Theor Chem Acc (2004) 112: 435–441
DOI 10.1007/s00214-004-0600-5

Theoretical
Chemistry Accounts

Regular article

Subshell-pair interelectronic angles of atoms in momentum space

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Received: 19 February 2004 / Accepted: 6 April 2004 / Published online: 28 July 2004

Abstract. Average angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ between linear momenta of an electron in a subshell nl and another electron in a subshell $n'l'$ are examined for the 102 atoms He through Lr in their ground states, where n and l are the principal and azimuthal quantum numbers, respectively. Congruency in the mathematical structures of the average interelectronic angles in position and momentum spaces leads to the theoretical results that $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with even $|l-l'|$ are exactly equal to 90°, while $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with odd $|l-l'|$ are always larger than 90°. Numerical analyses of 3,275 subshell-pair angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with odd $|l-l'|$ in the 102 atoms clarify that deviations of the total average interelectronic angles from 90° are mainly governed by subshell pairs with $|n-n'| \leq 1$ and $|l-l'| = 1$, in contrast to the position-space results where only subshell pairs with $n = n'$ and $|l-l'| = 1$ are important.

Keywords: Interelectronic angles – Subshell pairs – Momentum space – Atoms

Introduction

For the elucidation of electron–electron interactions in atomic systems, we have so far examined [1, 2, 3, 4, 5, 6, 7, 8] electron-pair relative-motion and center-of-mass-motion densities along with their moments in position and momentum spaces. We found that the electron-pair densities in position space are unimodal functions due to the predominant $1s1s$ subshell-pair contribution, whereas the electron-pair densities in momentum space are classified into two or three types based on their modalities, which originate from a few outermost subshell pairs. Thus, the position-space densities mainly reflect the motion of innermost $1s$ electrons, while the momentum-space densities provide us with the information about valence electrons. It is important to study the electron-pair properties in both spaces to analyze the interaction of inner and outer electron pairs. However, all of these studies focused on *distances* to characterize the interelectronic interaction in many-electron systems.

Recently, we have started a systematic examination of interelectronic *angles* in position and momentum spaces to clarify another aspect of the electron–electron interaction. Interelectronic angle densities $A(\theta_{12})$ and average angles $\langle\theta_{12}\rangle$ in position space have been studied [9] for the 102 atoms He through Lr in their ground states, where θ_{12} stands for the angle between position vectors of electrons 1 and 2 measured from the nucleus. Numerical examinations of the average interelectronic angles $\langle\theta_{12}\rangle$ for the 102 atoms clarified that $\langle\theta_{12}\rangle$ of all the atoms except for He, Li, and Be are larger than 90° with the maximum value 93.17° at the N atom. A decomposition of the average angle $\langle\theta_{12}\rangle$ into the subshell-pair contributions $\langle\theta_{12}\rangle_{nl,n'l'}$ from two electrons in subshells nl and $n'l'$ was also carried out [10], where n and l are the principal and azimuthal quantum numbers, respectively. The results showed [10] that: (i) $\langle\theta_{12}\rangle_{nl,n'l'}$ is exactly equal to 90° if $|l-l'|$ is even, while it is larger than 90° if $|l-l'|$ is odd; (ii) $\langle\theta_{12}\rangle_{nl,n'l'}$ remain almost unchanged when atomic number Z increases; (iii) deviations of $\langle\theta_{12}\rangle$ from 90° are mostly determined by *sp*, *pd*, and *df* subshell-pair contributions in the same shell.

In momentum space, the average angles $\langle\bar{\theta}_{12}\rangle$ and average cosines $\langle\cos\bar{\theta}_{12}\rangle$ of He, Li, and Be atoms as well as some of their isoelectronic ions have been calculated [11, 12, 13, 14, 15, 16, 17, 18] in ad hoc manners, where the symbol $\bar{\theta}_{12}$ denotes the angle between linear momenta of electrons 1 and 2. Mathematical structures of $\langle\bar{\theta}_{12}\rangle$ and $\langle\cos\bar{\theta}_{12}\rangle$ have been recently clarified [19, 20] and their Hartree–Fock values were examined for the 102 atoms He through Lr in their ground states. When Z increases, the angle $\langle\bar{\theta}_{12}\rangle$ first increases, takes the max-

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imum value (92.87°) at the O atom, and then decreases monotonically from the F atom to the Lr atom.

In the present short paper, we decompose the total average interelectronic angles $\langle\bar{\theta}_{12}\rangle$ into subshell-pair angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ between linear momenta of an electron in a subshell nl and another electron in a subshell $n'l'$. We then discuss the dependence of $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ on the quantum numbers n and l and on atomic number Z. The predominant subshell pairs are also clarified, which govern the interelectronic angle $\langle\bar{\theta}_{12}\rangle$ in momentum space. The next section outlines theoretical structures of $\langle\bar{\theta}_{12}\rangle$ and $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ within the Hartree–Fock framework. In the section Numerical results and discussion, numerical analyses are carried out for $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of the 102 atoms He through Lr in their ground states. We will find that deviations of $\langle\bar{\theta}_{12}\rangle$ from 90° are mainly determined by subshell-pair contributions with $|n–n'| \leq 1$ and $|l–l'| = 1$.

Subshell-pair interelectronic angles in momentum space

The theoretical structure of the interelectronic angle $\langle\bar{\theta}_{12}\rangle$ in momentum space is analogous [20] to that of $\langle\theta_{12}\rangle$ in position space. Therefore, we present only an essence of the theory of the average interelectronic angles in momentum space. In this section, angles are given in radians.

We assume that a momentum-space wave function of an N-electron ($N \geq 2$) atom consists of N orthonormal spin-orbitals $\phi_a(\mathbf{p})\eta_a(s)$ and that a spatial function $\phi_a(\mathbf{p})$ is the product of a radial $P_a(p) = P_{n_a l_a}(p)$ and a spherical harmonic $Y_{l_a m_a}(\bar{\theta}, \bar{\phi})$ functions, where m_a is the magnetic quantum number and $(p, \bar{\theta}, \bar{\phi})$ is the polar coordinates of the electron linear momentum $\mathbf{p}$. In terms of the spin-orbital-pair contributions $\langle\bar{\theta}_{12}\rangle_{ab}$, the total average interelectronic angle $\langle\bar{\theta}_{12}\rangle$ is given [10, 20] by

$$\langle\bar{\theta}_{12}\rangle = \frac{2}{N(N-1)} \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} \langle\bar{\theta}_{12}\rangle_{ab} \tag{1a}$$

$$\langle\bar{\theta}_{12}\rangle_{ab} = \frac{\pi}{2} - \delta_{m_{sa} m_{sb}} \left|\bar{S}(a,b)\right|^2 \sum_{k=|l_a-l_b|}^{l_a+l_b} \frac{2k+1}{2} b^k(l_a m_a, l_b m_b) I_k \tag{1b}$$

$$\bar{S}(a,b) = \int_0^\infty \mathrm{d}p\, p^2 P_a^*(p) P_b(p) = \bar{S}^*(b,a) \tag{1c}$$

where m_{sa} is the spin quantum number of the spin function $\eta_a(s)$, δ_{ab} is the Kronecker delta, b^k $(lm,l'm')$is the Condon–Shortley parameter [21, 22], and the summation index k runs over every other integers between the specified values. The I_k values are given [10] by

$$I_{2j} = \pi\delta_{j0} \tag{2a}$$

$$I_{2j+1} = -\pi\left[\frac{(2j-1)!!}{(2j+2)!!}\right]^2 \tag{2b}$$

for non-negative integers j. Note that all I_k with even k (≥ 2) vanish. The second term on the right-hand side of Eq. (1b) means the deviation of $\langle\bar{\theta}_{12}\rangle_{ab}$ from $\pi/2$. If $m_{sa} \neq m_{ab}$, $|l_a–l_b| =$ even, or $b^k = 0$, the second term vanishes. We, therefore, have

$$\langle\bar{\theta}_{12}\rangle_{ab} = \frac{\pi}{2} \tag{3a}$$

If $m_{sa} = m_{ab}$ and $|l_a–l_b| =$ odd, we obtain

$$\langle\bar{\theta}_{12}\rangle_{ab} > \frac{\pi}{2} \tag{3b}$$

since $b^k(lm,l'm')$ is positive and I_k ($k > 0$) is negative.

The subshell-pair interelectronic angle $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ is given by

$$\begin{aligned}\langle\bar{\theta}_{12}\rangle_{nl,n'l'} &= \tfrac{1}{N_{nl,n'l'}} \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} \delta_{nn_a}\delta_{ll_a}\delta_{n'n_b}\delta_{l'l_b}\langle\bar{\theta}_{12}\rangle_{ab} \\ &= \tfrac{\pi}{2} + C_{ll'}\left|\bar{S}(nl,n'l')\right|^2\end{aligned} \tag{4}$$

where $N_{nl,n'l'}$, is the number of electron pairs for the electrons in two subshells nl and $n'l'$, $C_{ll'}$ is a constant which depends only on l and l', and $\bar{S}(nl,n'l')$ is the overlap integral between radial functions $P_{nl}(p)$ and $P_{n'l'}(p)$ of subshells nl and $n'l'$. Since C'_{ll} and $|\bar{S}(nl,n'l')|^2$ are equal to or greater than zero, the angle $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ is equal to or larger than $\pi/2$. Note that for subshell pairs which have the same combination of l and l', the deviation of $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ from $\pi/2$ is proportional to $|\bar{S}(nl,n'l')|^2$. When we consider the 102 atoms He through Lr in their experimental ground states, no subshells with g or higher azimuthal quantum numbers appear. Thus, the interelectronic angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of *ss*, *sd*, *pp*, *pf*, *dd*, *ff* subshell pairs with even $|l–l'|$ are equal to $\pi/2$ precisely, whereas those of *sp*, *sf*, *pd*, *df* subshell pairs with odd $|l–l'|$ are larger than $\pi/2$. In the former case, the linear momentum vectors $\mathbf{p}_a$ and $\mathbf{p}_b$ of two electrons are perpendicular on average, and in the latter case, the linear momenta have more probability to be on opposite sides of the origin in momentum space than on the same side. The physical picture of the subshell-pair angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with even and odd $|l–l'|$ is analogous to that of the counterpart angles $\langle\theta_{12}\rangle_{nl,n'l'}$ in position space [10].

Numerical results and discussion

The experimental ground electronic configurations and *LS* terms [23] were considered for all the 102 atoms He through Lr. For these states, the radial functions $R_a(r)$ in position space were first generated by the numerical Hartree–Fock method based on a modified version of the MCHF72 program [24]. The radial functions $P_a(p)$ in momentum space were then obtained by the Hankel transformation of $R_a(r)$,

$$P_a(p) = (-\mathrm{i})^{l_a}(2/\pi)^{1/2}\int_0^{\infty} \mathrm{d}r\, r^2 j_{l_a}(pr)R_a(r) \tag{5}$$

using the algorithm of Talman [25], where $j_l(x)$ is the spherical Bessel function of the first kind. The $b^k(lm,l'm')$ values were taken from Refs. [21, 22]. The angles $\langle\bar{\theta}_{12}\rangle_{ab}$ were calculated from Eqs. (1b) and (4). In the present section, angles are given in degrees.

We take the Rn atom ($Z=86$) to exemplify the difference between subshell-pair interelectronic angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$. The Rn atom has six *s*, five *p*, three *d*, and one *f* subshells in the ground state. Thus, there is a total of 120 subshell pairs arising from these 15 subshells. The angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of the 66 subshell pairs with even $|l-l'|$ are precisely equal to 90°. On the other hand, those of the other 54 subshell pairs with odd $|l-l'|$ are larger than 90°, which are listed in Table 1. For convenience, we separate the 54 subshell pairs in Table 1 into four groups according to the combination of l and l', that is, 30 *sp*, 15 *pd*, six *sf*, and three *df* subshell pairs. The $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ values of *nsnp* ($n=2$–6), *ns*($n+1$)*p* ($n=1$–5), 5*s*4*p*, *npnd* ($n=3$–5), *np*($n+1$)*d* ($n=2$–4), 4*d*4*f*, and 3*d*4*f* subshell pairs are larger than 91°. This means that for the Rn atom the deviation of the total average interelectronic angle from 90° is mainly governed by the subshell pairs with $|n-n'| \le 1$ and $|l-l'|=1$, in contrast with the cases in position space, where the subshell pairs with $|l-l'|=1$ in the same shell are significant [10]. The constants $C_{ll'}$ (in degrees) for *sp*, *pd*, *sf*, and *df* subshell pairs of the Rn atom are $C_{sp}=45/4=11.25$, $C_{pd}=315/64\cong 4.922$, $C_{sf}=45/64\cong 0.7031$, and $C_{df}=405/128\cong 3.164$, respectively. We confirmed that in the subshell pairs with the same combination of l and l', the deviation of $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ from 90° is directly proportional to the modulus squared of the overlap integral $\bar{S}(nl,n'l')$.

The difference between the subshell-pair angles in position and momentum spaces for an atom is defined by

$$\begin{aligned}\Delta_{nl,n'l'} &= \langle\bar{\theta}_{12}\rangle_{nl,n'l'} - \langle\theta_{12}\rangle_{nl,n'l'} \\ &= C_{ll'}[|\bar{S}(nl,n'l)|^2 - |S(nl,n'l')|^2]\end{aligned} \tag{6}$$

where the symbol $S(nl, n'l')$ denotes the overlap integral between radial functions for subshells nl and $n'l'$ in position space. Equation (6) indicates that the difference $\Delta_{nl,n'l'}$ is determined only by the difference between the moduli squared of the radial overlap integrals in position and momentum spaces, since the value of the coefficient $C_{ll'}$ is common in both spaces. Table 1 also includes the differences $\Delta_{nl,n'l'}$ of the Rn atom. The differences $\Delta_{nl,n'l'}$ of subshell pairs with $n=n'$ and $|n-n'|=1$ are generally of found to be negative and positive, respectively. For *nsnp* ($n=2$–6) and *ns*($n+1$)*p* ($n=1$–5) subshell pairs, the mag-

Table 1. The average inter electronic angles $<\bar{\theta}_{12}>_{nl,n'l'}$ in momentum space and their differences $\Delta_{nl,n'l'}$ from the position-space values for 54 subshell pairs with odd $|l-l'|$ of the Rn atom

Subshell pair	$\lvert n-n'\rvert$	$<\bar{\theta}_{12}>_{nl,n'l'}$	$\Delta_{nl,n'l'}$	Subshell pair	$\lvert n-n'\rvert$	$<\bar{\theta}_{12}>_{nl,n'l'}$	$\Delta_{nl,n'l'}$
sp				*pd*			
2*s*2*p*	0	92.090	−6.645	3*p*3*d*	0	91.129	−2.134
3*s*3*p*		92.222	−8.222	4*p*4*d*		92.064	−2.392
4*s*4*p*		92.753	−8.266	5*p*5*d*		93.470	−1.110
5*s*5*p*		93.957	−7.145	2*p*3*d*	1	93.480	1.844
6*s*6*p*		96.539	−4.016	3*p*4*d*		92.226	2.042
1*s*2*p*	1	97.539	5.175	4*p*3*d*		90.137	0.134
2*s*3*p*		96.739	6.433	4*p*5*d*		91.093	1.093
3*s*2*p*		90.659	0.631	5*p*4*d*		90.177	0.168
3*s*4*p*		96.043	6.006	6*p*5*d*		90.073	−0.077
4*s*3*p*		90.967	0.962	2*p*4*d*	2	90.192	−0.070
4*s*5*p*		94.911	4.910	3*p*5*d*		90.079	0.052
5*s*4*p*		91.045	1.041	5*p*3*d*		90.013	0.012
5*s*6*p*		93.134	3.103	6*p*4*d*		90.009	0.009
6*s*5*p*		90.865	0.813	2*p*5*d*	3	90.033	−0.004
1*s*3*p*	2	90.264	−0.160	6*p*3*d*		90.001	0.001
2*s*4*p*		90.049	−0.017				
4*s*2*p*		90.069	0.063	*sf*			
3*s*5*p*		90.007	−0.001	4*s*4*f*	0	90.030	−0.393
5*s*3*p*		90.067	0.066	3*s*4*f*	1	90.155	−0.093
4*s*6*p*		90.000	0.000	5*s*4*f*		90.001	−0.018
6*s*4*p*		90.045	0.045	2*s*4*f*	2	90.472	0.461
1*s*4*p*	3	90.140	0.040	6*s*4*f*		90.000	0.000
2*s*5*p*		90.109	0.096	1*s*4*f*	3	90.044	0.044
5*s*2*p*		90.016	0.015				
3*s*6*p*		90.054	0.053	*df*			
6*s*3*p*		90.011	0.011	4*d*4*f*	0	91.457	−0.857
1*s*5*p*	4	90.016	−0.004	3*d*4*f*	1	91.655	0.838
2*s*6*p*		90.002	0.001	5*d*4*f*		90.015	−0.010
6*s*2*p*		90.002	0.002				
1*s*6*p*	5	90.003	0.001				

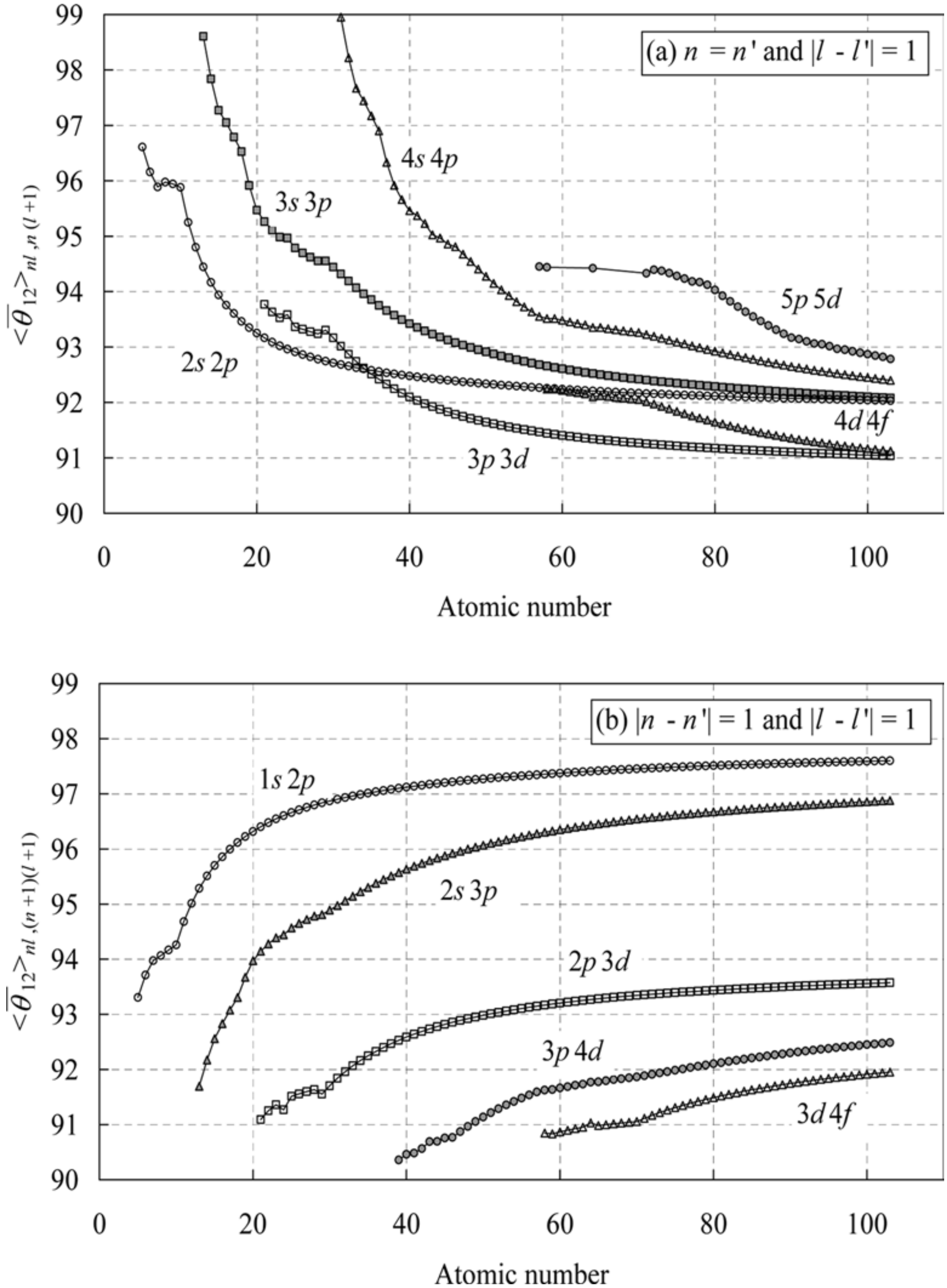

Fig. 1. The Z-dependence of some representative subshell-pair interelectronic angles $\langle\overline{\theta}_{12}\rangle_{nl,n'l'}$. (a) $n=n'$and $|l-l'|=1$. (b) $|n-n'|=1$ and $|l-l'|=1$

nitudes of $\Delta_{nl,n'l'}$ are larger than 3.10°. The values of $\Delta_{nl,n'l'}$ for 5*s*4*p*, *npnd* ($n=3$–5), and $np(n+1)d$ ($n=2$–4) are between 2.40° and 1.04°. The remaining 37 subshell pairs have $\Delta_{nl,n'l'}$ smaller than 0.97°. The maximum value of these $|\Delta_{nl,n'l'}|$ is 8.27° at the 4*s*4*p* subshell pair. This shows that the interactions between electrons in the *nsnp* ($n=2$–6) and $ns(n+1)p$ ($n=1$–5) subshell pairs in momentum space are very different from those in position space. At present, we do not have any physical interpretations for the dependence of $\Delta_{nl,n'l'}$ on the combination of *nl* and $n'l'$.

There are 7,569 subshell pairs for the 102 atoms in their ground states. They are divided into 4,294 subshell pairs with even $|l-l'|$ and 3,275 subshell pairs with odd $|l-l'|$. The former and the latter are classified into 101 and 87 kinds according to a combination of *nl* and $n'l'$, respectively. For the 101 kinds of subshell pairs with even $|l-l'|$, the $\langle\overline{\theta}_{12}\rangle_{nl,n'l'}$ are always equal to 90° independent of Z. On the other hand, we observed three types in the Z-dependences of $\langle\overline{\theta}_{12}\rangle_{nl,n'l'}$ for the 87 kinds of subshell pairs with odd $|l-l'|$. (i) For *nsnp* ($n=2$–6), *npnd* ($n=3$–6), and *ndnf* ($n=4$, 5) subshell pairs, the angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ decrease when Z increases. Figure 1(a) plots the Z-dependence of some representative $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with $n=n'$ and $|l{-}l'|=1$. The results show that interactions between electrons in subshells nl and $n\ l'$ in the same shell become smaller as Z becomes larger. The angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ for this group of subshell pairs are found to increase with increasing n without exceptions. (ii) For $ns(n+1)p$ ($n=1$–5), $np(n+1)d$ ($n=2$–4), and $3d4f$ subshell pairs, the $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ increase when Z increases, in contrast with the Z-dependence of the subshell pairs discussed in (i). The Z-dependence of the average interelectronic angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of selected subshell pairs with $|n{-}n'|=1$ and $|l{-}l'|=1$ is depicted in Fig. 1(b). We also found that the angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of the $ns(n+1)p$ and $np(n+1)d$ subshell pairs in an atom decrease with increasing n without exceptions. (iii) Though there are some exceptions, the $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ values of the other subshell pairs remain almost unchanged when Z changes.

Table 2 summarizes the mean values of the angles $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ of 87 subshell pairs with odd $|l{-}l'|$ over the 102 atoms. The 87 subshell pairs are divided into 42 *sp*, 23 *pd*, 14 *sf*, and eight *df* subshell pairs. The $nsnp$ ($n=2$–7), $ns(n+1)p$ ($n=1$–6), $npnd$ ($n=3$–6), $np(n+1)d$ ($n=2$–4), $ndnf$ ($n=4$, 5), and $3d4f$ subshell pairs have $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ larger than 91.0°. All the *sf* subshell pairs and 47 subshell pairs with $|n{-}n'|\geq 2$ have $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ values between 90.0° and 90.5°.

The results in Fig. 1 and Table 2 suggest that the Hartree–Fock angles $\langle\bar{\theta}_{12}\rangle$ are estimated from some *sp*, *pd*, and *df* subshell pair contributions $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ with

Table 2. The mean values of the average interelectronic angles $\langle\bar{\theta}_{12}\rangle_{nl,n',l'}$ for 87 kinds of subshell pairs with odd $|l-l'|$of the 102 atoms He through L_1 in their ground states

Subshell pair	$\|n{-}n'\|$	No. of pairs	Mean value	Subshell pair	$\|n{-}n'\|$	No. of pairs	Mean value
sp				*pd*			
2s2p	0	99	92.717	3p3d	0	83	91.723
3s3p		91	93.280	4p4d		65	92.664
4s4p		73	93.832	5p5d		36	93.595
5s5p		55	94.930	6p6d		6	94.479
6s6p		23	95.994	2p3d	1	83	92.942
7s7p		1	98.021	3p4d		65	91.767
1s2p	1	99	96.924	4p3d		73	90.113
2s3p		91	95.829	4p5d		36	90.999
3s2p		93	90.586	5p4d		55	90.136
3s4p		73	95.205	5p6d		6	90.355
4s3p		85	90.798	6p5d		23	90.104
4s5p		55	94.256	2p4d	2	65	90.163
5s4p		66	90.854	3p5d		36	90.070
5s6p		23	93.475	5p3d		55	90.010
6s5p		49	90.708	4p6d		6	90.027
6s7p		1	91.873	6p4d		23	90.011
7s6p		17	90.570	7p5d		1	90.004
1s3p	2	91	90.216	2p5d	3	36	90.030
2s4p		73	90.040	3p6d		6	90.011
4s2p		85	90.051	6p3d		23	90.002
3s5p		55	90.004	7p4d		1	90.001
5s3p		66	90.050	2p6d	4	6	90.003
4s6p		23	90.000	7p3d		1	90.000
6s4p		49	90.035	*sf*			
5s7p		1	90.000	4s4f	0	46	90.022
7s5p		17	90.024	5s5f		13	90.008
1s4p	3	73	90.107	3s4f	1	46	90.214
2s5p		55	90.087	4s5f		13	90.449
5s2p		66	90.011	5s4f		46	90.004
3s6p		23	90.070	6s5f		13	90.017
6s3p		49	90.008	2s4f	2	46	90.425
4s7p		1	90.022	3s5f		13	90.226
7s4p		17	90.005	6s4f		46	90.000
1s5p	4	55	90.012	7s5f		13	90.000
2s6p		23	90.003	1s4f	3	46	90.038
6s2p		49	90.002	2s5f		13	90.000
3s7p		1	90.000	7s4f		17	90.000
7s3p		17	90.001	1s5f	4	13	90.001
1s6p	5	23	90.004	*df*			
2s7p		1	90.001	4d4f	0	46	91.667
7s2p		17	90.000	5d5f		13	92.593
1s7p	6	1	90.000	3d4f	1	46	91.441
				4d5f		13	90.411
				5d4f		35	90.025
				6d5f		4	90.259
				3d5f	2	13	90.092
				6d4f		6	90.001

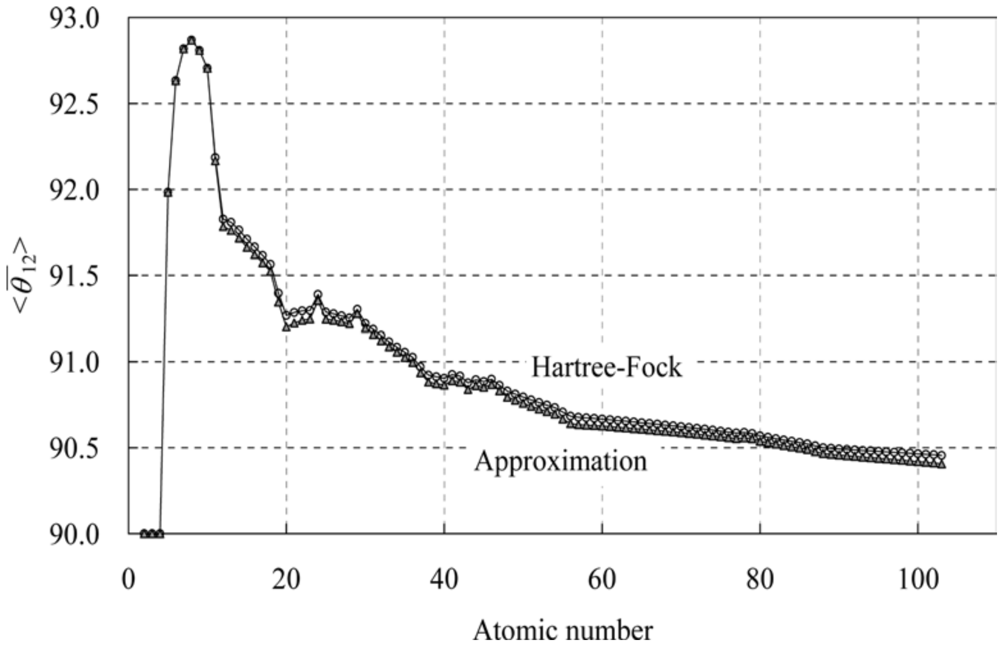

Fig. 2. The Hartree–Fock inter electronic angles $\langle\bar{\theta}_{12}\rangle$ and the approximations $\langle\bar{\theta}_{12}\rangle_{\mathrm{ap}}$ for the 102 ground-state atoms

$|n-n'| \le 1$. We therefore introduce an approximation $\langle\bar{\theta}_{12}\rangle_{ap}$ given by

$$\langle\bar{\theta}_{12}\rangle_{ap} = \frac{2}{N(N-1)}\left\{\sum_{n=2}^{7} N_{nsnp}\langle\bar{\theta}_{12}\rangle_{nsnp} + \sum_{n=3}^{6} N_{npnd}\langle\bar{\theta}_{12}\rangle_{npnd} + \sum_{n=4}^{5} N_{ndnf}\langle\bar{\theta}_{12}\rangle_{ndnf} + \sum_{n=1}^{6} N_{ns(n+1)p}\langle\bar{\theta}_{12}\rangle_{ns(n+1)p} + \sum_{n=2}^{4} N_{np(n+1)d}\langle\bar{\theta}_{12}\rangle_{np(n+1)d} + N_{3d4f}\langle\bar{\theta}_{12}\rangle_{3d4f} + N_{\mathrm{others}} \times 90\right\} \quad (7)$$

where N_{others} stands for the number of electron pairs in the possible subshell pairs except for the 22 subshell pairs in Eq. (7). Figure 2 compares the approximate values $\langle\bar{\theta}_{12}\rangle_{\mathrm{ap}}$ with the Hartree–Fock values. For He through Ne, the angle $\langle\bar{\theta}_{12}\rangle_{\mathrm{ap}}$ is equal to the Hartree–Fock value. In the range from Na to Lr, the approximate values are always smaller than the Hartree–Fock values. However, the maximum relative error is only 0.073% at the Ca atom and hence the approximation (7) well reproduces the Hartree–Fock values of the 102 atoms. The 22 subshell pairs in momentum space are thus confirmed to give predominant contributions to the total average interelectronic angles. In position space, only 12 subshell pairs with $n = n'$ are important [10].

The average inner product sum $\langle\Sigma_{a<b}\mathbf{p}_a\cdot\mathbf{p}_b\rangle$ of the electron linear momenta equals [26] the mass polarization energy ϵ_{mp} multiplied by the nuclear mass M, which appears as a total energy correction due to the finite nuclear mass. In the Hartree–Fock framework, $\langle\Sigma_{a<b}\mathbf{p}_a\cdot\mathbf{p}_b\rangle$ is expressed by the sum of subshell-pair contributions $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle_{nl,n'l'}$ between linear momenta of an electron in a subshell nl and another electron in a subshell $n'l'$. We are interested in a possible correlation between the subshell-pair contributions $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle_{nl,n'l'}$ and $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$. For this purpose, we consider a quantity $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle^{\mathrm{ap}}_{nl,n'l'}$ defined by

$$\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle^{\mathrm{ap}}_{nl,n'l'} = \langle p\rangle_{nl}\langle p\rangle_{n'l'}\langle\cos\bar{\theta}_{12}\rangle_{nl,n'l'} \quad (8a)$$

where

$$\langle p\rangle_{nl} = \int_0^\infty \mathrm{d}p\, p^3|P_{nl}(p)|^2$$

is the average linear momentum of an electron in a subshell nl and the average cosine $\langle\cos\bar{\theta}_{12}\rangle_{nl,n'l'}$ is obtained from $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$ using an approximate relation [27]

$$\langle\bar{\theta}_{12}\rangle_{nl,n'l'} \cong 90 - \frac{135}{2}\langle\cos\bar{\theta}_{12}\rangle_{nl,n'l'} \quad (8b)$$

We have examined the $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle_{nl,n'l'}$ and $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle^{\mathrm{ap}}_{nl,n'l'}$ values for the 120 subshell pairs of the Rn atom. For the 66 subshell pairs with even $|l-l'|$, the two values are zero and the approximation (8a) correctly reproduces the Hartree–Fock results. For the 54 subshell pairs with odd $|l-l'|$ of the Rn atom, however, the correlation between $\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle_{nl,n'l'}$ and $\langle\bar{\theta}_{12}\rangle_{nl,n'l'}$, examined through Eqs. (8a) and (8b), is found to be non-uniform: for subshell pairs such as $5s4f$, $3d4p$, and $3d4f$, the agreement of the two values is good, but for subshell pairs such as $2s2p$, $3s3p$, and $3p3d$, the agreement is very poor.

An approximate formula $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle^{\mathrm{ap}}_{nl,n'l'}$, corresponding to Eq. (8a), can also be introduced for the subshell-pair contributions $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle_{nl,n'l'}$ in position space. When the approximations in momentum and position spaces are compared for the Rn atom, the accuracies are found to be more or less the same: For the 66 subshell pairs with even $|l-l'|$, $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle^{\mathrm{ap}}_{nl,n'l'} = \langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle_{nl,n'l'}$, but for the 54 subshell pairs with odd $|l-l'|$, the correlation between $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle_{nl,n'l'}$ and $\langle \theta_{12} \rangle_{nl,n',l'}$ is again non-uniform.

Summary

For the 102 atoms He through Lr in their ground states, the average interelectronic angles $\langle \bar{\theta}_{12} \rangle_{nl,n'l'}$ between linear momenta of an electron in a subshell *nl* and another electron in a subshell *n′l′* were examined based on the numerical Hartree–Fock calculations. In momentum space, the deviations of the total average interelectronic angles $\langle \bar{\theta}_{12} \rangle$ from 90° are mainly determined by $\langle \bar{\theta}_{12} \rangle_{nl,n'l'}$ of the six *sp*, four *pd*, two *df* subshell pairs in the same shell and the six *sp*, three *pd*, one *df* subshell pairs in neighboring shells.

Acknowledgments. We thank Mr. T. Shimazaki for his assistance in the compilation of data. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

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