Calculations of maxima of probability distributions from expectation values

I. ANGULAR DISTRIBUTION

A. Definitions

Let us consider a wavefunction of S-state of a two-electron atom,

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = N^{-1/2} \phi(r_1, r_2, \theta), \tag{1}$$

where

$$N = 16\pi^2 \int_0^{\pi} \left[\int_0^{\infty} \left(\int_0^{\infty} \left| \phi^2(r_1, r_2, \theta) \right| r_1^2 \, dr_1 \right) r_2^2 \, dr_2 \right] \sin\theta \, d\theta \tag{2}$$

is a normalization factor.

The angular probability distribution is defined as

$$P(\theta) = \frac{16\pi^2}{N} \int_0^{\infty} \left(\int_0^{\infty} \left| \phi^2(r_1, r_2, \theta) \right| r_1^2 \, dr_1 \right) r_2^2 \, dr_2. \tag{3}$$

If there are no angular correlations (no dependence on θ), then $P(\theta) = 1/2$ is a constant function. Generally, as a periodic function, it could be expanded in Fourier series

$$P(\theta) = \frac{1}{2\mathcal{N}} \sum_{n=0}^{\infty} c_n \cos n\theta, \tag{4}$$

where $\sin n\theta$ are absent because the function is even ($P(\theta) = P(-\theta)$) and where

$$\mathcal{N} = \sum_{k=0}^{\infty} \frac{c_{2k}}{1 - 4k^2} \tag{5}$$

is a normalization factor.

B. Approximation

Here, we approximate the angular distribution just by two terms of the Fourier series (4),

$$P(\theta) = \frac{1}{2}(1 + c\cos\theta) \tag{6}$$

that could be accurate when angular correlations are small.

II. THE MOST PROBABLE ANGLE

$\theta_{\max}$ is defined as the value of θ where a function $\theta \mapsto P(\theta)\sin(\theta)$ reaches its maximum. For the given approximation (6),

$$\cos\theta_{\max} = \frac{\sqrt{1+8c^2}-1}{4c}. \tag{7}$$

If $c \ll 1$, then $\cos\theta_{\max} \approx c$, and

$$\theta_{\max} \approx \frac{\pi}{2} - c. \tag{8}$$

III. DETERMINATION OF THE ANGULAR DISTRIBUTION FROM THE EXPECTATION VALUE OF $\cos\theta$

The expectation value is defined as

$$\overline{\cos\theta} = \int_0^\theta P(\theta)\cos\theta\sin\theta\,d\theta. \tag{9}$$

The angle θ_c is defined through the equation $\cos\theta_c = \overline{\cos\theta}$. For the given approximation (6),

$$\cos\theta_c = \frac{c}{3}. \tag{10}$$

If $c \ll 1$,

$$\theta_c \approx \frac{\pi}{2} - \frac{c}{3}. \tag{11}$$

IV. THE MOST PROBABLE ANGLE FOR HELIUM ATOM

According to [1], $\overline{\cos\theta} = -0.06420261$ for helium that corresponds to the angle $\theta_c = 93.6811°$. The angular distribution is approximated by equation (6) with $c = -0.192608$. The most probable angle is determined through equation (7), $\theta_{\max} \approx 100.376°$, or by an approximate equation (8), $\theta_{\max} \approx 101.043°$. We did not find the most probable angle in literature.

A. Alternative averaging

Average angle is

$$\overline{\theta} = \int_0^\pi P(\theta)\theta\sin\theta\,d\theta = \frac{\pi}{2} - \frac{\pi}{8}c. \tag{12}$$

For helium, it gives $\overline{\theta} = 94.33°$. It does not agree with the result of a paper [2], $\overline{\theta} = 99.811\,844°$.

Using data for various expectation values from [1], $\langle r_1^{-2} \rangle = 6.017409$, $\langle r_1^{-1} \rangle = 1.688317$, $\langle r_1 \rangle = 0.929472$, $\langle r_1^2 \rangle = 1.193483$, $\langle r_1^3 \rangle = 1.967946$, $\langle r_1^4 \rangle = 3.973565$, $\langle (r_1 r_2)^{-1} \rangle = 2.708655$, $\langle \boldsymbol{r}_1 \boldsymbol{r}_2 \rangle = -0.064737$, we could calculate several incomplete averages like

$$\cos \tilde{\theta}_n \equiv \langle \boldsymbol{r}_1 \boldsymbol{r}_2 \rangle \langle r_1^n \rangle^{-2/n}, \quad n = -2, -1, 1, 2, 3, 4 \tag{13}$$

or

$$\cos \tilde{\theta}_{1,2} \equiv \langle \boldsymbol{r}_1 \boldsymbol{r}_2 \rangle \left\langle (r_1 r_2)^{-1} \right\rangle . \tag{14}$$

B. Large D limit of θ

In the limit of $D \to \infty$,

$$\theta_{D\to\infty} = -\frac{1 + \sqrt{1 + 128Z^2}}{64Z^2} = \frac{\pi}{2} + \frac{1}{4\sqrt{2}Z} + \frac{1}{64Z^2} + 0.0016Z^{-3} + \dots, \tag{15}$$

where Z is the nuclear charge. For helium, $Z = 2$ and $\theta_{D\to\infty} = 95.3006°$.

C. Comparison of different averages and maximal angles

Numerical data are collected in Table I. The last line lists Bohr's model [3].

[1] A. M. Frolov, Phys. Rev. A **57**, 2436 (1998).

[2] P. Froelich, S. A. Alexander, Phys. Rev. A **42**, 2550 (1990).

[3] N. Bohr, Phil. Mag. **26**, 857 (1913).

TABLE I. Angle θ in helium atom

	Value (degrees)	Method
θ_{max}	100.376	equation (7)
θ_{max}	101.043	equation (8)
θ_{c}	93.681	equation (9)
$\overline{\theta}$	94.334	equation (12)
$\overline{\theta}$	99.812	[2]
$\tilde{\theta}_{-2}$	112.925	equation (13)
$\tilde{\theta}_{-1}$	100.633	equation (13)
$\tilde{\theta}_{1}$	94.297	equation (13)
$\tilde{\theta}_{2}$	93.109	equation (13)
$\tilde{\theta}_{3}$	92.363	equation (13)
$\tilde{\theta}_{4}$	91.861	equation (13)
$\tilde{\theta}_{1,2}$	100.099	equation (14)
$\theta_{D\to\infty}$	95.301	equation (15)
θ_{Bohr}	180	[3]