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# Interelectronic angle densities of atoms 

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In many-electron systems, the interelectronic angle density $A\left(\theta_{12}\right)$ represents the probability density function for the interelectronic angle $\theta_{i j}$ spanned by position vectors $\mathbf{r}_{i}$ and $\mathbf{r}_{j}$ of any two electrons to be $\theta_{12}$. It is shown that in general the interelectronic angle density $A\left(\theta_{12}\right)$ is expressed by a linear combination of Legendre polynomials $P_{n}\left(\cos \theta_{12}\right)$. 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 $\left\langle\theta_{12}\right\rangle$ 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 $\Psi\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{N}\right)$, the spinless two-electron density function (see, e.g., Ref. 1),
$\Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\frac{N(N-1)}{2} \int d s_{1} d s_{2} d \mathbf{x}_{3} \ldots d \mathbf{x}_{N}\left|\Psi\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{N}\right)\right|^{2}$,
is a convenient starting point to examine the electronelectron interaction in an explicit manner, where $\mathbf{x}_{i} \equiv\left(\mathbf{r}_{i}, s_{i}\right)$ is the combined position-spin coordinates of the electron $i$. The density function $\Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ 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 $A\left(\theta_{12}\right)$ defined by

$$
\begin{equation*}
A\left(\theta_{12}\right) \equiv \int \frac{d \mathbf{r}_{1} d \mathbf{r}_{2}}{d \theta_{12}} \frac{\Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)}{\sin \theta_{12}}, \tag{2}
\end{equation*}
$$

where $d \mathbf{r}_{1} d \mathbf{r}_{2} / d \theta_{12}$ means symbolically that the integration is performed over five variables except $\theta_{12}$ after one of the four angular variables of the vectors $\mathbf{r}_{1}=\left(r_{1}, \theta_{1}, \phi_{1}\right)$ and $\mathbf{r}_{2}=\left(r_{2}, \theta_{2}, \phi_{2}\right)$ is appropriately replaced with the intervector angle $\theta_{12}$ through the relation

$$
\begin{equation*}
\cos \theta_{12}=\cos \theta_{1} \cos \theta_{2}+\sin \theta_{1} \sin \theta_{2} \cos \left(\phi_{1}-\phi_{2}\right) \tag{3}
\end{equation*}
$$

The interelectronic angle density $A\left(\theta_{12}\right)$ is the probability density function that the angle $\theta_{i j}\left(0 \leqslant \theta_{i j} \leqslant \pi\right)$ subtended by the position vectors $\mathbf{r}_{i}$ and $\mathbf{r}_{j}$ of any two electrons $i$ and $j$ becomes $\theta_{12}$, and is normalized as

$$
\begin{equation*}
\int_{0}^{\pi} d \theta_{12} \sin \theta_{12} A\left(\theta_{12}\right)=\frac{N(N-1)}{2} . \tag{4}
\end{equation*}
$$

The density function $A\left(\theta_{12}\right)$ is a useful tool to know explicitly the distribution of the interelectronic angle in atoms and molecules. However, the examination of $A\left(\theta_{12}\right)$ in the literature is very limited. Only for the $\mathrm{He}, \mathrm{Li}, \mathrm{Be}$ atoms and some of their isoelectronic ions, the correlation contribution in $A\left(\theta_{12}\right)$ 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 $A\left(\theta_{12}\right)$ of atoms and molecules: The density can be expressed as a linear combination of Legendre polynomials $P_{n}\left(\cos \theta_{12}\right)$. 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 $\left\langle\theta_{12}\right\rangle$ are reported. Hartree atomic units are used throughout.

## II. MATHEMATICAL STRUCTURE OF INTERELECTRONIC ANGLE DENSITIES

For the study of the interelectronic angle density $A\left(\theta_{12}\right)$ 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

$$
\begin{equation*}
A\left(\theta_{12}\right)=B(x) \tag{5a}
\end{equation*}
$$

and

$$
\begin{equation*}
\int_{-1}^{+1} d x B(x)=\frac{N(N-1)}{2}, \tag{5b}
\end{equation*}
$$

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 $\operatorname{set}^{8}$ in this interval, we expand the function $B(x)$ in a Legendre series,

$$
\begin{equation*}
B(x)=\sum_{n=0}^{\infty} c_{n} P_{n}(x) \tag{6}
\end{equation*}
$$

By virtue of the orthonormality of the Legendre polynomials, ${ }^{8}$

$$
\begin{equation*}
\int_{-1}^{+1} d x P_{m}(x) P_{n}(x)=\frac{2}{2 n+1} \delta_{m n}, \tag{7}
\end{equation*}
$$

the expansion coefficients $c_{n}$ in Eq. (6) are obtained as

$$
\begin{equation*}
c_{n}=\frac{2 n+1}{2} \int_{-1}^{+1} d x P_{n}(x) B(x)=\frac{2 n+1}{2} q_{n}, \tag{8}
\end{equation*}
$$

where $\delta_{m n}$ is the Kronecker's delta and

$$
\begin{equation*}
q_{n}=\left\langle P_{n}\left(\cos \theta_{12}\right)\right\rangle \equiv \int d \mathbf{r}_{1} d \mathbf{r}_{2} P_{n}\left(\cos \theta_{12}\right) \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \tag{9}
\end{equation*}
$$

Particular cases of Eq. (8) are $c_{0}=N(N-1) / 4$ and $c_{1}$ $=3\left\langle\cos \theta_{12}\right\rangle / 2$, because $P_{0}(x)=1$ and $P_{1}(x)=x$. The expectation value $\left\langle\cos \theta_{12}\right\rangle$ was often examined in the literature (see Ref. 9 and the references therein).

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

$$
\begin{equation*}
A\left(\theta_{12}\right)=\sum_{n=0}^{\infty} \frac{2 n+1}{2} q_{n} P_{n}\left(\cos \theta_{12}\right) \tag{10}
\end{equation*}
$$

which shows that the interelectronic angle density $A\left(\theta_{12}\right)$ can be expressed as a linear combination of the Legendre polynomials $P_{n}\left(\cos \theta_{12}\right)$. 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 $\Psi\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{N}\right)$. Therefore, the summation in Eq. (10) runs from $n=0$ to $\infty$ 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 righthand side of Eq. (10) is a constant $N(N-1) / 4$ and gives a uniform distribution independent of $\theta_{12}$. The remaining terms with $n \geqslant 1$ are responsible for the $\theta_{12}$ dependence of the interelectronic angle density $A\left(\theta_{12}\right)$.

For particular values of $x=-1,0$, and +1 , the Legendre polynomials have values $P_{n}(-1)=(-1)^{n}, \quad P_{2 m}(0)$ $=(-1)^{m}(2 m-1)!!/(2 m)!!, P_{2 m+1}(0)=0$, and $P_{n}(1)=1$. Therefore, special cases of Eq. (10) for $\theta_{12}=0, \pi / 2$, and $\pi$ are
$A(0)=\sum_{n=0}^{\infty} \frac{2 n+1}{2} q_{n}$,
$A(\pi / 2)=\sum_{m=0}^{\infty}(-1)^{m} \frac{4 m+1}{2} \frac{(2 m-1)!!}{(2 m)!!} q_{2 m}$,
$A(\pi)=\sum_{n=0}^{\infty}(-1)^{n} \frac{2 n+1}{2} q_{n}$,
where only $q_{n}$ with even $n$ contribute to $A(\pi / 2)$.
From Eq. (10), the average interelectronic angle $\left\langle\theta_{12}\right\rangle$, defined by

$$
\begin{equation*}
\left\langle\theta_{12}\right\rangle \equiv \frac{2}{N(N-1)} \int_{0}^{\pi} d \theta_{12} \sin \theta_{12} \theta_{12} A\left(\theta_{12}\right), \tag{12}
\end{equation*}
$$

is obtained as

$$
\begin{equation*}
\left\langle\theta_{12}\right\rangle=\frac{1}{N(N-1)} \sum_{n=0}^{\infty}(2 n+1) q_{n} I_{n} \tag{13a}
\end{equation*}
$$

$$
\begin{equation*}
I_{n}=\int_{-1}^{+1} d x \arccos x P_{n}(x), \tag{13b}
\end{equation*}
$$

where $I_{n}$ is evaluated to be

$$
\begin{align*}
I_{2 m}=\pi & \delta_{m 0}  \tag{13c}\\
I_{2 m+1}= & \pi \sum_{i=0}^{m}(-1)^{m-i} \frac{(2 m+2 i+1)!!}{(2 i+2)!(2 m-2 i)!!} \\
& \times\left[\frac{(2 i+1)!!}{(2 i+2)!!}-1\right] \tag{13d}
\end{align*}
$$

for non-negative integers $m$.
We next examine the detailed expression of the expectation value $q_{n}=\left\langle P_{n}\left(\cos \theta_{12}\right)\right\rangle$ appearing in Eq. (10) for determinantal wave functions of atoms. For a multideterminant wave function $\Psi\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{N}\right)$ composed of a set of orthonormal spin-orbitals $\psi_{a}(\mathbf{r}) \eta_{a}(s)$, the two-electron density function $\Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ is given by

$$
\begin{equation*}
\Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\sum_{a, b, c, d} C_{a b c d} \psi_{a}^{*}\left(\mathbf{r}_{1}\right) \psi_{b}^{*}\left(\mathbf{r}_{2}\right) \psi_{c}\left(\mathbf{r}_{1}\right) \psi_{d}\left(\mathbf{r}_{2}\right), \tag{14}
\end{equation*}
$$

where $C_{a b c d}$ are expansion coefficients. Then the most general two-electron integral occurring in the calculation of $q_{n}$ is

$$
\begin{align*}
\langle a b| P_{n}\left(\cos \theta_{12}\right)|c d\rangle \equiv & \int d \mathbf{r}_{1} d \mathbf{r}_{2} \psi_{a}^{*}\left(\mathbf{r}_{1}\right) \psi_{b}^{*}\left(\mathbf{r}_{2}\right) \\
& \times P_{n}\left(\cos \theta_{12}\right) \psi_{c}\left(\mathbf{r}_{1}\right) \psi_{d}\left(\mathbf{r}_{2}\right) \tag{15}
\end{align*}
$$

which includes four different orbitals $\psi_{a}, \psi_{b}, \psi_{c}$, and $\psi_{d}$. 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 $Y_{a}(\Omega) \equiv Y_{l_{a} m_{a}}(\Omega)$ functions, where $(r, \Omega)$ with $\Omega=(\theta, \phi)$ is the polar coordinates of the vector $\mathbf{r}$. Then, Eq. (15) reduces to
$\langle a b| P_{n}\left(\cos \theta_{12}\right)|c d\rangle=S(a, c) S(b, d) A_{n}(a, b ; c, d)$,
where

$$
\begin{align*}
& S(a, b) \equiv \int_{0}^{\infty} d r r^{2} R_{a}^{*}(r) R_{b}(r)=S^{*}(b, a)  \tag{16b}\\
& A_{n}(a, b ; c, d) \equiv \int d \Omega_{1} d \Omega_{2} Y_{a}^{*}\left(\Omega_{1}\right) Y_{b}^{*}\left(\Omega_{2}\right) \\
& \times P_{n}\left(\cos \theta_{12}\right) Y_{c}\left(\Omega_{1}\right) Y_{d}\left(\Omega_{2}\right) \tag{16c}
\end{align*}
$$

Since an addition theorem ${ }^{10,11}$ states that
$P_{n}\left(\cos \theta_{12}\right)=\frac{4 \pi}{2 n+1} \sum_{m=-n}^{n} Y_{n m}^{*}\left(\Omega_{1}\right) Y_{n m}\left(\Omega_{2}\right)$,
the two-electron angular integral (16c) is calculated to be

$$
\begin{equation*}
A_{n}(a, b ; c, d)=\delta_{m_{a}+m_{b}, m_{c}+m_{d}} c^{n}(a, c) c^{n}(d, b), \tag{18a}
\end{equation*}
$$

where $c^{n}(a, b) \equiv c^{n}\left(l_{a} m_{a}, l_{b} m_{b}\right)$ 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 | $-0.325630$ |  |  |  |
| 6 | -0.655 956 | $-0.200000$ |  |  |
| 7 | -0.987 024 | -0.600 000 |  |  |
| 8 | -1.308 649 | -0.600 000 |  |  |
| 9 | -1.632680 | -0.800 000 |  |  |
| 10 | -1.958681 | - 1.200000 |  |  |
| 11 | -1.980 422 | -1.200 000 |  |  |
| 12 | -1.989 237 | -1.200 000 |  |  |
| 13 | -2.289 028 | -1.200 000 |  |  |
| 14 | -2.610932 | -1.400 000 |  |  |
| 15 | -2.939 924 | -1.800 000 |  |  |
| 16 | -3.258 081 | -1.800 000 |  |  |
| 17 | -3.582797 | $-2.000000$ |  |  |
| 18 | -3.911468 | -2.400 000 |  |  |
| 19 | -3.944 916 | -2.400 000 |  |  |
| 20 | -3.964 762 | -2.400 000 |  |  |
| 21 | -4.305 206 | -2.588200 | -0.217 089 |  |
| 22 | -4.676045 | -2.940 186 | -0.454512 | -0.020 408 |
| 23 | -5.052 497 | -3.273280 | -0.695 844 | -0.163 265 |
| 24 | - 5.691390 | -4.056 751 | -1.109594 | -0.714286 |
| 25 | -5.817697 | -4.064 451 | -1.186 966 | -0.714286 |
| 26 | -6.184 605 | -4.256521 | -1.422 477 | -0.714286 |
| 27 | -6.558 435 | -4.612 129 | -1.662570 | -0.734 694 |
| 28 | -6.934 005 | -4.947 472 | -1.903851 | -0.877 551 |
| 29 | -7.562 663 | -5.619296 | -2.310 036 | -1.428 571 |
| 30 | -7.691604 | -5.740 843 | -2.390 725 | -1.428571 |
| 31 | -8.075 758 | -5.768 693 | -2.452 234 | -1.428571 |
| 32 | -8.454 398 | -5.985 353 | -2.492 174 | -1.428571 |
| 33 | -8.820 481 | -6.396 421 | -2.518 429 | -1.428571 |
| 34 | -9.161 796 | -6.404 304 | -2.535928 | -1.428571 |
| 35 | -9.502 447 | -6.609 850 | -2.547886 | -1.428571 |
| 36 | -9.842 167 | -7.013 855 | -2.556 075 | -1.428571 |
| 37 | -9.889 905 | -7.017884 | -2.560254 | -1.428 571 |
| 38 | -9.922 331 | -7.020 856 | -2.562 871 | -1.428571 |
| 39 | -10.208603 | -7.207798 | -2.743 070 | -1.428571 |
| 40 | -10.547981 | -7.552 276 | -2.958 952 | -1.448980 |
| 41 | -11.131044 | -8.193109 | -3.338640 | -1.857 143 |
| 42 | $-11.515259$ | -8.660 473 | $-3.583711$ | -2.142857 |
| 43 | -11.654 278 | -8.653 008 | -3.666 128 | -2.142857 |
| 44 | -12.265397 | -9.112713 | -4.062 687 | -2.163 265 |
| 45 | -12.650618 | -9.414 194 | -4.309 158 | -2.306 122 |
| 46 | -13.258868 | -9.941820 | -4.702 473 | -2.857 143 |
| 47 | -13.432539 | -10.160 290 | -4.810 030 | -2.857 143 |
| 48 | -13.551225 | -10.314 096 | -4.882 168 | -2.857143 |
| 49 | -13.948270 | $-10.348400$ | -4.948229 | -2.857 143 |
| 50 | -14.341524 | -10.570 048 | -4.997 079 | -2.857 143 |
| 51 | - 14.723014 | -10.985 429 | -5.033 435 | -2.857 143 |
| 52 | -15.080 339 | -10.997292 | -5.060 749 | -2.857 143 |
| 53 | -15.435185 | -11.206 316 | -5.081830 | -2.857 143 |
| 54 | $-15.787279$ | -11.613380 | $-5.098191$ | -2.857 143 |

$$
\begin{align*}
c^{n}\left(l_{a} m_{a}, l_{b} m_{b}\right) \equiv & \sqrt{\frac{4 \pi}{2 n+1}} \int d \Omega Y_{l_{a} m_{a}}^{*}(\Omega) \\
& \times Y_{n, m_{a}-m_{b}}(\Omega) Y_{l_{b} m_{b}}(\Omega) \tag{18b}
\end{align*}
$$

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:

$$
\begin{align*}
& n+l_{a}+l_{c}=\text { even integer, } \quad n+l_{b}+l_{d}=\text { even integer, } \\
& \left|l_{a}-l_{c}\right| \leqslant n \leqslant l_{a}+l_{c}, \quad\left|l_{b}-l_{d}\right| \leqslant n \leqslant l_{b}+l_{d} \tag{19}
\end{align*}
$$

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 $\langle a b| P_{n}\left(\cos \theta_{12}\right)|a b\rangle$ and $\langle a b| P_{n}\left(\cos \theta_{12}\right)|b a\rangle$ appear. From the general expressions (16a) and (18a), we immediately find that

$$
\begin{equation*}
\langle a b| P_{n}\left(\cos \theta_{12}\right)|a b\rangle=a^{n}(a, b), \tag{20a}
\end{equation*}
$$

for the direct term and

$$
\begin{equation*}
\langle a b| P_{n}\left(\cos \theta_{12}\right)|b a\rangle=|S(a, b)|^{2} b^{n}(a, b), \tag{20b}
\end{equation*}
$$

TABLE II. Nonzero $q_{n}$ values for the atoms with $Z=55-103$. Note that $q_{0}=N(N-1) / 2$.

| $Z$ | $q_{1}$ | $q_{2}$ | $q_{3}$ | $q_{4}$ |
| ---: | ---: | :---: | ---: | :--- |

for the exchange term, where $a^{n}(a, b) \equiv c^{n}(a, a) c^{n}(b, b)$ and $b^{n}(a, b) \equiv\left[c^{n}(a, b)\right]^{2}$ 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 $\min \left(2 l_{a}, 2 l_{b}\right)$, while Eq. (20b) only for every other integers $n$ between $\left|l_{a}-l_{b}\right|$ and $l_{a}+l_{b}$.

## III. NUMERICAL RESULTS FOR ATOMS

The experimental ground electronic configurations and $L S$ terms ${ }^{12,13}$ were considered for all the 102 atoms He (atomic number $Z=2$ ) through $\operatorname{Lr}(Z=103)$. For these states, the radial functions $R_{a}(r)$ were generated by the nu-
merical 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 $\left\langle P_{n}\left(\cos \theta_{12}\right)\right\rangle$, 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 $A\left(\theta_{12}\right)$ for the five rare-gas atoms $\mathrm{Ne}, \mathrm{Ar}, \mathrm{Kr}, \mathrm{Xe}$, and Rn . The densities are normalized to unity, instead of $N(N$ $-1) / 2$, and the uniform contribution from the $P_{0}\left(\cos \theta_{12}\right)=1$ term is excluded.
condition (19), the maximal $n$ of nonzero $q_{n}$ is therefore 6 at most. The first three atoms $\mathrm{He}, \mathrm{Li}$, 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 $\left|q_{n}\right|$ decrease with increasing $n$. For a given $n,\left|q_{n}\right|$ 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 $A\left(\theta_{12}\right)$ are exemplified in Fig. 1 for the five rare-gas atoms $\mathrm{Ne}, \mathrm{Ar}, \mathrm{Kr}, \mathrm{Xe}$, and Rn, where $A\left(\theta_{12}\right)$ 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 $P_{0}\left(\cos \theta_{12}\right)=1$ term of Eq. (10) to clarify the deformation of $A\left(\theta_{12}\right)$ from the uniform distribution. In Fig. 1, we find that the interelectronic angle density is small for a smaller $\theta_{12}$ and large for a larger $\theta_{12}$ in all the
atoms, though the degree of the deformation decreases as $Z$ increases. Thus two electrons in an atom have a tendency to be on opposite sides of the nucleus without exceptions. The minimum in $A\left(\theta_{12}\right)$ 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 $\mathrm{Ne}, \mathrm{Ar}, \mathrm{Kr}, \mathrm{Xe}$, and Rn atoms, respectively.

Using Eq. (13), we have also calculated the average interelectronic angle $\left\langle\theta_{12}\right\rangle$. The results for the 102 atoms are plotted in Fig. 2 as a function of $Z$. For the first three atoms with $Z=2-4,\left\langle\theta_{12}\right\rangle$ 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 $\left\langle\theta_{12}\right\rangle$ is always greater than 90 degrees. When $Z$ increases from 5 to $103,\left\langle\theta_{12}\right\rangle$ 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 $P_{1}\left(\cos \theta_{12}\right)=\cos \theta_{12}$ term in Eq. (10) gives a predominant contribution to the deformation of the density $A\left(\theta_{12}\right)$ from the uniformity and hence to the increase


FIG. 2. The average interelectronic angle $\left\langle\theta_{12}\right\rangle$ as a function of atomic number $Z$.
of $\left\langle\theta_{12}\right\rangle$ from 90 degrees. A previous study ${ }^{9}$ showed that the major contributions to the coefficient $q_{1}=\left\langle\cos \theta_{12}\right\rangle$ come from $s p$ electron pairs in the same shell, and the $Z$ dependence of $\left\langle\theta_{12}\right\rangle$ 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 $\left\langle\theta_{12}\right\rangle$ shows a close parallelism with that of $\arccos \left(\left\langle\cos \theta_{12}\right\rangle\right)$ given in Ref. 9.

The inclusion of the electron correlation changes the interelectronic angle densities $A\left(\theta_{12}\right)$ from the Hartree-Fock results. In the literature, correlated $A\left(\theta_{12}\right)$ 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 $\theta_{12}(<\pi / 2)$ to a large $\theta_{12}(>\pi / 2)$. On the other hand, the correlated $\left\langle\cos \theta_{12}\right\rangle=q_{1}$ values are reported to be $-0.0642,-0.0641$, and -0.3582 for the $\mathrm{He},{ }^{15-17} \mathrm{Li},{ }^{18}$ and $\mathrm{Be}^{19}$ atoms, respectively. The values for the He and Be atoms are consistent with the correlation effect observed in $A\left(\theta_{12}\right)$, if we recall that the corresponding Hartree-Fock values are zero. Clearly, the correlated average interelectronic angles $\left\langle\theta_{12}\right\rangle$ are greater than 90 degrees, though the values are not reported in the literature. ${ }^{2,15-19}$ Since the Hartree-Fock $\left\langle\theta_{12}\right\rangle$ 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 $A\left(\theta_{12}\right)$ is generally expressed by a linear combination of Legendre polynomials $P_{n}\left(\cos \theta_{12}\right)$. 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 $\left\langle\theta_{12}\right\rangle$ were reported. The effect of the electron correlation was discussed for three light atoms.

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## 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 $A\left(\theta_{12}\right)$, given by Eq. (2), is rewritten as

$$
\begin{equation*}
A\left(\theta_{12}\right)=\int d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime} \delta\left(\theta_{12}-\theta_{12}^{\prime}\right) \frac{\Gamma\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right)}{\sin \theta_{12}^{\prime}} \tag{A1}
\end{equation*}
$$

where $\theta_{12}^{\prime}$ is the angle between the vectors $\mathbf{r}_{1}^{\prime}$ and $\mathbf{r}_{2}^{\prime}$. Using an identity

$$
\begin{equation*}
\delta\left(\theta-\theta^{\prime}\right)=\delta\left(\cos \theta-\cos \theta^{\prime}\right) \sin \theta \tag{A2}
\end{equation*}
$$

we first obtain

$$
\begin{equation*}
A\left(\theta_{12}\right)=\int d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime} \delta\left(\cos \theta_{12}-\cos \theta_{12}^{\prime}\right) \Gamma\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \tag{A3}
\end{equation*}
$$

We next apply the formal expansion of the Dirac delta function $\delta\left(x-x^{\prime}\right)$ in terms of a complete set of Legendre polynomials $P_{n}(x)$,

$$
\begin{equation*}
\delta\left(x-x^{\prime}\right)=\sum_{n=0}^{\infty} \frac{2 n+1}{2} P_{n}(x) P_{n}\left(x^{\prime}\right), \tag{A4}
\end{equation*}
$$

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