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Interelectronic angle densities of atoms in momentum space

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Abstract. For the 102 atoms from He to Lr in their ground states, the Hartree–Fock interelectronic angle densities, $\bar{A}(\bar{\theta}_{12})$, in momentum space are reported, where $\bar{\theta}_{12}$ is the angle between the momentum vectors \mathbf{p}_1 and \mathbf{p}_2 of two electrons. In the first three atoms, He–Be, $\bar{A}(\bar{\theta}_{12})$ is found to be uniform independent of $\bar{\theta}_{12}$, while in the remaining 99 atoms, $\bar{A}(\bar{\theta}_{12})$ is larger for a large $\bar{\theta}_{12}$ than for a small $\bar{\theta}_{12}$. Accordingly, the average interelectronic angles in momentum space are 90° precisely for the three atoms and greater than 90° for the 99 atoms.

Keywords: Interelectronic angles – Two-electron densities – Atoms – Momentum space

Introduction and definitions

In the study of electron correlations in few-electron atoms, the interelectronic angle densities were introduced [1, 2, 3, 4, 5, 6] to clarify the distribution of the angle spanned by the position or momentum vectors of two electrons. In position space, the interelectronic angle density, $A(\theta_{12})$, is defined [7] by

$$A(\theta_{12}) \equiv (\sin \theta_{12})^{-1} \int d\mathbf{r}'_1 d\mathbf{r}'_2 \delta(\theta_{12} - \theta'_{12}) \Gamma(\mathbf{r}'_1, \mathbf{r}'_2), \quad (1)$$

where $\delta(x)$ is the Dirac delta function and θ'_{12} is the angle between the vectors \mathbf{r}'_1 and \mathbf{r}'_2 . For a normalized N -electron ($N \geq 2$) wave function $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$, the spinless two-electron density function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (1) is given by

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{N(N-1)}{2} \int ds_1 ds_2 dx_3 \dots dx_N |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2, \quad (2)$$

where $\mathbf{x}_i \equiv (\mathbf{r}_i, s_i)$ is the combined position-spin coordinates of the electron i . The function $A(\theta_{12})$ is the probability density function that the interelectronic angle θ_{ij} ($0 \leq \theta_{ij} \leq \pi$) subtended by the position vectors \mathbf{r}_i and \mathbf{r}_j of any two electrons i and j becomes θ_{12} , and is normalized as

$$\int_0^\pi d\theta_{12} \sin \theta_{12} A(\theta_{12}) = \frac{N(N-1)}{2}, \quad (3)$$

where the value on the right-hand side is the number of electron pairs. Note that the interelectronic angle in position space is apparently dependent on the location of the coordinate origin, though the nuclear position is a natural choice in atomic systems.

$A(\theta_{12})$ is a useful tool to know explicitly the distribution of the interelectronic angle in atoms and molecules. Nevertheless, the examination of $A(\theta_{12})$ in the literature is very limited. Only for He and Be atoms and some of their isoelectronic ions was the correlation contribution in $A(\theta_{12})$ studied in an ad hoc manner [1, 2, 3]. Very recently, however, it has been shown [7] that $A(\theta_{12})$ can be expressed as a linear combination of Legendre polynomials $P_n(\cos \theta_{12})$ in general:

$$A(\theta_{12}) = \sum_{n=0}^{\infty} \frac{2n+1}{2} q_n P_n(\cos \theta_{12}), \quad (4)$$

and

$$q_n = \int d\mathbf{r}_1 d\mathbf{r}_2 P_n(\cos \theta_{12}) \Gamma(\mathbf{r}_1, \mathbf{r}_2). \quad (5)$$

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The Hartree–Fock limit densities have been reported [7] for the 102 atoms from He ($Z=2$) to Lr ($Z=103$) in their ground states, where Z stands for atomic number.

The interelectronic angle density $\bar{A}(\bar{\theta}_{12})$ is defined in momentum space as well. Corresponding to Eqs. (1) and (3), we have

$$\bar{A}(\bar{\theta}_{12}) \equiv (\sin \bar{\theta}_{12})^{-1} \int d\mathbf{p}'_1 d\mathbf{p}'_2 \delta(\bar{\theta}_{12} - \bar{\theta}'_{12}) \bar{\Gamma}(\mathbf{p}'_1, \mathbf{p}'_2) \quad (6)$$

and

$$\int_0^\pi d\bar{\theta}_{12} \sin \bar{\theta}_{12} \bar{A}(\bar{\theta}_{12}) = \frac{N(N-1)}{2}, \quad (7)$$

where $\bar{\theta}_{12}$ is the angle between the momentum vectors \mathbf{p}_1 and \mathbf{p}_2 of two electrons and $\bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2)$ is the spinless two-electron density function associated with a momentum-space wave function $\Phi(\mathbf{y}_1, \dots, \mathbf{y}_N)$, where $\mathbf{y}_i \equiv (\mathbf{p}_i, s_i)$ is the combined momentum-spin coordinates of electron i . In contrast to its position-space counterpart, the interelectronic angle in momentum space has no apparent origin-dependence under the zero translation condition of a system. In the present paper, we study the momentum-space interelectronic angle densities for the 102 ground-state atoms from He to Lr within the Hartree–Fock framework. The mathematical structure of the density $\bar{A}(\bar{\theta}_{12})$ and our computational procedures are outlined in Sect. 2. The results for the atoms are presented and discussed in Sect. 3 in comparison with their position-space counterparts. Hartree atomic units are used.

Theoretical and computational outlines

The mathematical structure of the interelectronic angle density $\bar{A}(\bar{\theta}_{12})$ in momentum space is isomorphic to that in position space. Following the formalism for the position-space density $A(\theta_{12})$ in Ref. [7], we substitute two relations,

$$\delta(\bar{\theta} - \bar{\theta}') = \delta(\cos \bar{\theta} - \cos \bar{\theta}') \sin \bar{\theta}, \quad (8a)$$

$$\delta(x - x') = \sum_{n=0}^{\infty} \frac{2n+1}{2} P_n(x) P_n(x'), \quad (8b)$$

into Eq. (6), where $P_n(x)$ are the Legendre polynomials. We then obtain in general that

$$\bar{A}(\bar{\theta}_{12}) = \sum_{n=0}^{\infty} \frac{2n+1}{2} \bar{q}_n P_n(\cos \bar{\theta}_{12}), \quad (9)$$

where the expansion coefficients \bar{q}_n are given by

$$\bar{q}_n = \langle P_n(\cos \bar{\theta}_{12}) \rangle \equiv \int d\mathbf{p}_1 d\mathbf{p}_2 P_n(\cos \bar{\theta}_{12}) \bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2). \quad (10)$$

A particular case of Eq. (10) is $\bar{q}_0 = N(N-1)/2$, because $P_0(x) = 1$. Therefore, the first term of $\bar{A}(\bar{\theta}_{12})$ in Eq. (9) is a constant, $N(N-1)/4$, and gives a uniform distribution independent of $\bar{\theta}_{12}$. The remaining terms with $n \geq 1$ are responsible for the $\bar{\theta}_{12}$ dependence of the interelectronic angle density $\bar{A}(\bar{\theta}_{12})$.

For a determinantal wave function $\Phi(\mathbf{y}_1, \dots, \mathbf{y}_N)$ composed of a set of orthonormal spin-orbitals $\phi_a(\mathbf{p})\eta_a(s)$, the two-electron density function $\bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2)$ is given by

$$\bar{\Gamma}(\mathbf{p}_1, \mathbf{p}_2) = \sum_{a,b,c,d} C_{abcd} \phi_a^*(\mathbf{p}_1) \phi_b^*(\mathbf{p}_2) \phi_c(\mathbf{p}_1) \phi_d(\mathbf{p}_2), \quad (11)$$

where C_{abcd} are expansion coefficients. Then the most general two-electron integral occurring in the calculation of $\bar{q}_n = \langle P_n(\cos \bar{\theta}_{12}) \rangle$ is

$$\langle ab | P_n(\cos \bar{\theta}_{12}) | cd \rangle \equiv \int d\mathbf{p}_1 d\mathbf{p}_2 \phi_a^*(\mathbf{p}_1) \phi_b^*(\mathbf{p}_2) P_n(\cos \bar{\theta}_{12}) \phi_c(\mathbf{p}_1) \phi_d(\mathbf{p}_2), \quad (12)$$

which includes four different momentum orbitals: ϕ_a , ϕ_b , ϕ_c , and ϕ_d . In atomic systems, we can generally assume that the spatial function $\phi_a(\mathbf{p})$ is a product of the radial $P_a(p) \equiv P_{n_a l_a}(p)$ and spherical harmonic $Y_a(\Omega) \equiv Y_{l_a m_a}(\Omega)$ functions, where (p, Ω) with $\Omega \equiv (\theta, \phi)$ is the polar coordinates of the vector \mathbf{p} , and n_a , l_a , and m_a are the principal, azimuthal, and magnetic quantum numbers, respectively, of the function $\phi_a(\mathbf{p})$. Then, Eq. (12) reduces to

$$\langle ab | P_n(\cos \bar{\theta}_{12}) | cd \rangle = \bar{S}(a, c) \bar{S}(b, d) A_n(a, b; c, d), \quad (13a)$$

where \bar{S} is the radial overlap integral in momentum space,

$$\bar{S}(a, b) \equiv \int_0^\infty dp p^2 P_a^*(p) P_b(p) = \bar{S}^*(b, a), \quad (13b)$$

and A_n is the angular integral,

$$A_n(a, b; c, d) \equiv \int d\Omega_1 d\Omega_2 Y_a^*(\Omega_1) Y_b^*(\Omega_2) P_n(\cos \bar{\theta}_{12}) Y_c(\Omega_1) Y_d(\Omega_2). \quad (13c)$$

A special case of Eq. (13b) for $a=b$ is $\bar{S}(a, a) = 1$. The two-electron angular integral (Eq. 13c) was calculated [7] to be

$$A_n(a, b; c, d) = \delta_{m_a+m_b, m_c+m_d} c^n(a, c) c^n(d, b), \quad (14)$$

where $c^n(a, b) \equiv c^n(l_a m_a, l_b m_b)$ is the Condon–Shortley parameter [8, 9]. The relation given in Eq. (13a) is

identical with that for position space [7], if the integral $\bar{S}(a, b)$ is replaced with the corresponding overlap integral $S(a, b)$ between the radial functions $R_a(r)$ and $R_b(r)$ in position space. Since $c^n(a, b)$ vanishes unless $n + l_a + l_c$ is an even integer, $n + l_b + l_d$ is an even integer, $|l_a - l_c| \leq n \leq l_a + l_c$, and $|l_b - l_d| \leq n \leq l_b + l_d$, the summation in Eq. (9) runs over a finite number of n in the case of atoms.

In a particular case of Hartree–Fock wave functions, only two types of integrals $\langle ab|P_n(\cos\bar{\theta}_{12})|ab\rangle$ and $\langle ab|P_n(\cos\bar{\theta}_{12})|ba\rangle$ appear. From Eqs. (13a, 13b, 13c) and (14), we immediately find that

$$\langle ab|P_n(\cos\bar{\theta}_{12})|ab\rangle = a^n(a, b) \quad (15a)$$

and

$$\langle ab|P_n(\cos\bar{\theta}_{12})|ba\rangle = |\bar{S}(a, b)|^2 b^n(a, b) \quad (15b)$$

for the direct and exchange terms, respectively, where $a^n(a, b) \equiv c^n(a, a)c^n(b, b)$ and $b^n(a, b) \equiv [c^n(a, b)]^2$ are the Condon–Shortley parameters [8, 9]. Because of the properties of $c^n(a, b)$, Eq. (15a) has nonzero values only for even integers n ranging from 0 to $\min(2l_a, 2l_b)$, while Eq. (15b) has nonzero values only for every other integer n between $|l_a - l_b|$ and $l_a + l_b$.

The experimental ground electronic configurations and LS terms [10, 11] were considered for all the 102 atoms from He ($Z=2$) to Lr ($Z=103$). For these states, the position-space radial functions $R_a(r) \equiv R_{n_a l_a}(r)$ were first generated by the numerical Hartree–Fock method based on a modified version of the MCHF72 program [12]. The radial functions $P_a(p)$ in momentum space were then obtained by the Hankel transformation of $R_a(r)$,

$$P_a(p) = (-i)^{l_a} (2/\pi)^{1/2} \int_0^\infty dr r^2 j_{l_a}(pr) R_a(r), \quad (16)$$

by using the algorithm of Talman [13], where $j_l(x)$ is the spherical Bessel function of the first kind. Finally, we used Eq. (15a) and (15b) to compute the spin-orbital-pair contributions to $\bar{q}_n = \langle P_n(\cos\bar{\theta}_{12}) \rangle$, where the values of the Condon–Shortley parameters $a^n(a, b)$ and $b^n(a, b)$ were taken from Refs. [8, 9].

Results and discussion

The numerical results of nonzero \bar{q}_n values are summarized in Table 1 for the second to fifth period atoms and in Table 2 for the sixth and seventh period atoms. The \bar{q}_0 value is not given, because it is $N(N-1)/2$, the number of electron pairs. Owing to the nonvanishing conditions of the Condon–Shortley parameters, the maximal n of nonzero \bar{q}_n is $2l_{\max}$ or $2l_{\max}-1$, where l_{\max} is the largest azimuthal quantum number of occupied orbitals in an atom. The first three atoms, He, Li, and

Table 1. Nonzero \bar{q}_n values for the atoms with $Z=5-54$. Note that $\bar{q}_0 = N(N-1)/2$. For $Z=2-4$, only \bar{q}_0 is nonvanishing

Z	\bar{q}_1	\bar{q}_2	\bar{q}_3	\bar{q}_4
5	-0.293820			
6	-0.585041	-0.200000		
7	-0.876746	-0.600000		
8	-1.190083	-0.600000		
9	-1.498162	-0.800000		
10	-1.803165	-1.200000		
11	-1.780045	-1.200000		
12	-1.785973	-1.200000		
13	-2.089513	-1.200000		
14	-2.377943	-1.400000		
15	-2.660101	-1.800000		
16	-2.961108	-1.800000		
17	-3.255228	-2.000000		
18	-3.545122	-2.400000		
19	-3.537362	-2.400000		
20	-3.566188	-2.400000		
21	-3.956035	-2.597810	-0.253898	
22	-4.350563	-2.956668	-0.510378	-0.020408
23	-4.743997	-3.294869	-0.765689	-0.163265
24	-5.491332	-4.105099	-1.267408	-0.714286
25	-5.529230	-4.093433	-1.274347	-0.714286
26	-5.923070	-4.292042	-1.528882	-0.714286
27	-6.316490	-4.653074	-1.783049	-0.734694
28	-6.709927	-4.993680	-2.037100	-0.877551
29	-7.459476	-5.799393	-2.539709	-1.428571
30	-7.496720	-5.796931	-2.544882	-1.428571
31	-7.805253	-5.790170	-2.536707	-1.428571
32	-8.086682	-5.986679	-2.525466	-1.428571
33	-8.358507	-6.385435	-2.515404	-1.428571
34	-8.648367	-6.385655	-2.507305	-1.428571
35	-8.933105	-6.586699	-2.501798	-1.428571
36	-9.215469	-6.988210	-2.498718	-1.428571
37	-9.209323	-6.991310	-2.495210	-1.428571
38	-9.244454	-6.994686	-2.492336	-1.428571
39	-9.620929	-7.195034	-2.736258	-1.428571
40	-10.015798	-7.555178	-2.992427	-1.448980
41	-10.739199	-8.218369	-3.486985	-1.857143
42	-11.143569	-8.698316	-3.747922	-2.142857
43	-11.191755	-8.683898	-3.754638	-2.142857
44	-11.927315	-9.240620	-4.257094	-2.163265
45	-12.318494	-9.572003	-4.510674	-2.306122
46	-13.053938	-10.366066	-5.005965	-2.857143
47	-13.097558	-10.356850	-5.014862	-2.857143
48	-13.128254	-10.367309	-5.005995	-2.857143
49	-13.425731	-10.362787	-4.991489	-2.857143
50	-13.702107	-10.561133	-4.977967	-2.857143
51	-13.971521	-10.961494	-4.967543	-2.857143
52	-14.260125	-10.963238	-4.959839	-2.857143
53	-14.544350	-11.165747	-4.955635	-2.857143
54	-14.826767	-11.568709	-4.954644	-2.857143

Be, do not appear in Table 1, since only s ($l=0$) orbitals are occupied and all \bar{q}_n , except \bar{q}_0 , vanish for these atoms. We find in Tables 1 and 2 that the nonzero \bar{q}_n are negative for all n except $n=0$. For a given Z , the magnitudes $|\bar{q}_n|$ decrease with increasing n , while for a given n , $|\bar{q}_n|$ increase with increasing Z in general. These trends of \bar{q}_n are similar to those [7] of q_n in position space. Some atoms with analogous valence electron configurations have the same \bar{q}_n value for the largest n , since it originates from the contribution of two electrons in the outermost subshell with l_{\max} . In the case of $n=2l_{\max}$, moreover, we obtain an interesting equality $q_n = \bar{q}_n$

Table 2. Nonzero \bar{q}_n values for the atoms with $Z = 55\text{--}103$. Note that $\bar{q}_0 = N(N-1)/2$

Z	\bar{q}_1	\bar{q}_2	\bar{q}_3	\bar{q}_4	\bar{q}_5	\bar{q}_6
55	-14.833830	-11.574825	-4.951470	-2.857143		
56	-14.883720	-11.581513	-4.948723	-2.857143		
57	-15.271724	-11.781072	-5.198418	-2.857143		
58	-15.690254	-12.180940	-5.523809	-3.078977	-0.211151	
59	-16.117360	-12.645644	-5.923305	-3.556748	-0.630802	-0.030020
60	-16.536653	-13.037325	-6.251738	-3.837863	-0.844552	-0.146571
61	-16.956194	-13.384455	-6.580323	-4.127238	-1.058248	-0.351416
62	-17.377743	-13.798167	-6.909791	-4.452447	-1.272764	-0.582751
63	-17.801269	-14.322899	-7.240111	-4.824503	-1.488103	-0.815851
64	-18.218355	-14.521777	-7.502908	-4.824481	-1.501686	-0.815851
65	-18.633461	-14.949894	-7.894715	-5.251656	-1.911223	-0.817617
66	-19.052299	-15.385533	-8.223188	-5.524504	-2.123957	-0.845871
67	-19.470984	-15.776674	-8.551615	-5.805622	-2.336527	-0.962421
68	-19.889475	-16.123321	-8.879977	-6.095010	-2.548921	-1.167267
69	-20.309029	-16.536591	-9.208796	-6.420227	-2.761756	-1.398601
70	-20.729967	-17.060928	-9.538206	-6.792293	-2.975196	-1.631702
71	-21.153070	-17.261735	-9.800900	-6.792537	-2.997539	-1.631702
72	-21.575575	-17.621762	-10.068414	-6.812313	-3.008954	-1.631702
73	-21.985572	-17.957416	-10.330599	-6.953992	-3.014192	-1.631702
74	-22.386375	-18.269998	-10.588524	-7.217859	-3.015849	-1.631702
75	-22.780425	-18.743162	-10.843237	-7.502065	-3.015456	-1.631702
76	-23.170062	-18.934535	-11.094969	-7.500604	-3.013954	-1.631702
77	-23.557081	-19.287446	-11.345525	-7.519667	-3.011902	-1.631702
78	-24.285941	-19.922981	-11.849146	-7.926496	-3.009764	-1.631702
79	-24.671286	-20.389676	-12.099780	-8.211165	-3.007655	-1.631702
80	-24.706852	-20.404638	-12.090512	-8.210435	-3.005541	-1.631702
81	-25.003313	-20.398004	-12.075948	-8.209961	-3.003538	-1.631702
82	-25.278687	-20.594559	-12.062415	-8.209697	-3.001649	-1.631702
83	-25.546790	-20.993546	-12.051991	-8.209614	-2.999883	-1.631702
84	-25.833541	-20.994308	-12.044223	-8.209667	-2.998244	-1.631702
85	-26.115904	-21.196243	-12.040107	-8.209857	-2.996726	-1.631702
86	-26.396511	-21.599003	-12.039433	-8.210162	-2.995326	-1.631702
87	-26.407311	-21.606323	-12.035712	-8.210450	-2.994053	-1.631702
88	-26.461998	-21.614799	-12.032311	-8.210765	-2.992890	-1.631702
89	-26.850155	-21.814649	-12.281243	-8.211062	-2.991929	-1.631702
90	-27.242698	-22.172551	-12.533783	-8.231779	-2.991107	-1.631702
91	-27.668937	-22.345188	-12.924823	-8.643340	-3.402876	-1.633468
92	-28.081998	-22.838509	-13.252631	-8.914681	-3.616814	-1.661722
93	-28.498799	-23.306308	-13.580645	-9.187007	-3.831567	-1.778272
94	-28.914628	-23.832328	-13.971341	-9.805041	-4.248665	-2.214452
95	-29.340322	-24.357324	-14.301657	-10.176908	-4.465692	-2.447552
96	-29.762605	-24.555059	-14.566156	-10.176843	-4.480084	-2.447552
97	-30.181023	-24.718931	-14.893328	-10.362194	-4.693828	-2.447552
98	-30.602418	-25.420125	-15.287433	-10.875830	-5.108672	-2.477573
99	-31.025363	-25.811153	-15.617015	-11.156454	-5.323903	-2.594123
100	-31.448386	-26.157621	-15.946677	-11.445299	-5.539085	-2.798969
101	-31.872178	-26.570618	-16.276660	-11.769903	-5.754564	-3.030303
102	-32.296745	-27.094571	-16.606945	-12.141276	-5.970349	-3.263403
103	-32.709188	-27.293082	-16.865878	-12.139765	-5.982070	-3.263403

between the expansion coefficients in position and momentum spaces, because $\bar{S}(a, b) = 1$ in Eq. (15b).

The interelectronic angle densities $\bar{A}(\bar{\theta}_{12})$ in momentum space are exemplified in Fig. 1 for the five rare-gas atoms Ne, Ar, Kr, Xe, and Rn, where $\bar{A}(\bar{\theta}_{12})$ are renormalized to unity, instead of $N(N-1)/2$, to compare the atoms with different numbers of electron pairs. Moreover, we have excluded in the figure the contribution from the first $P_0(\cos\bar{\theta}_{12}) = 1$ term of Eq. (9) to clarify the deformation of $\bar{A}(\bar{\theta}_{12})$ from the uniform distribution. In Fig. 1, we find that the interelectronic angle density is small for a smaller $\bar{\theta}_{12}$ and large for a larger $\bar{\theta}_{12}$ in all the atoms, though the degree of the deformation decreases as Z increases. Thus two electrons in an atom

have a tendency to have opposite momenta without exceptions. The minimum in $\bar{A}(\bar{\theta}_{12})$ is observed at $\bar{\theta}_{12} = 0^\circ$ for all five atoms, while the maximum is at $\bar{\theta}_{12} = 107, 107, 122, 127,$ and 134° for the Ne, Ar, Kr, Xe, and Rn atoms, respectively. In the Hartree-Fock approximation, the characteristics of $\bar{A}(\bar{\theta}_{12})$ are very similar to those of its position-space partner $A(\theta_{12})$ reported in Ref. [7].

We have also calculated the average interelectronic angle $\langle \bar{\theta}_{12} \rangle$ in momentum space, defined by

$$\langle \bar{\theta}_{12} \rangle \equiv \frac{2}{N(N-1)} \int_0^\pi d\bar{\theta}_{12} \sin \bar{\theta}_{12} \bar{\theta}_{12} \bar{A}(\bar{\theta}_{12}). \quad (17)$$

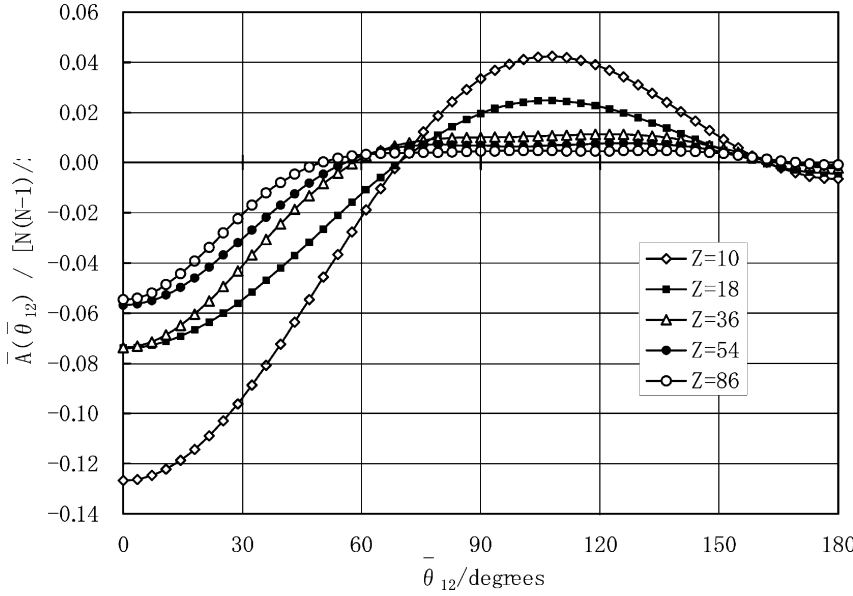


Fig. 1. The interelectronic angle densities $\bar{A}(\bar{\theta}_{12})$ in momentum space for the five rare-gas atoms Ne, Ar, Kr, Xe, and Rn. The densities are normalized to unity, instead of $N(N-1)/2$, and the uniform contribution from the $P_0(\cos\bar{\theta}_{12})=1$ term is excluded

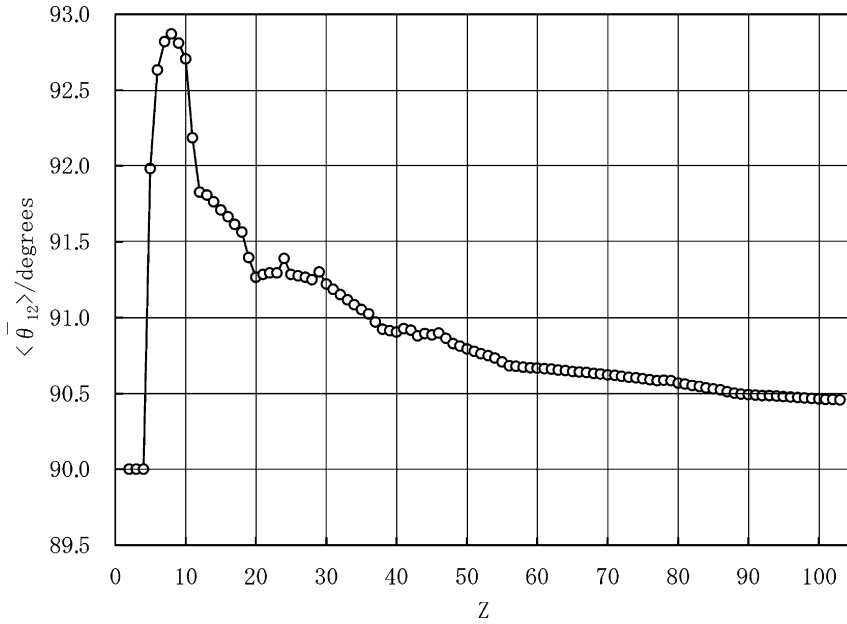


Fig. 2. The average interelectronic angle $\langle \bar{\theta}_{12} \rangle$ in momentum space as a function of atomic number Z

The results for the 102 atoms are plotted in Fig. 2 as a function of Z . For the first three atoms with $Z=2-4$, $\langle \bar{\theta}_{12} \rangle$ is 90° precisely and the momentum vectors \mathbf{p}_i and \mathbf{p}_j of two electrons are perpendicular in an average sense. For the remaining 99 atoms, on the other hand, the average angle $\langle \bar{\theta}_{12} \rangle$ is always greater than 90° . When Z increases from 5 to 103, $\langle \bar{\theta}_{12} \rangle$ first increases, has a maximum (92.9°) at $Z=8$, and then decreases towards a minimum (90.5°) at $Z=103$. The Z -dependence of $\langle \bar{\theta}_{12} \rangle$ shows close parallelism with that of $\langle \theta_{12} \rangle$ in position space, except that $\langle \theta_{12} \rangle$ has a maximum (93.2°) at $Z=7$ [7].

As expected from the expansion coefficients \bar{q}_n summarized in Tables 1 and 2, the second $P_1(\cos\bar{\theta}_{12})=\cos\bar{\theta}_{12}$ term in Eq. (9) gives a predominant contribution to the deformation of the density $\bar{A}(\bar{\theta}_{12})$

from the uniformity (Fig. 1) and hence to the increase of $\langle \bar{\theta}_{12} \rangle$ from 90° (Fig. 2). A finer analysis shows that the major contributions to the coefficient $\bar{q}_1 = \langle \cos\bar{\theta}_{12} \rangle$ come from sp electron pairs in the same shell or in neighboring shells, and the Z -dependence of $\langle \bar{\theta}_{12} \rangle$ in Fig. 2 is roughly explained by the relative significance of these electron pairs in the possible $N(N-1)/2$ electron pairs. In fact, the average angles $\langle \bar{\theta}_{12} \rangle$ have a good linear correlation with the ratios \bar{q}_1/\bar{q}_0 .

The similarity observed in the Hartree-Fock approximation between the position-space and momentum-space quantities, q_n and \bar{q}_n , $A(\theta_{12})$ and $\bar{A}(\bar{\theta}_{12})$, $\langle \theta_{12} \rangle$ and $\langle \bar{\theta}_{12} \rangle$, has theoretical origin. As discussed in the previous section, the Hartree-Fock coefficients q_n and \bar{q}_n are the sums of the direct and exchange contributions. The direct terms are determined solely by the

angular integrals A_n and are common in position and momentum spaces. On the other hand, the exchange terms depend on the radial overlap integrals $S(a, b)$ in position space and $\bar{S}(a, b)$ in momentum space. However, we find that $S(a, b) = \bar{S}(a, b)$ for two orbitals with $l_a = l_b$, when we recall the closure relation [14] of the spherical Bessel functions,

$$\frac{2a^2}{\pi} \int_0^\infty dr r^2 j_l(ar) j_l(br) = \delta(a - b), \quad (18)$$

together with Eq. (16). Therefore, the differences in the q_n and \bar{q}_n values and the resultant interelectronic angle properties arise only from the exchange terms of two orbitals with different azimuthal quantum numbers.

The inclusion of the electron correlation changes the interelectronic angle densities $\bar{A}(\bar{\theta}_{12})$ from the Hartree–Fock results. In the literature, a correlated ground-state $\bar{A}(\bar{\theta}_{12})$ is found [5] only for the Li atom. In this atom, the electron correlation works to modify the uniform Hartree–Fock density in such a manner that the density migrates from a large $\bar{\theta}_{12}$ ($> \pi/2$) to a small $\bar{\theta}_{12}$ ($< \pi/2$). The average interelectronic angle $\langle \bar{\theta}_{12} \rangle$ was calculated [5] to be 89.1° , which is smaller than the Hartree–Fock value of 90° . Thus the correlated electrons prefer parallel momenta to perpendicular or opposite momenta. Correspondingly, the correlated $\langle \cos \bar{\theta}_{12} \rangle = \bar{q}_1$ value is reported [5] as 0.04772. In position space, the electron correlation was found [7] to increase the average angles $\langle \bar{\theta}_{12} \rangle$ and to decrease the negative $\langle \cos \bar{\theta}_{12} \rangle = \bar{q}_1$ values for He–Be. The correlation contribution in momentum space is opposite to that in position space, as long as the Li atom is concerned. Correlated studies on the interelectronic angle densities of other atoms are now in progress in our laboratory.

Summary

The Hartree–Fock interelectronic angle densities $\bar{A}(\bar{\theta}_{12})$ in momentum space have been reported for the 102 atoms from He to Lr in their ground states. In the first three atoms, He, Li, and Be, $\bar{A}(\bar{\theta}_{12})$ is uniform independent of $\bar{\theta}_{12}$, while in the remaining 99 atoms, $\bar{A}(\bar{\theta}_{12})$ is larger for a large $\bar{\theta}_{12}$ than for a small $\bar{\theta}_{12}$. Accordingly, the average interelectronic angles $\langle \bar{\theta}_{12} \rangle$ in momentum space are 90° precisely for the three atoms and greater than 90° for the 99 atoms. The effect of the electron correlation was discussed for the Li atom.

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References

1. McWeeny R, Sutcliffe BT (1963) Proc R Soc Lond Ser A 273:103
2. Banyard KE, Ellis DJ (1972) Mol Phys 24:1291
3. Banyard KE, Ellis DJ (1975) J Phys B 8:2311
4. Youngman PK, Banyard KE (1987) J Phys B 20:3313
5. Banyard KE, Youngman PK (1987) J Phys B 20:5585
6. Keeble DRT, Banyard KE (1997) J Phys B 30:13
7. Koga T (2002) J Chem Phys 117:10493
8. Condon EU, Shortley GH (1970) The theory of atomic spectra. Cambridge University Press, London
9. Condon EU, Odabasi H (1980) Atomic structure. Cambridge University Press, Cambridge
10. Moore CE (1970) Ionization potentials and ionization limits derived from the analysis of optical spectra. NSRDS-NBS 34. National Bureau of Standards US, Washington, DC
11. Anderson HL (1989) A physicist's desk reference. AIP, New York, p 94
12. Froese Fischer C (1972) Comput Phys Commun 4:107
13. Talman JD (1983) Comput Phys Commun 30:93
14. Arfken GB, Weber HJ (2001) Mathematical methods for physicists, 5th edn. Harcourt/Academic, San Diego, p 735