Electron Densities: Pictorial Analogies for Apparent Ambiguities in Probability Calculations

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Many articles published in this *Journal* have greatly contributed to a better interpretation of electron density in atoms (*1–12*). The aim of this paper is to present supplementary analogies to clarify differences in probability and probability density calculations for hydrogen-like wave functions. Students who first encounter quantum mechanical details of atomic structure seldom have a feeling for these concepts and they often encounter apparent ambiguities in this field.

Radial Wave Functions

To analyze the maximum probability of finding an electron described by a Ψ_{1s} wave function, texts usually plot the probability density ($|\Psi_{1s}|^2$) as a function of r, obtaining an increasing function as one approaches the nucleus (*14*). On the other hand, to determine the probability of finding the electron between the distances r and $r + dr$, regardless of angle, integration over θ and φ variables is performed. The r-value that maximizes the so-called radial distribution function leads to a more intuitive result: the maximum probability of finding an electron regardless of the angle is found at a distance a (Bohr radius) from the nucleus (*13, 14*). Sometimes students do not understand the physical implications of the above calculations. *Is the probability of finding an electron described by a Ψ_{1s} wave function greater at the nucleus or at the Bohr radius?*

Differences between the probability density and the most probable distance from the nucleus regardless of the angle are the key for comprehension. Pictorial analogies are very useful at this stage (*11*). A pictorial analogy that proved very clarifying in our quantum chemistry courses consisted of presenting a two-dimensional forest in which trees were distributed with radial symmetry (Fig. 1), so that tree density was higher as one approached the center. The picture was presented as it would be seen from a helicopter. Students were asked about the distance from the center where the probability of finding trees was maximum. They immediately recognized that this was satisfied for a given distance (d in Fig. 1) by walking in circles (i.e., regardless φ angle). This was correlated with the typical graph of $|R(r)|^2 r^2$ as a function of r that is usually presented in books (*14*). Students also realized that when they are walking toward the center of the forest, the probability of finding trees per unit area has an increasing value (as was found in the literature for $|\Psi_{1s}|^2$) and that it is not in contradiction with the previous observation. It must be emphasized, however, that this analogy illustrates a two-dimensional situation (variables r and φ), whereas hydrogen wave functions depend on three coordinates (r, θ, and φ).

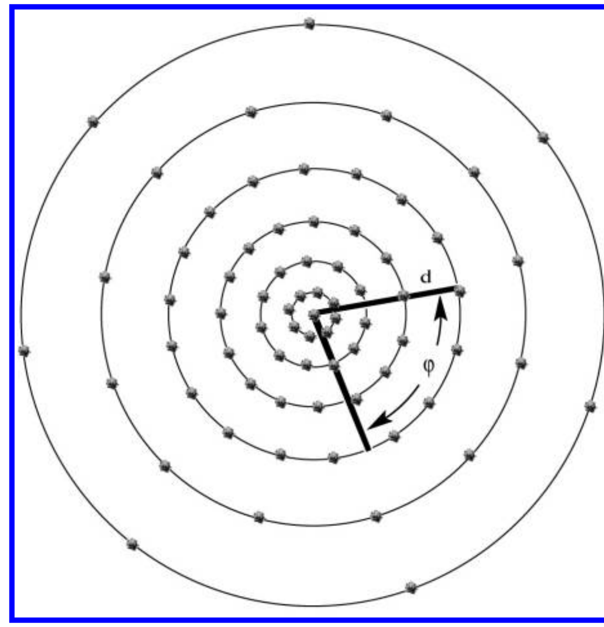

Figure 1. Forest analogy to discuss probability distribution function for the Ψ_{1s} hydrogen wave function.

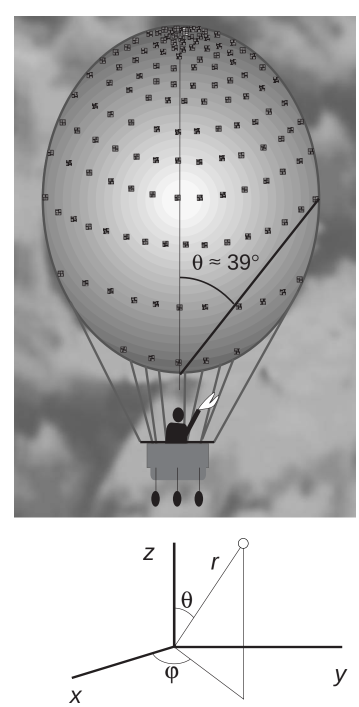

Figure 2. Balloon analogy to discuss probability distribution for the Ψ_{2p_z} hydrogen wave function.

Angular Wave Functions

On discussing the directionality of p orbitals, the maximum angular probability is often calculated. Quantum chemistry texts directly analyze $|\Psi_{(r,\theta,\varphi)}|^2$. For a Ψ_{2p_z} orbital $|\Psi_{2p_z}|^2$ has a maximum for $\theta = 0, \pi$ and the expected result is obtained: Ψ_{2p_z} is oriented along the *z* axis. However, in analogy with Ψ_{1s} analysis, students usually work on the probability of finding the electron between *r* and *r* + d*r*, θ and θ + dθ, and φ and φ + dφ. As they are interested in the dependence of probability on θ regardless of *r* and φ values, they integrate over these two variables on the whole space. They finally find the θ value, which maximizes the resultant function *P*(θ):

$$P(\theta)\mathrm{d}\theta = \int_{r=0}^{\infty}\int_{\varphi=0}^{2\pi} |\Psi_{2p_z}|^2 r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\varphi = \text{constant}\cdot\cos^2\theta\cdot\sin\theta \, \mathrm{d}\theta$$

P(θ) maximum for θ = atan (sqrt (2)/2) ≈ 39° is found. This result usually strikes students: *How can θ_{max} be 39° if p_z is supposed to be oriented along the* z *axis?* What was the error in their calculations? Actually there is no error. The result θ ≈ 39° is not in contradiction with θ = 0, π found for $|\Psi_{2p_z}|^2$ maximum.

Physical concepts involved in both calculations are valuable to initiate a classroom discussion. The different concepts of probability have to be distinguished. A pictorial analogy to describe these results is presented in Figure 2. A balloon full of small squares is shown to students. As we can see in the figure, square density is higher on the *z* axis. Nevertheless, if an imaginary stick were taken and moved in circles (i.e., varying φ values between 0 and 2π), the higher number of squares would be counted for θ ≈ 39°. Analysis was performed on Ψ_{2p_z} as an example, but similar derivations may be discussed with other angular wave functions.

Final Comment

These analogies are not orbital representations; they are only simplified pictures to allow better understanding of probability concepts and their differences.

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