

Solving Schrödinger's Equation for the Hydrogen Atom

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Abstract

Since the dawn of quantum mechanics, correctly predicting the emission spectrum of Hydrogen has been a crucial test for any atomic model. Wave mechanics are the standard for understanding quantum systems, and one of their most important discoveries is the Schrödinger equation—a PDE used to describe atomic behavior. We solved the three-dimensional, time-independent Schrödinger equation for a Hydrogen atom, an interesting two-body system (proton + electron). We found the allowed wavelengths of the atom's emission spectra as the eigenvalues of a Sturm-Liouville problem. Then, we determined the emission spectrum of Hydrogen experimentally using diffraction grating, the known spectra for Helium/Mercury, and a polynomial interpolant to test the accuracy of our theoretical predictions. Our largest absolute error was 1.2%, and most were much smaller.

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1 Introduction

The core goal of this project is to compare theoretical predictions of Hydrogen's emission spectrum to experimental measurements. We derive the wave function for Hydrogen analytically using Fourier's methods. In particular, we use spherical coordinates and apply separation of variables to construct three second-order ordinary differential equations whose products form the complete three-dimensional wave function. We utilize Sturm-Liouville theory, Legendre polynomials, Laguerre polynomials, and solution methods for equidimensional problems. This theoretical treatment results in a number of eigenstates corresponding to allowed energy levels of the Hydrogen atom. By examining the differences between nearby energy levels, we can predict the energy emitted in a photon when electrons transition downward. This ultimately yields an emission spectrum consistent with the Rydberg formula.

Next, we experimentally estimate Hydrogen's emission spectrum by taking pictures of a Hydrogen lamp through a diffraction grating. The resulting images have Hydrogen's spectral lines visible. By repeating this process for Helium and Mercury, and using the known wavelengths of their spectral lines as a reference, an interpolant is constructed via polynomial least squares regression to estimate wavelength from characteristics of the collected spectrum images. Applying this interpolant to Hydrogen yields a final experimental estimate that we compare to our theoretical predictions.

Upon comparison, we find that our theoretical and experimental results match closely, with a maximum error of 1.2% in the wavelength of each spectral line, with most much lower.

2 Derivation & Solution of the Schrödinger Equation

Schrödinger's equation was one of the most influential discoveries in quantum mechanics. It is a crucial piece of the project of describing quantum systems. Like the classical Hamiltonian equations of motion $\dot{q} = \frac{\partial \mathcal{H}}{\partial p}$, $\dot{p} = -\frac{\partial \mathcal{H}}{\partial q}$, Schrödinger's equation describes the evolution of a physical system over time. For our purposes, we will formulate Schrödinger's equation with a Hamiltonian which describes our system of interest, a single Hydrogen atom, and solve the resulting partial differential equation for a wave function Ψ . The wave function describes the quantum state of an isolated quantum system and, from it, we can derive the discrete allowable energy levels of the electron. These "quantized" energy states ultimately correspond to specific wavelengths in Hydrogen's emission spectrum, and we use our solution of the Schrödinger equation to calculate these spectral lines.

2.1 Problem Definition

The Schrödinger equation, as written in terms of an arbitrary Hamiltonian (describing the dynamics of the system), can be expressed as

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{\mathcal{H}} |\Psi\rangle \quad (1)$$

Here, $|\Psi\rangle$ is the wavefunction, which maps the system's configurations to probability amplitudes over time. For our purposes, a three-dimensional system of two particles, the Hamiltonian is the sum of the kinetic energies of the particles and the potential energy which describes their interaction. We also note for readers that \hbar is a physical constant, the reduced Planck constant. In reality, the Hamiltonian may be somewhat complicated—so we start with a simplifying assumption for our system. We consider only the motion *about* the center of mass, rather than the motion *of* the center of mass. Without expanding, we note that these quantities are separable and result in different equations with different Hamiltonians. This separation is largely algebraic, and requires only gradients and a (quantum) understanding of momentum. Since most treatments begin with the Hamiltonian specified and since we are primarily concerned with the solution of Schrödinger's equation, we note the Hamiltonian (for our simplified one-body problem) below without expanding.

$$\hat{\mathcal{H}} = \hat{T} + \hat{U} = \frac{\hat{p}^2}{2\mu} + V(\vec{r}), \quad \hat{p} = -i\hbar \nabla \quad \text{and} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2)$$

Above, \hat{p} describes the momentum of the system and μ is its reduced mass. For the hydrogen atom, $\mu \approx 0.9995 m_e$. Additionally, we describe the case of an electron near a much heavier nucleus fixed at the origin with charge Ze . Then, the Coulomb potential results in (where ρ is the distance to the origin)

$$\implies \hat{\mathcal{H}} = \frac{-\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0\rho} \quad (3)$$

Substituting this back into Schrödinger's equation yields

$$i\hbar \frac{d}{dt} \Psi = -\frac{\hbar^2}{2\mu} \nabla^2 \Psi - \frac{Ze^2}{4\pi\epsilon_0\rho} \Psi \quad (4)$$

Continuing for a time, we consider the substitution below to make the derivation cleaner.

$$V(\rho) = -\frac{Ze^2}{4\pi\epsilon_0\rho} \Psi \quad (5)$$

2.2 Separation of Variables

While Ψ is in principle a function of time, our Hamiltonian (and thus our physical situation) is time-independent. This indicates that our next step should be to separate time-dependence from the solution, resulting in a time-independent wavefunction ψ and a function $u(t)$. This step also introduces the eigenvalue E , representing the energy associated with a particular configuration.

$$\Psi(\vec{r}, t) = \psi(\vec{r})u(t) \implies i\hbar\psi \frac{du}{dt} = (\hat{\mathcal{H}}\psi)u \quad (6)$$

Consequently, the time-dependent wavefunction becomes the product of a time-independent solution and a simple oscillation:

$$\implies \frac{i\hbar}{u} \frac{du}{dt} = \frac{\hat{\mathcal{H}}\psi}{\psi} = \lambda \implies u(t) = \exp(-i\lambda t/\hbar), \quad \hat{\mathcal{H}}\psi = E\psi \quad (7)$$

The potential energy, $V(\rho)$, depends only on the radius from the origin so spherical coordinates are a natural choice. Without stating them explicitly, we use well-known facts about the definition of spherical coordinates and their gradient operator to arrive at Schrödinger's equation expressed in spherical coordinates. Also, without going into the physical details, we note a simplification using the angular momentum operator \mathbf{L}^2 which will simplify the derivation

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{\rho^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\rho^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\rho^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi(\rho, \theta, \phi) + V(r)\Psi(\rho, \theta, \phi) = E\Psi(\rho, \theta, \phi) \quad (8)$$

$$\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (9)$$

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{\rho^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 \rho^2} \mathbf{L}^2 \right] \Psi(\rho, \theta, \phi) + V(r)\Psi(\rho, \theta, \phi) = E\Psi(\rho, \theta, \phi) \quad (10)$$

We begin with the standard solution step, separation of variables: $\Psi(\rho, \theta, \phi) = R(\rho)Y(\theta, \phi)$. We substitute this separation into the equation above and proceed with basic algebra to find

$$\frac{1}{R(\rho)} \frac{d}{d\rho} \left(\rho^2 \frac{dR(\rho)}{d\rho} \right) - \frac{2\mu}{\hbar^2} [E - V(\rho)]\rho^2 = \frac{1}{\hbar^2} \frac{1}{Y(\theta, \phi)} \mathbf{L}^2 Y(\theta, \phi) \equiv A \quad (11)$$

We define the separation constant A because two equal equations of independent variables can only differ by a constant. We re-arrange slightly to arrive at two independent separated solutions which look more familiar

$$\left[-\frac{\hbar^2}{2\mu\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d}{d\rho} \right) + V(r) + A \frac{\hbar}{2\mu\rho^2} \right] R(\rho) = ER(\rho) \quad (12)$$

$$\mathbf{L}^2 Y(\theta, \phi) = A\hbar^2 Y(\theta, \phi) \quad (13)$$

Readers should notice that, at this point, (13) is an eigenvalue problem because it has a single unknown constant A. We apply separation of variables a second time: $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. After additional algebra, we arrive at the following separated solutions (note that we introduced a new separation constant B for the equation describing $\Phi(\phi)$)

$$\left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) - B \frac{1}{\sin^2 \theta} \right] \Theta(\theta) = -A\Theta(\theta) \quad (14)$$

$$\frac{d^2\Phi(\phi)}{d\phi^2} = -B\Phi(\phi) \quad (15)$$

At this point, we have three second-order ordinary differential equations to solve.

2.3 The Azimuthal Equation

We note that the Azimuthal Equation (as described by (15)) is a common boundary value problem (and a regular Sturm-Liouville problem) whose solutions are well-known and can be determined from substituting the assumed solution $\Phi(\phi) = e^{r\phi}$ and solving for the roots of the characteristic polynomial. We find that the solutions are the complex exponentials

$$\Phi(\phi) = c_1 e^{\pm i\sqrt{B}\phi} \quad (16)$$

We noted above that the Azimuthal equation is a boundary value problem, however, at this point we have yet to provide any boundaries and, thus, have yet to provide a solution. However, we can derive boundary conditions if we assume our wave function is well-defined and single-valued. This is not a trivial assumption, but for our purposes, it is an essential one—and accurately describes the physical system we're considering. Since the wave-function must be single-valued, we can impose the periodicity condition $\Phi(\phi + 2\pi) = \Phi(\phi)$ and, by implication, $\frac{d\Phi}{d\phi}(\phi + 2\pi) = \frac{d\Phi}{d\phi}(\phi)$. Thus \sqrt{B} must be real and, utilizing Sturm-Liouville properties, we can write

$$\Phi_m(\phi) = \sum_{m=1}^{\infty} c_{1m} \sin(m\phi) + \sum_{m=0}^{\infty} c_{2m} \cos(m\phi) \quad (17)$$

For clarity, note that we have introduced that \sqrt{B} must be an integer, which we call m , so that our solutions have the correct period. We also note the equivalent form (with an independent constant)

$$\Phi_m(\phi) = c_1 e^{im\phi} \quad (18)$$

Before continuing, we also note that we have a (hidden) additional condition from our assumption that the wave function is well-defined. Since the squared modulus of a wave function describes the probability density of a particle in (complex) space when that wave function depends on position, we solve for the normalization constant using a well-known result from probability.

$$1 = \int_0^{2\pi} \Phi_m^*(\phi) \Phi_m(\phi) d\phi = 2\pi |c_1|^2 \quad (19)$$

Above, we used that the absolute value of a complex number is $\sqrt{z^* \cdot z}$ where $z \in \mathcal{C}$ and $*$ is the adjoint operator. We let $c_1 = \frac{1}{\sqrt{2\pi}}$ to arrive at the solution

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (20)$$

In reality, we will re-compute the coefficients for the series solution in Section 2.5. However, this fact will be useful for describing an alternate solution form (and checking our work).

2.4 The Polar Equation

In solving the azimuthal equation we found that $\sqrt{B} = m \implies B = m^2$. Now, we once again have a single separation constant in the polar equation. Thus, it forms a boundary value problem we solve. We note the polar equation with this substitution below

$$\left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = -A\Theta(\theta) \quad (21)$$

We have seen equations in this form before, so we make the (non-obvious) substitution $x = \cos(\theta)$. After some algebraic manipulation (which we will not provide here, given it is well-described in many sources) we arrive at

$$\frac{d\Theta}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left(A - \frac{m^2}{(1-x^2)} \right) \Theta(x) = 0 \quad (22)$$

We note from references (Haberman) that this equation has solutions $A = n(n+1)$ for $n \in \mathbb{N}$ and bounded solutions given by Legendre polynomials of the first kind for $n \geq m$. We exclude Legendre polynomials of the second kind given the physical nature of the problem:

$$\Theta(\theta) = P_n^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_n(x) \quad (23)$$

Thus, taking advantage of Sturm-Liouville properties, we can write

$$\Theta(\theta) = \sum_{m=0}^{\infty} \sum_{n=m}^{\infty} c_{nm} P_n^m(\cos(\theta)) \quad (24)$$

Before continuing, we note some important properties of Legendre functions (McIntyre) which will allow us to determine c_{nm} .

$$P_\ell^{-m}(x) = P_\ell^m(x) \quad (25)$$

$$P_\ell^m(-x) = (-1)^{\ell-m} P_\ell^m(x) \quad (26)$$

$$\int_{-1}^1 P_\ell^m(x) P_q^m(x) dx = \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \delta_{\ell q} \quad (27)$$

We recall our original substitution for x to find (28), where $\sin \theta$ mysteriously appears because $(1 - \cos^2 \theta)^{\frac{m}{2}} = (\sin \theta)^{\frac{m}{2}} = \sin^m \theta$. Thus, using (25), (26), and (27) we find the orthogonality condition (29).

$$\int_0^\pi \Theta_\ell^m(\theta) \Theta_q^m(\theta) \sin \theta d\theta = \delta_{\ell q} \quad (28)$$

$$\int_{-1}^1 P_\ell^m(x) P_q^m(x) dx = \begin{cases} 0 & \ell \neq q \\ (-1)^{\ell-m} \frac{2}{2\ell+1} \frac{(\ell+|m|)!}{(\ell-|m|)!} & \ell = q \end{cases} \quad (29)$$

So, by applying orthogonality to the equation 28 we can solve for the normalizing constant c_{nm} .

$$c_{nm} = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2n+1}{2} \frac{(n-|m|)!}{(n+|m|)!}} \quad (30)$$

2.5 The Angular Equation

Given the families of product solutions we found above for $\Phi(\phi)$ and $\Theta(\theta)$ we return to solve for the angular equation given by $Y(\theta, \phi) = \Phi(\phi)\Theta(\theta)$. We form

$$Y(\theta, \phi) = \sum_{m=1}^{\infty} \sum_{n=m}^{\infty} c_{1nm} P_n^m \cos \theta \sin m\phi + \sum_{m=1}^{\infty} \sum_{n=m}^{\infty} c_{2nm} P_n^m \cos \theta \cos m\phi \quad (31)$$

However, we note that using the singular form (without sin/cos) of $Y(\theta, \phi)$ allows us to compute the coefficients more easily because in sections 2.4 and 2.5 we computed coefficients using the assumption the wave function was well-defined (19) and properties of Legendre functions (30). We remind readers that, as previously noted, when a wave function depends on position it must be orthogonal. Thus, we find

$$Y_n^m(\theta, \phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2n+1}{4\pi} \frac{(n-|m|)!}{(n+|m|)!}} P_n^m \cos \theta e^{im\phi} \quad (32)$$

2.6 The Radial Equation

Now, we return to the radial equation which has become a solvable eigenvalue problem with the substitution $A = n(n+1)$. We remind readers of its form below

$$\left[-\frac{\hbar^2}{2\mu\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d}{d\rho} \right) + V(r) + n(n+1) \frac{\hbar^2}{2\mu\rho^2} \right] R(\rho) = ER(\rho) \quad (33)$$

Recall from above that $V(\rho) = -\frac{Ze^2}{4\pi\epsilon_0\rho}$, the Coulomb potential energy. We re-introduce that value here and make several substitutions to simplify the resulting differential equation, as recommended by McIntyre.

1. Let $r = \frac{\rho}{a}$ where a is the characteristic length scale of the hydrogen atom, $a = \frac{4\pi\epsilon_0\hbar^2}{\mu Ze^2}$, so that r is a dimensionless radius
2. Let $-\gamma^2 = \frac{E}{\left(\frac{\hbar^2}{2\mu a^2}\right)}$, a dimensionless energy parameter.

With these simplifications, we present the modified radial differential equation

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[-\gamma^2 + \frac{2}{r} - \frac{n(n+1)}{r^2} \right] R(r) = 0 \quad (34)$$

We begin by noting asymptotic solutions, which are especially instructive because—given its nature—the wave function should be finite everywhere. For $r \gg 1$, r^{-1} and r^{-2} terms are dominated so we solve

$$\frac{d^2 R}{dr^2} - \gamma^2 R \approx 0 \quad (35)$$

This simple boundary value problem has well-known solutions $R(r) = e^{-\gamma r}$.

For $1 \gg r$ (approaching the singular point at $r = 0$), the r^{-2} term dominates. So, we solve

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} - \frac{n(n+1)}{r^2} R \approx 0 \quad (36)$$

This is an equidimensional problem. Thus, solutions are of the form $R(r) = r^q$. We present the characteristic equation and its solutions below

$$q(q-1)r^{q-2} + \frac{2}{r}qp^{q-1} - \frac{n(n+1)}{r^2}p^q = 0 \quad (37)$$

$$q(q+1) - n(n+1) = 0 \implies q = n \text{ and } q = -(n+1) \quad (38)$$

Observe that, for $1 \gg r$, the solution $p^{-(n+1)}$ becomes unbounded. So, we have the limiting form $R(r) = r^n$. If we combine these asymptotic solutions we obtain $R(r) = r^n e^{-\gamma r}$, which remains well-behaved for $r = 0$ and $r \rightarrow \infty$. To complete the solution, we need to describe the behavior for intermediate r . So, posit a function $H(r)$ exists which is well-behaved at $r = 0$ and $r \rightarrow \infty$ (or blows up more slowly).

Now, we seek to determine $H(r)$ by substituting our trial function $R(r) = r^n e^{-\gamma r} H(r)$ into (34). We start by computing the necessary derivatives using the chain rule

$$\frac{dR}{dr} = r^{n-1} e^{-\gamma r} [nH(r) - \gamma r H(r) + r H'(r)] \quad (39)$$

$$\frac{d^2 R}{dr^2} = r^{n-1} e^{-\gamma r} [-(2 + 2\gamma + 2\gamma r)H(r) + (2 + 2r - r\gamma r)H'(r) + r H''(r)] \quad (40)$$

By collecting terms we arrive at

$$r \frac{d^2 H}{dr^2} + 2(n+1 - \gamma r) \frac{dH}{dr} + 2(1 - \gamma - \gamma r)H(r) = 0 \quad (41)$$

Assume that $H(r)$ can be expressed as the power series $H(r) = \sum_{i=0}^{\infty} c_i r^i$, an infinite-degree polynomial. We note that this is a relatively justifiable assumption—if $H(r)$ could not be represented by elementary functions (which can be approximated by power series) it would be very difficult to find. We proceed with term-by-term differentiation—which is justifiable, given our earlier assumptions that the wave equation is well-defined.

$$\frac{dH}{dr} = \sum_{i=0}^{\infty} i c_i r^{i-1} = \sum_{i=0}^{\infty} (i+1) c_{i+1} r^i \quad (42)$$

$$\frac{d^2 H}{dr^2} = \sum_{i=0}^{\infty} i(i+1) c_{i+1} r^{i+1} \quad (43)$$

We substitute (again) to find the not particularly helpful-looking

$$\sum_{i=0}^{\infty} i(i+1) c_{i+1} r^i + 2(n-1) \sum_{i=0}^{\infty} (i+1) c_{i+1} r^i - 2\gamma \sum_{i=0}^{\infty} i c_i r^i + 2(1-\gamma-\gamma n) \sum_{i=0}^{\infty} c_i r^i = 0 \quad (44)$$

But, if we notice that in order for all terms of the series to sum to zero, the coefficient of each power of r must be zero then we can obtain a recurrence relation.

$$\begin{aligned} (2n+i+2)(j+1)c_{i+1} + [2(1-\gamma-\gamma n) - 2\gamma i]c_i &= 0 \\ (2n+i+2)(j+1)c_{i+1} &= [2(\gamma+\gamma n-1) + 2\gamma i]c_i \\ (2n+i+2)(j+1)c_{i+1} &= [2\gamma + 2\gamma n + 2\gamma i - 2]c_i \\ c_{i+1} &= \frac{2\gamma(1+i+n) - 2}{(2n+i+2)(i+1)} c_i \end{aligned} \quad (45)$$

Before we solve for c_0 , let us verify that $H(r)$ has the asymptotic properties described above. For large i the recurrence relation becomes $c_{i+1} = \frac{2\gamma i}{i^2} c_i = \frac{2\gamma}{i} c_i$. Note that, for large i , this approximately represents the exponential function, given by $e^{\alpha x} = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} x^n$. So, for large i , $H(r) \approx e^{2\gamma r}$ which, when substituted into $R(r) = r^n e^{-\gamma r} H(r)$ leads to the function $R(r) = r^n e^{-\gamma r}$. Unfortunately, this result in unbounded as $i \rightarrow \infty$. So, we can impose a limit on the maximum number of terms in the series.

$$2\gamma(1+i_{\max}+n) - 2 = 0 \quad (46)$$

$$\implies \ell = i_{\max} + n + 1 \text{ where } \ell \text{ is an integer} \quad (47)$$

Although on its on it is not particularly mathematically meaningful, based on the physical system we are modeling we recognize that ℓ is the so-called principal quantum number of the hydrogen atom. We draw some conclusions about the principal quantum number below:

1. $\ell = 1, 2, 3, \dots, \infty$
2. We can solve $\gamma = \frac{1}{\ell}$ to find that $-\frac{1}{\ell^2} = \frac{E}{\left(\frac{\hbar^2}{2\mu a^2}\right)} = \frac{E}{\left(\frac{\hbar^2}{2\mu}\right)} \left(\frac{4\pi\epsilon_0 \hbar^2}{\mu Z e^2}\right)$. Thus, we have a discrete quantization of the energy based on ℓ $E_{\ell} = -\frac{1}{2\ell} \left(\frac{Z e^2}{4\pi\epsilon_0}\right) \frac{\mu}{\hbar^2}$
3. For finite values of ℓ , n cannot exceed $\ell - i_{\max} - 1$ so we impose the upper bound on n , $n = 0, 1, 2, \dots, \ell - 1$.

Returning to the radial equation, recall that

$$R(r) = r^n e^{-\gamma r} H(r) \quad (48)$$

At this point, we begin to return dimensions to the problem. Let

$$a = \frac{4\pi\epsilon_0 \hbar^2}{m_e Z e^2} = \frac{a_0}{Z}, \text{ with } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.0529 nm \quad (49)$$

We call a_0 the Bohr radius, and it can be experimentally measured. We let m_e represent the mass of the electron which is a good approximation for μ . Technically, $\mu \approx 0.9995 m_e$ but we reserve this precision for calculations. Then we have $r = \frac{\rho}{a} = \frac{Z r}{a_0}$. Thus,

$$R_{\ell n} = \left(\frac{Z \rho}{a_0}\right)^n e^{-\frac{Z r}{a_0}} H\left(\frac{Z \rho}{H_0}\right) \quad (50)$$

Now, we want to find polynomials $H(Z_0/a_0)$ for each state. Continuing the recurrence relation we derived earlier, we may write the radial wave functions in terms of associated Laguerre polynomials $L_q^p(x)$ defined as

$$L_q^p = \frac{d^p}{dx^p} L_q(x) \quad (51)$$

Note that associated Laguerre polynomials are defined using ordinary Laguerre polynomials

$$L_q(x) = e^x \frac{d^q}{dx^q} (x^q e^{-x}) \quad (52)$$

Using these definitions, we note the radial unity condition and redefine the radial wave functions

$$\int_0^\infty [R_n^\ell(\rho)]^2 \rho^2 d\rho = 1 \quad (53)$$

$$R_{\ell n} = - \left\{ \left(\frac{2Z}{\ell a_0} \right)^3 \frac{(\ell - n - 1)!}{2\ell[(\ell + n)!]^3} \right\}^{\frac{1}{2}} e^{-\frac{Z\rho}{\ell a_0}} \left(\frac{2Z\rho}{\ell a_0} \right)^n L_{\ell+n}^{2n+1} \left(\frac{2Z\rho}{\ell a_0} \right) \quad (54)$$

2.7 3D Eigenstate Wave Function

Finally, we multiply our separated solutions to find $\psi(\rho, \theta, \phi)_{m,n,\ell}$.

$$\begin{aligned} \psi(\rho, \theta, \phi)_{m,n,\ell} = & - \left\{ \left(\frac{2Z}{\ell a_0} \right)^3 \frac{(\ell - n - 1)!}{2\ell[(\ell + n)!]^3} \right\}^{\frac{1}{2}} e^{-\frac{Z\rho}{\ell a_0}} \left(\frac{2Z\rho}{\ell a_0} \right)^n L_{\ell+n}^{2n+1} \left(\frac{2Z\rho}{\ell a_0} \right) \\ & (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2n+1}{4\pi} \frac{(n-|m|)!}{(n+|m|)!}} P_n^m \cos \theta e^{im\phi} \\ & \text{for } \ell \in 0, 1, \dots, n \in 0, 1, \ell - 1, m \in -n, \dots, n \end{aligned} \quad (55)$$

Note: We omit the series notation for space and clarity. However, note that $\psi(\rho, \theta, \phi)$ is given by the sums over ℓ, n , and m .

2.8 Energy Levels of the Hydrogen Atom

Determining the wavelengths of light emitted/absorbed by transitioning between energy states does not actually require the entire eigenstate wave function, although it encodes this information. The solution to the radial equation produced a discrete (quantized) set of allowable energy values. We let $Z=1$ and recall $\mu \approx m_e$.

$$E_\ell = -\frac{1}{2\ell^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{\hbar^2} \text{ for } \ell \in 0, 1, \dots \quad (56)$$

Photon emissions in the visible spectrum exist for transitions $6 \rightarrow 2$, $5 \rightarrow 2$, $4 \rightarrow 2$, and $3 \rightarrow 2$. The energy of the emitted photons is given by the difference in energy of the states

$$E_{\text{photon}} = |E_{nf} - E_{ni}| = \frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| \quad (57)$$

Then we can solve for the wavelength using the relationships given by McIntyre

$$\lambda = \frac{1}{R_\infty \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|} \text{ with } R_\infty = \frac{m_e}{4\pi\hbar^3 c} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \quad (58)$$

We call R_∞ the Rydberg constant. It was discovered empirically and is now one of the most precisely measured physical constants. We use $R_\infty = 10973731.56852773 \text{ m}^{-1}$ as its value. We include our theoretical estimates for the wavelengths of emitted photons below in the results.

2.9 Alternative Derivation Methods

The problem can be simplified significantly if we assume spherical symmetry during the derivation. Interestingly, this assumption, while inaccurate, still yields an identical set of allowed energies, and thus an identical emission spectrum.

We begin with (7). Substituting our previously defined Hamiltonian yields

$$\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{Ze^2}{4\pi\epsilon_0\rho} \psi + E\psi = 0 \quad (59)$$

Separating $\psi(\vec{r})$ in spherical coordinates implies $\psi(\rho, \theta, \phi) = f(\rho)g(\theta)h(\phi)$, where θ is the polar angle and ϕ is the azimuthal angle. In this method, we will only consider spherically symmetric solutions, meaning we take $g(\theta) = h(\phi) = 1$ such that the solution has only radial dependence. When we expand the Laplacian operator in spherical coordinates, we obtain

$$\begin{aligned} & \frac{\hbar^2}{2\mu} \left(\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{df}{d\rho} \right) \right) + \left(\frac{Ze^2}{4\pi\epsilon_0\rho} + E \right) f = 0 \\ \implies & \rho^2 \frac{d^2 f}{d\rho^2} + 2\rho \frac{df}{d\rho} + \frac{2\mu\rho^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0\rho} + E \right) f = 0 \end{aligned} \quad (60)$$

Next, we perform the substitution $x = \rho \frac{\mu Ze^2}{4\pi\epsilon_0\hbar^2} \implies \rho = \frac{4\pi\epsilon_0\hbar^2}{\mu Ze^2} x$ in order to concentrate dimensional constants to one term. The result is (defining the constant k for simplification)

$$x^2 \frac{d^2 f}{dx^2} + 2x \frac{df}{dx} + 2xf + \underbrace{\frac{32\pi^2\epsilon_0^2\hbar^2}{\mu Z^2 e^4} E}_{=k} x^2 f = 0 \quad (61)$$

Rewriting and simplifying slightly, we are left with a simplified form of the radial equation, which should constrain the possible values of E .

$$x \frac{d^2 f}{dx^2} + 2 \frac{df}{dx} + kExf = 0 \quad (62)$$

In order to obtain a form closer to that of a known differential equation from (62), and ultimately determine the allowed values of E , we make the substitution $F(x) = f(x)e^{sx} \implies f(x) = F(x)e^{-sx}$ for some arbitrary $s \in \mathbb{R}$. Upon substitution, we obtain

$$x \frac{d^2 F}{dx^2} + (2 - 2sx) \frac{dF}{dx} + (s^2 x - 2s + 2 + kEx) F = 0 \quad (63)$$

Making an additional substitution $y = 2sx$ yields

$$\implies y \frac{d^2 F}{dy^2} + (2 - y) \frac{dF}{dy} + (s^{-1} - 1)F + \frac{s^2 + kE}{4s^2} yF = 0 \quad (64)$$

This is similar to the differential equation satisfied by the associated Laguerre polynomials L_n^α , which is (for $\alpha = 1$):

$$y \frac{d^2 L_n^{(1)}}{dy^2} + (2 - y) \frac{dL_n^{(1)}}{dy} + nL_n^{(1)}(y) = 0, \quad n \in \mathbb{W} \quad (65)$$

The radial equation (64) is similar to this, but with an additional term involving yF . However, this term can be eliminated if we pick E such that $s^2 + kE = 0 \implies E = -s^2/k$. Imposing this condition, we find

$$y \frac{d^2 F}{dy^2} + (2 - y) \frac{dF}{dy} + (s^{-1} - 1)F = 0$$

However, in (65), Laguerre polynomial solutions only exist for $n \in \mathbb{W}$, which implies that we must have the restriction $(s^{-1} - 1) \in \mathbb{W} \implies s^{-1} \in \mathbb{N}$. If we let $n \in \mathbb{N}$, $s = n^{-1}$, we see that (62) has constrained the possible choices of the energy E to be $E = -1/(kn^2)$. Substituting our definition of k , and letting $Z = 1$, we find an identical expression for the allowed energies

$$E = -\frac{\mu}{2n^2} \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \quad (66)$$

3 Experimental Results

3.1 Laboratory Methods

In order to confirm our theoretical predictions of the allowed energy levels of the Hydrogen Atom, the emission spectrum of Hydrogen needed to be experimentally measured. Given that a dedicated spectrometer was not available, a measurement of the emission spectrum was made using a camera and a diffraction grating.

Hydrogen, Helium, and Mercury lamps were provided by the physics department as part of a standard undergraduate experimental physics lab, and pictures were taken using a phone camera through a diffraction grating of unknown specification, taking care to use identical camera settings for each picture. Assuming the diffraction grating is uniform, the distance between the camera lens and the diffraction grating would not have an effect on the positioning of spectral lines within the resulting image, as the angular deflection for a given wavelength is the same. Hence, the diffraction grating was manually held in front of the camera just close enough that it covered the entire field of view.

After taking these images, GIMP (GNU Image Manipulation Program) was used to measure distances between the tube and the spectral lines as they appeared in each image, in pixels (px), denoted d . The result for each lamp, annotated with pixel distances for each relevant spectral line, is given in Figure 1.

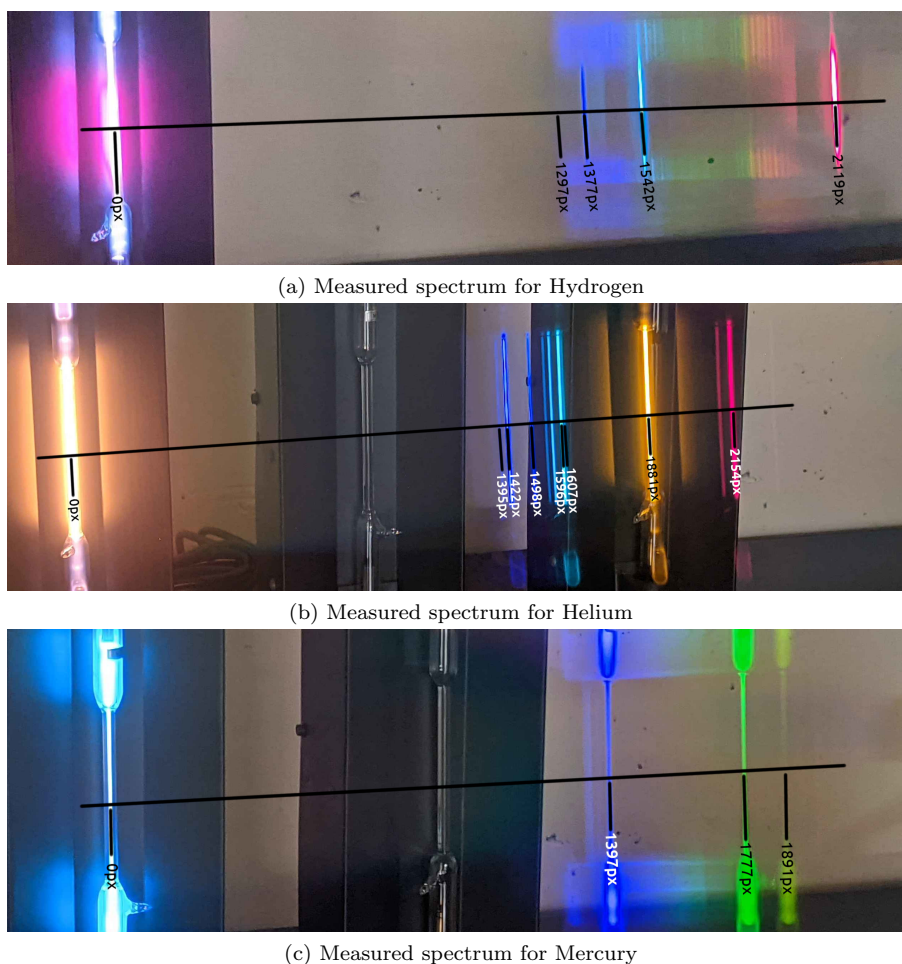


Figure 1: Annotated diffraction grating images for available lamps

The measured spectral lines for Helium and Mercury were then cross-referenced with known spectra, resulting in a number of d - λ pairs. Given that both image displacement and wavelength are ideally proportional to $\sin \theta$, where θ is the deflection angle through the diffraction grating, the image displacements of spectral lines should be proportional to their respective wavelengths. However, the camera's lens distortion means that they are not perfectly proportional to each other, and a more sophisticated method of interpolation was necessary to accurately deduce the emission spectrum from the Hydrogen lamp.

3.2 Polynomial Interpolation

We implemented a standard least-squares polynomial regression using python and `scikit-learn` (code in Appendix B) on observed data for He/Hg spectra (found in Appendix A). In particular, we predicted wavelength using image displacement—whose calculation is described above. Polynomial interpolation is a technique from numerical analysis that interpolates a bivariate data set by the polynomial of lowest possible degree which passes through all of the points. In particular, given a set of data points $\{(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)\}$ and a function $p(x_j) = a_0 + a_1x + \dots + a_nx^n$ we call it an interpolant if $p(x_j) = y_j$ for each $j \in \{0, 1, \dots, n\}$. In practice, we try to minimize the error term $\sum_j |p(x_j) - y_j|^2$ by using an ordinary least-squares regression to fit the polynomial to experimentally observed data. Additionally, given the observed shape of the data, we use a polynomial of degree 2 (a quadratic function) to avoid overfitting or unwanted oscillatory behavior. Thus, we don't make rigorous theoretical guarantees regarding convergence, etc. But—for our purposes—a polynomial of degree two fits the data quite well. See Figure 2 below, which plots the experimental data (in black), quadratic fit, and predicted hydrogen wavelengths (in red).

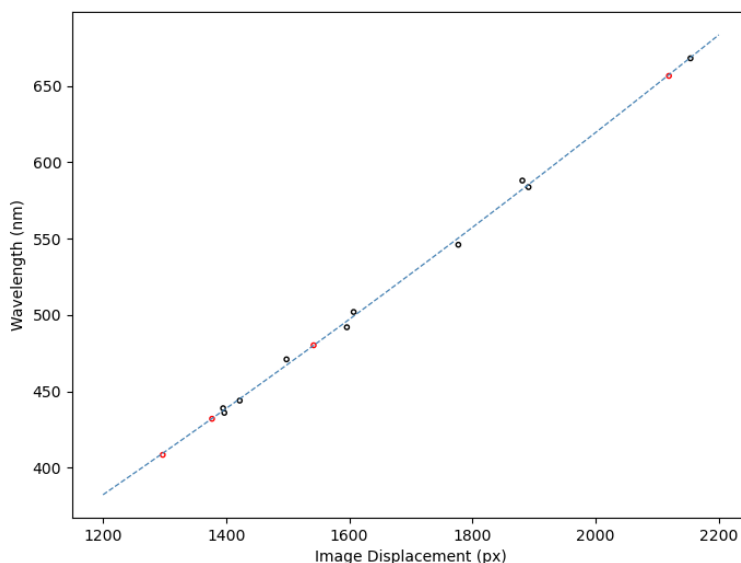


Figure 2: Polynomial Interpolation

We briefly outline our results for the hydrogen atom in Table 1 below.

Element	Displacement (px)	Predicted λ (nm)
H	1297	409.6
H	1377	432.3
H	1542	480.1
H	2119	657.3

Table 1: Polynomial Interpolation Results for Hydrogen

3.3 Results

After using the polynomial regression to deduce the wavelength of Hydrogen's spectral lines from the measurements displayed in figure 1a, we are left with four sufficiently strong ones in the visible range. In order to identify the electronic transition that these emission lines correspond to, we manually searched for small integers such that nearly consecutive transitions between the corresponding energy levels would approximately yield our experimental wavelength measurements (using (58)). Once we identified the transitions, we could then calculate an expected emission wavelength. The resulting summary can be found in Table 2.

All of these transitions are consecutive, as well as finishing in the $n = 2$ state, meaning these spectral lines are the first four in the Balmer spectral series for Hydrogen, as expected. In addition, the accuracy

Hydrogen Spectral Lines			
Measured λ	Transition	Expected λ	Error %
409.6 nm	$6 \rightarrow 2$	410.1 nm	-0.12%
432.3 nm	$5 \rightarrow 2$	433.9 nm	-0.37%
480.1 nm	$4 \rightarrow 2$	486.0 nm	-1.2%
657.3 nm	$3 \rightarrow 2$	656.1 nm	0.18%

Table 2: Summary of experimental results

is quite good (within 2% for all four spectral lines) indicating that both the theoretical and experimental components are behaving as expected.

4 Summary & Conclusions

Here, we have been able to successfully apply methods of PDEs, Sturm-Liouville theory, and known eigenvalue problems to theoretically calculate the allowed energies for a Hydrogen atom in terms of universal constants, which we then experimentally verified via a measurement of the emission spectrum. This particular application of quantum mechanics presents several conclusions, the most fundamental of which is simply the expected result that the Schrödinger equation holds a significant amount of power to explain experimental observations. While the Schrödinger equation is an incomplete description of the universe (e.g. it does not account for special relativity, nor does it hold at very high energies), in this particular case it is "good enough" to describe the behavior of a single Hydrogen atom at relatively low energies, and can describe this case purely analytically.

We can also draw a conclusion as to some of the chemistry occurring within the Hydrogen lamp. Namely, Hydrogen is naturally found as H_2 , which has a much different structure and would likely have a completely different set of allowed energies. However, our experimentally observed spectrum is very close to that predicted of single Hydrogen atoms, which implies that the high voltage in the lamp provides enough energy for H_2 to break apart into single Hydrogen atoms, which then have electronic transitions excited.

Originally, Hydrogen's spectral series were explained using the Rydberg formula

$$\lambda_e = (R_\infty(n_1^{-2} - n_2^{-2}))^{-1}, \quad n_1, n_2 \in \mathbb{N}$$

This formula originated purely because it seemed to fit the spectral lines well, and not due to a result from quantum mechanics. However, our final theoretical result validates this as a means to compute spectral lines of Hydrogen-like elements, and expressed R_∞ in terms of other universal constants. In this way, we can conclude that the Rydberg formula is a result of the Schrödinger equation in this case, even though it was not originally derived that way.

Finally, our attempts to match Helium and Mercury's spectral lines to our theoretical analysis were unsuccessful, implying that the interaction between other electrons in non-Hydrogen-like elements requires a much more complicated theoretical treatment.

Given more time, it would be interesting to experimentally confirm the applicability of these results to other Hydrogen-like atoms (i.e. alkali metals and other ions). In addition, using the Schrödinger or Dirac equations to predict the emission spectra of both Helium and Mercury could serve to enhance our understanding of these methods, although its complexity may necessitate numerical solution. While our final accuracy was relatively good, it may have been better if actual spectrometers were available as opposed to a camera and diffraction grating. More time given to this project may have allowed us to acquire the equipment necessary to make more accurate experimental measurements.

5 Acknowledgments

All authors contributed to all parts of the paper. Cassidy All completed the general solution using Fourier methods and constructed the final polynomial interpolant. Ray Anchordoquy collected the diffraction grating images, analyzed them to produce image displacements, and provided the alternate solution method.

6 References

- [1] Richard Haberman. *Applied Partial Differential Equations with Fourier Series and Boundary Value Problems*. Pearson Education Inc., 2013.
- [2] David H McIntyre. *Quantum Mechanics: A Paradigms Approach*. Cambridge University Press, 2012.

Appendix A Experimentally Observed Data

Element	Displacement (px)	Known λ (nm)
H	1297	N/A
H	1377	N/A
H	1542	N/A
H	2119	N/A
He	1395	439
He	1422	444
He	1498	471
He	1596	492
He	1607	502
He	1881	588
He	2154	668
Hg	1397	436
Hg	1777	546
Hg	1891	584

Table 3: Complete Experimental Results

Appendix B Polynomial Interpolation Code

```

import numpy as np
import matplotlib.pyplot as plt
from sklearn.linear_model import LinearRegression
from sklearn.preprocessing import PolynomialFeatures

# Data for He/Hg
X = np.array([1395, 1422, 1498, 1596, 1607, 1881, 2154, 1397, 1777, 1891])

X = X.reshape(-1, 1)
y = np.array([439, 444, 471, 492, 502, 588, 668, 436, 546, 583.7])
y = y.reshape(-1)

# Data for Hydrogen
hydro_distr = np.array([1297, 1377, 1542, 2119]).reshape(-1, 1)

poly = PolynomialFeatures(degree=2, include_bias=False)
poly_features = poly.fit_transform(X)
poly_model = LinearRegression()
poly_model.fit(poly_features, y)

# Define prediction function
def poly_interp(x):
    return poly_model.coef_[1] * x**2 + poly_model.coef_[0] * x + poly_model.intercept_

interp = lambda x: poly_interp(x)
fast_interp = np.vectorize(interp)

# Get data for curve
x_seq = np.linspace(1200, 2200, 1000).reshape(-1, 1)
interp_seq = fast_interp(x_seq)

# Plot He/Hg data, curve, and Hydrogen points
fig, ax = plt.subplots(figsize=(8, 6))
ax.scatter(X, y, marker=".", fc="none", ec="black")
ax.scatter(hydro_distr, fast_interp(hydro_distr), marker=".", fc="none", ec="red")
ax.plot(x_seq, interp_seq, ls="dashed", color="steelblue", lw=0.9)
ax.set_xlabel("Image-Displacement-(px)")
ax.set_ylabel("Wavelength-(nm)")

plt.show()

# Print predictions
for x in hydro_distr:
    pred = poly_interp(x)
    print("Prediction:-" + str(pred))

```