, and D denote the outermost subshells of the respective symmetries, and the symbol S' denotes the second outermost s subshell. While the SS contribution has type-A distribution, the other four contributions have type-B distributions. When the SS subshell-pair contribution is large, the intracule density belongs to type A. When one of the subshell-pair contributions SS', SP, PP, and PD is large, $\bar{h}(v)$ becomes type-B density. The modality of type-C density comes from a combined contributions from SS and SP subshell pairs or from SS and PD subshell pairs. These results are in marked contrast to those of the position-space intracule densities $h(u)$; for all the 96 singly-charged ions, the densities $h(u)$ are monotonically decreasing functions [8] due to the predominant 1s1s subshell-pair contributions.

The electron-electron coalescence density $\bar{h}(0)$ is (see, Refs. [18,19] and references therein) the probability density of finding any two electrons at the same momentum. Figure 2(a) depicts the densities $\bar{h}(0)$ for the 53 cations and 43 anions together with the corresponding densities for the neutral atoms [18,19]. The densities $\bar{h}(0)$ of all the 96 ions are found to be highly dependent on the several outermost-subshell pairs, as shown for the neutral atoms [19]. The density $\bar{h}(0)$ decreases as the number of electrons increases toward a rare-gas (anions), rare-gas plus s^1 (cations), or s^1d^{10} (cations) electronic configuration, and there is a jump-up when one (cations) or two (anions) electrons are added to form a fully-occupied valence s^2 configuration. An inequality

$$\bar{h}^+(0) < \bar{h}^0(0) < \bar{h}^-(0)\,, \tag{5}$$

is seen to be true without exceptions for isoelectronic species, where the superscripts +, 0, and - refer to the cationic, neutral, and anionic species, respectively. Equation (5) means that among isoelectronic species a decrease in the nuclear charge Z increases the probability of finding any two electrons at the same momentum.

Table 1 summarizes the intracule moments $< v^k >$ with k = -2 to +2 for the 96 singly-charged ions. The moment $< v^{-2} >$ shows a periodic N-dependence analogous to the electron-electron coalescence density $\bar{h}(0)$ shown in Fig. 2(a). The moment $< v^{-1} >$ decreases with increasing N, although there are several exceptions. On the other hand, the moments $< v^k >$ with positive k have monotonically increasing behavior. Figure 2(b) shows the N-dependence of the average relative momentum $< v >$ for all the 96 ions and the corresponding 53 neutral atoms. A detailed comparison of the moments $< v^k >$ of the 96 singly-charged ions with those [4] of the 53 neutral atoms has shown that inequalities,

$$< v^k >^+ \ < < v^k >^0 \ < < v^k >^-, \qquad \text{when } k < 0, \tag{6a}$$

$$< v^k >^- \ < < v^k >^0 \ < < v^k >^+, \qquad \text{when } k > 0, \tag{6b}$$

hold among isoelectronic species with no exceptions. Equation (6) implies that among a isoelectronic series, a species with a larger Z has more diffuse intracule density than the one with a smaller Z.

Analogously, we have examined the modality of the extracule densities $\bar{d}(P)$ for the 96 ions and have found that the cationic densities are classified into two groups, whereas all the anions have a single type of densities.

Type A. Unimodal density with a maximum at $P = 0$. All the 43 anions and the following 41 cations have densities of this type: Group-1, 5, 6, 9 to 11, 13 to 18 cations, Y^+, and Ru^+. These 84 ions commonly have a doubly-occupied outermost s subshell. Figure 3(a) shows the extracule density of Br^- which has a type A distribution.

Type B. Unimodal density with a local minimum at $P = 0$ and a maximum $P > 0$. The next 12 cations with a singly-occupied outermost s subshell have type-B densities: Group-2, 4, 7, 12 cations, Sc^+, and Fe^+. The extracule density for Tc^+ is given in Fig. 3(b).

A comparison of the intracule and extracule densities for each ion shows that the two densities of the next 19 cations and 9 anions have type-A modality: 13 ions with an s^k configuration (k = 1 and 2), three cations with a p^1 configuration except Sn^+, four anions with a d^k configuration (k = 2-4) except Nb^-, eight cations with an s^1d^k configuration (k = 1, 2, 5, 6, 10). On the other hand, the modality of the intracule density of 34 cations and 34 anions is different from that of the extracule density. The next 32 cations and 21 anions have a type-B intracule density and a type-A extracule density: 40 ions with a p^k configuration (k = 2-6), Sn^+ with a p^1 configuration, 11 cations with a d^k configuration (k = 4, 5, 7-10), and Y^- with a d^1p^1 configuration. The two cations Ga^+ and In^+ with a d^{10} configuration and 13 transition anions with a d^k configuration (k = 4-10) except V^- have a type-C intracule density and a type-A extracule density. The change in the modalities of the intracule and extracule densities is observed mainly for an ion with a valence p^k ($k \geq 2$) or d^k ($k \geq 4$) configuration.

A separation of the extracule density into subshell-pair contributions has shown that the origin of the above modalities is similar to that of the intracule densities; the modality of the extracule density depends on the valence electronic configuration of an ion, and is governed by a few outermost subshell pairs SS, SS', SP, S'P, SD and PD. The SS, SP, S'P, and PD contributions have type-A distributions, and the other two contributions have type-B distributions. The modality of a type-A extracule density is due to SS, SP, or PD subshell pair. On the other hand, the type-B modality originates mainly from SS' subshell pair, S'P+SS', or PD+SD subshell pairs.

For the 96 singly-charged and 53 neutral atoms, Figure 4(a) plots the N-dependence of electron-electron counterbalance density $\bar{d}(0)$, which is [18,19] the probability density for any pair of electrons to have exactly opposite momenta. The N-dependence of $\bar{d}(0)$ is seen to be analogous to those of $\bar{h}(0)$ shown in Figure 2(a). For the five ions with N = 2 to 4, $\bar{d}(0)$ is confirmed to equal $8\bar{h}(0)$ exactly, as shown in the neutral atoms [18,19]. An inequality

$$\bar{d}^+(0) < \bar{d}^0(0) < \bar{d}^-(0), \tag{7}$$

is found to be valid among isoelectronic species without exceptions. The relation leads to a conclusion that an isoelectronic species with a smaller Z has a larger probability of finding any two electrons exactly at the opposite momenta.

Table 2 summarizes the extracule moments $< P^k >$ for the 96 ions, where k

ranges from -2 to +2. The dependence of $< P^k >$ on N is analogous to that of the intracule moments $< v^k >$. The average extracule radius $< P >$ is shown in Fig. 4(b) as a function of the number of electrons N for the 96 ions and compared with the results for the neutral atoms reported in Ref. [5]. By comparison of the extracule moments for the ionic and neutral atoms, we have found among isoelectronic species that

$$< P^k >^+ \; < < P^k >^0 \; < < P^k >^-, \qquad \text{when } k < 0, \tag{8a}$$

$$< P^k >^- \; < < P^k >^0 \; < < P^k >^+, \qquad \text{when } k > 0. \tag{8b}$$

For the 53 neutral atoms from He to Xe, an approximate relation

$$< v^k > / < P^k > \cong 2^k, \tag{9}$$

has been reported [5] between the intracule $< v^k >$ and extracule $< P^k >$ moments. The equality in Eq. (9) is rigorous for the species with N = 2 to 4. We have confirmed that the relation (9) also holds for the ions. For the neutral atoms with $2 \leq N \leq 54$, the average values of $< v^k > / < P^k >$ are [5] 0.212 (n = -2), 0.478 (n = -1), 2.03 (n = +1), and 4.07 (n = +2), respectively. For the cations and anions, the corresponding values have been found to be almost the same when n = -1, +1, and +2. When n = -2, the values for cations and anions are 0.209 and 0.214, respectively.

3-3-4. CONCLUSION

We have systematically examined the spherically-averaged intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities in momentum space, together with their moments $< v^k >$ and $< P^k >$, for the singly-charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground states. The electron-electron coalescence $\bar{h}(0)$ and counterbalance $\bar{d}(0)$ densities have been reported as well. For all the 96 ions, the modalities of the densities $\bar{h}(v)$ and $\bar{d}(P)$ have been classified into three and two types, respectively, and are highly affected by a few outermost subshell pairs. Comparing the 53 cations, 43 anions, and 53 neutral atoms with $2 \leq N \leq 54$, we have found several important inequalities among isoelectronic species. Moreover, the approximate but useful relation $< v^k > / < P^k > \cong 2^k$ is confirmed to hold for the ions as well.

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Table 1. Intracule moments $\langle v^k \rangle$ for singly-charged cations and anions. Note that the normalization is $\langle v^0 \rangle = 1$ instead of $N(N\text{-}1)/2$.

	Cation					Anion				
Z		$k=-2$	$k=-1$	$k=+1$	$k=+2$		$k=-2$	$k=-1$	$k=+1$	$k=+2$
1						H^-	6.10058	1.83339	0.822267	0.975859
3	Li^+	0.307010	0.425024	3.29607	14.4728	Li^-	5.38487	1.17535	2.14303	7.42823
4	Be^+	0.239773	0.383317	3.70895	19.0365					
5	B^+	0.522488	0.453208	4.01444	24.2376	B^-	1.05274	0.682547	3.07076	16.4176
6	C^+	0.357611	0.404919	4.39092	30.0100	C^-	0.615639	0.550291	3.52839	21.7008
7	N^+	0.258892	0.361431	4.78302	36.2653	N^-	0.457686	0.478765	3.95620	27.4016
8	O^+	0.195777	0.324744	5.18510	42.9955	O^-	0.342046	0.419510	4.38501	33.5803
9	F^+	0.165862	0.300624	5.56936	50.0547	F^-	0.261205	0.371613	4.81417	40.2322
10	Ne^+	0.139116	0.277597	5.96390	57.5893					
11	Na^+	0.116918	0.256717	6.36557	65.5947	Na^-	0.689087	0.377402	5.57509	54.5821
12	Mg^+	0.114212	0.250703	6.68790	73.5020					
13	Al^+	0.158387	0.256260	6.99050	81.6306	Al^-	0.387358	0.351027	6.23924	69.8920
14	Si^+	0.156666	0.254764	7.28421	89.9344	Si^-	0.307455	0.332403	6.55564	77.8936
15	P^+	0.148728	0.251079	7.57120	98.4535	P^-	0.282618	0.321515	6.85913	86.1006
16	S^+	0.138549	0.245933	7.85342	107.190	S^-	0.251464	0.308911	7.15673	94.5325
17	Cl^+	0.136432	0.242523	8.12673	116.104	Cl^-	0.222003	0.296061	7.44962	103.189
18	Ar^+	0.130181	0.237676	8.39762	125.235					
19	K^+	0.122191	0.232000	8.66669	134.584	K^-	0.438670	0.305265	7.99328	121.016
20	Ca^+	0.124261	0.231805	8.91036	143.958					
21	Sc^+	0.112496	0.223711	9.17186	153.493	Sc^-	0.283677	0.274659	8.53796	139.435
22	Ti^+	0.101170	0.215137	9.43679	163.213	Ti^-	0.248985	0.260231	8.81593	148.919
23	V^+	0.0854722	0.202781	9.71960	173.119	V^-	0.218983	0.247260	9.09332	158.586
24	Cr^+	0.0776599	0.195315	9.98708	183.206	Cr^-	0.194464	0.235295	9.37162	168.443
25	Mn^+	0.0752029	0.191762	10.2369	193.457	Mn^-	0.171570	0.225209	9.64416	178.457
26	Fe^+	0.0696263	0.185476	10.5004	203.869	Fe^-	0.153146	0.215710	9.91795	188.660
27	Co^+	0.0620999	0.177065	10.7796	214.471	Co^-	0.137595	0.206934	10.1916	199.046
28	Ni^+	0.0576730	0.171470	11.0449	225.256	Ni^-	0.124308	0.198814	10.4650	209.615
29	Cu^+	0.0535524	0.166063	11.3114	236.229	Cu^-	0.113012	0.191193	10.7391	220.374
30	Zn^+	0.0514151	0.162732	11.5638	247.367					
31	Ga^+	0.0565703	0.161582	11.8096	258.651	Ga^-	0.102953	0.187030	11.2507	242.376
32	Ge^+	0.0576592	0.160247	12.0512	270.054	Ge^-	0.0946154	0.183939	11.4985	253.591
33	As^+	0.0579419	0.159001	12.2883	281.593	As^-	0.0953795	0.182434	11.7405	264.935
34	Se^+	0.0576320	0.157731	12.5217	293.267	Se^-	0.0932722	0.180493	11.9786	276.417
35	Br^+	0.0592448	0.157038	12.7504	305.059	Br^-	0.0900175	0.178304	12.2132	288.035
36	Kr^+	0.0597184	0.156127	12.9762	316.983					
37	Rb^+	0.0594124	0.155030	13.1994	329.039	Rb^-	0.162978	0.183304	12.6647	311.604
38	Sr^+	0.0620984	0.155504	13.4135	341.146					
39	Y^+	0.0718436	0.157061	13.6231	353.349	Y^-	0.130306	0.180540	13.1028	335.574
40	Zr^+	0.0583860	0.152303	13.8441	365.674	Zr^-	0.111874	0.173604	13.3269	347.726
41	Nb^+	0.0536940	0.148913	14.0635	378.109	Nb^-	0.104413	0.170210	13.5457	359.993
42	Mo^+	0.0515094	0.146865	14.2768	390.656	Mo^-	0.0979597	0.166828	13.7635	372.376
43	Tc^+	0.0514445	0.146180	14.4823	403.302	Tc^-	0.0917173	0.163889	13.9785	384.860
44	Ru^+	0.0486041	0.143241	14.6976	416.061	Ru^-	0.0863785	0.160917	14.1927	397.461
45	Rh^+	0.0469716	0.141327	14.9068	428.931	Rh^-	0.0815923	0.158006	14.4059	410.174
46	Pd^+	0.0453309	0.139399	15.1151	441.913	Pd^-	0.0772523	0.155163	14.6182	423.002
47	Ag^+	0.0436551	0.137426	15.3229	455.011	Ag^-	0.0733228	0.152350	14.8299	435.945
48	Cd^+	0.0430435	0.136438	15.5229	468.196					
49	In^+	0.0456194	0.136204	15.7197	481.475	In^-	0.0704949	0.151277	15.2344	462.109
50	Sn^+	0.0464541	0.135842	15.9145	494.833	Sn^-	0.0677967	0.150305	15.4328	475.329
51	Sb^+	0.0469248	0.135481	16.1069	508.282	Sb^-	0.0692418	0.149976	15.6282	488.635
52	Te^+	0.0470962	0.135082	16.2973	521.819	Te^-	0.0691482	0.149411	15.8214	502.032
53	I^+	0.0483758	0.134952	16.4850	535.436	I^-	0.0682850	0.148687	16.0127	515.519
54	Xe^+	0.0490696	0.134711	16.6709	549.141					
55	Cs^+	0.0493221	0.134368	16.8552	562.933					

Table 2. Extracule moments $< P^k >$ for singly-charged cations and anions. Note that the normalization is $< P^0 > = 1$ instead of $N(N\text{-}1)/2$.

	Cation					Anion				
Z		$k=-2$	$k=-1$	$k=+1$	$k=+2$		$k=-2$	$k=-1$	$k=+1$	$k=+2$
1						H^-	24.4023	3.66678	0.411133	0.243965
3	Li^+	1.22804	0.850048	1.64804	3.61821	Li^-	21.5395	2.35070	1.07152	1.85706
4	Be^+	0.959094	0.766634	1.85448	4.75913					
5	B^+	2.08995	0.906416	2.00722	6.05939	B^-	5.90412	1.51434	1.51294	4.06868
6	C^+	1.75539	0.864978	2.16523	7.41440	C^-	3.40621	1.21506	1.73069	5.34876
7	N^+	1.34759	0.785162	2.34309	8.89634	N^-	2.46594	1.05119	1.93616	6.73008
8	O^+	1.03591	0.707470	2.53203	10.5004	O^-	1.80419	0.915345	2.14338	8.22487
9	F^+	0.869912	0.653947	2.71585	12.1943	F^-	1.35420	0.806096	2.35188	9.83385
10	Ne^+	0.720992	0.601671	2.90682	14.0066					
11	Na^+	0.598652	0.554084	3.10273	15.9367	Na^-	2.85158	0.783358	2.73249	13.3303
12	Mg^+	0.543444	0.531283	3.26697	17.8739					
13	Al^+	0.694371	0.535545	3.42092	19.8715	Al^-	2.10538	0.752988	3.06353	17.0810
14	Si^+	0.772260	0.538822	3.56902	21.9123	Si^-	1.64611	0.711880	3.22125	19.0452
15	P^+	0.758025	0.533181	3.71356	24.0080	P^-	1.47519	0.686964	3.37265	21.0622
16	S^+	0.711626	0.522606	3.85553	26.1589	S^-	1.28788	0.658130	3.52114	23.1361
17	Cl^+	0.693844	0.515034	3.99290	28.3551	Cl^-	1.11987	0.628904	3.66730	25.2667
18	Ar^+	0.654950	0.503954	4.12896	30.6059					
19	K^+	0.608420	0.490962	4.26402	32.9115	K^-	1.85985	0.633099	3.94054	29.6622
20	Ca^+	0.591706	0.486414	4.38723	35.2283					
21	Sc^+	0.538820	0.469958	4.51691	37.5806	Sc^-	1.22464	0.570749	4.21067	34.2038
22	Ti^+	0.485991	0.452156	4.64816	39.9782	Ti^-	1.07713	0.541189	4.34810	36.5418
23	V^+	0.425559	0.428901	4.78657	42.4176	V^-	0.948836	0.514369	4.48531	38.9254
24	Cr^+	0.385546	0.412759	4.91913	44.9062	Cr^-	0.843248	0.489518	4.62300	41.3561
25	Mn^+	0.361015	0.402682	5.04461	47.4399	Mn^-	0.745166	0.468407	4.75800	43.8264
26	Fe^+	0.333043	0.389181	5.17530	50.0098	Fe^-	0.665660	0.448507	4.89362	46.3437
27	Co^+	0.302883	0.372831	5.31238	52.6229	Co^-	0.598320	0.430092	5.02921	48.9065
28	Ni^+	0.279873	0.360618	5.44408	55.2854	Ni^-	0.540632	0.413031	5.16473	51.5150
29	Cu^+	0.258703	0.348846	5.57643	57.9947	Cu^-	0.491429	0.397016	5.30067	54.1707
30	Zn^+	0.242738	0.340295	5.70307	60.7491					
31	Ga^+	0.257565	0.336386	5.82654	63.5412	Ga^-	0.528835	0.391806	5.55629	59.6098
32	Ge^+	0.275826	0.334328	5.94775	66.3631	Ge^-	0.481791	0.385245	5.68023	62.3839
33	As^+	0.282543	0.331981	6.06678	69.2199	As^-	0.478535	0.381850	5.80134	65.1911
34	Se^+	0.282857	0.329333	6.18393	72.1110	Se^-	0.462199	0.377411	5.92053	68.0333
35	Br^+	0.289818	0.327790	6.29874	75.0320	Br^-	0.441385	0.372409	6.03802	70.9100
36	Kr^+	0.290578	0.325691	6.41207	77.9866					
37	Rb^+	0.287366	0.323149	6.52410	80.9746	Rb^-	0.700322	0.378666	6.26456	76.7492
38	Sr^+	0.292209	0.323003	6.63177	83.9768					
39	Y^+	0.326627	0.325234	6.73719	87.0035	Y^-	0.653855	0.375538	6.48392	82.6906
40	Zr^+	0.277102	0.316597	6.84749	90.0590	Zr^-	0.493587	0.359033	6.59574	85.7024
41	Nb^+	0.261112	0.310479	6.95699	93.1423	Nb^-	0.461595	0.352067	6.70508	88.7437
42	Mo^+	0.250079	0.306120	7.06379	96.2547	Mo^-	0.433465	0.345076	6.81395	91.8143
43	Tc^+	0.244228	0.303771	7.16702	99.3933	Tc^-	0.406269	0.338932	6.92140	94.9106
44	Ru^+	0.233929	0.298263	7.27448	102.558	Ru^-	0.382715	0.332711	7.02849	98.0361
45	Rh^+	0.225202	0.294116	7.37917	105.752	Rh^-	0.361458	0.326604	7.13507	101.190
46	Pd^+	0.216535	0.289936	7.48342	108.974	Pd^-	0.342091	0.320632	7.24118	104.373
47	Ag^+	0.207828	0.285669	7.58742	112.225	Ag^-	0.324470	0.314719	7.34700	107.584
48	Cd^+	0.201461	0.282880	7.68787	115.499					
49	In^+	0.208552	0.281699	7.78677	118.797	In^-	0.349333	0.313874	7.54974	114.080
50	Sn^+	0.218527	0.281212	7.88457	122.115	Sn^-	0.333920	0.311799	7.64918	117.363
51	Sb^+	0.223542	0.280557	7.98120	125.456	Sb^-	0.338254	0.311038	7.74714	120.667
52	Te^+	0.225496	0.279728	8.07676	128.820	Te^-	0.335060	0.309714	7.84402	123.995
53	I^+	0.231380	0.279418	8.17102	132.204	I^-	0.328425	0.308027	7.93990	127.345
54	Xe^+	0.234019	0.278832	8.26435	135.609					
55	Cs^+	0.234354	0.278006	8.35683	139.037					

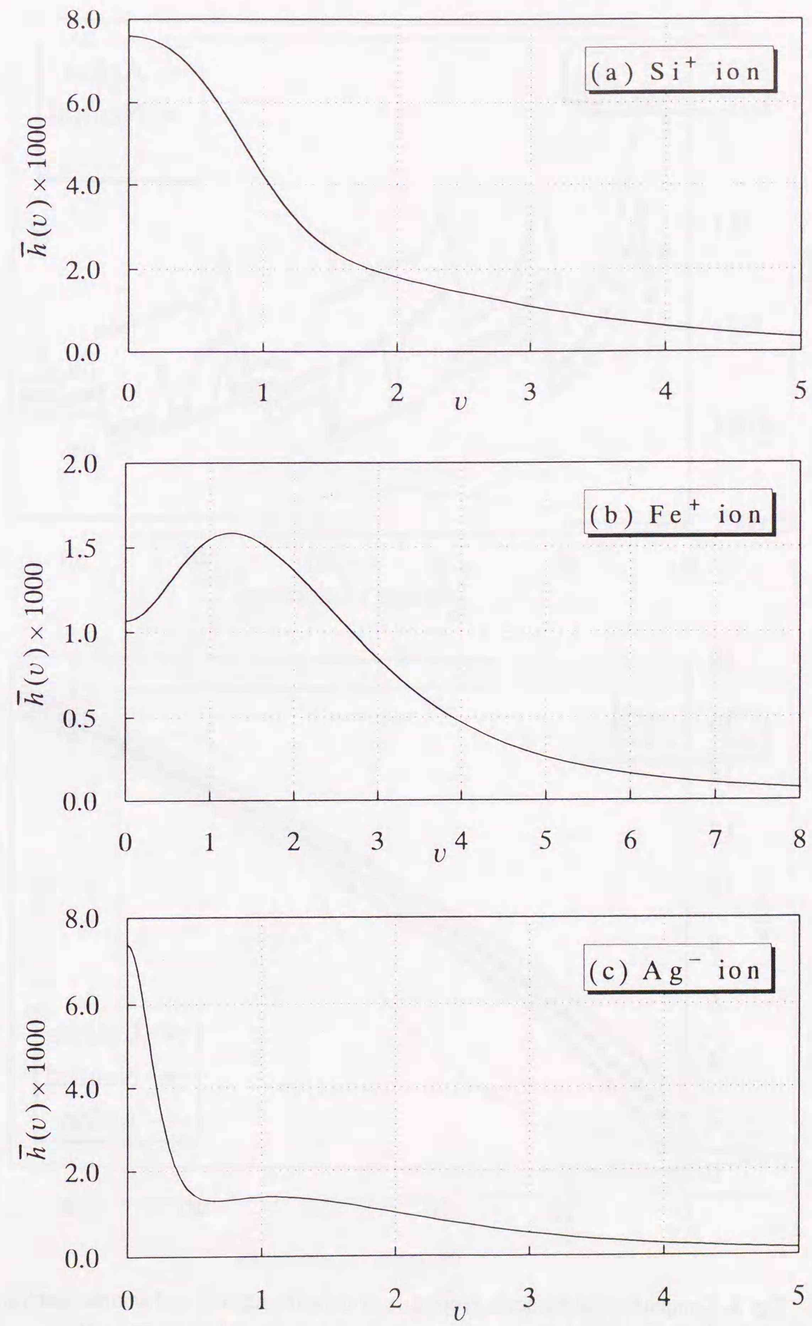
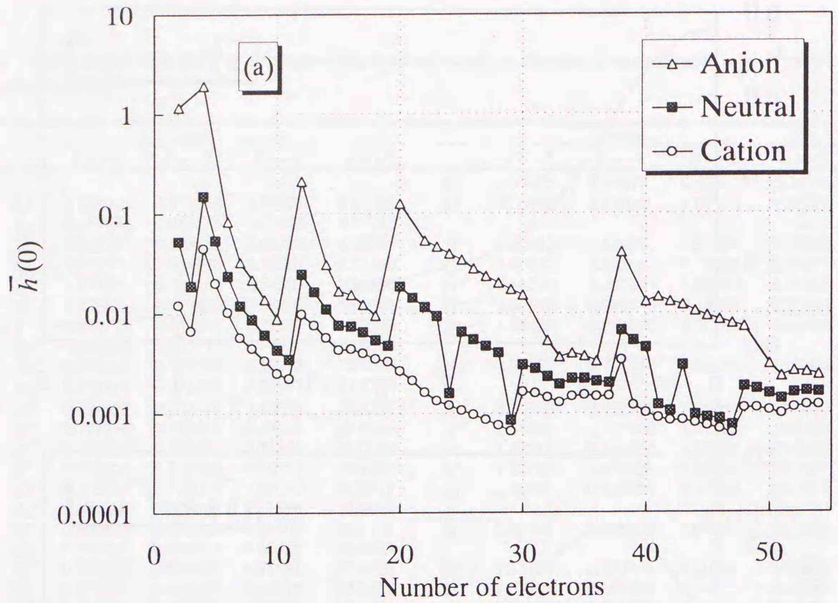


Fig. 1. An illustration of the three modalities of intracule densities in singly-charged ions. (a) The Si^+ ion with type A modality. (b) The Fe^+ ion with type B modality. (c) The Ag^- ion with type C modality.



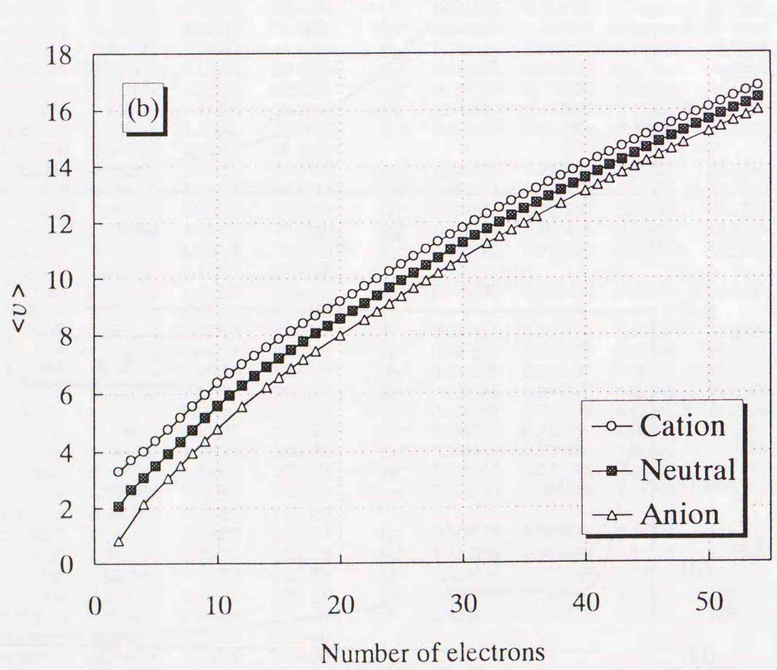
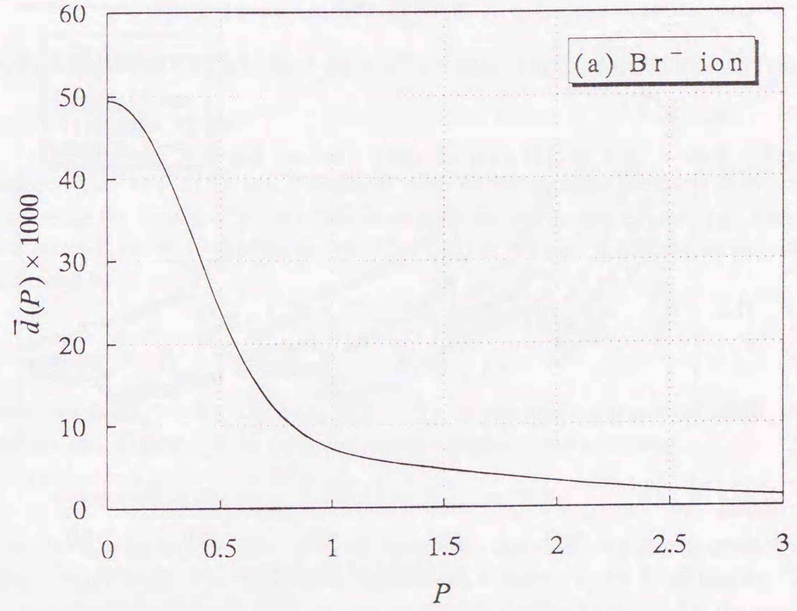


Fig. 2. Comparison of intracule properties of cationic, neutral, and anionic species. All the parent intracule densities are normalized to unity. (a) Electron-electron coalescence densities $\bar{h}(0)$. (b) The average relative momentum $<v>$.



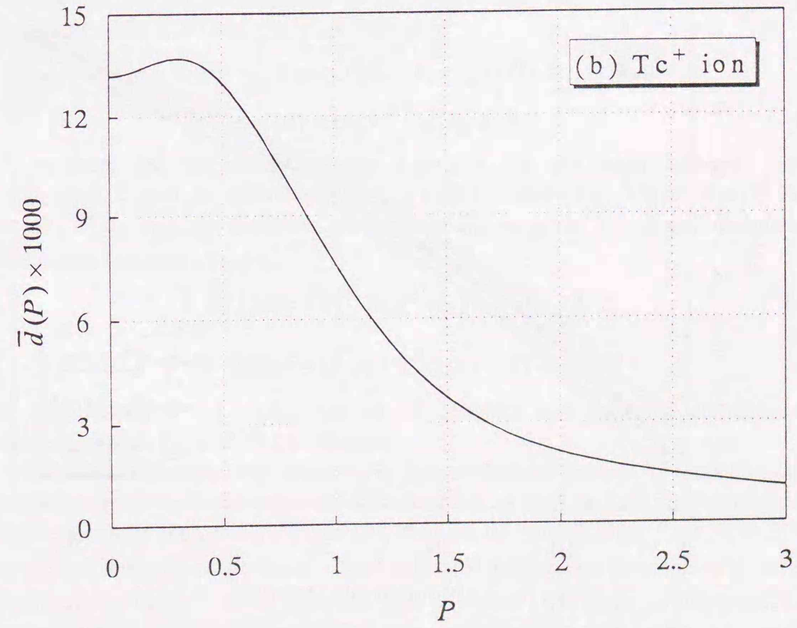
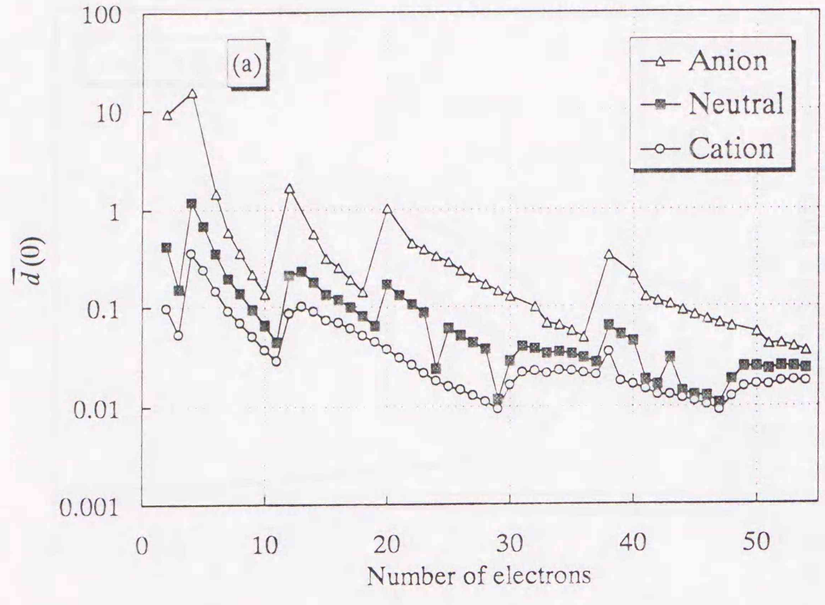


Fig. 3. An illustration of the two modalities of extracule densities in singly-charged ions. (a) The Br^- ion with type A modality. (b) The Tc^+ ion with type B modality.



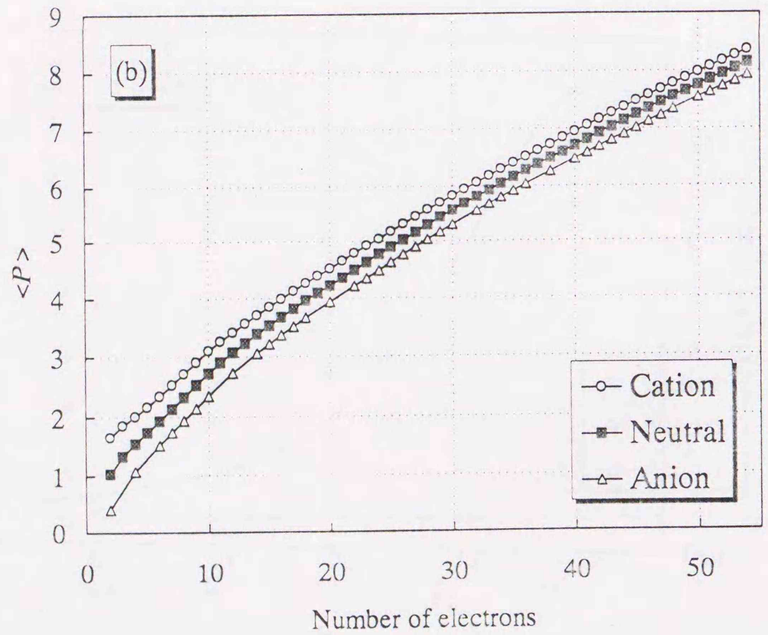


Fig. 4. Comparison of extracule properties of cationic, neutral, and anionic species. All the parent extracule densities are normalized to unity. (a) Electron-electron counterbalance density $\bar{d}(0)$. (b) The average extracule radius $<P>$.

PART 3.
CHAPTER 4.

CORRELATED EXTRACULE DENSITIES FOR TWO-ELECTRON ATOMS

3-4-1. INTRODUCTION

The intracule $I(\mathbf{u})$ and extracule $E(\mathbf{R})$ densities [1], as well as their spherical averages $h(u)$ and $d(R)$, are a couple of electron-pair densities useful to analyze and characterize the motion of a pair of electrons in atoms and molecules (see, *e.g.*, Ref. [2] for a review). For an N-electron system $(N \geq 2)$, the intracule densities $I(\mathbf{u})$ and $h(u)$ are defined by

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

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

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,

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

in which $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ is the combined space-spin coordinate of the electron i and $\Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$ is the electronic wave function of a system under consideration. The intracule densities $I(\mathbf{u})$ and $h(u)$ are the probability density functions for the relative vector $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ and its magnitude $u = |\mathbf{r}_1 - \mathbf{r}_2|$, respectively. On the other hand, the extracule densities $E(\mathbf{R})$ and $d(R)$ are defined by

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

$$d(R) \equiv (4\pi)^{-1} \int d\Omega_R \; E(\mathbf{R}) \, , \tag{3}$$

and represent the probability density functions for the center-of-mass vector $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and its magnitude $R = |\mathbf{r}_1 + \mathbf{r}_2|/2$, respectively, where $\mathbf{R} \equiv (R, \Omega_R)$ with $\Omega_R \equiv (\theta_R, \phi_R)$. By definition, the intracule and extracule densities are normalized to the number of electron pairs,

$$\int d\mathbf{u} \; I(\mathbf{u}) = 4\pi \int_0^\infty du \; u^2 \; h(u) = N(N-1)/2 \; , \tag{4a}$$

$$\int d\mathbf{R} \; E(\mathbf{R}) = 4\pi \int_0^\infty dR \; R^2 \; d(R) = N(N-1)/2 \; . \tag{4b}$$

For various studies and applications of the intracule and extracule densities, see references given in Refs. [2-4], for example.

Within the Hartree-Fock framework, systematic examinations of the spherically-averaged intracule $h(u)$ and extracule $d(R)$ densities, as well as their momentum-space counterparts, have been recently performed [5,6] for the neutral atoms from He to Xe in their ground states. Accurate Hartree-Fock values of the intracule moments $<u^n>$ and the extracule moments $<R^n>$ have also been published [3,4] for these atoms based on numerical Hartree-Fock calculations. For few-electron atoms such as He, Li, and Be, some intracule densities $h(u)$ and their moments $<u^n>$ were also reported from

explicitly-correlated near-exact wave functions, as summarized in Ref. [3]. Studies on the extracule properties are very limited compared to the intracule properties, though there are a few more references [7-11] which were not cited in Refs. [2-4]. In particular, all the extracule studies in the literature are based on the Hartree-Fock or configuration-interaction approximation, and no extracule densities $d(R)$ and their moments $< R^n >$ are known from explicitly-correlated wave functions even for the He atom.

In Chapter 4, we report explicitly-correlated near-exact results of the extracule density $d(R)$, its moments $< R^n >$, and the electron-electron counterbalance density $d(0)$ for the helium atom and its isoelectronic analogs in their ground states. For this purpose, we describe in the next section a method to obtain $d(R)$ from explicitly-correlated wave functions, when their two-electron density functions $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ can be expressed by the Hylleraas coordinates s, t, and u. In Section 3-4-3, numerical results are presented and discussed for two-electron atoms based on highly-accurate Kinoshita wave functions. Hartree atomic units are used throughout this chapter.

3-4-2. CORRELATED EXTRACULE DENSITIES

We consider a particular class of explicitly-correlated wave functions whose two-electron density functions $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ are expressed as a function of the Hylleraas coordinates s, t, and u,

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2) = \Gamma(s,t,u) \ , \tag{5a}$$

where

$$s = |\mathbf{r}_1| + |\mathbf{r}_2| \ , \quad t = |\mathbf{r}_1| - |\mathbf{r}_2| \ , \quad u = |\mathbf{r}_1 - \mathbf{r}_2| \ . \tag{5b}$$

Note that $\Gamma(s,t,u)$ is an even function with respect to the variable t for the antisymmetric property of electronic wave functions. For such functions, the six-fold integration over the whole space of the two three-dimensional variables $\mathbf{r}_1$ and $\mathbf{r}_2$ reduces to the three-fold integration,

$$d\mathbf{r}_1 d\mathbf{r}_2 \ \rightarrow \ \pi^2 (s^2 - t^2)\, u \, ds \, dt \, du \ , \tag{6a}$$

under the following triangular condition to the integration ranges,

$$0 \le |t| \le u \le s < \infty \ . \tag{6b}$$

Since the center-of-mass variable $R = |\mathbf{r}_1 + \mathbf{r}_2|/2$ is related to the Hylleraas coordinates by

$$4R^2 = s^2 + t^2 - u^2 \ , \tag{7}$$

Eqs.(6a) and (6b) are equivalent to

$$d\mathbf{r}_1 d\mathbf{r}_2 \ \rightarrow \ 4\pi^2 (s^2 - t^2)\, R \, ds \, dt \, dR \ , \tag{8a}$$

$$0 \le |t| \le 2R \le s < \infty \ , \tag{8b}$$

if the variable u is replaced with the variable R. The definition (3) of the extracule densities $E(\mathbf{R})$ and $d(R)$ implies that the density $d(R)$ is obtained by integrating $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ over all variables *except* R and divided by $4\pi R^2$. For the special case of Eq.(5a), we thus have the desired result,

$$d(R) = \frac{2\pi}{R} \int_0^{2R} dt \int_{2R}^{\infty} ds \, (s^2 - t^2)\, \Gamma(s,t,\sqrt{s^2 + t^2 - 4R^2}) \ , \tag{9}$$

where we have used the fact that $\Gamma(s,t,u)$ is even with respect to t. Once the extracule density $d(R)$ is obtained, the associated moments $< R^n >$ follow immediately from

$$< R^n > \equiv 4\pi \int_0^{\infty} dR \ R^{n+2} \, d(R) \ . \tag{10}$$

Note that $< R^0 > = N(N-1)/2$, the number of electron pairs.

A special case of $E(\mathbf{R})$ at $\mathbf{R}=\mathbf{0}$ or $d(R)$ at $R=0$ yields the electron-electron counterbalance density $E(\mathbf{0})=d(0)$, which is the probability density of finding any two electrons exactly at the opposite positions with respect to the coordinate origin (*i.e.*, the nucleus in atoms) [12,13]. Very recently, the existence of the electron-electron counterbalance hole was found [14] in the Hartree-Fock theory, in addition to the well-known electron-electron coalescence or Fermi hole. Applying an appropriate limiting procedure to Eq. (9), we obtain the electron-electron counterbalance density to be

$$d(0) = 4\pi \int_0^{\infty} ds \, s^2 \, \Gamma(s,0,s) \ . \tag{11}$$

An exactly analogous discussion finds that the corresponding intracule density $h(u)$ is given by

$$h(u) = \frac{\pi}{2u} \int_0^u dt \int_u^{\infty} ds \, (s^2 - t^2)\, \Gamma(s,t,u) \ . \tag{12}$$

Comparison of Eqs (9) and (12) shows that if the two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is independent of u, we have a simple, rigorous, and interesting relation

$$d(R) = 8h(2R) \ , \tag{13}$$

which has been also found [6] to be valid in the Hartree-Fock approximation for the ground-state He, Li, Be atoms and their isoelectronic analogs. We note that even when $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is independent of u, $h(u)$ depends on u since in Eq. (12) the integration intervals for the variables s and t include u. A special case of Eq.(13) for $R=0$ gives a relation $d(0)=8h(0)$ between the electron-electron counterbalance and coalescence densities. When Eq.(13) holds, we find a proportionality relation between the extracule and intracule moments,

$$< u^n > / < R^n > = 2^n \ . \tag{14}$$

For two-electron atoms, radially-correlated wave functions described below will be found to satisfy Eqs.(13) and (14) rigorously.

3-4-3. APPLICATION TO TWO-ELECTRON ATOMS

3-4-3-1. CHOICE OF CORRELATED WAVE FUNCTIONS

For S states of a two-electron atom, Hylleraas showed [15-17] that the exact (nonrelativistic) wave function can be expressed by the three variables s, t, and u defined by Eq.(5b) and proposed an expansion

$$\Phi_M(\mathbf{r}_1,\mathbf{r}_2) = \exp(-\zeta s) \sum_{i=1}^{M} c_i \, s^{l_i} \, t^{m_i} \, u^{n_i} \ , \tag{15}$$

where M specifies the number of expansion terms and the powers $\{l_i, m_i, n_i\}$ are nonnegative integers under the restriction that $\{m_i\}$ are all even for singlet states while all odd for triplet states. Since the two-electron density $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is merely the norm-squared of the wave function for two-electron systems, the Hylleraas function (15) fits the method developed in Section 3-4-2. Due to the presence of the square root term $\sqrt{s^2 + t^2 - 4R^2}$ in the integrand of Eq.(9), however, the analytical determination of the

extracule density $d(R)$ by Eq.(9) combined with Eq.(15) requires the powers $\{n_i\}$ of u must be all even.

In order to see the accuracy of the Hylleraas expansion with even $\{n_i\}$, we have constructed for the He atom the optimal 10- and 20-term functions composed of the best combinations of $\{l_i, m_i, n_i\}$ and the best values of ζ and $\{c_i\}$, by using the technique described in Refs. [18,19]. The resultant He energies have been found to be -2.901 508 450 and -2.903 054 137 hartrees, respectively, for M=10 and 20. Since the optimal Hylleraas energies [18] are -2.902 772 273 hartrees with 4 terms and -2.903 384 915 hartrees with 5 terms, the even-n_i restriction is concluded to be an extremely poor approximation. Therefore, we have decided to abandon analytical integrations of Eq.(9) and to employ numerical integrations instead.

The use of numerical integrations in Eq.(9) adds freedom to the choice of the parent wave function. In the present study, we have chosen the Kinoshita functions [20] given by

$$\Psi_M(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\zeta s) \sum_{i=1}^{M} c_i \, s^{l_i} \left(\frac{t}{u}\right)^{m_i} \left(\frac{u}{s}\right)^{n_i} , \qquad (16)$$

which generalizes the Hylleraas expansion through negative powers of the variables s and u. The Kinoshita expansion is known [19,21] to give very accurate results with a fewer number M of terms compared to the other expansions.

The effect of the electron correlation in atomic systems may be classified into radial and angular contributions. The radial correlation means that the electrons have a tendency to be at different distances from the nucleus. On the other hand, the angular correlation means that the electrons have a tendency to be on opposite sides of the nucleus. Since the angular correlation enters through the variable u in the Hylleraas coordinates, the removal of all the terms including u yields radially-correlated wave functions. In the present Kinoshita framework given by Eq.(16), radially-correlated functions are simply obtained by adding a constraint $m_i = n_i$. Comparison of the results from the radially- and fully-correlated wave functions will clarify in Section 3-4-3-3 that the radial and angular correlations have different contributions to the extracule density $d(R)$.

3-4-3-2. COMPUTATIONAL DETAILS

Radially-correlated Kinoshita functions for the ground states of the two-electron atoms with atomic number Z=1-10 have been taken from Ref. [22]. For a given number M of expansion terms, these functions have the fully-optimized powers $\{l_i, m_i = n_i\}$ as well as the exponent ζ and the coefficients $\{c_i\}$. The largest M values are 65 for Z=1, 50 for Z=2 and 3, and 40 for Z=4-10. These expansions essentially achieve the radial correlation limit [22].

Fully-correlated Kinoshita functions for the same species as above have been taken from Ref. [21]. In these functions, the powers $\{l_i\}$ and $\{n_i\}$ were extended from integers to half-integers, and all the variational parameters $\{l_i, m_i, n_i\}$, ζ, and $\{c_i\}$ were also fully optimized for a given value of M. The largest expansion contains 100 terms for Z=1-10. The associated energies demonstrate the accuracy of the Kinoshita functions employed in this study. In the case of the He atom, for example, the present

100-term function gives -2.903 724 377 033 hartrees which is only 1×10^{-12} hartrees above the most accurate literature values (see, *e.g.*, Ref. [23]) obtained by using more than 200 terms with more complicated functional forms.

The numerical integrations over s and t, involved in Eqs. (9) and (11), were performed by using the double-exponential technique [24] to obtain the extracule density $d(R)$ and the electron-electron counterbalance density $d(0)$. For numerical quadrature formulas, the double-exponential method [24] introduces a variable transformation such that a finite or semi-infinite integral interval changes into the infinite interval and that an integrand has a double exponential asymptotic decay as the new variable approaches to $\pm\infty$. The R value in $d(R)$ was discretized by the formula

$$R_i = (2Z)^{-1} \exp(x_i) , \quad x_i = x_{\min} + h(i-1) , \quad (i = 1, \ldots, N_p) \qquad (17)$$

where the discretization parameters were taken to be h=0.05, $N_p = 512$, and $x_{\min} = -21.6$ for Z=1 and $x_{\min} = -22.1$ for Z=2-10 in order to facilitate the comparison with the Hartree-Fock results already reported [4,6]. The error in any $d(R_i)$ was designed to be less than 1×10^{-15}. The numerical integration in Eq.(10) was carried out by the simple trapezoidal rule over the transformed abscissas x_i, and the resultant moments $< R^n >$ have the accuracy of more than 7 significant figures.

3-4-3-3. RESULTS AND DISCUSSION

In both radially-correlated and correlated calculations of two-electron atoms, it is known that the energy convergence is faster for a larger Z, when the number M of expansion terms is increased. For the first three members of two-electron atoms, Table 1 summarizes the manner of convergence of the radially-correlated extracule densities in terms of the quantities $d(0)$ and $< R^n >$ with n=−2 to +2. The energies E associated with the parent wave functions are also tabulated there for convenience. For the He and Li^+ atoms, we find that the moments are convergent in seven significant figures with 40- or 50-term functions, though the local quantity $d(0)$ is slightly less stable. In the case of the hydrogen anion H^-, however, the convergence of the extracule properties is poorer, except for $< R^{-1} >$ and $< R >$, than the neutral and cationic species even at M=65. Nevertheless, six significant figures for $< R^{-2} >$ and $< R^2 >$ and five significant figures for $d(0)$ appear to be reliable. Analogously, Table 2 exemplifies the manner of convergence of the extracule density for the fully-correlated Kinoshita functions. For He and Li^+, the extracule density $d(R)$ is seen to be essentially convergent with the 100-term functions. Again, the convergence is less satisfactory for H^- even when 100 terms are used in the Kinoshita expansion.

For the H^-, He, and Li^+ atoms, Figure 1 depicts the radially-correlated and correlated extracule densities obtained from the largest Kinoshita expansions, and compares them with the Hartree-Fock results obtained by the numerical Hartree-Fock procedure [5]. In all the cases, the spherically-averaged extracule density $d(R)$ is a monotonically decreasing function with a maximum at R=0. Comparison of the Hartree-Fock and radially-correlated densities clarifies that the radial correlation contributes to shift the density from a small R to a large R region. Since the radial correlation increases the probability of finding the two electrons at different distances from the nucleus, the probability of finding the center-of-mass of the electrons is decreased around the origin

(*i.e.*, the nucleus), whichever the two electrons are on the same side or on the opposite sides of the nucleus. The electron-electron counterbalance density $d(0)$ decreases accordingly. These effects of the radial correlation are most remarkable in the H^- anion and decrease as Z increases.

Comparison of the radially-correlated and correlated extracule densities in Figure 1 shows that the angular correlation works to increase the extracule density in a small R region. The result appears to be natural, since the angular correlation increases the probability of finding the two electrons on the opposite sides of the nucleus, leading to an increased probability for the electronic center-of-mass being around the nucleus. The angular correlation effect is again largest for the H^- anion, and there the correlated density is found to lie approximately at the middle of the Hartree-Fock and radially-correlated densities. For the neutral and cationic species, however, we see that the correlated density is rather close to the Hartree-Fock density. As discussed before [25] for the neutral Li atom, an appropriate balance between the radial and angular correlations in correlated calculations is suggested to be important for the reliable description of electron densities and related properties. We note that the different contributions of the radial and angular correlations to the extracule density $d(R)$, observed above, are in accord with the conjecture given in a previous work [13] on the electron-electron counterbalance density $d(0)$.

For the two-electron atoms with Z=1-10, Table 3 summarizes and compares the electron-electron counterbalance density $d(0)$ and the extracule moments $< R^n >$ (n=−2 to +4) obtained from the Hartree-Fock (HF), radially-correlated (rc), and correlated (c) wave functions. For the counterbalance density $d(0)$, we find an inequality,

$$d_{\rm rc}(0) < d_{\rm c}(0) < d_{\rm HF}(0) \ , \tag{18}$$

is valid for all species, where the subscripts HF, rc, and c distinguish the parent wave functions. As anticipated from Figure 1, $d_{\rm c}(0) \cong d_{\rm HF}(0)$ is a good approximation, except for H^-, with the maximum error of 4.3% for He.

For the H^- anion, the extracule moments satisfy inequality relations $\langle R^n \rangle_{\rm rc} < \langle R^n \rangle_{\rm c} < \langle R^n \rangle_{\rm HF}$ when n is negative and $\langle R^n \rangle_{\rm HF} < \langle R^n \rangle_{\rm c} < \langle R^n \rangle_{\rm rc}$ when n is positive, but neither $\langle R^n \rangle_{\rm HF}$ nor $\langle R^n \rangle_{\rm rc}$ are acceptable approximations to $\langle R^n \rangle_{\rm c}$. In a previous paper [22], it was discussed from an energetic point of view that the radial correlation is exceptionally more important than the angular correlation for the H^- anion. However, the correlation effect on the extracule moments does not imply that the radial correlation is the major part of the electron correlation in H^-.

For the extracule moments $< R^n >$ of the neutral and cationic two-electron species, the situation is different. We find in Table 3 that

$$\langle R^n \rangle_{\rm rc} < \langle R^n \rangle_{\rm HF} < \langle R^n \rangle_{\rm c} \ , \quad \text{for } n=-2 \text{ and } -1, \tag{19a}$$

$$\langle R^n \rangle_{\rm c} < \langle R^n \rangle_{\rm HF} < \langle R^n \rangle_{\rm rc} \ , \quad \text{for } n=1 \text{ and } 2, \tag{19b}$$

and

$$\langle R^n \rangle_{\rm c} < \langle R^n \rangle_{\rm rc} < \langle R^n \rangle_{\rm HF} \ , \quad \text{for } n=3 \text{ and } 4, \tag{19c}$$

with only two exceptions for $< R^{-2} >$ and $< R^3 >$ of He. Equations (19a) and (19b) mean that in small and intermediate R regions, $d_{\rm HF}(R)$ is closer to $d_{\rm c}(R)$ than $d_{\rm rc}(R)$ as observed in Figures 1(b) and 1(c). The numerical values in Table 3 show that at least for $<R>$ and $< R^{-1} >$ the Hartree-Fock values may be used as acceptable estimates of the exact nonrelativistic values. On the other hand, Eq.(19c) means that for a large R region, $d_{\rm rc}(R)$ is closer to $d_{\rm c}(R)$ than $d_{\rm HF}(R)$, and the contribution of the radial correlation is important for higher extracule moments.

In Section 3-4-2, we have shown that the relations $d(R) = 8h(2R)$ and $< u^n > / < R^n > = 2^n$ hold exactly, when the two-electron density $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is a function of only s and t and independent of the interelectronic variable u. Thus the relations are valid at the Hartree-Fock and radially-correlated levels. However, this is not true for correlated wave functions. For two-electron atoms, we have seen in Figure 1 that the correlated extracule density $d(R)$ is monotonically decreasing with a maximum at R=0. In contrast, the correlated intracule density $h(u)$ has been known [26,27] to be a unimodal function with a maximum at u>0. At the correlated level, therefore, the extracule $d(R)$ and intracule $h(u)$ densities are qualitatively different and the simple relations no longer hold, as an explicit comparison of $d(R)$ and $8h(2R)$ is given in Figure 2 based on the optimum 100-term Kinoshita wave functions with half-integer powers. However, the difference between $d(R)$ and $8h(2R)$ is observed mainly in a small R region and diminishes as Z increases. Thus an approximation $< u^n > / < R^n > \cong 2^n$ may be used, for a positive value of n, to estimate roughly the extracule moments from the intracule ones and *vice versa*. The proportionality between the extracule and intracule properties is summarized in Table 4 for two-electron atoms.

3-4-4. CONCLUSION

For two-electron atoms with Z=1-10 in their ground states, explicitly-correlated near-exact results have been reported for the extracule density $d(R)$, its moments $< R^n >$, and the electron-electron counterbalance density $d(0)$, based on the highly accurate Kinoshita wave functions. From the comparison of the Hartree-Fock, radially-correlated, and correlated results, different contributions of the radial and angular correlations to the extracule density have been clarified. As long as the counterbalance density $d(0)$ and the moments $< R^n >$ with n=−2 to +2 are concerned, an incorporation of the radial correlation only results in a larger deviation from the correlated values than the Hartree-Fock approximation. In the Hartree-Fock and radially-correlated description of two-electron atoms, there exist interesting relations $d(R) = 8h(2R)$ and $< u^n > / < R^n > = 2^n$ between the extracule $d(R)$ and intracule $h(u)$ densities and their moments. Unfortunately, these equalities do not hold at the correlated exact level. Nevertheless, a relation $< u^n > / < R^n > \cong 2^n$ may be a rough but useful approximation for positive values of n.

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Table 1. Convergence of radially-correlated extracule densities for H^-, He, and Li^+. A(n) means $A \times 10^n$.

Species	M	$-E$	$d(0)$	$\langle R^{-2} \rangle$	$\langle R^{-1} \rangle$	$\langle R \rangle$	$\langle R^2 \rangle$
H^-	10	0.514 479 536	4.086 414(-2)	6.486 042(-1)	5.964 936(-1)	2.502 546	8.667 529
	20	496 021	.089 532(-2)	.480 443(-1)	.960 242(-1)	.506 958	.732 179
	30	267	.086 812(-2)	.479 947(-1)	237(-1)	972	.733 170
	40	341	682(-2)	957(-1)	220(-1)	995	380
	50	352	970(-2)	.480 049(-1)	215(-1)	.507 014	699
	60	355	895(-2)	043(-1)	214(-1)	014	685
	65	355	877(-2)	037(-1)	213(-1)	016	729
He	10	2.879 027 441	1.246 048	6.644 084	1.973 322	6.939 481(-1)	6.053 693(-1)
	20	028 713	231	561	320	.940 153(-1)	.055 585(-1)
	30	759	127	400	321	.939 988(-1)	137(-1)
	40	764	121	391	321	991(-1)	160(-1)
	50	764	123	393	321	992(-1)	160(-1)
Li^+	10	7.252 490 548	5.485 025	1.783 903(+1)	3.234 659	4.227 190(-1)	2.242 095(-1)
	20	491 877	634	970(+1)	657	250(-1)	142(-1)
	30	985	967	986(+1)	658	231(-1)	108(-1)
	40	996	.486 026	989(+1)	658	231(-1)	109(-1)
	50	996	050	990(+1)	658	231(-1)	109(-1)

Table 2. Convergence of correlated extracule densities for H^-, He, and Li^+. A(n) means $A \times 10^n$.

Species	M	$-E$	$d(0)$	$\langle R^{-2}\rangle$	$\langle R^{-1}\rangle$	$\langle R\rangle$	$\langle R^2\rangle$
H^-	5	0.527 546 851 024	7.570 618(-2)	9.585 973(-1)	7.249 654(-1)	2.012 891	5.387 201
	10	743 228 813	.293 794(-2)	.451 289(-1)	.214 819(-1)	.032 103	.575 298
	20	750 451 865	.298 043(-2)	.445 785(-1)	.211 303(-1)	.035 508	.608 537
	30	750 960 782	.299 568(-2)	955(-1)	.210 861(-1)	894	.612 497
	50	751 014 653	.300 935(-2)	.446 197(-1)	828(-1)	944	.613 171
	100	016 523	930(-2)	237(-1)	836(-1)	945	193
He	5	2.903 569 904 286	1.476 609	7.336 903	2.064 174	6.669 222(-1)	5.606 735(-1)
	10	721 712 458	.460 882	.307 022	.061 067	.684 014(-1)	.643 196(-1)
	20	724 228 359	.462 145	.309 203	260	026(-1)	750(-1)
	30	361 888	312	209	248	028(-1)	754(-1)
	50	376 757	359	273	251	023(-1)	732(-1)
	100	377 033	363	275	251	023(-1)	732(-1)
Li^+	5	7.279 690 994 991	6.069 683	1.893 941(+1)	3.325 038	4.122 901(-1)	2.135 676(-1)
	10	908 853 989	.050 145	.892 117(+1)	.323 346	.128 856(-1)	.144 918(-1)
	20	913 266 793	.057 231	774(+1)	610	927(-1)	.145 128(-1)
	30	389 769	425	783(+1)	608	927(-1)	129(-1)
	50	412 432	498	794(+1)	612	926(-1)	128(-1)
	100	668	510	794(+1)	612	926(-1)	128(-1)

Table 3. Comparison of the Hartree-Fock, radially-correlated, and correlated extracule moments. For each species, the first line gives the Hartree-Fock results, the middle line the radially-correlated results, and the last line the correlated results. $\langle R^0\rangle$ is normalized to unity. A(n) means $A \times 10^n$.

Species	$-E$	$d(0)$	$\langle R^{-2}\rangle$	$\langle R^{-1}\rangle$	$\langle R\rangle$	$\langle R^2\rangle$	$\langle R^3\rangle$	$\langle R^4\rangle$
H^-	0.487 929 734	1.038 678(-1)	1.160 953	7.909 697(-1)	1.869 637	4.705 549	1.508 079(+1)	5.921 988(+1)
	0.514 496 355	4.086 877(-2)	6.480 037(-1)	5.960 213(-1)	2.507 016	8.733 729	4.044 388(+1)	2.396 547(+2)
	0.527 751 017	7.300 930(-2)	9.446 237(-1)	7.210 836(-1)	2.035 945	5.613 193	2.001 550(+1)	8.923 141(+1)
He	2.861 679 996	1.524 832	7.368 179	2.051 538	6.810 622(-1)	5.924 142(-1)	6.261 191(-1)	7.784 555(-1)
	2.879 028 764	1.246 123	6.644 393	1.973 321	6.939 992(-1)	6.055 160(-1)	6.340 607(-1)	7.736 257(-1)
	2.903 724 377	1.462 363	7.309 275	2.061 251	6.684 023(-1)	5.643 732(-1)	5.742 096(-1)	6.830 523(-1)
Li^+	7.236 415 201	6.161 923	1.890 557(+1)	3.303 373	4.191 574(-1)	2.226 603(-1)	1.427 731(-1)	1.070 973(-1)
	7.252 491 996	5.486 050	1.783 990(+1)	3.234 658	4.227 231(-1)	2.242 109(-1)	1.424 008(-1)	1.051 226(-1)
	7.279 913 413	6.057 510	1.892 794(+1)	3.323 612	4.128 926(-1)	2.145 128(-1)	1.337 669(-1)	9.715 118(-2)
Be^{2+}	13.611 299 43	1.592 501(+1)	3.577 588(+1)	4.554 137	3.029 080(-1)	1.159 152(-1)	5.340 122(-2)	2.871 527(-2)
	13.626 859 40	1.467 593(+1)	3.436 009(+1)	4.488 987	3.045 236(-1)	1.163 058(-1)	5.316 326(-2)	2.822 920(-2)
	13.655 566 24	1.577 307(+1)	3.587 560(+1)	4.578 845	2.993 084(-1)	1.125 807(-1)	5.076 358(-2)	2.662 716(-2)
B^{3+}	21.986 234 47	3.272 395(+1)	5.797 940(+1)	5.804 555	2.371 729(-1)	7.094 217(-2)	2.550 928(-2)	1.069 332(-2)
	22.001 513 83	3.072 586(+1)	5.621 105(+1)	5.741 272	2.380 863(-1)	7.108 276(-2)	2.539 446(-2)	1.053 642(-2)
	22.030 971 58	3.251 927(+1)	5.815 557(+1)	5.831 764	2.348 529(-1)	6.927 122(-2)	2.447 935(-2)	1.005 746(-2)
C^{4+}	32.361 192 88	5.846 860(+1)	8.551 619(+1)	7.054 819	1.948 911(-1)	4.785 096(-2)	1.411 074(-2)	4.847 267(-3)
	32.376 295 97	5.554 580(+1)	8.339 422(+1)	6.992 685	1.954 763(-1)	4.791 333(-2)	1.405 150(-2)	4.785 428(-3)
	32.406 246 60	5.820 603(+1)	8.576 852(+1)	7.083 630	1.932 753(-1)	4.689 863(-2)	1.362 978(-2)	4.603 845(-3)
N^{5+}	44.736 163 96	9.506 883(+1)	1.183 863(+2)	8.305 001	1.654 077(-1)	3.444 268(-2)	8.608 518(-3)	2.505 068(-3)
	44.751 146 05	9.104 561(+1)	1.159 102(+2)	8.243 644	1.658 140(-1)	3.447 443(-2)	8.575 415(-3)	2.476 950(-3)
	44.781 445 15	9.474 328(+1)	1.187 146(+2)	8.334 929	1.642 190(-1)	3.384 969(-2)	8.354 823(-3)	2.396 264(-3)
O^{6+}	59.111 142 70	1.444 345(+2)	1.565 897(+2)	9.555 134	1.436 744(-1)	2.597 229(-2)	5.632 929(-3)	1.421 842(-3)
	59.126 036 56	1.391 351(+2)	1.537 591(+2)	9.494 338	1.439 728(-1)	2.599 012(-2)	5.613 127(-3)	1.407 630(-3)
	59.156 595 12	1.440 409(+2)	1.569 940(+2)	9.585 884	1.427 638(-1)	2.557 845(-2)	5.486 768(-3)	1.367 454(-3)
F^{7+}	75.486 126 41	2.084 754(+2)	2.001 264(+2)	1.080 524(+1)	1.269 899(-1)	2.028 204(-2)	3.885 054(-3)	8.658 627(-4)
	75.500 953 09	2.017 242(+2)	1.969 411(+2)	1.074 486(+1)	1.272 182(-1)	2.029 280(-2)	3.872 530(-3)	8.580 707(-4)
	75.531 712 36	2.080 087(+2)	2.006 067(+2)	1.083 662(+1)	1.262 702(-1)	2.000 730(-2)	3.795 026(-3)	8.362 771(-4)
Ne^{8+}	93.861 113 52	2.891 015(+2)	2.489 965(+2)	1.205 532(+1)	1.137 778(-1)	1.627 600(-2)	2.791 662(-3)	5.569 869(-4)
	93.875 887 35	2.807 229(+2)	2.454 563(+2)	1.199 528(+1)	1.139 580(-1)	1.628 287(-2)	2.783 374(-3)	5.524 328(-4)
	93.906 806 52	2.885 565(+2)	2.495 526(+2)	1.208 720(+1)	1.131 947(-1)	1.607 681(-2)	2.733 227(-3)	5.397 925(-4)

Table 4. Proportionality between the extracule and intracule properties.

Method, Species	$h(0)/d(0)$	$\langle u^n\rangle/\langle R^n\rangle$ $n=-2$	-1	$+1$	$+2$	$+3$	$+4$
Hartree – Fock Radially - correlated	0.125	0.25	0.5	2	4	8	16
Correlated							
H^-	0.038	0.164	0.431	2.167	4.490	9.023	17.820
He	0.073	0.200	0.459	2.128	4.459	9.244	19.005
Li^+	0.088	0.216	0.472	2.088	4.322	8.885	18.178
Be^{2+}	0.097	0.224	0.478	2.067	4.245	8.678	17.677
B^{3+}	0.102	0.229	0.483	2.054	4.198	8.548	17.358
C^{4+}	0.106	0.232	0.485	2.045	4.166	8.459	17.140
N^{5+}	0.108	0.235	0.488	2.039	4.142	8.395	16.981
O^{6+}	0.110	0.237	0.489	2.034	4.125	8.346	16.861
F^{7+}	0.112	0.238	0.490	2.030	4.111	8.308	16.767
Ne^{8+}	0.113	0.239	0.491	2.027	4.100	8.278	16.691

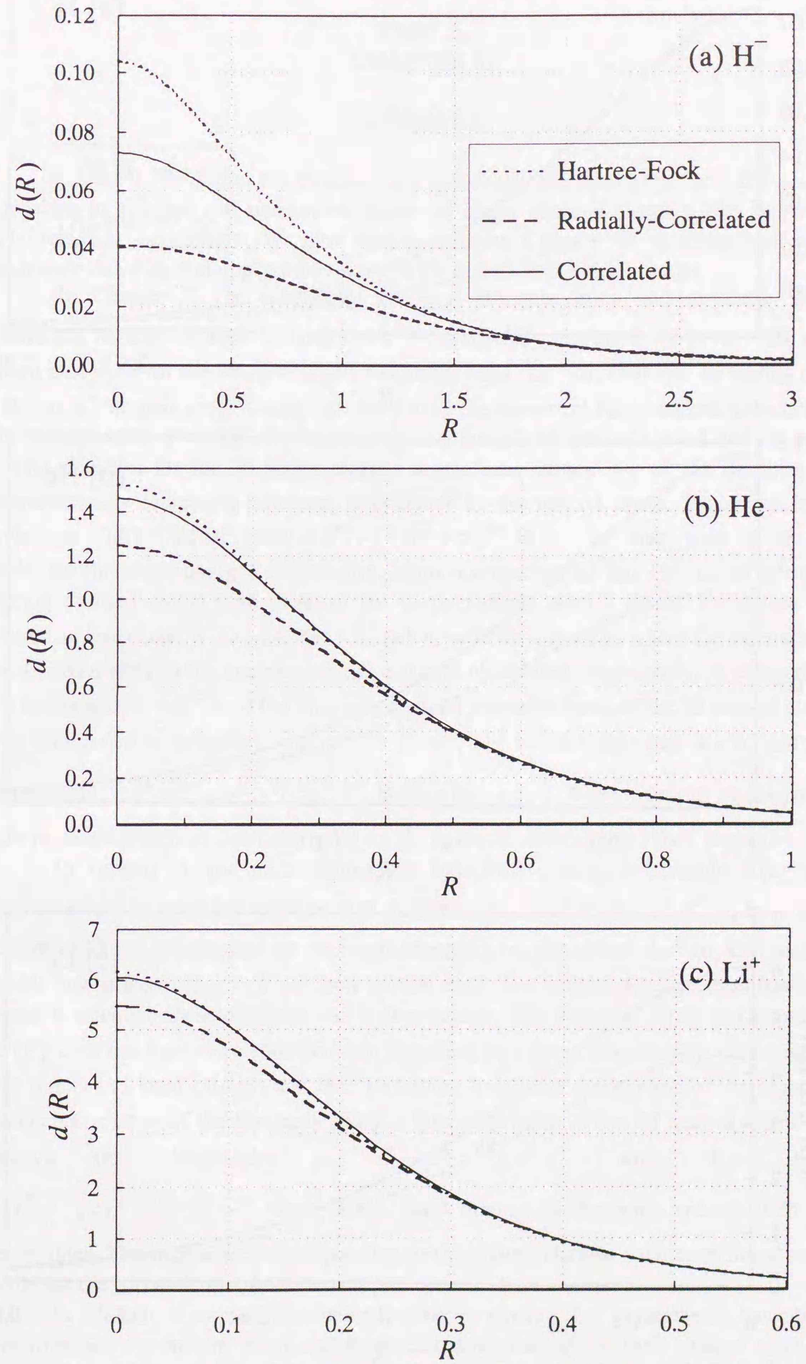


Fig. 1. Comparison of the Hartree-Fock, radially-correlated, and correlated extracule densities $d(R)$ for (a) H^-, (b) He, and (c) Li^+.

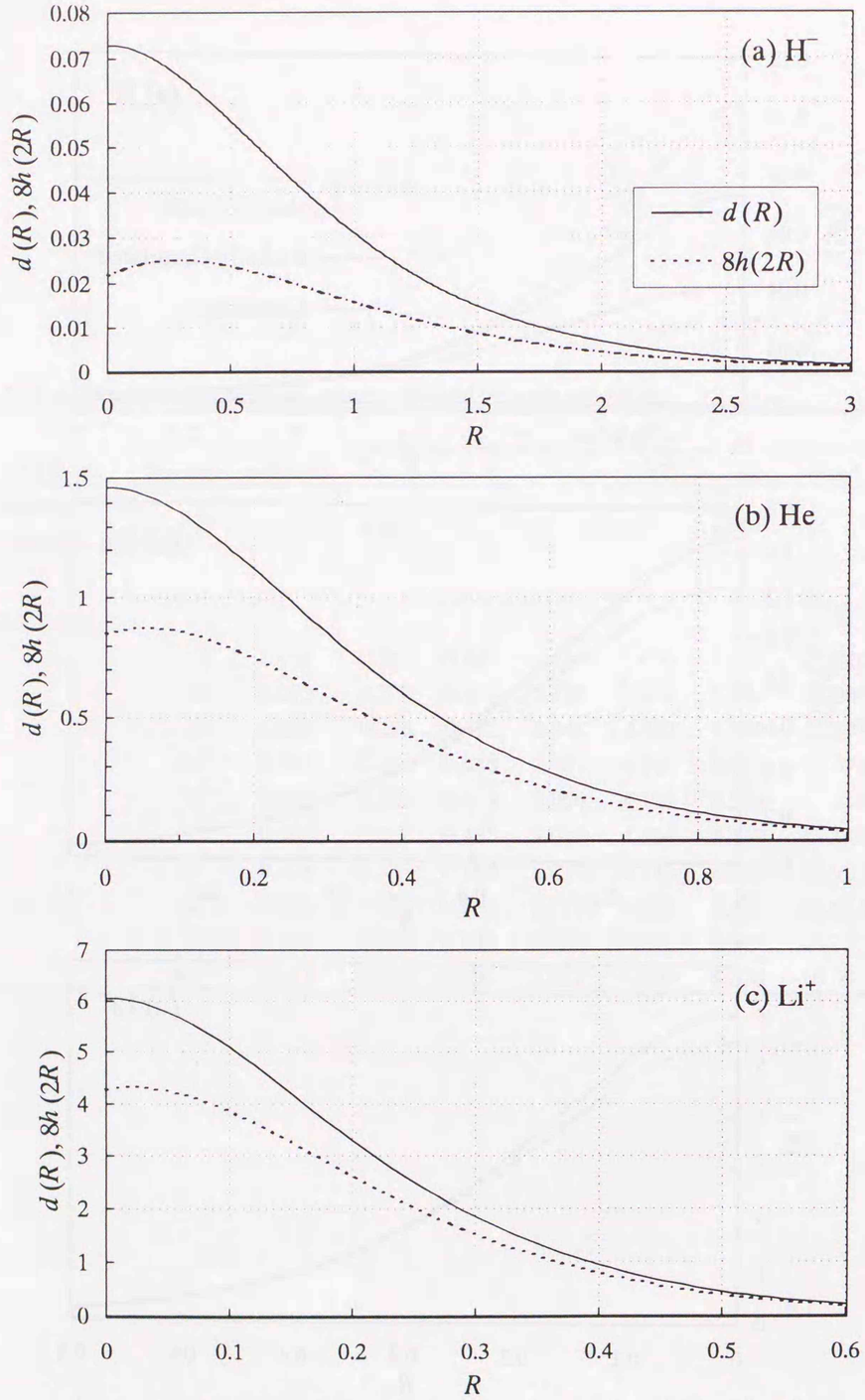


Fig. 2. Comparison of the correlated near-exact densities $d(R)$ and $8h(2R)$ for (a) H^-, (b) He, and (c) Li^+.

PART 3.
CHAPTER 5.

SUMMARY

In Part 3, the author has examined the spherically averaged intracule and extracule densities in position and momentum spaces of singly charged atoms within numerical Hartree-Fock calculations. We have also constructed a theory for obtaining near exact extracule densities and applied the theory to He and its isoelectronic series.

In Chapter 2, the spherically averaged intracule $h(u)$ and extracule $d(R)$ densities, as well as their moments $<u^k>$ and $<R^k>$ with $k=-2$ to $+2$, have been examined for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground state. We have used the numerical Hartree-Fock calculations to examine these quantities. Systematic examinations of the intracule $h(u)$ and extracule $d(R)$ densities for the 96 singly charged atoms have shown that all the densities are monotonically decreasing functions, as observed for the neutral atoms. The approximate relations $d(R) \cong 8h(2R)$ and $<u^k>/<R^k> \cong 2^k$ have been confirmed to be also valid for the singly charged cations and anions. Comparing the intracule densities of the singly charged atoms with those of the corresponding neutral atoms, the author has found an inequality $h^-(u) < h^0(u) < h^+(u)$ is valid for a small u, where the superscripts $-$, 0, and + refer to the anionic, neutral, and cationic species, respectively. A comparison of the moments $<u^k>$ of the 96 singly charged ions with those of the 53 neutral atoms has shown that an inequality $<u^k>^- \lessgtr <u^k>^0 \lessgtr <u^k>^+$ is valid when $k<0$, and that an equality $<u^k>^+ \lessgtr <u^k>^0 \lessgtr <u^k>^-$ holds when $k>0$. A few relations similar to the above inequalities have been also valid for the extracule densities and their moments.

In Chapter 3, the momentum-space spherically averaged intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities, together with their moments $<v^k>$ and $<P^k>$, have been constructed and investigated for the singly charged 53 cations from Li^+ to Cs^+ and 43 stable anions from H^- to I^- in their ground state. The Hartree-Fock method has been used to calculate these densities and their moments. The intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities have been classified into three and two types, respectively, according to the number of local extrema and their locations. A detailed comparison of the intracule moments $<v^k>$ of the 96 singly charged ions with those of the 53 neutral atoms has shown that inequalities $<v^k>^+ \lessgtr <v^k>^0 \lessgtr <v^k>^-$ when $k<0$ and $<v^k>^- \lessgtr <v^k>^0 \lessgtr <v^k>^+$ when $k>0$ hold among isoelectronic species with no exceptions. The inequalities corresponding to the above relations have been found to be valid for the extracule moments as well.

In Chapter 4, explicitly-correlated extracule density and its moments have been reported for the helium atom and its isoelectronic analogs in their ground state. A comparison of the Hartree-Fock density with correlated density has clarified that the

correlation contributes to shift the density from a small R to a large R region. A detailed comparison of the extracule moments of correlated densities with Hartree-Fock densities has found that for $k = -2$ and -1, the correlated moments are greater than the Hartree-Fock ones, and that for a positive k the reverse relations are valid.

GENERAL CONCLUSION

As shown in GENERAL INTRODUCTION, many researchers have devoted much time to various chemical and physical problems based on the electron-pair densities. Their studies have provided us with a new concept for examining electronic structures, and with profound understanding of the interactions between electrons in atoms and molecules. Most of the studies on electron-pair densities, however, are limited to the intracule density in position space for light atoms and small molecules. The several reasons for this are: We can directly compare computational position-space intracule density with experimental one. Since one of the expectation values obtained from the density is exactly equal to the electron-electron repulsion energy, the position-space intracule density is a convenient function to discuss electron correlations of atoms and molecules. The reason why studies on the electron-pair density in momentum space are less than those in position space may be that the momentum-space wave function must, in general, be constructed from the counterpart in position space. In the present thesis, we have developed a theory for constructing intracule and extracule densities, as well as their moments, for atoms and atomic ions in both position and momentum spaces when the wave function is expressed by a single Slater determinant, or a linear combination of Slater determinants. The author have applied the theory for the atoms and atomic ions with $2 \leq N \leq 54$, where N means the number of electrons, and systematically examined their densities and moments. We have also reported a theory of calculating near-exact extracule density in position space for the wave function explicitly containing an interelectronic distance r_{12} term. The theory has been applied to the He and its isoelectronic series.

In Part 1, we have defined the electron-electron coalescence and counterbalance densities of atoms in position and momentum spaces, and examined these densities and the average electron density within the Hartree-Fock framework. In Chapter 2, the electron-electron coalescence $I(\mathbf{0}) = h(0)$ and counterbalance $E(\mathbf{0}) = d(0)$ densities, as well as the average electron density $<\rho>$, have been derived for the atoms He through Ne in their experimental ground state. The numerical Hartree-Fock calculations have been used to examined these densities. We have found that inequalities $I(\mathbf{0}) \cong <\rho>/4$ and $E(\mathbf{0}) \cong 2<\rho>$ are good approximations within the Hartree-Fock framework, where the equality holds only for He, Be, and their isoelectronic species. These relations mean that the electron-electron coalescence and counterbalance densities can be estimated by the average electron density. In Chapter 3, we have reported that the electron-electron coalescence and counterbalance densities, as well as the average electron densities, in position and momentum spaces for the atoms He through Xe in their ground state. We have used the numerical Hartree-Fock calculations to compute these densities. In position space, the electron-electron coalescence $h(0)$ and counterbalance $d(0)$ densities, and the average electron density $<\rho>$ increase monotonically with increasing atomic number Z. We have found that a relation $h(0) \cong <\rho>/4$ is very accurate for all the atoms He through Xe. Decomposing the total coalescence density into its subshell-pair contributions, we have clarified that the coalescence density $h(0)$ is strongly influenced by electron pairs in inner subshells, particularly in the 1s subshell, for all the 53 atoms. On the other hand, the momentum-space electron-electron coalescence $\bar{h}(0)$ and counterbalance $\bar{d}(0)$ densities, and the

average electron density $<\gamma>$ have shown periodic behaviors as a function of Z. The relations $\bar{h}(0) \leq <\gamma>/4$ and $\bar{h}(0) \leq \bar{d}(0)/8$ hold in momentum space. An detailed analysis has shown that the coalescence density $\bar{h}(0)$ is governed by a few pairs of outermost subshells.

In Part 2, the author has aimed to develop a theory for the calculation of the intracule and extracule densities, as well as their intracule and extracule moments, in position and momentum spaces of atomic systems when the wave function is given by a Slater determinant or a linear combination of Slater determinants. The author has also systematically examined the electron-pair densities and their moments for the neutral atoms with $2 \leq N \leq 54$. In Chapter 2, we have presented a theory of constructing spherically averaged intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space of atomic systems for the wave function expressed by a Slater determinant. The theory has been applied to the atoms He through Xe in their ground state, and their electron-pair densities have been calculated based on the Hartree-Fock method. Systematic examinations on the behaviors of the electron-pair densities have found that the position-space intracule densities $h(u)$ are a unimodal function with a maximum at $u=0$ for all the 53 atoms. In momentum space, on the other hand, the intracule densities $\bar{h}(v)$ are found to be classified into three types: Eighteen atoms have a unimodal density with a maximum at $v=0$. Thirty-two atoms have a unimodal density with a local minimum at $v=0$ and a maximum at $v>0$. Only three atoms have a bimodal density with a primary maximum at $v=0$ and a secondary maximum at $v>0$. Decomposing the intracule density into its subshell-pair contributions has shown that the largest contributions to $h(u)$ come from the four innermost subshell pairs 1*s*1*s*, 1*s*2*p*, 2*p*2*p*, and 1*s*2*s*, and that the density $\bar{h}(v)$ is governed by a few outermost subshell pairs. In Chapter 3, we have reported two methods for accurate Hartree-Fock values of interelectronic moments $<u^k>$ in position space and $<v^k>$ in momentum space of atomic systems having a single Slater determinant wavefunction. First and second methods use, respectively, the spherically averaged intracule density and its characteristic function to calculate the moments. We have systematically examined the moments $<u^k>$ with $k=-2$ to $+4$ and $<v^k>$ with $k=-2$ to $+3$ for atoms from He to Xe in their ground state. An interelectronic moment $<u^k>$ with a positive k generally decreases with an increasing Z, but the behavior is quite irregular except for the second period atoms. A moment $<u^k>$ with a negative k generally increases with an increasing Z. On the other hand, a moment $<v^k>$ with a positive k increases monotonically as Z increases. A moment $<v^k>$ with a negative k generally decreases with increasing Z. In Chapter 4, the author has constructed a theory of calculating the spherically averaged extracule densities $d(R)$ in position space and $\bar{d}(P)$ in momentum space for atoms when the wave function is given by a Slater determinant. The theory has been used to examine these densities for the atoms from He to Xe in their ground state based on the numerical Hartree-Fock method. In position space, the extracule density $d(R)$ is a unimodal function with a maximum at $R=0$ for all the 53 atoms due to the predominant 1*s*1*s* subshell-pair contribution. In momentum space, on the other hand, the extracule densities $\bar{d}(P)$ have been found to be classified into two

types; forty-two atoms have a unimodal density with a maximum at $P=0$, and 11 atoms have a unimodal density with a local minimum at $P=0$ and a maximum at $P>0$. A decomposition of the $\bar{d}(P)$ density into the subshell pairs has clarified that the momentum-space extracule density is governed by a few outermost subshell pairs. In Chapter 5, two methods have been presented for the calculation of extracule moments $<R^k>$ in position space and $<P^k>$ in momentum space of atomic systems for a single-Slater-determinant wavefunction. The first method uses the spherically averaged extracule densities, while the second method uses their characteristic functions. The two methods have been applied to the neutral atoms from He to Xe in their ground state, and the moments $<R^k>$ with $k=-2$ to $+4$ and $<P^k>$ with $k=-2$ to $+3$ have been reported based on the numerical Hartree-Fock calculations. A comparison of the extracule moments $<R^k>$ with the corresponding intracule moments $<u^k>$ for $k=-2$ to $+4$ has shown that a relation $<u^k>/<R^k> \cong 2^k$ is a good approximation for all the 53 atoms. Similarly, an approximate relation $<v^k>/<P^k> \cong 2^k$ is valid for $k=-2$ to $+3$ in momentum space. In Chapter 6, the author has generalized a method for evaluating the four kinds of electron-pair densities to the case where an N-electron wavefunction is given by a linear combination of Slater determinants. As an illustrative application, the author has discussed the difference of the electron-pair motion in the ^1P and ^3P states of the helium atom. Compared to the moments $<u^k>$ of ^1P state, the ^3P moments $<u^k>$ are larger when $k<0$ and smaller when $k>0$. The similar trends have been observed for the extracule moments $<R^k>$ in position space and $<P^k>$ in momentum space. The momentum-space moments $<v^k>$ have resulted in the reverse trend.

In Part 3, the author has examined the spherically averaged intracule and extracule densities in both position and momentum spaces of singly charged atomic ions within numerical Hartree-Fock calculations. We have calculated the position-space spherically averaged extracule density of two-electron systems with the correlated wave function as well. In Chapter 2, the spherically averaged intracule $h(u)$ and extracule densities $d(R)$, as well as their moments $<u^k>$ and $<R^k>$ with $k=-2$ to $+2$, have been examined for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground state. The numerical Hartree-Fock calculations have been used to compute these properties. Systematic examinations of the intracule and extracule densities for the 96 singly charged ions have shown that all the densities are monotonically decreasing functions, as observed for the neutral atoms. The approximate relations $d(R) \cong 8h(2R)$ and $<u^k>/<R^k> \cong 2^k$ have been confirmed to be also valid for the singly charged cations and anions. Comparing the intracule densities of the singly charged atoms with those of the corresponding neutral atoms, we have found an inequality $h^-(u) < h^0(u) < h^+(u)$ is valid for a small u, where the superscripts –, 0, and + refer to the anionic, neutral, and cationic species, respectively. Comparing of the moments $<u^k>$ of the 96 singly charged ions with those of the 53 neutral atoms, we have found inequalities $<u^k>^- \langle <u^k>^0 \langle <u^k>^+$ when $k<0$ and

$< u^k >^+ \left\langle < u^k >^0 \right\langle < u^k >^-$ when $k > 0$ with no exceptions. A few relations similar to the above inequalities have been also valid for the extracule densities. In Chapter 3, the momentum-space spherically averaged intracule $\bar{h}(u)$ and extracule densities $\bar{d}(P)$, together with their moments $< u^k >$ and $< P^k >$, have been constructed and investigated for the singly charged 53 cations from Li^+ to Cs^+ and 43 stable anions from H^- to I^- in their ground state within the Hartree-Fock framework. The intracule $\bar{h}(u)$ and extracule $\bar{d}(P)$ densities have been classified into three and two types, respectively, according to the number of local extrema and their locations. A detailed comparison of the intracule moments $< u^k >$ of the 96 singly charged ions with those of the 53 neutral atoms has shown that inequalities $< u^k >^+ \left\langle < u^k >^0 \right\langle < u^k >^-$ when $k < 0$ and $< u^k >^- \left\langle < u^k >^0 \right\langle < u^k >^+$ when $k > 0$ hold among isoelectronic species with no exceptions. The inequalities corresponding to the above relations have found to be valid for the extracule moments. In Chapter 4, explicitly-correlated near-exact results of the extracule density and its moments have been reported for the helium atom and its isoelectronic analogs in their ground state. Comparing Hartree-Fock densities with the correlated densities has clarified that the correlation contributes to shift the density from a small R to a large R region. A comparison of the extracule moments of correlated densities with Hartree-Fock densities has found that for $k = -2$ and -1 the correlated moments are greater than the Hartree-Fock ones, and that for a positive k the reverse relations are valid.

