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Approximate formulas for the characteristics of interelectronic angle densities

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Abstract. The accuracies of approximate formulas are examined for several characteristics of the interelectronic angle density $A(\theta_{12})$, where θ_{12} $(0 \le \theta_{12} \le \pi)$ is the angle subtended by the position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ of two electrons. Numerical results for 102 atoms show that simple approximations have sufficient accuracies for the moments $\langle \theta_{12}^n \rangle$ with $n=1$–4, the central moments μ_n with $n=2$, 4, and the kurtosis, when measured by the absolute and relative errors. For heavy atoms, however, the relative errors for the third central moment μ_3 and the skewness are large.

Keywords: Interelectronic angle densities – Moments – Variance – Skewness – Kurtosis – Atoms

Introduction

For an N-electron $(N \ge 2)$ system, the interelectronic angle density $A(\theta_{12})$ is defined [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] 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, θ_{12}' is the angle spanned by the position vectors $\mathbf{r}_1'$ and $\mathbf{r}_2'$, and $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the spinless two-electron density function [11] normalized to the number of electron pairs $N(N-1)/2$. The density $A(\theta_{12})$ is the probability density function that the angle θ_{ij} $(0 \le \theta_{ij} \le \pi)$ subtended by the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ of any two electrons i and j becomes θ_{12}, and is normalized as

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

The interelectronic angle density function $A(\theta_{12})$ is a useful tool to characterize the spatial distribution of electron pairs in atoms and molecules through the interelectronic angle θ_{12}. However, the examination of these densities is very limited in the literature. Only for the He, Li, and Be atoms and some of their isoelectronic ions, the correlation contribution in $A(\theta_{12})$ was studied in an ad hoc manner [1, 2, 3, 4, 5, 6]. Exceptions are Refs. [7, 8], in which the mathematical structure of the interelectronic angle densities is clarified. The densities $A(\theta_{12})$ of the 102 neutral atoms from He to Lr in their ground states were discussed [8] at the Hartree–Fock limit level. A subshell-pair analysis of the average interelectronic angles $\langle \theta_{12} \rangle$ was reported in Ref. [9] for the 102 atoms and several general results for equivalent electrons in atoms were given in Ref. [10].

In Ref. [8], it was shown that the interelectronic angle density $A(\theta_{12})$, given by Eq. (1), is rewritten as a linear combination of Legendre polynomials $P_k(\cos\theta_{12})$,

$$A(\theta_{12}) = \sum_{k=0}^{\infty} \frac{2k+1}{2} \, q_k P_k(\cos\theta_{12}), \quad (3)$$

where the expansion coefficients q_k are

$$q_k \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 P_k(\cos\theta_{12})\Gamma(\mathbf{r}_1, \mathbf{r}_2). \quad (4)$$

Owing to the special functional form of $A(\theta_{12})$, the first few coefficients q_k of the linear combination have approximate relations with the characteristics of the density $A(\theta_{12})$. The present short paper discusses the accuracies of these approximate formulas for the 102 atoms in their ground states. It will be found that simple approximations have sufficient accuracies for practical applications in most cases. Angles are given in radians.

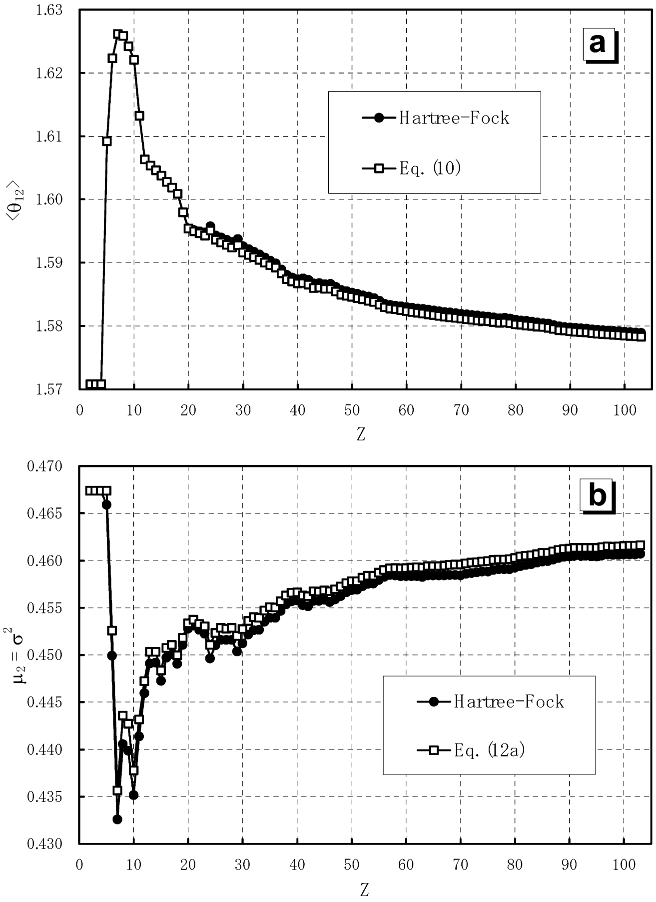

Fig. 1a,b. Comparison of the calculated and estimated properties as a function of atomic number Z. **a** Average interelectronic angle $\langle\theta_{12}\rangle$. **b** Second central moment μ_2 or variance σ^2

Characteristics of interelectronic angle densities

The definitions of several characteristics and the corresponding approximate formulas for the interelectronic angle density $A(\theta_{12})$ are summarized in the following.

Taking the normalization condition (Eq. 2) into account, we define the expectation value $\langle f(\theta_{12})\rangle$ of an angular function $f(\theta_{12})$ by

$$\langle f(\theta_{12})\rangle \equiv \frac{2}{N(N-1)} \int_0^\pi d\theta_{12} \sin\theta_{12} f(\theta_{12}) A(\theta_{12}). \tag{5}$$

For $f(\theta_{12}) = \theta_{12}^n$ with a nonnegative integer n, combination of Eqs. (3) and (5) gives the interelectronic angular moments $\langle\theta_{12}^n\rangle$ as

$$\langle\theta_{12}^n\rangle = \sum_{k=0}^{\infty} \frac{2k+1}{2} \frac{q_k}{q_0} I_{n,k}, \tag{6}$$

where $q_0 = N(N-1)/2$ from Eq. (4) and

$$I_{n,k} \equiv \int_0^\pi d\theta_{12} \sin\theta_{12} \theta_{12}^n P_k(\cos\theta_{12}) = \int_{-1}^{1} dx \arccos^n x P_k(x). \tag{7}$$

Since the square-integrability of the functions $\arccos^n x$ and $A(\theta_{12})$ means

$$\sqrt{\frac{2k+1}{2}} I_{n,k} \to 0, \quad \sqrt{\frac{2k+1}{2}} q_k \to 0, \quad \text{when } k \to \infty \tag{8}$$

we keep the first n terms in the summation of Eq. (6) to obtain an approximate formula

$$\langle\theta_{12}^n\rangle \cong \sum_{k=0}^{n} \frac{2k+1}{2} \frac{q_k}{q_0} I_{n,k} \tag{9}$$

for the angular moment.

A particular case of Eq. (9) for $n = 1$ is found to be

$$\langle\theta_{12}\rangle \cong \frac{\pi}{2} - \frac{3\pi}{8} \frac{q_1}{q_0}. \tag{10}$$

The average interelectronic angle $\langle\theta_{12}\rangle$ is conveniently estimated from the first two of the expansion coefficients q_k. Since q_0 is positive, Eq. (10) implies that the sign of the coefficient q_1 determines whether $\langle\theta_{12}\rangle$ is smaller or larger than $\pi/2$. If we note an equality $q_1/q_0 = \langle\cos\theta_{12}\rangle$, Eq. (10) also provides an approximate connection between the average angle $\langle\theta_{12}\rangle$ and the average cosine $\langle\cos\theta_{12}\rangle$. Another important aspect of Eq. (10) is that it relates the average interelectronic angle with the statistical angular correlation coefficient. On the basis of concepts from mathematical statistics and probability theory, Kutzelnigg et al. [12] introduced statistical correlation coefficients $\tau[g]$ as simple numerical indices which provide overall measures for the statistical correlation of electrons, where $g = g(\mathbf{r})$ is a probe function. When $g(\mathbf{r}) = \mathbf{r}/r$ is chosen, it is known [13, 14, 15, 16] that the correlation coefficient $\tau[\mathbf{r}/r]$ reduces to $\langle\cos\theta_{12}\rangle$ and measures the angular correlation (against the radial correlation) of electrons. Therefore, Eq. (10) clarifies that the average interelectronic angles $\langle\theta_{12}\rangle$ smaller and larger than $\pi/2$ have one-to-one correspondences with the positive and negative electron correlations observed in the coefficient $\tau[\mathbf{r}/r]$; namely, $\langle\theta_{12}\rangle - \pi/2 \cong -(3\pi/8)\tau[\mathbf{r}/r]$.

When $f(\theta_{12}) = (\theta_{12} - \langle\theta_{12}\rangle)^n$, Eq. (5) defines the nth central moments μ_n of the interelectronic angle density $A(\theta_{12})$:

$$\mu_n \equiv \left\langle (\theta_{12} - \langle\theta_{12}\rangle)^n \right\rangle = \sum_{k=0}^{n} \frac{(-1)^{n-k} n!}{k!(n-k)!} \langle\theta_{12}^k\rangle \langle\theta_{12}\rangle^{n-k}, \tag{11}$$

Table 1. Characteristics of the interelectronic angle densities and the errors of the approximate formulas for the 102 atoms from He to Lr

Property	Values for the 102 atoms			Average errors of the approximations	
	Minimum	Average	Maximum	Absolute	Relative (%)
$\langle\theta_{12}\rangle$	1.5708	1.5881	1.6262	0.0006	−0.03
$\langle\theta_{12}^2\rangle$	2.9348	2.9783	3.0840	0.0011	−0.04
$\langle\theta_{12}^3\rangle$	6.0784	6.1747	6.4397	0.0026	0.04
$\langle\theta_{12}^4\rangle$	13.4869	13.6997	14.3577	0.0010	−0.01
$\mu_2=\sigma^2$	0.4326	0.4559	0.4674	0.0011	0.23
μ_3	−0.0198	−0.0036	0.0002	0.0009	149.50
μ_4	0.4287	0.4607	0.4793	0.0008	0.18
γ_1	−0.0673	−0.0121	0.0006	0.0030	148.67
γ_2	−0.8062	−0.7835	−0.7092	0.0064	0.82

where μ_2 is nothing but the variance σ^2 of the density. Substituting Eq. (6) into Eq. (11) and keeping the terms linear in q_k/q_0 with $k \le n$, we find that the central moments μ_n for $n = 2$–4 are approximated by

$$\mu_2 = \sigma^2 \cong \frac{\pi^2-8}{4} + \frac{10}{9}\frac{q_2}{q_0}, \tag{12a}$$

$$\mu_3 \cong \frac{3\pi\left(\pi^2-9\right)}{16}\frac{q_1}{q_0} + \frac{7\pi\left(4\pi^2-81\right)}{1024}\frac{q_3}{q_0}, \tag{12b}$$

and

$$\mu_4 \cong \frac{\pi^4-48\pi^2+384}{16} + \frac{5\left(9\pi^2-80\right)}{27}\frac{q_2}{q_0} + \frac{4\left(225\pi^2-1622\right)}{1875}\frac{q_4}{q_0}. \tag{12c}$$

Equations (12a), (12b), and (12c) also enable us to know the skewness γ_1 and kurtosis γ_2,

$$\gamma_1 = \mu_3/\sigma^3, \tag{13a}$$

$$\gamma_2 = \left(\mu_4/\sigma^4\right) - 3, \tag{13b}$$

of the interelectronic angle density $A(\theta_{12})$ directly from the first five coefficients q_k, where γ_1 and γ_2 measure the degree of asymmetry and the degree of peakedness (relative to a normal distribution), respectively.

Numerical results and discussion

To check the accuracy of the approximate relations in a systematic manner, we examined the interelectronic angle densities $A(\theta_{12})$ of the 102 ground-state atoms from He to Lr at the Hartree–Fock limit level. The required data were taken from Ref. [8].

We first consider the angular moments $\langle\theta_{12}^n\rangle$ for $n = 1$–4. In the case of $n = 1$, the Hartree–Fock and approximate $\langle\theta_{12}\rangle$ values are explicitly compared in Fig. 1a as a function of atomic number Z. When $Z \le 20$, the approximate formula, Eq. (10), gives values identical to the Hartree–Fock ones. When $Z \ge 21$, the estimated $\langle\theta_{12}\rangle$ are always smaller than the Hartree–Fock values, but correctly reproduce the Z-dependence of $\langle\theta_{12}\rangle$. The absolute error of Eq. (10) is maximum (0.0010) at $Z = 29$ and the average over the 102 atoms is 0.0006. The relative error is only −0.03% on average, with the maximum (−0.06%) at $Z = 29$. We thus find that Eq. (10) is very accurate. Analogous results are obtained for the other moments $\langle\theta_{12}^n\rangle$ with $n = 2$–4, as summarized in Table 1. Therefore, Eq. (9) is concluded to give a sufficiently accurate estimation of $\langle\theta_{12}^n\rangle$ as long as $n = 1$–4 is concerned.

The second central moments μ_2 (or the variance σ^2) obtained from the Hartree–Fock calculation and estimated from Eq. (12a) are compared in Fig. 1b. When $Z \le 4$, the two values coincide. When $Z \ge 5$, the approximate μ_2 are larger than the Hartree–Fock values with no exceptions. However, the absolute error is 0.0011 on average, with the maximum 0.0031 at $Z = 7$. The relative error is 0.23% on average with the maximum 0.71% at $Z = 7$. We thus find that Eq. (12a) yields a sufficiently accurate estimation of $\mu_2 = \sigma^2$. Analogous results are obtained for the fourth central moment μ_4, as summarized in Table 1. On the other hand, the accuracy of the approximate formula, Eq. (12b), for the third central moment μ_3 is different from that for μ_2 or μ_4. As shown in Table 1, the absolute error of Eq. (12b) for μ_3 is similar to that of Eq. (12a) for μ_2 or Eq. (12c) for μ_4, but the magnitude of μ_3 is very small compared with the magnitudes of μ_2 and μ_4, reflecting a small asymmetry in the interelectronic angle densities. In particular, $|\mu_3|$ is smaller than 0.001 for $Z \ge 63$; therefore, the relative error for μ_3 is calculated to be large. When the relative error is used as a measure, we conclude that Eqs. (12a) and (12c) are accurate enough but Eq. (12b) is not.

We also estimated the skewness γ_1 by combining the two approximate formulas, Eqs. (12a) and (12b), and the kurtosis γ_2 by combining Eqs. (12a) and (12c). The calculated and estimated values are compared in Fig. 2 as a function of Z. Except for the first three atoms with $Z = 2$–4, both γ_1 and γ_2 are estimated to be smaller than the Hartree–Fock values, but the Z-dependences are

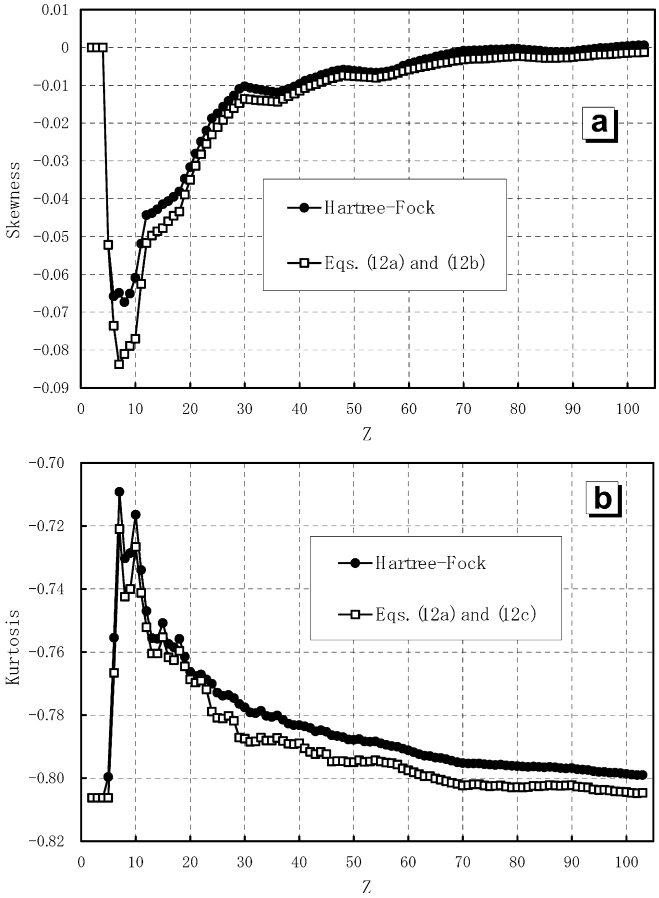

Fig. 2a,b. Comparison of the calculated and estimated properties as a function of atomic number Z. **a** Skewness γ_1. **b** Kurtosis γ_2

correctly reproduced. Since two approximate formulas are combined in the estimation of γ_1 and γ_2, the absolute errors are larger than the cases of $\langle\theta_{12}^n\rangle$ and μ_n as shown in Table 1. For $Z \geq 63$, the magnitude of the Hartree–Fock γ_1 is smaller than 0.005 and the relative error is calculated to be very large. On the other hand, the relative error for γ_2 is 0.82% on average with the maximum of 1.67% at $Z=8$.

At the correlated level of calculations, we could not find the literature data appropriate for the present purpose, except for those in Ref. [17] where the average angles $\langle\theta_{12}\rangle$ were studied for a series of two-electron atoms. In these correlated cases, the values estimated by Eq. (10) are smaller, as in the Hartree–Fock cases, than the calculated values. However, the maximum absolute and relative errors are only 0.0004 and −0.02%, respectively, and Eq. (10) is again concluded to be an excellent approximation.

Summary

The first few coefficients q_k appearing in the general expression of the interelectronic angle density $A(\theta_{12})$ have approximate relations with the characteristics of the density $A(\theta_{12})$. The numerical tests on the 102 atoms have shown that the approximate formulas have sufficient accuracies for $\langle\theta_{12}^n\rangle$ with $n=1$–4 and μ_n with $n=2$, 4, when measured by the absolute and relative errors. The estimation of γ_2 is slightly less accurate. For heavy atoms, however, the relative errors for μ_3 and γ_1 are large.

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