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メタデータ	言語: English 出版者: American Institute of Physics 公開日: 2012-03-07 キーワード (Ja): キーワード (En): atomic structure, Legendre polynomials, ground states, HF calculations 作成者: 古賀, 俊勝 メールアドレス: 所属:
URL	http://hdl.handle.net/10258/828

JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 23 15 DECEMBER 2002

Interelectronic angle densities of atoms

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(Received 9 July 2002; accepted 23 September 2002)

In many-electron systems, the interelectronic angle density $A(\theta_{12})$ represents the probability density function for the interelectronic angle θ_{ij} spanned by position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ of any two electrons to be θ_{12}. It is shown that in general the interelectronic angle density $A(\theta_{12})$ is expressed by a linear combination of Legendre polynomials $P_n(\cos\theta_{12})$. Explicit formulas for the expansion coefficients are presented for atoms described by determinantal wave functions. The results are applied to the 102 atoms He through Lr in their ground states within the Hartree–Fock framework, and the expansion coefficients as well as the average interelectronic angles $\langle\theta_{12}\rangle$ are reported. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1521433]

I. INTRODUCTION

For an N-electron ($N \geqslant 2$) system described by a wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$, the spinless two-electron density function (see, e.g., Ref. 1),

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

is a convenient starting point to examine the electron–electron interaction in an explicit manner, where $\mathbf{x}_i \equiv (\mathbf{r}_i, s_i)$ is the combined position-spin coordinates of the electron i. The density function $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is normalized to $N(N-1)/2$, the number of electron pairs. In the study of electron correlations in few-electron atoms, Banyard and co-workers[2–6] (see also Ref. 7) introduced the interelectronic angle density $A(\theta_{12})$ defined by

$$A(\theta_{12}) \equiv \int \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{d\theta_{12}} \frac{\Gamma(\mathbf{r}_1,\mathbf{r}_2)}{\sin\theta_{12}}, \tag{2}$$

where $d\mathbf{r}_1\, d\mathbf{r}_2/d\theta_{12}$ means symbolically that the integration is performed over five variables except θ_{12} after one of the four angular variables of the vectors $\mathbf{r}_1=(r_1,\theta_1,\phi_1)$ and $\mathbf{r}_2=(r_2,\theta_2,\phi_2)$ is appropriately replaced with the intervector angle θ_{12} through the relation

$$\cos\theta_{12}=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2). \tag{3}$$

The interelectronic angle density $A(\theta_{12})$ is the probability density function that the angle θ_{ij} ($0 \leqslant \theta_{ij} \leqslant \pi$) 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

$$\int_0^\pi d\theta_{12}\sin\theta_{12}\; A(\theta_{12})=\frac{N(N-1)}{2}. \tag{4}$$

The density function $A(\theta_{12})$ is a useful tool to know explicitly the distribution of the interelectronic angle in atoms and molecules. However, the examination of $A(\theta_{12})$ in the literature is very limited. Only for the He, Li, Be atoms and some of their isoelectronic ions, the correlation contribution in $A(\theta_{12})$ was studied in an ad hoc manner.[2–7]

In the present paper, we first clarify the general mathematical structure of the interelectronic angle density $A(\theta_{12})$ of atoms and molecules: The density can be expressed as a linear combination of Legendre polynomials $P_n(\cos\theta_{12})$. Detailed formulas for the expansion coefficients are presented for atoms described by multideterminantal wave functions, such as Hartree–Fock and configuration interaction wave functions. The results are then applied to the 102 atoms from He to Lr in their ground states within the Hartree–Fock framework, and the expansion coefficients as well as the average interelectronic angles $\langle\theta_{12}\rangle$ are reported. Hartree atomic units are used throughout.

II. MATHEMATICAL STRUCTURE OF INTERELECTRONIC ANGLE DENSITIES

For the study of the interelectronic angle density $A(\theta_{12})$ defined by Eq. (2), it appears simplest to introduce a new variable $x=\cos\theta_{12}$ ($-1 \leqslant x \leqslant +1$) and a new function $B(x)$ such that

$$A(\theta_{12})=B(x) \tag{5a}$$

and

$$\int_{-1}^{+1} dx\, B(x)=\frac{N(N-1)}{2}, \tag{5b}$$

corresponding to Eq. (4). We implicitly assume that the function $B(x)$ and its first derivative are continuous functions of x in the interval $-1 \leqslant x \leqslant +1$.

Since the Legendre polynomials $P_n(x)$ constitute a complete set[8] in this interval, we expand the function $B(x)$ in a Legendre series,

$$B(x)=\sum_{n=0}^{\infty} c_n P_n(x). \tag{6}$$

By virtue of the orthonormality of the Legendre polynomials,[8]

$$\int_{-1}^{+1} dx\, P_m(x)P_n(x)=\frac{2}{2n+1}\delta_{mn}, \tag{7}$$

the expansion coefficients c_n in Eq. (6) are obtained as

$$c_n=\frac{2n+1}{2}\int_{-1}^{+1}dx\,P_n(x)B(x)=\frac{2n+1}{2}q_n, \tag{8}$$

where δ_{mn} is the Kronecker's delta and

$$q_n=\langle P_n(\cos\theta_{12})\rangle\equiv\int d\mathbf{r}_1\,d\mathbf{r}_2\;\;P_n(\cos\theta_{12})\Gamma(\mathbf{r}_1,\mathbf{r}_2). \tag{9}$$

Particular cases of Eq. (8) are $c_0=N(N-1)/4$ and $c_1=3\langle\cos\theta_{12}\rangle/2$, because $P_0(x)=1$ and $P_1(x)=x$. The expectation value $\langle\cos\theta_{12}\rangle$ was often examined in the literature (see Ref. 9 and the references therein).

Combining Eqs. (5a), (6), and (8), we obtain the desired result,

$$A(\theta_{12})=\sum_{n=0}^{\infty}\frac{2n+1}{2}q_nP_n(\cos\theta_{12}), \tag{10}$$

which shows that the interelectronic angle density $A(\theta_{12})$ can be expressed as a linear combination of the Legendre polynomials $P_n(\cos\theta_{12})$. An alternative derivation of Eq. (10) is given in the Appendix. Note that we did not set any restrictions to the form of the parent wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$. Therefore, the summation in Eq. (10) runs from $n=0$ to ∞ in general. However, we will soon find that the summation terminates at some finite n in the case of atomic systems described by a finite number of Slater determinants. We also note that the first $n=0$ term on the right-hand side of Eq. (10) is a constant $N(N-1)/4$ and gives a uniform distribution independent of θ_{12}. The remaining terms with $n\geqslant 1$ are responsible for the θ_{12} dependence of the interelectronic angle density $A(\theta_{12})$.

For particular values of $x=-1$, 0, and $+1$, the Legendre polynomials have values $P_n(-1)=(-1)^n$, $P_{2m}(0)=(-1)^m(2m-1)!!/(2m)!!$, $P_{2m+1}(0)=0$, and $P_n(1)=1$. Therefore, special cases of Eq. (10) for $\theta_{12}=0$, $\pi/2$, and π are

$$A(0)=\sum_{n=0}^{\infty}\frac{2n+1}{2}q_n, \tag{11a}$$

$$A(\pi/2)=\sum_{m=0}^{\infty}(-1)^m\frac{4m+1}{2}\frac{(2m-1)!!}{(2m)!!}q_{2m}, \tag{11b}$$

$$A(\pi)=\sum_{n=0}^{\infty}(-1)^n\frac{2n+1}{2}q_n, \tag{11c}$$

where only q_n with even n contribute to $A(\pi/2)$.

From Eq. (10), the average interelectronic angle $\langle\theta_{12}\rangle$, defined by

$$\langle\theta_{12}\rangle\equiv\frac{2}{N(N-1)}\int_0^{\pi}d\theta_{12}\sin\theta_{12}\theta_{12}A(\theta_{12}), \tag{12}$$

is obtained as

$$\langle\theta_{12}\rangle=\frac{1}{N(N-1)}\sum_{n=0}^{\infty}(2n+1)q_nI_n, \tag{13a}$$

$$I_n=\int_{-1}^{+1}dx\,\arccos x\,P_n(x), \tag{13b}$$

where I_n is evaluated to be

$$I_{2m}=\pi\delta_{m0}, \tag{13c}$$

$$I_{2m+1}=\pi\sum_{i=0}^{m}(-1)^{m-i}\frac{(2m+2i+1)!!}{(2i+2)!(2m-2i)!!}\times\left[\frac{(2i+1)!!}{(2i+2)!!}-1\right], \tag{13d}$$

for non-negative integers m.

We next examine the detailed expression of the expectation value $q_n=\langle P_n(\cos\theta_{12})\rangle$ appearing in Eq. (10) for determinantal wave functions of atoms. For a multideterminant wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ composed of a set of orthonormal spin–orbitals $\psi_a(\mathbf{r})\eta_a(s)$, the two-electron density function $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$ is given by

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2)=\sum_{a,b,c,d}C_{abcd}\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2), \tag{14}$$

where C_{abcd} are expansion coefficients. Then the most general two-electron integral occurring in the calculation of q_n is

$$\langle ab|P_n(\cos\theta_{12})|cd\rangle\equiv\int d\mathbf{r}_1\,d\mathbf{r}_2\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\times P_n(\cos\theta_{12})\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2), \tag{15}$$

which includes four different orbitals ψ_a, ψ_b, ψ_c, and ψ_d. In atomic systems, we can generally assume that the spatial function $\psi_a(\mathbf{r})$ is a product of the radial $R_a(r)$ and spherical harmonic $Y_a(\Omega)\equiv Y_{l_am_a}(\Omega)$ functions, where (r,Ω) with $\Omega=(\theta,\phi)$ is the polar coordinates of the vector $\mathbf{r}$. Then, Eq. (15) reduces to

$$\langle ab|P_n(\cos\theta_{12})|cd\rangle=S(a,c)S(b,d)A_n(a,b;c,d), \tag{16a}$$

where

$$S(a,b)\equiv\int_0^{\infty}dr\,r^2R_a^*(r)R_b(r)=S^*(b,a), \tag{16b}$$

$$A_n(a,b;c,d)\equiv\int d\Omega_1\,d\Omega_2\,Y_a^*(\Omega_1)Y_b^*(\Omega_2)\times P_n(\cos\theta_{12})Y_c(\Omega_1)Y_d(\Omega_2). \tag{16c}$$

Since an addition theorem[10,11] states that

$$P_n(\cos\theta_{12})=\frac{4\pi}{2n+1}\sum_{m=-n}^{n}Y_{nm}^*(\Omega_1)Y_{nm}(\Omega_2), \tag{17}$$

the two-electron angular integral (16c) is calculated to be

$$A_n(a,b;c,d)=\delta_{m_a+m_b,m_c+m_d}c^n(a,c)c^n(d,b), \tag{18a}$$

where $c^n(a,b)\equiv c^n(l_am_a,l_bm_b)$ is the Condon–Shortley parameter[10,11] defined by

TABLE I. Nonzero q_n values for the atoms with $Z=5-54$. Note that $q_0=N(N-1)/2$. For $Z=2-4$, only q_0 is nonvanishing.

Z	q_1	q_2	q_3	q_4
5	−0.325 630			
6	−0.655 956	−0.200 000		
7	−0.987 024	−0.600 000		
8	−1.308 649	−0.600 000		
9	−1.632 680	−0.800 000		
10	−1.958 681	−1.200 000		
11	−1.980 422	−1.200 000		
12	−1.989 237	−1.200 000		
13	−2.289 028	−1.200 000		
14	−2.610 932	−1.400 000		
15	−2.939 924	−1.800 000		
16	−3.258 081	−1.800 000		
17	−3.582 797	−2.000 000		
18	−3.911 468	−2.400 000		
19	−3.944 916	−2.400 000		
20	−3.964 762	−2.400 000		
21	−4.305 206	−2.588 200	−0.217 089	
22	−4.676 045	−2.940 186	−0.454 512	−0.020 408
23	−5.052 497	−3.273 280	−0.695 844	−0.163 265
24	−5.691 390	−4.056 751	−1.109 594	−0.714 286
25	−5.817 697	−4.064 451	−1.186 966	−0.714 286
26	−6.184 605	−4.256 521	−1.422 477	−0.714 286
27	−6.558 435	−4.612 129	−1.662 570	−0.734 694
28	−6.934 005	−4.947 472	−1.903 851	−0.877 551
29	−7.562 663	−5.619 296	−2.310 036	−1.428 571
30	−7.691 604	−5.740 843	−2.390 725	−1.428 571
31	−8.075 758	−5.768 693	−2.452 234	−1.428 571
32	−8.454 398	−5.985 353	−2.492 174	−1.428 571
33	−8.820 481	−6.396 421	−2.518 429	−1.428 571
34	−9.161 796	−6.404 304	−2.535 928	−1.428 571
35	−9.502 447	−6.609 850	−2.547 886	−1.428 571
36	−9.842 167	−7.013 855	−2.556 075	−1.428 571
37	−9.889 905	−7.017 884	−2.560 254	−1.428 571
38	−9.922 331	−7.020 856	−2.562 871	−1.428 571
39	−10.208 603	−7.207 798	−2.743 070	−1.428 571
40	−10.547 981	−7.552 276	−2.958 952	−1.448 980
41	−11.131 044	−8.193 109	−3.338 640	−1.857 143
42	−11.515 259	−8.660 473	−3.583 711	−2.142 857
43	−11.654 278	−8.653 008	−3.666 128	−2.142 857
44	−12.265 397	−9.112 713	−4.062 687	−2.163 265
45	−12.650 618	−9.414 194	−4.309 158	−2.306 122
46	−13.258 868	−9.941 820	−4.702 473	−2.857 143
47	−13.432 539	−10.160 290	−4.810 030	−2.857 143
48	−13.551 225	−10.314 096	−4.882 168	−2.857 143
49	−13.948 270	−10.348 400	−4.948 229	−2.857 143
50	−14.341 524	−10.570 048	−4.997 079	−2.857 143
51	−14.723 014	−10.985 429	−5.033 435	−2.857 143
52	−15.080 339	−10.997 292	−5.060 749	−2.857 143
53	−15.435 185	−11.206 316	−5.081 830	−2.857 143
54	−15.787 279	−11.613 380	−5.098 191	−2.857 143

$$c^n(l_am_a,l_bm_b)\equiv\sqrt{\frac{4\pi}{2n+1}}\int d\Omega\, Y^*_{l_am_a}(\Omega)\times Y_{n,m_a-m_b}(\Omega)Y_{l_bm_b}(\Omega). \tag{18b}$$

It is important to note that due to the property[10,11] of $c^n(a,b)$, the integral $A_n(a,b;c,d)$ vanishes unless the following four conditions are satisfied simultaneously:

$$\begin{aligned} &n+l_a+l_c=\text{even integer}, \quad n+l_b+l_d=\text{even integer},\\ &|l_a-l_c|\leqslant n\leqslant l_a+l_c, \quad |l_b-l_d|\leqslant n\leqslant l_b+l_d. \end{aligned} \tag{19}$$

Therefore, the summation in Eq. (10) 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 $\langle ab|P_n(\cos\theta_{12})|ab\rangle$ and $\langle ab|P_n(\cos\theta_{12})|ba\rangle$ appear. From the general expressions (16a) and (18a), we immediately find that

$$\langle ab|P_n(\cos\theta_{12})|ab\rangle=a^n(a,b), \tag{20a}$$

for the direct term and

$$\langle ab|P_n(\cos\theta_{12})|ba\rangle=|S(a,b)|^2b^n(a,b), \tag{20b}$$

TABLE II. Nonzero q_n values for the atoms with $Z=55-103$. Note that $q_0=N(N-1)/2$.

Z	q_1	q_2	q_3	q_4	q_5	q_6
55	−15.838 101	−11.622 148	−5.106 825	−2.857 143		
56	−15.875 383	−11.629 446	−5.112 841	−2.857 143		
57	−16.181 314	−11.813 556	−5.305 932	−2.857 143		
58	−16.593 217	−12.210 834	−5.609 698	−3.077 688	−0.185 302	
59	−16.976 061	−12.684 907	−6.029 841	−3.552 180	−0.553 197	−0.030 020
60	−17.360 985	−13.072 579	−6.343 290	−3.830 977	−0.747 146	−0.146 571
61	−17.747 886	−13.415 802	−6.657 593	−4.118 093	−0.942 191	−0.351 416
62	−18.140 040	−13.825 253	−6.974 122	−4.440 767	−1.140 013	−0.582 751
63	−18.537 532	−14.345 298	−7.292 885	−4.809 953	−1.340 644	−0.815 851
64	−18.951 614	−14.526 985	−7.533 683	−4.809 464	−1.395 525	−0.815 851
65	−19.302 908	−14.967 293	−7.918 264	−5.234 515	−1.726 764	−0.817 617
66	−19.692 223	−15.399 837	−8.233 746	−5.505 600	−1.923 306	−0.845 871
67	−20.081 681	−15.788 001	−8.549 309	−5.785 022	−2.119 956	−0.962 421
68	−20.471 158	−16.131 789	−8.864 902	−6.072 780	−2.316 647	−1.167 267
69	−20.863 247	−16.541 962	−9.181 596	−6.396 173	−2.514 711	−1.398 601
70	−21.258 591	−17.062 861	−9.499 652	−6.766 143	−2.714 475	−1.631 702
71	−21.670 114	−17.246 557	−9.731 638	−6.764 946	−2.785 640	−1.631 702
72	−22.100 965	−17.588 905	−9.984 362	−6.785 778	−2.839 915	−1.631 702
73	−22.526 089	−17.912 432	−10.239 286	−6.930 021	−2.881 518	−1.631 702
74	−22.945 654	−18.217 005	−10.494 925	−7.197 201	−2.913 841	−1.631 702
75	−23.364 713	−18.684 890	−10.753 435	−7.484 971	−2.939 272	−1.631 702
76	−23.760 057	−18.874 210	−10.999 018	−7.487 155	−2.959 231	−1.631 702
77	−24.159 203	−19.225 575	−11.248 886	−7.509 646	−2.975 249	−1.631 702
78	−24.817 919	−19.703 900	−11.669 830	−7.919 206	−2.991 219	−1.631 702
79	−25.226 378	−20.154 234	−11.928 054	−8.206 774	−3.001 311	−1.631 702
80	−25.357 000	−20.341 298	−12.006 008	−8.208 947	−3.006 961	−1.631 702
81	−25.772 918	−20.380 162	−12.083 831	−8.211 147	−3.011 380	−1.631 702
82	−26.184 448	−20.606 168	−12.144 741	−8.213 186	−3.014 757	−1.631 702
83	−26.583 329	−21.025 709	−12.192 774	−8.215 012	−3.017 387	−1.631 702
84	−26.956 896	−21.041 542	−12.230 954	−8.216 584	−3.019 474	−1.631 702
85	−27.326 853	−21.254 207	−12.262 266	−8.217 956	−3.021 134	−1.631 702
86	−27.692 907	−21.664 601	−12.288 151	−8.219 141	−3.022 465	−1.631 702
87	−27.752 775	−21.678 481	−12.302 230	−8.220 040	−3.023 563	−1.631 702
88	−27.798 735	−21.690 734	−12.312 618	−8.220 770	−3.024 455	−1.631 702
89	−28.100 108	−21.875 669	−12.502 433	−8.221 338	−3.025 232	−1.631 702
90	−28.434 984	−22.219 128	−12.714 975	−8.242 210	−3.025 866	−1.631 702
91	−28.880 574	−22.401 574	−13.108 915	−8.650 846	−3.353 504	−1.633 468
92	−29.234 812	−22.888 969	−13.423 577	−8.918 289	−3.536 532	−1.661 722
93	−29.597 915	−23.350 150	−13.737 913	−9.186 259	−3.725 512	−1.778 272
94	−29.884 289	−23.881 527	−14.093 055	−9.796 633	−4.066 455	−2.214 452
95	−30.273 450	−24.397 502	−14.406 926	−10.162 393	−4.262 096	−2.447 552
96	−30.725 223	−24.575 479	−14.665 446	−10.161 108	−4.332 520	−2.447 552
97	−31.096 132	−24.733 811	−14.969 892	−10.343 225	−4.523 569	−2.447 552
98	−31.429 793	−25.441 898	−15.344 944	−10.849 441	−4.843 569	−2.477 573
99	−31.824 801	−25.826 053	−15.661 500	−11.125 586	−5.042 446	−2.594 123
100	−32.222 194	−26.165 718	−15.979 056	−11.410 004	−5.242 598	−2.798 969
101	−32.623 602	−26.571 516	−16.298 192	−11.729 888	−5.444 863	−3.030 303
102	−33.029 195	−27.087 780	−16.618 936	−12.096 173	−5.649 324	−3.263 403
103	−33.455 959	−27.270 507	−16.861 009	−12.097 061	−5.720 015	−3.263 403

for the exchange term, 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.[10,11] Because of the condition (19), Eq. (20a) has nonzero values only for even integers n ranging from 0 to $\min(2l_a,2l_b)$, while Eq. (20b) only for every other integers n between $|l_a-l_b|$ and l_a+l_b.

III. NUMERICAL RESULTS FOR ATOMS

The experimental ground electronic configurations and LS terms[12,13] were considered for all the 102 atoms He (atomic number $Z=2$) through Lr ($Z=103$). For these states, the radial functions $R_a(r)$ were generated by the numerical Hartree–Fock method based on a modified version of the MCHF72 program.[14] Equations (20a) and (20b) were used to compute the contributions of two spin–orbitals to $\langle P_n(\cos\theta_{12})\rangle$, where the $a^n(a,b)$ and $b^n(a,b)$ values were taken from Refs. 10 and 11.

The numerical results of nonzero q_n values are summarized in Table I for the second through fifth period atoms and in Table II for the sixth and seventh period atoms. The q_0 value is not given, because it is $N(N-1)/2$, the number of electron pairs. When we consider the ground states of the 102 atoms, the occupied orbitals have the azimuthal quantum numbers $l=0-3$ in the Hartree–Fock theory. Due to the

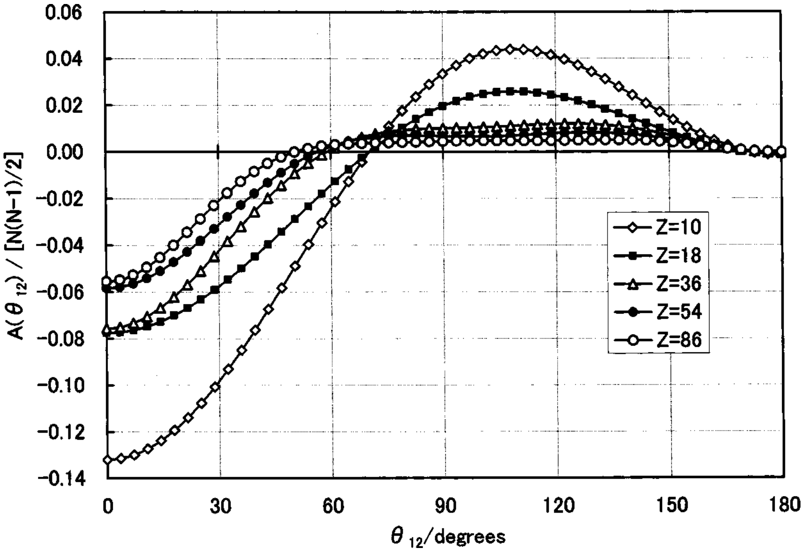

FIG. 1. The interelectronic angle densities $A(\theta_{12})$ for the five rare-gas atoms Ne, Ar, Kr, Xe, and Rn. The densities are normalized to unity, instead of $N(N-1)/2$, and the uniform contribution from the $P_0(\cos\theta_{12})=1$ term is excluded.

condition (19), the maximal n of nonzero q_n is therefore 6 at most. The first three atoms He, Li, and Be do not appear in Table I, since only $s(l=0)$ orbitals are occupied and all q_n, except q_0, vanish for these atoms. We find in Tables I and II that the nonzero q_n are negative for all n except $n=0$. For a given Z, the magnitudes $|q_n|$ decrease with increasing n. For a given n, $|q_n|$ increase with increasing Z in general. Some atoms with analogous valence electron configurations have the same q_n value for the largest n, since it originates from the contribution of two electrons in the outermost subshell with the maximal l.

The interelectronic angle densities $A(\theta_{12})$ are exemplified in Fig. 1 for the five rare-gas atoms Ne, Ar, Kr, Xe, and Rn, where $A(\theta_{12})$ 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 $P_0(\cos\theta_{12})=1$ term of Eq. (10) to clarify the deformation of $A(\theta_{12})$ from the uniform distribution. In Fig. 1, we find that the interelectronic angle density is small for a smaller θ_{12} and large for a larger θ_{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 be on opposite sides of the nucleus without exceptions. The minimum in $A(\theta_{12})$ is observed at $\theta_{12}=0$ degrees for all the five atoms, while the maximum is at $\theta_{12}=109$, 109, 124, 129, and 136 degrees for the Ne, Ar, Kr, Xe, and Rn atoms, respectively.

Using Eq. (13), we have also calculated the average interelectronic angle $\langle\theta_{12}\rangle$. The results for the 102 atoms are plotted in Fig. 2 as a function of Z. For the first three atoms with $Z=2-4$, $\langle\theta_{12}\rangle$ is 90 degrees precisely and the position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ of two electrons are perpendicular in an average sense. For the remaining 99 atoms, on the other hand, the average angle $\langle\theta_{12}\rangle$ is always greater than 90 degrees. When Z increases from 5 to 103, $\langle\theta_{12}\rangle$ first increases, takes a maximum (93.2 degrees) at $Z=7$, and then decreases towards a minimum (90.5 degrees) at $Z=103$. As anticipated from Fig. 1, the second $P_1(\cos\theta_{12})=\cos\theta_{12}$ term in Eq. (10) gives a predominant contribution to the deformation of the density $A(\theta_{12})$ from the uniformity and hence to the increase

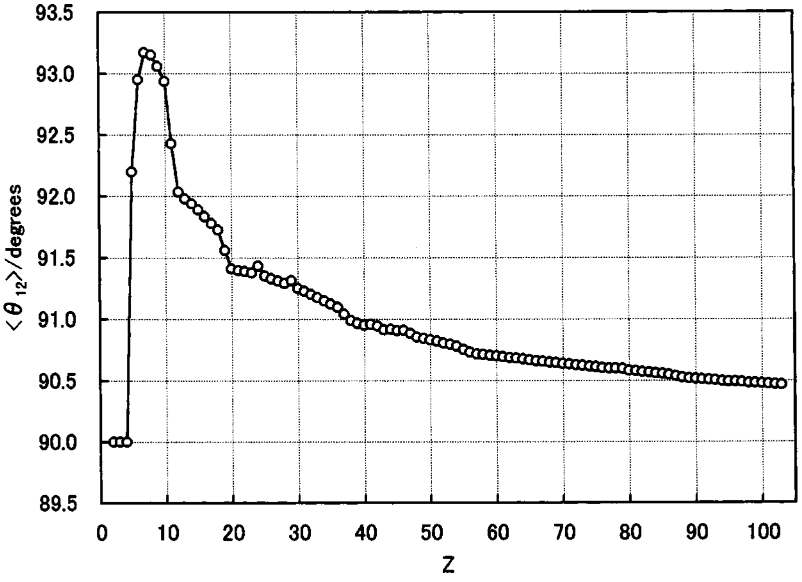

FIG. 2. The average interelectronic angle $\langle\theta_{12}\rangle$ as a function of atomic number Z.

of $\langle \theta_{12} \rangle$ from 90 degrees. A previous study[9] showed that the major contributions to the coefficient $q_1 = \langle \cos \theta_{12} \rangle$ come from sp electron pairs in the same shell, and the Z dependence of $\langle \theta_{12} \rangle$ 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 Z dependence of $\langle \theta_{12} \rangle$ shows a close parallelism with that of $\arccos(\langle \cos \theta_{12} \rangle)$ given in Ref. 9.

The inclusion of the electron correlation changes the interelectronic angle densities $A(\theta_{12})$ from the Hartree–Fock results. In the literature, correlated $A(\theta_{12})$ is found[2] only for the He and Be atoms. In both atoms, the electron correlation works to modify the uniform Hartree–Fock density in such a manner that the density migrates from a small θ_{12} ($<\pi/2$) to a large θ_{12} ($>\pi/2$). On the other hand, the correlated $\langle \cos \theta_{12} \rangle = q_1$ values are reported to be -0.0642, -0.0641, and -0.3582 for the He,[15–17] Li,[18] and Be[19] atoms, respectively. The values for the He and Be atoms are consistent with the correlation effect observed in $A(\theta_{12})$, if we recall that the corresponding Hartree–Fock values are zero. Clearly, the correlated average interelectronic angles $\langle \theta_{12} \rangle$ are greater than 90 degrees, though the values are not reported in the literature.[2,15–19] Since the Hartree–Fock $\langle \theta_{12} \rangle$ values are 90 degrees for the atoms, the electron correlation works to increase the interelectronic angles.

IV. SUMMARY

We showed that the interelectronic angle density $A(\theta_{12})$ is generally expressed by a linear combination of Legendre polynomials $P_n(\cos \theta_{12})$. Explicit formulas for the expansion coefficients were presented for atoms described by determinantal wave functions. The results were applied to the 102 atoms He through Lr in their ground states within the Hartree–Fock framework, and the expansion coefficients as well as the average interelectronic angles $\langle \theta_{12} \rangle$ were reported. The effect of the electron correlation was discussed for three light atoms.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

APPENDIX:ALTERNATIVE DERIVATION OF INTERELECTRONIC ANGLE DENSITIES

If we use techniques of the Dirac delta function $\delta(x)$, we can derive Eq. (10) in an alternative but less familiar way. The interelectronic angle density $A(\theta_{12})$, given by Eq. (2), is rewritten as

$$A(\theta_{12}) = \int d\mathbf{r}_1' \, d\mathbf{r}_2' \, \delta(\theta_{12} - \theta_{12}') \frac{\Gamma(\mathbf{r}_1', \mathbf{r}_2')}{\sin \theta_{12}'}, \tag{A1}$$

where θ_{12}' is the angle between the vectors $\mathbf{r}_1'$ and $\mathbf{r}_2'$. Using an identity

$$\delta(\theta - \theta') = \delta(\cos \theta - \cos \theta') \sin \theta, \tag{A2}$$

we first obtain

$$A(\theta_{12}) = \int d\mathbf{r}_1' \, d\mathbf{r}_2' \, \delta(\cos \theta_{12} - \cos \theta_{12}') \Gamma(\mathbf{r}_1', \mathbf{r}_2'). \tag{A3}$$

We next apply the formal expansion of the Dirac delta function $\delta(x - x')$ in terms of a complete set of Legendre polynomials $P_n(x)$,

$$\delta(x - x') = \sum_{n=0}^{\infty} \frac{2n+1}{2} P_n(x) P_n(x'), \tag{A4}$$

to Eq. (A3) together with the substitutions $x = \cos \theta_{12}$ and $x' = \cos \theta_{12}'$. Then we arrive at Eq. (10) again.

[1] A. J. Thakkar, in *Density Matrices and Density Functionals*, edited by R. M. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), pp. 553–581.
[2] K. E. Banyard and D. J. Ellis, Mol. Phys. **24**, 1291 (1972).
[3] K. E. Banyard and D. J. Ellis, J. Phys. B **8**, 2311 (1975).
[4] P. K. Youngman and K. E. Banyard, J. Phys. B **20**, 3313 (1987).
[5] K. E. Banyard and P. K. Youngman, J. Phys. B **20**, 5585 (1987).
[6] D. R. T. Keeble and K. E. Banyard, J. Phys. B **30**, 13 (1997).
[7] R. McWeeny and B. T. Sutcliffe, Proc. R. Soc. London, Ser. A **273**, 103 (1963).
[8] G. B. Arfken and H. J. Weber, *Mathematical Methods for Physicists*, 5th ed. (Harcourt/Academic, San Diego, 2001).
[9] T. Koga, Chem. Phys. Lett. **363**, 598 (2002).
[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1970).
[11] E. U. Condon and H. Odabasi, *Atomic Structure* (Cambridge University Press, Cambridge, 1980).
[12] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*. NSRDS-NBS 34 (Nat. Bur. Stand., Washington, DC, 1970).
[13] H. L. Anderson, *A Physicist's Desk Reference* (AIP Press, New York, 1989), p. 94.
[14] C. Froese Fischer, Comput. Phys. Commun. **4**, 107 (1972).
[15] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 1 (1977).
[16] P. E. Regier and A. J. Thakkar, J. Phys. B **18**, 3061 (1985).
[17] H. E. Montgomery, Jr., Chem. Phys. Lett. **294**, 468 (1998).
[18] K. E. Banyard and K. H. Al-Bayati, J. Phys. B **19**, 2211 (1986).
[19] K. E. Banyard and R. J. Mobbs, J. Chem. Phys. **75**, 3433 (1981).