

Approximating the electron cloud wavefunction for s-orbital electrons in Schrödinger's model

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1 Introduction

The development of quantum mechanics during the early 20th century fundamentally transformed our understanding of atomic structure. In 1926, Erwin Schrödinger published his celebrated wave equation [1], providing a rigorous mathematical framework for describing electron behaviour in atoms and replacing the classical notion of fixed orbits with probability distributions called orbitals. This approach marked a significant departure from Niels Bohr's earlier model [2], which treated electrons as particles travelling in well-defined circular orbits. Instead, Schrödinger's quantum mechanical description characterises electrons as wave-like entities whose positions are inherently probabilistic.

At the heart of Schrödinger's model lies the wavefunction $\Psi(r, \theta, \phi)$, whose square modulus yields the probability density of locating an electron at any given point in space. For s-orbitals, which represent the simplest atomic orbitals exhibiting perfect spherical symmetry, the wavefunction depends solely on the radial distance r from the nucleus [4]. A thorough understanding of these radial wavefunctions proves essential for comprehending atomic structure, chemical bonding and spectroscopy, whilst also providing a convenient shortcut to approximate their behaviour using only a single variable.

Louis de Broglie's revolutionary matter wave hypothesis [3], proposed in 1924, suggested that particles possess wave-like properties characterised by wavelength $\lambda = h/(mv)$, where h represents Planck's constant, m denotes mass and v indicates velocity. This groundbreaking idea proposed that electrons in atoms form standing waves, with only certain wavelengths fitting precisely into circular paths around the nucleus, thereby providing a physical explanation for Bohr's angular momentum quantisation condition [5].

This article develops an analytical approximation for the radial probability density function of s-orbital electrons by synthesising de Broglie's standing wave picture with probabilistic constraints. Although the exact solutions to Schrödinger's equation for hydrogen involve Laguerre polynomials and exhibit multiple nodes for higher orbitals, this simplified model successfully captures essential behaviour: zero probability at the nucleus, a maximum at the most probable radius, and exponential decay at

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large distances. The approach presented here offers considerable pedagogical value by demonstrating how physical reasoning, guided by appropriate boundary conditions and normalisation requirements, can lead to approximate yet insightful mathematical models of quantum phenomena.

2 Mathematical framework and assumptions

The construction of a physically valid probability density function begins with establishing the essential mathematical properties that any such function must satisfy.

2.1 Fundamental requirements

Let Ψ_n denote the radial probability density function on $[0, \infty)$ for an electron occupying the n th s-orbital, where $n \in \mathbb{Z}^+$ represents the principal quantum number. We assume that Ψ is differentiable on $(0, \infty)$. Since Ψ is a radial function, we denote the input by r and it measures the distance from the nucleus.

As a legitimate probability density function, Ψ_n must satisfy two crucial requirements:

- (a) **Normalisation:** the total probability of finding the electron somewhere in space equals one; that is,

$$\int_0^\infty \Psi_n(r) dr = 1.$$

- (b) **Non-negativity:** we have that $\Psi_n(r) \geq 0$ for all $r \geq 0$; that is, the values probabilities cannot assume negative values.

2.2 Physical constraints from quantum mechanics

Beyond purely mathematical requirements, physical considerations impose additional constraints on acceptable solutions:

- (c) **Boundary condition:** the wavefunction must vanish at the nucleus for s-orbitals in this simplified model, giving $\Psi_n(0) = 0$.
- (d) **Maximum value:** the probability density attains its maximum value somewhere. In other words, there must exist a radius r_n , called the most probable radius, such that

$$\Psi_n(r_n) \geq \Psi_n(r)$$

for all $r \geq 0$.

- (e) **Asymptotic behaviour:** the probability must decay to zero as distance increases without bound. This can be expressed as

$$\lim_{r \rightarrow \infty} \Psi_n(r) = 0.$$

2.3 de Broglie's standing wave condition

De Broglie's hypothesis [3] establishes that an electron in a stable orbital must form a standing wave pattern, with an integer number of wavelengths fitting precisely into the orbital circumference. This imposes one further restriction:

(f) **de Broglie's condition:** the most probable radius r_n satisfies

$$r_n = \frac{n\lambda}{2\pi},$$

where λ denotes the de Broglie wavelength and n represents the principal quantum number.

This relationship provides an essential link between the quantum number n and the characteristic length scale of the orbital. For the hydrogen atom specifically, the Bohr radius $a_0 = 52.9$ pm represents the most probable radius for the ground state [2].

3 Derivation of the probability density function

One function that satisfies conditions (b), (c), (d) and (e) is the function Ψ defined by $\Psi(r) = kre^{-ar}$, where $a, k \in \mathbb{R}^+$ represent constants whose values remain to be determined using the other conditions.

To locate the position of the most probable radius r_n , we first differentiate Ψ_n using the product rule to get

$$\Psi'_n(r) = \frac{d}{dr}(kre^{-ar}) = k(e^{-ar} + r(-a)e^{-ar}) = ke^{-ar}(1 - ar).$$

Since $k > 0$ and $e^{-ar} > 0$ for all values of r , the condition $\Psi'_n(r) = 0$ implies $r = 1/a$. Moreover, $\Psi'_n(r) < 0$ for $0 < r < 1/a$ and $\Psi'_n(r) > 0$ for $r > 1/a$ which implies that the maximum occurs at the most probable radius $r_n = 1/a$. Combining this result with de Broglie's standing wave condition (f), we get that

$$\frac{1}{a} = \frac{n\lambda}{2\pi},$$

from which the parameter a is given by

$$a = \frac{2\pi}{n\lambda}.$$

Since there is a dependency on n , we shall write $\Psi = \Psi_n$ which is defined by

$$\Psi_n(r) = kr \exp\left(-\frac{2\pi r}{n\lambda}\right).$$

To find the parameter k , we employ the normalisation condition

$$k \int_0^\infty re^{-ar} dr = 1.$$

To evaluate the integral, we use integration by parts. By letting $u = r$ and $dv = e^{-ar} dr$ we obtain

$$\begin{aligned}
1 &= k \int_0^\infty r e^{-ar} dr \\
&= k \left[-\frac{r}{a} e^{-ar} - \frac{1}{a^2} e^{-ar} \right]_0^\infty \\
&= k \left(\lim_{R \rightarrow \infty} \left(-\frac{R}{a} e^{-aR} - \frac{1}{a^2} e^{-aR} \right) - \left(0 - \frac{1}{a^2} \right) \right) \\
&= \frac{k}{a^2}
\end{aligned}$$

since $\lim_{R \rightarrow \infty} R e^{-aR} = 0$ for $a > 0$. Therefore, the value of k is

$$k = a^2 = \left(\frac{2\pi}{n\lambda} \right)^2 = \frac{4\pi^2}{n^2\lambda^2}.$$

Combining all derived results, one probability density function for the n th s-orbital takes the form

$$\Psi_n(r) = a^2 r e^{-ar} = \frac{4\pi^2}{n^2\lambda^2} r \exp \left(-\frac{2\pi r}{n\lambda} \right).$$

For atoms containing multiple occupied s-orbitals, the total probability density function becomes the sum

$$P_{\text{total}}(r) = \sum_{n=1}^N \Psi_n(r) = \sum_{n=1}^N \frac{4\pi^2}{n^2\lambda^2} r \exp \left(-\frac{2\pi r}{n\lambda} \right)$$

where N denotes the number of occupied s-orbitals in the atom under consideration.

4 Visualisation and physical interpretation

4.1 Graphical representation

Figure 1 illustrates the behaviour of $\Psi_n(r)$ for the first three s-orbitals using physically realistic parameters appropriate for the hydrogen atom. Employing de Broglie's standing wave condition together with the Bohr radius value of $r_1 = 52.9$ pm for $n = 1$ [2], we obtain the wavelength

$$\lambda = 2\pi r_1 = 2\pi(52.9 \text{ pm}) \approx 332.4 \text{ pm}.$$

This wavelength, representing the de Broglie wavelength of an electron in the first Bohr orbit, serves as the foundation for all visualisations presented here.

Several key features become evident upon examining the figure. First, radial scaling demonstrates that as n increases, the most probable radius $r_n = n\lambda/2\pi$ increases

proportionally, reflecting the larger spatial extent of orbitals at higher energy levels. For hydrogen specifically, this yields

$$r_1 = 52.9 \text{ pm}, \quad r_2 = 105.8 \text{ pm}, \quad r_3 = 158.7 \text{ pm}.$$

Second, the peak height behaviour shows that the maximum value

$$\Psi_n(r_n) = a^2 r_n e^{-ar_n} = \frac{a}{e} = \frac{2\pi}{en\lambda}$$

decreases as n increases, reflecting the increasingly diffuse nature of the electron cloud at higher energy levels. Third, exponential decay characterises all functions beyond their maxima, with each function exhibiting a characteristic decay length of $1/a = n\lambda/2\pi$.

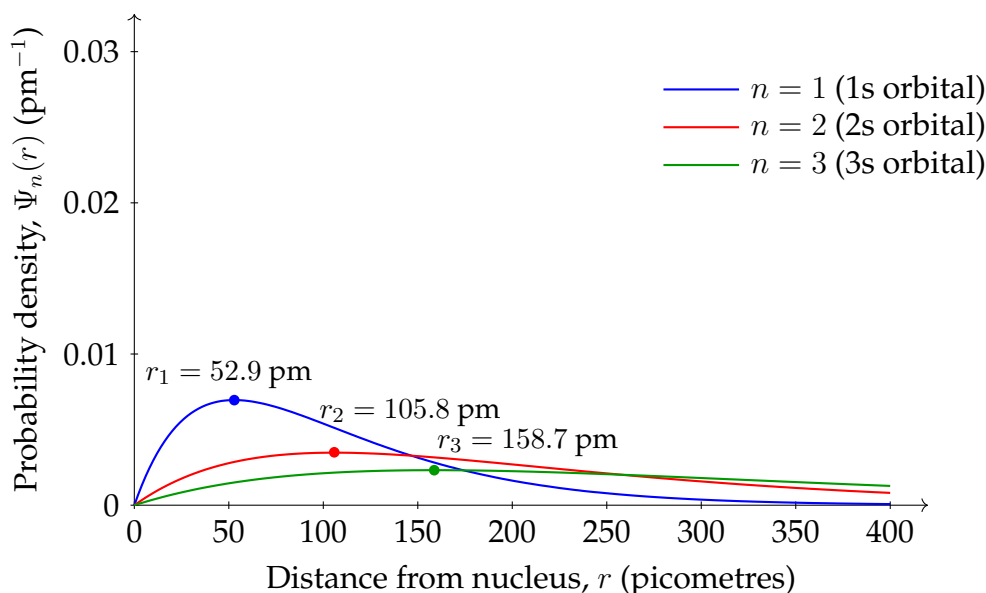


Figure 1: The plots of radial probability density functions Ψ_n for the first three s-orbitals of the hydrogen atom, calculated using the de Broglie wavelength $\lambda \approx 332.4$ pm derived from the Bohr radius.

4.2 Comparison with exact solutions

There are several aspects of this simplified model that differ to the exact solutions to Schrödinger's equation [1] for hydrogen s-orbitals. The exact wavefunctions for $n \geq 2$ has $n - 1$ radial nodes, which are spherical surfaces where the probability density vanishes identically. The simple exponential form presented here lacks these nodes entirely.

As for the behaviour at the origin, the exact 1s wavefunction assumes a non-zero value at $r = 0$, whereas the approximation presented here vanishes at that point. However, it should be noted that the radial probability density does vanish at the origin for all orbitals in Schrödinger's theory.

Lastly, the exact solutions involve a product of Laguerre polynomials with exponential functions, providing substantially more complex radial dependence than the single exponential employed here. Despite these differences, this simple approximation is able to demonstrate the fundamental wave-particle duality of electrons and the quantisation of energy levels through de Broglie's standing wave condition.

5 Discussion

There are several key physical principles that can be observed from the derived probability density function Ψ_n :

Wave-particle duality appears through the incorporation of de Broglie's wavelength from the parameter $a = 2\pi/(n\lambda)$, bridging the particle picture of classical mechanics with the wave picture of quantum theory;

Quantisation appears explicitly through the discrete principal quantum number n , which determines both the characteristic size of each orbital (with r_n being proportional to n) and the normalisation constant (with k being proportional to $1/n^2$);

The spreading of the probability distribution throughout space reflects Heisenberg's uncertainty principle [6], embodying the fundamental concept that the electron does not possess a precisely defined position but rather exists as a probability distribution in space.

Since our analysis only employed basic calculus and probability theory, this lets students derive a meaningful quantum mechanical result without confronting partial differential equations which are present in the full Schrödinger theory.

The limitations inherent in this model suggest several promising directions for further study. Extension to higher angular momentum states, encompassing p, d and f orbitals, requires incorporating angular dependence and accounting for centrifugal effects arising from electron motion. Multi-electron atoms present additional complications, as electron repulsion significantly modifies orbital shapes in atoms beyond hydrogen. Relativistic effects become increasingly important for heavy atoms, particularly affecting inner-shell electrons where velocities approach significant fractions of the speed of light.

The development of our understanding of atomic structure illustrates beautifully the evolution of scientific thinking over time. Bohr's model [2], published in 1913, successfully explained the discrete spectrum of hydrogen but lacked a convincing physical mechanism for quantisation. De Broglie's matter wave hypothesis [3] of 1924 provided this missing mechanism, whilst Schrödinger's equation [1], formulated in 1926, gave the theory complete mathematical rigour. Max Born's probabilistic interpretation [7], also developed in 1926, greatly extended the conceptual framework by establishing that $|\Psi|^2$ represents probability density. This progression demonstrates eloquently how successive refinements, each building carefully on previous insights whilst addressing their limitations, lead ultimately to deeper understanding of natural phenomena.

6 Conclusion

Under conditions (a) to (f), an analytical approximation for the radial probability density function of s-orbital electrons is found to be

$$\Psi_n(r) = \frac{4\pi^2}{n^2\lambda^2} r \exp\left(-\frac{2\pi r}{n\lambda}\right).$$

This expression, obtained by synthesising de Broglie's standing wave hypothesis with probabilistic constraints, captures the essential features of electron distributions in atoms: zero probability at the nucleus, a maximum at the most probable radius $r_n = n\lambda/(2\pi)$, and exponential decay at large distances. For hydrogen atoms with $\lambda \approx 332.4$ pm, this model predicts most probable radii of 52.9 pm, 105.8 pm and 158.7 pm for the first three s-orbitals, demonstrating agreement with Bohr model predictions.

Although greatly simplified compared to exact Schrödinger solutions, this model provides an accessible introduction to quantum mechanical wavefunctions whilst simultaneously illustrating fundamental concepts including wave-particle duality, quantisation and probabilistic interpretation. The derivation showcases how basic calculus serves physical understanding of atoms. By starting from qualitative behaviour and systematically imposing appropriate constraints, the analysis arrives at a quantitative approximation connecting abstract quantum behaviour to measurable probability distributions.

Future work might extend this framework to incorporate radial nodes for higher orbitals, explore angular momentum contributions for non-s orbitals, or investigate how electron interactions modify these simple distributions in multi-electron atoms. The electron's dual nature as simultaneously a wave and a particle remains one of quantum mechanics' most profound and wondrous insights. This probability density function, although admittedly approximate, captures this duality mathematically, providing a valuable bridge between the abstract formalism of Schrödinger's equation and the deceptively simple question: where might the electron be found?

Glossary

Asymptotic behaviour: The limiting behaviour of a function as its argument approaches infinity or some other boundary value.

Bohr radius: The most probable distance between the nucleus and the electron in a hydrogen atom in its ground state, approximately 52.9 picometres.

Boundary condition: A constraint that a solution to a differential equation must satisfy at the boundaries of its domain.

de Broglie wavelength: The wavelength associated with a particle, given by $\lambda = h/(mv)$ where h is Planck's constant, m is mass, and v is velocity.

Exponential decay: A decrease in quantity at a rate proportional to its current value,

described mathematically by functions of the form $e^{-\alpha x}$.

Integration by parts: A technique for evaluating integrals based on the product rule for differentiation, expressed as $\int u dv = uv - \int v du$.

Laguerre polynomials: A sequence of orthogonal polynomials that appear in the exact solutions to Schrödinger's equation for the hydrogen atom.

Matter waves: Wave-like properties associated with particles, as proposed by Louis de Broglie in 1924.

Normalisation: The process of scaling a probability distribution so that the total probability equals one.

Orbital: A region of space around an atomic nucleus where an electron is likely to be found, described mathematically by a wavefunction.

Probability density function: A function whose value at any point represents the relative likelihood of a random variable taking on that value.

Principal quantum number: An integer $n \geq 1$ that specifies the energy level and approximate size of an orbital in an atom.

Quantisation: The restriction of a physical quantity to discrete values rather than a continuous range.

Radial node: A spherical surface in an orbital where the wavefunction and probability density equal zero.

s-orbital: An atomic orbital with spherical symmetry, possessing zero angular momentum quantum number.

Standing wave: A wave pattern that remains stationary in space, formed by the interference of two waves travelling in opposite directions.

Wavefunction: A mathematical function describing the quantum state of a particle, typically denoted Ψ , whose square modulus gives probability density.

Wave-particle duality: The concept that all matter and energy exhibit both wave-like and particle-like properties.

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