# MATH 131P WINTER 2025 FINAL PROJECT

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## Quantum Analysis of the Hydrogen Atom

## 1. Introduction

The hydrogen atom, consisting of a single electron bound to a single proton, is the simplest atomic system in quantum mechanics. Historically, it has served as the gateway to revolutionary insights into the foundations of quantum theory. The mathematical definition of the hydrogen atom through Schrödinger's equation uncovers fundamental properties such as discrete energy levels, quantized electronic orbitals, and certain electron spatial distributions.

In this paper, we present a rigorous mathematical exploration of the hydrogen atom, solving Schrödinger's equation utilizing spherical harmonics and Laguerre polynomials, largely based on the work of N. H. Asmar[1]. We will state and prove several relevant theorems, provide demonstrative examples, and show the implications of these solutions in physical and chemical contexts.

## 2. Preliminary Mathematical Background

Before exploring the hydrogen atom in more detail, we will review essential concepts necessary for a comprehensive understanding of quantum mechanical descriptions.

### 2.1. Schrödinger's Equation.

Schrödinger's equation is a central Partial Differential Equation in quantum mechanics [4, 1] and is generally expressed as :

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2\mu}\nabla^2\psi + V(\mathbf{r})\psi, \tag{1}$$

where $\psi(\mathbf{r}, t)$ is the wavefunction, $\hbar$ is the reduced Planck's constant, $\mu$ is the mass of the particle, and $V(\mathbf{r})$ is the potential energy function.

The wavefunction $\psi$ is interpreted probabilistically where its magnitude squared $|\psi(\mathbf{r}, t)|^2$ gives the probability density for finding the particle at position $\mathbf{r}$ and time $t$. For a solution to be considered physically meaningful, normalization must hold as such:

$$\int |\psi(\mathbf{r}, t)|^2 \, d^3r = 1.$$

2.2. **Spherical Coordinates and Separation of Variables.** In problems exhibiting spherical symmetry, we will often use spherical coordinates $(r, \theta, \phi)$. Their relationship with Cartesian coordinates is as follows:

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta. \tag{3}$$

Separation of variables is a standard method for solving PDEs where the solution is expressed as a product of functions each dependent on only one coordinate. This is relevant for spherical symmetry problems. This is typically written:

$$\psi(r, \theta, \phi, t) = R(r)\, Y(\theta, \phi)\, T(t). \tag{4}$$

2.3. **Normalization Example.** Consider a hypothetical wavefunction of the form:

$$\psi(r, \theta, \phi) = Ae^{-r/a_0}\sin\theta, \tag{5}$$

where $A$ is a normalization constant and $a_0$ is a length scale. The normalization condition is:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |A|^2 e^{-2r/a_0} \sin^3\theta\, r^2\, dr\, d\theta\, d\phi = 1. \tag{6}$$

Performing this integral gives a value for $A$ ensuring normalization.

## 3. Setting up the Hydrogen Atom Problem

The hydrogen atom,can be simplified due to the signiifcantly large mass difference between its singular proton and singular electron.. Given that the proton is substantially heavier, we assume it to be fixed at the origin, simplifying the scenario to solving Schrödinger's equation solely for the electron. Refer to Figure 1 for a visualization of the hydrogen atoms with spherical coordinates.

The electron's potential energy in a hydrogen atom arises from electrostatic attraction (Coulomb potential):

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \tag{7}$$

where $e$ is the elementary charge, and $\epsilon_0$ is vacuum permittivity. In atomic units ($4\pi\epsilon_0 = 1$), this simplifies to:

$$V(r) = -\frac{e^2}{r}. \tag{8}$$

Thus, Schrödinger's equation in spherical coordinates reduces to the radial Schrödinger equation.

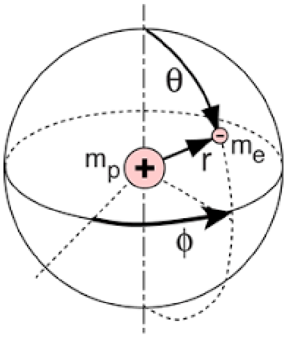

Figure 1. Electron-Proton Configuration in Spherical Coordinates

## 4. Radial and Angular Equations

To solve Schrödinger's equation for the hydrogen atom, we will utilize the inherent spherical symmetry by employing separation of variables. We assume the wavefunction can be factorized as such:

$$\psi(r,\theta,\phi,t) = R(r)Y(\theta,\phi)e^{-iEt/\hbar}. \tag{9}$$

Substituting this into Schrödinger's equation and dividing by the wavefunction itself, we separate variables and obtain two independent ordinary differential equations: one depending solely on the radial coordinate $r$, and the other solely on the angular coordinates $\theta$ and $\phi$.

4.1. **Lemma (Angular Equation).** The angular part of Schrödinger's equation satisfies:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + n(n+1)Y = 0, \tag{10}$$

where $n$ is an integer quantum number related to angular momentum.

4.2. **Proof.** We begin with the time-independent Schrödinger equation (1).

Since the potential (8) depends only on the radial coordinate, the system has spherical symmetry. It is natural to use spherical coordinates $(r,\theta,\phi)$, in which the Laplacian is given by:

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}.$$

We now assume that the wavefunction can be separated as:

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi).$$

Substituting this into Schrödinger's equation and dividing both sides by $R(r)Y(\theta,\phi)$, we get:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{r^2Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)\right] - \frac{e^2}{r} = E.$$

Multiplying by $\frac{2\mu r^2}{\hbar^2}$, we obtain:

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)+\frac{2\mu e^2 r}{\hbar^2}=\frac{2\mu E r^2}{\hbar^2}.$$

Since the left-hand side depends separately on $r$ and on $(\theta,\phi)$, each part must be equal to a constant. We define this separation constant as $\ell(\ell+1)$ (which correspond to angular momentum eigenvalues). Thus, we isolate the angular part:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}+\ell(\ell+1)Y=0. \tag{11}$$

This is the angular portion of the Schrödinger equation in spherical coordinates. Its solutions, $Y_\ell^m(\theta,\phi)$, are the spherical harmonics, which form a complete orthonormal set on the sphere.

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## 5. ANGULAR EQUATION AND SPHERICAL HARMONICS

The solutions to the angular equation are spherical harmonics, which describe quantized angular momentum states on the unit sphere [3].

5.1. **Definition: Spherical Harmonics.** Spherical harmonics, denoted as $Y_n^m(\theta,\phi)$, are defined as:

$$Y_n^m(\theta,\phi)=\sqrt{\frac{(2n+1)(n-m)!}{4\pi(n+m)!}}P_n^m(\cos\theta)e^{im\phi}, \tag{12}$$

where $P_n^m(\cos\theta)$ are associated Legendre polynomials.

5.2. **Properties of Spherical Harmonics.** Spherical harmonics satisfy the critical orthogonality and normalization conditions given by:

$$\int_0^{2\pi}\int_0^{\pi} Y_n^m(\theta,\phi)\overline{Y_{n'}^{m'}(\theta,\phi)}\sin\theta\,d\theta d\phi=\delta_{nn'}\delta_{mm'}. \tag{13}$$

5.3. **Example Spherical Harmonics.** We will give the computations and visualizations (Figure 2) for $Y_1^0(\theta,\phi)$ and $Y_1^1(\theta,\phi)$:

$$Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_1^1(\theta,\phi)=-\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{i\phi}. \tag{14}$$

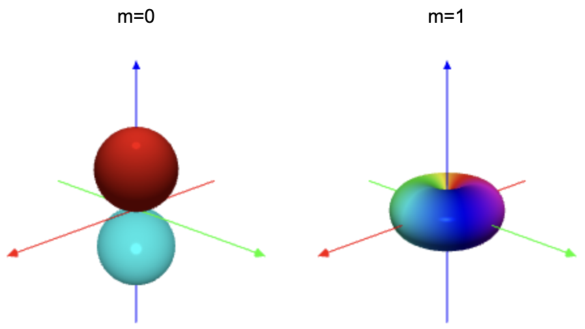

FIGURE 2. $Y_1^0(\theta, \phi)$ $Y_1^1(\theta, \phi)$

## 6. RADIAL EQUATION AND SOLUTIONS VIA LAGUERRE POLYNOMIALS

The radial equation, via separation of variables, emerges as:

$$\frac{d^2u}{dr^2} + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{n(n+1)}{r^2}\right]u = 0, \quad \text{where } u(r) = rR(r). \tag{15}$$

Solutions involve special functions known as generalized Laguerre polynomials, characterized by orthogonality and recurrence relations, making them particularly well-suited for describing bound-state quantum systems such as hydrogen.

6.1. **Definition: Laguerre Polynomials.** The generalized Laguerre polynomials $L_k^\alpha(x)$ satisfy:

$$x\frac{d^2L_k^\alpha(x)}{dx^2} + (\alpha + 1 - x)\frac{dL_k^\alpha(x)}{dx} + kL_k^\alpha(x) = 0. \tag{16}$$

6.2. **Theorem: Radial Solutions.** The radial solutions incorporate Laguerre polynomials:

$$R_{vn}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(v-n-1)!}{2v[(v+n)!]^3}} e^{-r/(na_0)} \left(\frac{2r}{na_0}\right)^n L_{v-n-1}^{2n+1}\left(\frac{2r}{na_0}\right). \tag{17}$$

6.3. **Proof.** We start with the radial part of the time-independent Schrödinger equation in spherical coordinates:

$$\frac{d^2u}{dr^2} + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right]u(r) = 0, \tag{18}$$

where $u(r) = rR(r)$, and $R(r)$ is the radial component of the wavefunction.

Now, define a dimensionless variable:

$$\rho = \frac{2r}{na_0}, \quad \text{where } a_0 = \frac{\hbar^2}{\mu e^2} \text{ is the Bohr radius.}$$

Next, we propose an ansatz (assumption about the form of the unknown function) for $u(r)$ of the form:

$$u(\rho) = \rho^{\ell+1} e^{-\rho/2} v(\rho),$$

where $v(\rho)$ is an unknown function to be determined. This ansatz is motivated by the known asymptotic behavior of the radial wavefunction: it should behave like $r^{\ell+1}$ near the origin and decay exponentially at infinity to ensure square integrability. The inclusion of an ansatz aids us in facilitating a solution.

Now we substitute the ansatz into the radial equation. After differentiating and simplifying, we find that $v(\rho)$ must satisfy the differential equation:

$$\rho \frac{d^2 v}{d\rho^2} + [2\ell + 2 - \rho] \frac{dv}{d\rho} + [n - \ell - 1] \, v(\rho) = 0. \tag{19}$$

This is the differential equation for the associated Laguerre polynomials $L_k^{2\ell+1}(\rho)$ with:

$$k = n - \ell - 1,$$

where $k$ must be a non-negative integer in order for the polynomial solution to terminate (i.e., to remain finite and normalizable at infinity).

Thus, for the wavefunction to be square integrable, we require:

$$n = k + \ell + 1, \quad k = 0, 1, 2, \ldots$$

This condition leads directly to the quantization of $n$, and hence to quantized energy levels.

The corresponding energy eigenvalues are found by substituting this quantization condition into the expression for energy derived earlier:

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots$$

The normalized radial wavefunction then becomes:

$$R_{n\ell}(r) = N_{n\ell} \left( \frac{2r}{na_0} \right)^{\ell} e^{-r/(na_0)} L_{n-\ell-1}^{2\ell+1} \left( \frac{2r}{na_0} \right),$$

where $N_{n\ell}$ is a normalization constant determined via the requirement that the total probability integrates to 1:

$$\int_0^\infty |R_{n\ell}(r)|^2 r^2 dr = 1.$$

This completes the derivation. We have shown that square-integrable solutions of the radial Schrödinger equation exist only for specific, quantized values of energy. These solutions correspond to bound states of the electron in a hydrogen atom.

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6.4. **Example: First Excited State.** For the first excited state ($v = 2$), the radial wavefunction is:

$$R_{20}(r) = \frac{1}{\sqrt{2}} \left(\frac{1}{a_0}\right)^{3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/(2a_0)}. \tag{20}$$

## 7. Energy Levels and Quantization

The solutions of Schrödinger's equation for the hydrogen atom yield discrete energy levels [2], indicating that the electron energy is quantized rather than continuous. These quantized energy levels arise from boundary conditions and normalization constraints.

7.1. **Theorem: Discrete Energy Levels.** The allowed energy levels for the hydrogen atom depend on the principal quantum number $v$:

$$E_v = -\frac{\mu e^4}{2\hbar^2 v^2}, \quad v = 1, 2, 3, \ldots \tag{21}$$

7.2. **Proof.** We begin with the radial equation in dimensionless form, after substituting $u(r) = rR(r)$ and defining a new variable $\rho = \frac{2r}{na_0}$:

$$\frac{d^2u}{d\rho^2} + \left(-\frac{1}{4} + \frac{\eta}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) u = 0.$$

A solution of the form $u(\rho) = \rho^{\ell+1} e^{-\rho/2} v(\rho)$ leads to the associated Laguerre differential equation for $v(\rho)$, which only has polynomial solutions when:

$$v = n + \ell + 1, \quad \text{with } n \in \mathbb{N}.$$

This condition quantizes the allowed energy levels as stated. ☐

7.3. **Example: Hydrogen-like Ions.** For a hydrogen-like ion such as He$^+$, we can calculate the energy levels as:

$$E_v^{He^+} = -Z^2 \frac{\mu e^4}{2\hbar^2 v^2}, \quad Z = 2. \tag{22}$$

## 8. Probability Density and Electron Distribution

The squared magnitude of the wavefunction defines the probability density function (PDF):

$$|\psi_{vnm}(r, \theta, \phi)|^2 = |R_{vn}(r)|^2 |Y_n^m(\theta, \phi)|^2. \tag{23}$$

This PDF gives a probabilistic interpretation of electron position.

8.1. **Example: Probability within Radius for Excited State.** For the state with quantum numbers $v = 3, n = 1$, the radial wavefunction is:

$$R_{31}(r) = \frac{4}{81\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{4r}{3a_0}\right) e^{-r/(3a_0)} \left(2 - \frac{r}{a_0}\right).$$

The probability of finding the electron within one Bohr radius $a_0$ thus is:

$$P(r < a_0) = \int_0^{a_0} 4\pi r^2 |R_{31}(r)|^2 \, dr,$$

which can be numerically evaluated, clearly illustrating the probabilistic interpretation.

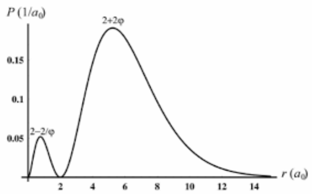

Figure 3. Radial Wave Probability Density for First Excited State

## 9. Applications of Hydrogen Atom Solutions

Solutions to the hydrogen atom problem have valuable implications and applications in many areas of modern physics and chemistry.

### 9.1. **Spectroscopy.**

Hydrogen atom solutions predict discrete spectral lines observed experimentally, historically validating quantum mechanics. Spectral lines (e.g., Balmer series, Lyman series) correlate to electron transitions between quantized energy levels.

### 9.2. **Quantum Chemistry.**

Quantum mechanical methods based on hydrogen solutions form foundational approximations (e.g., atomic orbitals used in molecular orbital theory), crucial for chemical bonding and molecular structure analyses.

### 9.3. **Atomic Clocks.**

Precise knowledge of atomic energy levels facilitates high-precision atomic clocks. These devices rely on electron transitions between quantized states for accuracy[5].

## 10. Conclusion

In this paper, we presented a detailed and rigorous analysis of the hydrogen atom through the lens of the time-independent Schrödinger equation. By employing separation of variables in spherical coordinates, we derived both the angular and radial equations governing the system. The angular part led to spherical harmonics, which describe the quantization of angular momentum, while the radial part yielded a second-order differential equation solved using generalized Laguerre polynomials [1].

From this analysis, we obtained the quantized energy levels of the hydrogen atom, recovering the expression for hydrogen's energy spectrum [2, 4]. We demonstrated how these results explain key physical phenomena, including the discrete nature of atomic spectral lines and the probabilistic spatial distribution of electrons.

Moreover, we extended this framework to hydrogen-like ions and computed examples of radial probability densities, illustrating the applicability of these mathematical methods to both physical interpretation and experimental verification [**Bransden2003**]. These results have direct implications in fields such as spectroscopy, quantum chemistry, and precision timekeeping via atomic clocks [5].

The content of this course and this paper relate to my personal interest in quantum physics and the standard model due to the relevance and necessity of PDE's in describing sub-atomic behavior. Exploring the hydrogen atom through Schrodinger's equation reinvigorated my personal interest in the subject and motivated me to continue reading and learning more to further develop and apply my personal understanding of the subject,.

## References

[1] N. H. Asmar. *Partial Differential Equations with Fourier Series and Boundary Value Problems*. 3rd. Dover Publications, 2017.

[2] David J. Griffiths and Darrell F. Schroeter. *Introduction to Quantum Mechanics*. 3rd. Cambridge University Press, 2018.

[3] J. J. Sakurai and Jim Napolitano. *Modern Quantum Mechanics*. 3rd. Cambridge University Press, 2017.

[4] R. Shankar. *Principles of Quantum Mechanics*. 2nd. Springer, 2012.

[5] John S. Townsend. *A Modern Approach to Quantum Mechanics*. 2nd. University Science Books, 2012.