REGULAR ARTICLE

Direct and exchange contributions to inner and outer radii in many-electron atoms

Toshikatsu Koga · Hisashi Matsuyama

Abstract Within the Hartree-Fock framework, the spinless two-electron density function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ consists of direct $\Gamma_{\text{di}}(\mathbf{r}_1, \mathbf{r}_2)$ and exchange $\Gamma_{\text{ex}}(\mathbf{r}_1, \mathbf{r}_2)$ parts. Accordingly, the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii in many-electron systems are rigorously separated into the direct and exchange contributions, i.e., $\langle r_< \rangle = \langle r_< \rangle_{\text{di}} + \langle r_< \rangle_{\text{ex}}$ and $\langle r_> \rangle = \langle r_> \rangle_{\text{di}} + \langle r_> \rangle_{\text{ex}}$. It is generally shown that $\langle r_< \rangle_{\text{di}} + \langle r_> \rangle_{\text{di}} = 2\langle r \rangle$ and $\langle r_< \rangle_{\text{ex}} + \langle r_> \rangle_{\text{ex}} = 0$, where $\langle r \rangle$ is the usual average radius of an electron. Numerical examinations of the direct and exchange contributions for the 102 atoms from He to Lr in their ground states find that the electron exchange works to decrease $\langle r_< \rangle$ and increase $\langle r_> \rangle$. However, the exchange parts are very small and the direct parts essentially govern the inner and outer radii.

Keywords Direct and exchange contributions · Inner radius · Outer radius · Radial separation · Atoms

1 Introduction

In many-electron systems, the mean distance of an electron from the coordinate origin is given by the average electron radius,

$$\langle r \rangle = \frac{1}{N} \int_0^\infty \mathrm{d}r\, r\, D(r), \tag{1a}$$

where $D(r)$ is the one-electron radial density (see, e.g., Ref. [1]) normalized to N, the number of electrons. For an

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N-electron wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ with $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ being the combined position-spin coordinate of the electron i, $D(r)$ is explicitly given by

$$D(r) = N\, r^2 \int \mathrm{d}s\, \mathrm{d}\Omega\, \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2, \tag{1b}$$

where (r, Ω) is the polar coordinate of the vector $\mathbf{r}$. The average radius $\langle r \rangle$ is a traditional one-electron index of the electron motion used popularly in the electronic structure theory of atoms and molecules, but its information content is limited since $\langle r \rangle$ is derived by averaging the motions of all the N electrons.

Deeper insights into the electronic motion would be obtained if two or more electrons are explicitly treated without an averaging procedure. In fact, it has recently been shown [2] that when any two electrons are considered simultaneously, the average radius $\langle r \rangle$ splits into inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii to reduce the electron–electron repulsion. The latter radii are defined [2] by

$$\langle r_< \rangle = \frac{2}{N(N-1)} \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2\, r_< D_2(r_1, r_2), \tag{2a}$$

$$\langle r_> \rangle = \frac{2}{N(N-1)} \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2\, r_> D_2(r_1, r_2), \tag{2b}$$

where $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$, and $D_2(r_1, r_2)$ is the two-electron radial density (see, e.g., Ref. [3]),

$$D_2(r_1, r_2) = \frac{N(N-1)}{2} r_1^2 r_2^2 \int \mathrm{d}s_1 \mathrm{d}s_2 \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \mathrm{d}\mathbf{x}_3 \ldots \mathrm{d}\mathbf{x}_N$$
$$\times |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2, \tag{2c}$$

normalized to $N(N-1)/2$, the number of electron pairs. The three average radii $\langle r \rangle$, $\langle r_< \rangle$, and $\langle r_> \rangle$ are related [2] by

$$\langle r_< \rangle = \langle r \rangle - \tfrac{1}{2}\langle |r_1 - r_2| \rangle, \tag{3a}$$

$$\langle r_> \rangle = \langle r \rangle + \tfrac{1}{2}\langle |r_1 - r_2| \rangle, \tag{3b}$$

where

$$\langle |r_1 - r_2| \rangle = \frac{2}{N(N-1)} \int\limits_0^\infty dr_1 \int\limits_0^\infty dr_2 |r_1 - r_2| D_2(r_1, r_2) \tag{4}$$

is the magnitude of the radial separation. Equations (3a) and (b) also imply an interesting relation $2\langle r \rangle = \langle r_< \rangle + \langle r_> \rangle$, which connects the one- and two-electron properties.

The splitting of the average radius $\langle r \rangle$ into the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii was studied [2] for the 102 atoms He through Lr in their ground states. The effect of electron correlation was discussed [2] for the He atom and its isoelectronic ions. An examination of the splitting of the average subshell radius $\langle r \rangle_{nl}$ into the inner $\langle r_< \rangle_{nl}$ and outer $\langle r_> \rangle_{nl}$ radii was reported [4] in connection with the double-zeta description of atomic wave functions, where n and l are the principal and azimuthal quantum numbers. Relations of the inner and outer radii with the electron-pair relative distance $\langle r_{12} \rangle = \langle |\mathbf{r}_1 - \mathbf{r}_2| \rangle$ and center-of-mass radius $\langle R \rangle = \langle |\mathbf{r}_1 + \mathbf{r}_2|/2 \rangle$ were discussed in Ref. [5]. It has been also pointed out [6] that the inner and outer radii are useful tools to distinguish electrons with different natures, as is the case of singly-excited $1snl$ states of the He atom.

In the present paper, we study direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii to see how the quantum-mechanical exchange effect, which is implicit in the one-electron property $\langle r \rangle$, emerges in the two-electron properties $\langle r_< \rangle$ and $\langle r_> \rangle$. Since the Hartree-Fock two-electron density is the sum of direct and exchange parts, the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii are rigorously separated into the direct and exchange contributions, i.e., $\langle r_< \rangle = \langle r_< \rangle_{di} + \langle r_< \rangle_{ex}$ and $\langle r_> \rangle = \langle r_> \rangle_{di} + \langle r_> \rangle_{ex}$. General sum rules are shown that $\langle r_< \rangle_{di} + \langle r_> \rangle_{di} = 2\langle r \rangle$ and $\langle r_< \rangle_{ex} + \langle r_> \rangle_{ex} = 0$. Numerical results of the direct and exchange contributions are reported for the 102 atoms from He to Lr in their ground states. The exchange parts are found to decrease $\langle r_< \rangle$, increase $\langle r_> \rangle$, and enlarge $\langle |r_1 - r_2| \rangle$. Hartree atomic units are used throughout.

2 Direct and exchange densities in Hartree-Fock theory

For an N-electron system ($N \geq 2$), we consider a Hartree-Fock wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ composed of a set of N orthonormal spin–orbitals $\psi_i(\mathbf{r})\eta_i(s)$.

Then the spinless two-electron density function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is [7] the sum of direct $\Gamma_{di}(\mathbf{r}_1, \mathbf{r}_2)$ and exchange $\Gamma_{ex}(\mathbf{r}_1, \mathbf{r}_2)$

contributions,

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int ds_1 ds_2 d\mathbf{x}_3 \ldots d\mathbf{x}_N |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2$$
$$= \Gamma_{di}(\mathbf{r}_1, \mathbf{r}_2) + \Gamma_{ex}(\mathbf{r}_1, \mathbf{r}_2), \tag{5}$$

where

$$\Gamma_{di}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Gamma_{di}^{ij}(\mathbf{r}_1, \mathbf{r}_2), \tag{6a}$$

$$\Gamma_{di}^{ij}(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{2}[F_{ii}(\mathbf{r}_1)F_{jj}(\mathbf{r}_2) + F_{jj}(\mathbf{r}_1)F_{ii}(\mathbf{r}_2)], \tag{6b}$$

$$\Gamma_{ex}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Gamma_{ex}^{ij}(\mathbf{r}_1, \mathbf{r}_2), \tag{6c}$$

$$\Gamma_{ex}^{ij}(\mathbf{r}_1, \mathbf{r}_2)$$
$$= -\tfrac{1}{2}\delta_s(i, j)[F_{ij}(\mathbf{r}_1)F_{ji}(\mathbf{r}_2) + F_{ji}(\mathbf{r}_1)F_{ij}(\mathbf{r}_2)], \tag{6d}$$

in which $F_{ij}(\mathbf{r}) = \psi_i * (\mathbf{r})\psi_j(\mathbf{r})$ and $\delta_s(i, j) = \int ds \eta_i^*(s)\eta_j(s)$. We note that

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma(\mathbf{r}_1, \mathbf{r}_2)$$
$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma_{di}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2}, \tag{7a}$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \Gamma_{ex}(\mathbf{r}_1, \mathbf{r}_2) = 0. \tag{7b}$$

The partitioning of the two-electron density $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ into the direct and exchange parts suggests the corresponding partitioning of the one-electron density $\rho(\mathbf{r})$,

$$\rho(\mathbf{r}) = \frac{2}{N-1} \int d\mathbf{r}_2 \Gamma(\mathbf{r}, \mathbf{r}_2) = \rho_{di}(\mathbf{r}) + \rho_{ex}(\mathbf{r}), \tag{8a}$$

where

$$\rho_{di}(\mathbf{r}) = \frac{2}{N-1} \int d\mathbf{r}_2 \Gamma_{di}(\mathbf{r}, \mathbf{r}_2) = \sum_{i=1}^{N} F_{ii}(\mathbf{r}), \tag{8b}$$

but

$$\rho_{ex}(\mathbf{r}) = \frac{2}{N-1} \int d\mathbf{r}_2 \Gamma_{ex}(\mathbf{r}, \mathbf{r}_2) = 0. \tag{8c}$$

There is no exchange contribution to the one-electron density. Clearly,

$$\int d\mathbf{r} \rho(\mathbf{r}) = \int d\mathbf{r} \rho_{di}(\mathbf{r}) = N. \tag{9}$$

If we apply the polar coordinates (r_i, Ω_i) to the vector $\mathbf{r}_i$ and integrate $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ and its components over the angular variables Ω_1 and Ω_2, we find that the two-electron radial density function $D_2(r_1, r_2)$ also consists of the direct $D_{2,di}(r_1, r_2)$ and exchange $D_{2,ex}(r_1, r_2)$ parts,

$$D_2(r_1, r_2) = r_1^2 r_2^2 \int d\Omega_1 d\Omega_2 \Gamma(\mathbf{r}_1, \mathbf{r}_2)$$
$$= D_{2,di}(r_1, r_2) + D_{2,ex}(r_1, r_2), \tag{10}$$

where

$$\int_0^\infty dr_1 \int_0^\infty dr_2 D_2(r_1, r_2)$$

$$= \int_0^\infty dr_1 \int_0^\infty dr_2 D_{2,\mathrm{di}}(r_1, r_2) = \frac{N(N-1)}{2}, \tag{11a}$$

$$\int_0^\infty dr_1 \int_0^\infty dr_2 D_{2,\mathrm{ex}}(r_1, r_2) = 0. \tag{11b}$$

The spin–orbital-pair components $D_{2,\mathrm{di}}^{ij}(r_1, r_2)$ and $D_{2,\mathrm{ex}}^{ij}(r_1, r_2)$ of $D_{2,\mathrm{di}}(r_1, r_2)$ and $D_{2,\mathrm{ex}}(r_1, r_2)$ are defined by integrating Eqs. (6b) and (d), respectively, over Ω_1 and Ω_2. Analogously, the one-electron radial density $D(r)$ is given by

$$D(r) = r^2 \int d\Omega \rho(\mathbf{r}) = D_{\mathrm{di}}(r). \tag{12}$$

For atomic systems, we can generally assume that the spatial function $\psi_i(\mathbf{r})$ is the product of a radial function $R_i(r) = R_{n_i l_i}(r)$ and a spherical harmonic function $Y_i(\Omega) = Y_{l_i m_i}(\Omega)$. In such cases, the spin–orbital-pair components $D_{2,\mathrm{di}}^{ij}(r_1, r_2)$ and $D_{2,\mathrm{ex}}^{ij}(r_1, r_2)$ are expressed as

$$D_{2,\mathrm{di}}^{ij}(r_1, r_2) = \tfrac{1}{2} r_1^2 r_2^2 [G_{ii}(r_1) G_{jj}(r_2) + G_{jj}(r_1) G_{ii}(r_2)], \tag{13a}$$

$$D_{2,\mathrm{ex}}^{ij}(r_1, r_2) = -\tfrac{1}{2} \delta_s(i, j) [c^0(i, j)]^2 r_1^2 r_2^2 [G_{ij}(r_1) G_{ji}(r_2) + G_{ji}(r_1) G_{ij}(r_2)], \tag{13b}$$

where $G_{ij}(r) = R_i^*(r) R_j(r)$ and

$$c^k(i, j) = c^k(l_i m_i; l_j m_j)$$
$$= \sqrt{\frac{4\pi}{2k+1}} \int d\Omega Y_{l_i m_i}^*(\Omega) Y_{k, m_i - m_j}(\Omega) Y_{l_j m_j}(\Omega) \tag{14}$$

is the Condon–Shortley parameter [8]. The radial density $D(r)$ is given by

$$D(r) = r^2 \sum_{i=1}^N G_{ii}(r) = D_{\mathrm{di}}(r). \tag{15}$$

3 Direct and exchange contributions to average radii

Once the two-electron radial density $D_2(r_1, r_2)$ is separated into the direct and exchange parts, the expectation value of any two-electron radial property $f(r_1, r_2)$ is decomposed into the corresponding two contributions. For a single pair of electrons, the expectation value $\langle f(r_1, r_2) \rangle$ and its direct

and exchange components are given by

$$\langle f(r_1, r_2) \rangle = \frac{2}{N(N-1)} \int_0^\infty dr_1 \int_0^\infty dr_2 f(r_1, r_2) D_2(r_1, r_2)$$
$$= \langle f(r_1, r_2) \rangle_{\mathrm{di}} + \langle f(r_1, r_2) \rangle_{\mathrm{ex}}, \tag{16a}$$

$$\langle f(r_1, r_2) \rangle_{\mathrm{di}} = \frac{2}{N(N-1)} \int_0^\infty dr_1 \int_0^\infty dr_2 f(r_1, r_2) D_{2,\mathrm{di}}(r_1, r_2), \tag{16b}$$

$$\langle f(r_1, r_2) \rangle_{\mathrm{ex}} = \frac{2}{N(N-1)} \int_0^\infty dr_1 \int_0^\infty dr_2 f(r_1, r_2) D_{2,\mathrm{ex}}(r_1, r_2). \tag{16c}$$

The expectation value of a one-electron radial property $g(r)$ is obtained by

$$\langle g(r) \rangle = \frac{1}{N} \int_0^\infty dr g(r) D(r) = \langle g(r) \rangle_{\mathrm{di}}, \quad \langle g(r) \rangle_{\mathrm{ex}} = 0. \tag{17}$$

Now, the direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii are obtained from Eq. (16) as

$$\langle r_< \rangle = \langle r_< \rangle_{\mathrm{di}} + \langle r_< \rangle_{\mathrm{ex}}, \tag{18a}$$

$$\langle r_< \rangle_{\mathrm{di}} = \langle r \rangle - \tfrac{1}{2} \langle |r_1 - r_2| \rangle_{\mathrm{di}}, \tag{18b}$$

$$\langle r_< \rangle_{\mathrm{ex}} = -\tfrac{1}{2} \langle |r_1 - r_2| \rangle_{\mathrm{ex}}, \tag{18c}$$

and

$$\langle r_> \rangle = \langle r_> \rangle_{\mathrm{di}} + \langle r_> \rangle_{\mathrm{ex}}, \tag{19a}$$

$$\langle r_> \rangle_{\mathrm{di}} = \langle r \rangle + \tfrac{1}{2} \langle |r_1 - r_2| \rangle_{\mathrm{di}}, \tag{19b}$$

$$\langle r_> \rangle_{\mathrm{ex}} = +\tfrac{1}{2} \langle |r_1 - r_2| \rangle_{\mathrm{ex}}, \tag{19c}$$

where we have used Eq. (13) and the fact that $\langle r \rangle_{\mathrm{di}} = \langle r \rangle$ and $\langle r \rangle_{\mathrm{ex}} = 0$ from Eq. (17). Since Eq. (11b) means that the function $D_{2,\mathrm{ex}}(r_1, r_2)$ takes both negative and positive values, we cannot judge whether $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ is positive or negative. However, we can claim without numerical examinations that the exchange contributions to the inner and outer radii are opposite. From Eqs. (18) and (19), it also follows that

$$\langle r_< \rangle_{\mathrm{di}} + \langle r_> \rangle_{\mathrm{di}} = 2\langle r \rangle, \tag{20a}$$

$$\langle r_< \rangle_{\mathrm{ex}} + \langle r_> \rangle_{\mathrm{ex}} = 0. \tag{20b}$$

The exchange contributions cancel each other out, and the sum of the direct contributions is precisely twice the average radius $\langle r \rangle$.

Table 1 The direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii exemplified for the six group-18 atoms

	He	Ne	Ar	Kr	Xe	Rn
$\langle r_< \rangle$						
Direct	0.622000	0.476586	0.452230	0.353180	0.333632	0.280325
Exchange	0	−0.000185	−0.000566	−0.000245	−0.000277	−0.000164
Sum	0.622000	0.476401	0.451664	0.352935	0.333355	0.280161
$\langle r_> \rangle$						
Direct	1.232547	1.101640	1.333420	1.104557	1.113065	0.967396
Exchange	0	0.000185	0.000566	0.000245	0.000277	0.000164
Sum	1.232547	1.101825	1.333986	1.104802	1.113342	0.967560

4 Numerical results and discussion for ground-state atoms

Using a modified version of the MCHF72 program [9], we have first performed numerical Hartree-Fock calculations and generated radial functions $R_i(r)$ for the 102 atoms He through Lr in their ground states [10]. For each atom, the direct $D_{2,\mathrm{di}}^{ij}(r_1, r_2)$ and exchange $D_{2,\mathrm{ex}}^{ij}(r_1, r_2)$ terms of a spin–orbital-pair component have been constructed by Eqs. (13a) and (13b). Gathering the direct and exchange contributions separately from all spin–orbital pairs, we have obtained the direct $D_{2,\mathrm{di}}(r_1, r_2)$ and exchange $D_{2,\mathrm{ex}}(r_1, r_2)$ parts of the two-electron radial density $D_2(r_1, r_2)$. Finally, the direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii have been calculated by Eqs. (16)–(19). The total values of $\langle r_< \rangle$ and $\langle r_> \rangle$ have been verified by comparison with the literature values [2]. The validity of the sum rules, Eqs. (20a) and (b), has also been confirmed numerically for all the 102 atoms.

Table 1 exemplifies the direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii for the six group-18 atoms, among which there is no exchange contribution in the He atom. The direct parts $\langle r_< \rangle_{\mathrm{di}}$ and $\langle r_> \rangle_{\mathrm{di}}$ are always positive. The exchange part $\langle r_< \rangle_{\mathrm{ex}}$ of the inner radius $\langle r_< \rangle$ is found to be negative and works to decrease the inner radius. The same is true for all the remaining atoms. However, the magnitude of $\langle r_< \rangle_{\mathrm{ex}}$ is very small and is at most 0.54% of $\langle r_< \rangle$. On the other hand, the exchange part $\langle r_> \rangle_{\mathrm{ex}}$ of the outer radius $\langle r_> \rangle$ is positive and works to increase the outer radius for all the atoms except He. The contribution $\langle r_> \rangle_{\mathrm{ex}}$ is also small and is at most 0.10% of $\langle r_> \rangle$. Consequently, the direct parts $\langle r_< \rangle_{\mathrm{di}}$ and $\langle r_> \rangle_{\mathrm{di}}$ essentially determine the inner and outer radii.

Because of the relations (18c) and (19c), the above numerical results imply that for the ground-state atoms, the exchange part $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ of the radial separation $\langle |r_1 - r_2| \rangle$ is non-negative, though it is small compared to $\langle |r_1 - r_2| \rangle_{\mathrm{di}}$. Thus, the non-classical electron exchange works to increase the radial separation $\langle |r_1 - r_2| \rangle = \langle r_> \rangle - \langle r_< \rangle$ or to pull two

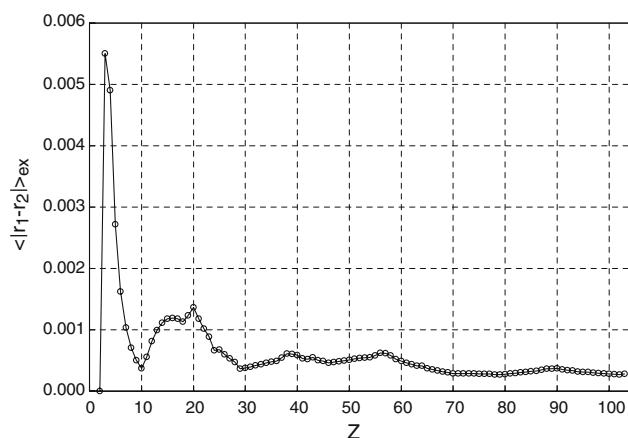**Fig. 1** The exchange contribution $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ to the radial separation $\langle |r_1 - r_2| \rangle$ as a function of Z

electrons apart radially. The result does not contradict the fact that the electron exchange reduces the electron–electron repulsion energy. Figure 1 plots $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ as a function of atomic number Z. The exchange contribution is maximal at the Li atom and has a tendency to decrease as Z increases, with a few local maxima at group-2 atoms.

In terms of a component $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}$ from a pair of spin–orbitals i and j with a non-zero exchange contribution, $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ is written as $N_{\mathrm{pair}}^{-1} \sum_{i<j} \langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}$, where $N_{\mathrm{pair}} = N(N-1)/2$ is the total number of spin–orbital pairs. If we introduce an average $[\langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}]^{\mathrm{av}}$ of non-zero $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}$ contributions, we obtain $\langle |r_1 - r_2| \rangle_{\mathrm{ex}} = (N_{\mathrm{ex}}/N_{\mathrm{pair}})[\langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}]^{\mathrm{av}}$, where N_{ex} is the number of spin–orbital pairs with non-zero exchange contributions. The average value $[\langle |r_1 - r_2| \rangle_{\mathrm{ex}}^{ij}]^{\mathrm{av}}$ varies from one atom to another. Nevertheless, we have examined a possible correlation of $\langle |r_1 - r_2| \rangle_{\mathrm{ex}}$ with the ratio $N_{\mathrm{ex}}/N_{\mathrm{pair}}$ for the 101 atoms Li through Lr. The result is depicted in Fig. 2. We find there is an approximate linear correlation between the two quantities. A regression analysis gives

$$\langle |r_1 - r_2| \rangle_{\mathrm{ex}} \cong 0.015699(N_{\mathrm{ex}}/N_{\mathrm{pair}}) - 0.000214, \quad (21)$$

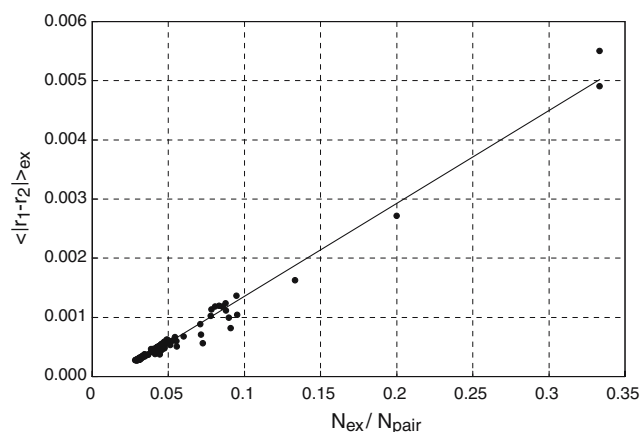**Fig. 2** The correlation between $\langle |r_1 - r_2| \rangle_{ex}$ and N_{ex}/N_{pair} for the 101 atoms Li through Lr

with the correlation coefficient 0.991. Therefore, $[\langle |r_1 - r_2| \rangle_{ex}^{ij}]^{av}$ is commonly approximated by 0.016 bohr, independent of Z, from which we can roughly estimate the exchange contributions to the inner and outer radii of the ground-state atoms.

5 Summary

The direct and exchange contributions to the inner $\langle r_< \rangle$ and outer $\langle r_> \rangle$ radii, as well as to the radial separation $\langle |r_1 - r_2| \rangle$, have been studied for many-electron systems. Numerical examinations of the 102 atoms from He to Lr in their ground states have shown that the exchange effects decrease $\langle r_< \rangle$, increase $\langle r_> \rangle$, and enlarge $\langle |r_1 - r_2| \rangle$. However, the exchange parts are very small and the direct parts essentially govern the inner and outer radii. The present numerical results have been obtained within the non-relativistic framework. Even when the relativistic effect is incorporated, we expect the observed trends remain unaltered though all the average radii would reduce slightly due to the so-called relativistic contraction of orbitals.

References

1. Bransden BH, Joachain CJ (1983) Physics of atoms and molecules. Longman, London, p 336
2. Koga T (2004) J Chem Phys 121:3939
3. Banyard KE, Baker CC (1969) J Chem Phys 51:2680
4. Koga T, Matsuyama H (2004) J Chem Phys 121:7708
5. Koga T, Matsuyama H (2005) J Chem Phys 122:024113
6. Matsuyama H, Koga T Theor Chem Acc (in press)
7. Koga T, Kawata Y (2002) J Chem Phys 117:9133
8. Condon EU, Shortley GH (1970) The theory of atomic spectra. Cambridge University Press, London, p 175
9. Froese Fischer C (1972) Comput Phys Commun 4:107
10. Avery J (2003) In: Wilson S (ed) Handbook of molecular physics and quantum chemistry, vol 1. Wiley, Chichester, pp 236–249