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Subshell-pair correlation coefficients of atoms in momentum space

Received: 20 April 2005 / Accepted: 28 July 2005 / Published online: 10 December 2005
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Abstract Angular correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ between linear momenta of an electron in a subshell nl and another electron in a subshell $n'l'$ are studied for the 102 neutral atoms He through Lr in their ground states, where n and l are the principal and azimuthal quantum numbers, respectively. We theoretically find that electron momenta are negatively correlated or uncorrelated; $\tau^{nl,n'l'}[\mathbf{p}] < 0$ when $|l - l'| = 1$, while $\tau^{nl,n'l'}[\mathbf{p}] = 0$ when $|l - l'| \neq 1$. Numerical examinations of the atoms show that except for the He–B atoms, negative correlations are largest between $1s$ and $2p$ subshells, which have the most diffuse electron distributions in momentum space.

Keywords Correlation coefficients · Subshell pairs · Momentum space · Atoms

1 Introduction

Statistical correlation coefficients introduced by Kutzelnigg et al. [1] provide useful tools for analyzing electron correlations in various wave functions. Even for the Hartree–Fock wave functions, we have nonvanishing correlation coefficients, which enable us to assess the Fermi correlation [2]. Thus, the meaning of correlation is essentially different from that of “electron correlation” defined by Löwdin [3], since the latter is the difference between the exact nonrelativistic and Hartree–Fock descriptions. The correlation coefficient $\tau[f]$ in position space is given [1] by

$$\tau[f] = \frac{2N \langle \sum_{i < j} f(\mathbf{r}_i) f(\mathbf{r}_j) \rangle - (N-1) \langle \sum_i f(\mathbf{r}_i) \rangle^2}{(N-1) \langle \sum_i f^2(\mathbf{r}_i) \rangle - \langle \sum_i f(\mathbf{r}_i) \rangle^2}, \quad (1)$$

where $f(\mathbf{r})$ is a probe function and the angular brackets $\langle \rangle$ indicate the expectation value over the N -electron ($N \geq 2$)

wave function $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ with $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ being the combined position-spin coordinates of the electron i . The correlation coefficient is [1] bounded as $-1 \leq \tau[f] \leq +1$ for any $f(\mathbf{r})$. Electrons are perfectly correlated if $\tau[f] = \pm 1$, while they are uncorrelated or independent if $\tau[f] = 0$.

A particularly important $\tau[f]$ is the angular correlation coefficient $\tau[\mathbf{r}]$, which is obtained by setting $f(\mathbf{r}) = \mathbf{r}$ in Eq. (1) and is given [1] for atomic systems by

$$\tau[\mathbf{r}] = \frac{2 \langle \sum_{i < j} \mathbf{r}_i \cdot \mathbf{r}_j \rangle}{(N-1) \langle \sum_i r_i^2 \rangle}, \quad (2)$$

where $\mathbf{r}_i \cdot \mathbf{r}_j = r_i r_j \cos \theta_{ij}$, $r_i = |\mathbf{r}_i|$, and θ_{ij} is the angle between position vectors of two electrons i and j . The correlation coefficients $\tau[\mathbf{r}]$ have been examined as a measure of angular correlations for He [4–11], Li [6, 10–13], Be [6, 10–16], B–Ne [6, 10–12], Na–Si [6, 11], and P–Lr [11]. Recently, correlation coefficients $\tau^{ij}[\mathbf{r}]$ between two spin-orbitals i and j and $\tau^{nl,n'l'}[\mathbf{r}]$ between two subshells nl and $n'l'$ have been studied [17], where n and l are the principal and azimuthal quantum numbers, respectively. It has been shown that $\tau^{ij}[\mathbf{r}]$ is negative for two parallel-spin orbitals with azimuthal quantum numbers different by unity, while zero otherwise. For the 102 atoms He (atomic number $Z = 2$) through Lr ($Z = 103$) in their ground states, the negative correlation in $\tau^{nl,n'l'}[\mathbf{r}]$ has been found to be largest between the outermost s and p subshells.

The correlation coefficient $\tau[\bar{f}]$ in momentum space is also defined, if we replace $f(\mathbf{r})$ with a momentum-space probe function $\bar{f}(\mathbf{p})$ and $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ with a momentum-space wave function $\Phi(\mathbf{y}_1, \dots, \mathbf{y}_N)$ in Eq. (1), where $\mathbf{y}_i = (\mathbf{p}_i, \sigma_i)$ is the combined momentum-spin coordinates of the electron i . A special case of $\tau[\bar{f}]$ for $\bar{f}(\mathbf{p}) = \mathbf{p}$ gives [1] the momentum-space angular correlation coefficient $\tau[\mathbf{p}]$ as

$$\tau[\mathbf{p}] = \frac{2 \langle \sum_{i < j} \mathbf{p}_i \cdot \mathbf{p}_j \rangle}{(N-1) \langle \sum_i p_i^2 \rangle}, \quad (3)$$

where $\mathbf{p}_i \cdot \mathbf{p}_j = p_i p_j \cos \bar{\theta}_{ij}$, $p_i = |\mathbf{p}_i|$, and $\bar{\theta}_{ij}$ is the angle between linear momenta of two electrons i and j . The coefficient $\tau[\mathbf{p}]$ is a measure of correlations between linear

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momenta of any two electrons. Examinations of $\tau[\mathbf{p}]$ have been reported for He [11, 18–21], Li [11, 13, 22], Be [11, 13, 16], B–Na [11], Mg [11, 20], and Al–Lr [11].

In the present paper, we study subshell-pair correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ between linear momenta of an electron in a subshell nl and another electron in a subshell $n'l'$. The next section outlines mathematical structures of $\tau[\mathbf{p}]$ and $\tau^{nl,n'l'}[\mathbf{p}]$ in the Hartree–Fock theory. In the third section, numerical results of $\tau^{nl,n'l'}[\mathbf{p}]$ are discussed for the 102 atoms He through Lr in their ground states. We will find that for a given pair of subshells nl and $n'l'$ ($n \neq n'$), the negative correlation in momentum space decreases with increasing $|n - n'|$, but for sp and pd subshell pairs in the same shell, it increases as n increases.

2 Subshell-pair correlation coefficients in momentum space

The theoretical structure of correlation coefficients $\tau[\mathbf{p}]$ in momentum space is analogous [17] to that of $\tau[\mathbf{r}]$ in position space. Therefore, we briefly summarize the Hartree–Fock theory of the correlation coefficients in momentum space.

We assume that a momentum-space wave function $\Phi(\mathbf{y}_1, \dots, \mathbf{y}_N)$ of an N -electron atom consists of N orthonormal spin-orbitals $\phi_i(\mathbf{p})\eta_i(\sigma)$ and that a spatial function $\phi_i(\mathbf{p})$ is the product of a radial $P_i(p) = P_{n_i l_i}(p)$ and a spherical harmonic $Y_{l_i m_i}(\bar{\theta}, \bar{\phi})$ functions, where $\eta_i(\sigma)$ is the spin function, m_i is the magnetic quantum number, and $(p, \bar{\theta}, \bar{\phi})$ is the polar coordinates of the electron linear momentum \mathbf{p} . As in position space [17], we have the correlation coefficient $\tau^{ij}[\mathbf{p}]$ of two spin-orbitals i and j in momentum space as

$$\tau^{ij}[\mathbf{p}] = -\frac{2\delta_s(i, j) |\langle \mathbf{p} \rangle_{ij}|^2}{\langle p^2 \rangle_{ii} + \langle p^2 \rangle_{jj}}, \quad (4a)$$

where

$$\langle X \rangle_{ij} = \int d\mathbf{p} \phi_i * (\mathbf{p}) X \phi_j(\mathbf{p}). \quad (4b)$$

When the two spin-orbitals have the same spin, the spin integral $\delta_s(i, j) = \int d\sigma \eta_i * (\sigma) \eta_j(\sigma)$ in Eq. (4a) is unity. When they have the opposite spins, $\delta_s(i, j)$ is zero. Equation (4a) leads to a few important results: (1) Since $\delta_s(i, j) = 1$ or 0, $\tau^{ij}[\mathbf{p}] \leq 0$ for any two spin-orbitals. This means that the angle θ_{12} between \mathbf{p}_1 of a spin-orbital i and \mathbf{p}_2 of another spin-orbital j is larger than $\pi/2$ on average. (2) The presence of the integral $\delta_s(i, j)$ indicates that $\tau^{ij}[\mathbf{p}]$ appears only from the exchange term. Thus, $\tau^{ij}[\mathbf{p}]$ in the Hartree approximation is equal to zero. (3) For the wave function assumed above, a selection rule [23] concludes that $\langle \mathbf{p} \rangle_{ij} = \mathbf{0}$ and hence $\tau^{ij}[\mathbf{p}] = 0$ unless $|l_i - l_j| = 1$. The spin-orbital-pair coefficient $\tau^{ij}[\mathbf{p}]$ and the total coefficient $\tau[\mathbf{p}]$ are related by

$$\begin{aligned} (N-1) \langle \sum_i p_i^2 \rangle &> \tau[\mathbf{p}] \\ &= \sum_{i < j} (\langle p^2 \rangle_{ii} + \langle p^2 \rangle_{jj}) \tau^{ij}[\mathbf{p}]. \end{aligned} \quad (5)$$

Gathering the $\tau^{ij}[\mathbf{p}]$ contributions, we have the subshell-pair correlation coefficient $\tau^{nl,n'l'}[\mathbf{p}]$ as

$$\tau^{nl,n'l'}[\mathbf{p}] = -2\delta_{1,|l-l'|} \bar{A}_{nl,n'l'} B_{nl,n'l'}, \quad (6)$$

where δ_{ij} is the Kronecker delta, the angular constant $B_{nl,n'l'}$ is defined in Ref. [17], and the radial contribution $\bar{A}_{nl,n'l'}$ is

$$\bar{A}_{nl,n'l'} = \frac{|\langle p \rangle_{nl,n'l'}|^2}{\langle p^2 \rangle_{nl} + \langle p^2 \rangle_{n'l'}} \quad (7a)$$

in which

$$\langle p \rangle_{nl,n'l'} = \int_0^\infty dp p^3 P_{nl} * (p) P_{n'l'}(p), \quad (7b)$$

$$\langle p^2 \rangle_{nl} = \int_0^\infty dp p^4 |P_{nl}(p)|^2. \quad (7c)$$

Corresponding to Eq. (5), the relation between $\tau^{nl,n'l'}[\mathbf{p}]$ and $\tau[\mathbf{p}]$ is given by

$$\begin{aligned} (N-1) \langle \sum_i p_i^2 \rangle &> \tau[\mathbf{p}] \\ &= \sum_{nl < n'l'} M_{nl,n'l'} (\langle p^2 \rangle_{nl} + \langle p^2 \rangle_{n'l'}) \tau^{nl,n'l'}[\mathbf{p}], \end{aligned} \quad (8)$$

where $M_{nl,n'l'}$ is the number of electron pairs in subshells nl and $n'l'$. Since $\bar{A}_{nl,n'l'}$ and $B_{nl,n'l'}$ are both positive, we find that $\tau^{nl,n'l'}[\mathbf{p}] \leq 0$, where the equality holds when $|l - l'| \neq 1$. For the 102 atoms He through Lr in their ground states, no subshells with g or higher azimuthal quantum numbers appear. Thus, the correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ for seven types of subshell pairs $ss, sd, sf, pp, pf, dd,$ and ff are zero, while $\tau^{nl,n'l'}[\mathbf{p}]$ for three types of subshell pairs $sp, pd,$ and df are negative. In particular, all the subshell pairs in the ground-state He, Li, and Be atoms are uncorrelated, since they have only s subshells. When either or both of two subshells are closed, $B_{nl,n'l'}$ depends only on l and l' values. A few explicit values [17] are $1/6$ for sp , $1/15$ for pd , and $3/70$ for df subshell pairs. For such subshell pairs with the same l and l' values, the relative magnitude of $\tau^{nl,n'l'}[\mathbf{p}]$ is determined by $\bar{A}_{nl,n'l'}$, since $B_{nl,n'l'}$ is common.

3 Numerical results and discussion

For the 102 atoms He through Lr, we considered the ground electronic configurations and LS terms [24]. The radial functions $R_i(r)$ in position space of these states were first generated by the numerical Hartree–Fock method based on a modified version of the MCHF72 program [25]. By the use of Talman’s algorithm [26], the radial functions $P_i(p)$ in momentum space were then obtained by the Hankel transformation of $R_i(r)$. The correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ were calculated from Eq. (6).

Table 1 The correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ in momentum space for 48 subshell pairs with $|l - l'| = 1$ of the Rn atom

Subshell pair	$-\tau^{nl,n'l'}[\mathbf{p}]$	Subshell pair	$-\tau^{nl,n'l'}[\mathbf{p}]$	Subshell pair	$-\tau^{nl,n'l'}[\mathbf{p}]$
1s2p	5.666(-2)	2p3s	3.849(-3)	2s2p	1.627(-4)
1s3p	1.159(-2)	2p4s	9.454(-4)	3s3p	8.262(-4)
1s4p	2.879(-3)	2p5s	2.099(-4)	4s4p	2.454(-3)
1s5p	5.736(-4)	2p6s	2.890(-5)	5s5p	5.689(-3)
1s6p	6.016(-5)			6s6p	1.102(-2)
		3p4s	6.300(-3)		
2s3p	3.062(-2)	3p5s	1.339(-3)	3p3d	8.204(-4)
2s4p	7.888(-3)	3p6s	1.880(-4)	4p4d	3.457(-3)
2s5p	1.634(-3)			5p5d	9.005(-3)
2s6p	1.740(-4)	4p5s	6.991(-3)		
		4p6s	9.651(-4)	4d4f	4.252(-3)
3s4p	1.648(-2)				
3s5p	3.667(-3)	5p6s	6.034(-3)		
3s6p	4.048(-4)				
		3d4p	1.033(-3)		
4s5p	6.585(-3)	3d5p	1.869(-4)		
4s6p	8.179(-4)	3d6p	2.001(-5)		
5s6p	1.135(-3)	4d5p	2.023(-3)		
		4d6p	2.053(-4)		
2p3d	3.187(-2)				
2p4d	6.266(-3)	5d6p	1.998(-3)		
2p5d	9.631(-4)				
		4f5d	5.504(-4)		
3p4d	1.137(-2)				
3p5d	1.977(-3)				
4p5d	1.965(-3)				
3d4f	1.559(-2)				

$A(n)$ means $A \times 10^n$

Using the heaviest rare-gas atom Rn ($Z = 86$) as an example, we discuss the characteristics of subshell-pair correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$. The Rn atom in the ground state has six s , five p , three d , and one f subshells. The total number of possible subshell pairs amounts to 120, which consist of 72 subshell pairs with $|l - l'| \neq 1$ and 48 subshell pairs with $|l - l'| = 1$. The correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ of the former are exactly zero, while those of the latter are negative. The correlation coefficients of the 48 subshell pairs with $|l - l'| = 1$ are shown in Table 1. Based on the quantum numbers of subshell pairs $nl n'l'$, we separate the 48 subshell pairs into three groups; the first group is 22 subshell pairs with $n < n'$ and $l' = l + 1$ (the left block in Table 1), the second is 17 subshell pairs with $n < n'$ and $l' = l - 1$ (the middle block in Table 1), and the third is nine subshell pairs with $n = n'$ and $l' = l + 1$ (the right block in Table 1).

In the first group, we find two rules for the dependence of $\tau^{nl,n'l'}[\mathbf{p}]$ on n and n' : (1) For subshell pairs with common n , l , and l' , the negative correlation decreases with increasing n' without exceptions. For example, we have $1s2p > 1s3p > 1s4p > 1s5p > 1s6p$. (2) For subshell pairs with common l , n' , and l' , the negative correlation increases as n increases, except for $np\ 5d$ subshell pairs. A typical example is $1s6p < 2s6p < 3s6p < 4s6p < 5s6p$. The two rules hold as well for the second group. We find another rule in the third group: (3) For subshell pairs with common l and l' , the negative correlation increases with increasing $n = n'$. An example is $2s2p < 3s3p < 4s4p < 5s5p < 6s6p$. The

three rules found for the Rn atom are valid for all the atoms examined, though there are minor exceptions. The rules imply that $\tau^{nl,n'l'}[\mathbf{p}]$ is mainly dependent on a radial overlap between momentum distributions associated with the subshells nl and $n'l'$, because the overlap largely affects $\bar{A}_{nl,n'l'}$ through the factor $\langle p \rangle_{nl,n'l'}$. We observe in general that for subshell pairs in different shells the overlap becomes larger when $|n - n'|$ decreases, and that for subshell pairs in the same shell the overlap becomes smaller when n decreases.

When we consider all the 102 atoms, there are 7,569 subshell pairs, which are classified into 188 pairs according to the combination of nl and $n'l'$. They are divided into uncorrelated 115 pairs with $|l - l'| \neq 1$ and negatively correlated 73 pairs with $|l - l'| = 1$. Among the 73 pairs, the $1s2p$ subshell pair is found to have the largest negative $\tau^{nl,n'l'}[\mathbf{p}]$ value, as seen in Table 1 for the Rn atom (-0.05666). The largest negative correlation of the $1s2p$ subshell pair is attributed to the facts that the angular constant B_{1s2p} is larger than those of pd and df subshell pairs and the constant \bar{A}_{1s2p} is large due to the meaningful radial overlap between the two subshells. Minor exceptions are the He–Be atoms where only s subshells are occupied and the B atom where the $2s2p$ pair is largest. These results are in contrast with those in position space, where $\tau^{nl,n'l'}[\mathbf{r}]$ is generally largest between the outermost s and p subshells [17].

We next examine how the correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ change from an atom to another. The 73 negatively correlated subshell pairs are divided into two groups, that is,

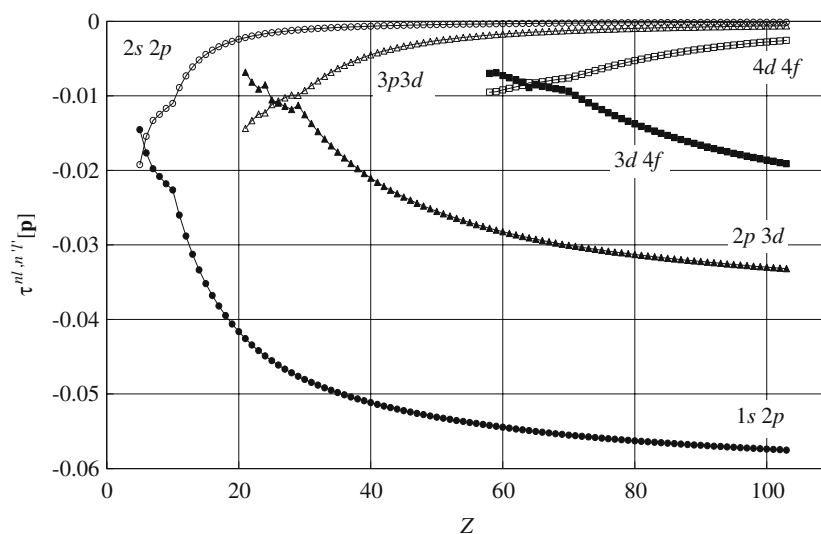


Fig. 1 The Z -dependence of six representative subshell-pair correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$

62 subshell pairs with $n \neq n'$ and eleven subshell pairs with $n = n'$. The former $\tau^{nl,n'l'}[\mathbf{p}]$ values are observed to decrease with increasing Z in general. This is also true [17] in position space for $\tau^{nl,n'l'}[\mathbf{r}]$ between two different shells. On the other hand, the latter $\tau^{nl,n'l'}[\mathbf{p}]$ values with $n = n'$ have an increasing trend when Z becomes larger. This is different from the Z -dependence of $\tau^{nl,n'l'}[\mathbf{r}]$ in position space, where the correlation coefficients are almost constant [17]. Since $B_{nl,n'l'}$ is independent of Z , the different Z -dependences of $\tau^{nl,n'l'}[\mathbf{p}]$ between pairs with $n \neq n'$ and $n = n'$ originate from different Z -dependences of $\bar{A}_{nl,n'l'}$. We find that the denominator of $\bar{A}_{nl,n'l'}$ always increases with an increasing Z , but the Z -dependence of the numerator of $\bar{A}_{nl,n'l'}$ is determined by whether $n \neq n'$ or $n = n'$. When Z increases, $\bar{A}_{nl,n'l'}$ of subshell pairs in different shells increases, while $\bar{A}_{nl,n'l'}$ of subshell pairs in the same shell decreases. In fact, the radial subshell interaction measured by the magnitude of the radial overlap becomes larger for subshell pairs with $n \neq n'$, while it becomes smaller for subshell pairs with $n = n'$, as Z increases. Figure 1 shows the Z -dependence of six representative $\tau^{nl,n'l'}[\mathbf{p}]$ with larger negative correlations.

4 Summary

The angular correlation coefficients $\tau^{nl,n'l'}[\mathbf{p}]$ 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 for the 102 atoms He through Lr in their ground states. The correlation in momentum space has been found to be different from that in position space. We have clarified the dependence of $\tau^{nl,n'l'}[\mathbf{p}]$ on the quantum

numbers. In momentum space, the correlation coefficient of most atoms is largest for the $1s2p$ subshell pair.

Acknowledgements 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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