# How can you mathematically determine and prove the emission spectrum of hydrogen?

## Introduction

### Rationale

The concept of emission spectra is one of the key foundational ideas learned early on in any chemistry class. I was first exposed to this a few years ago in my General Chemistry class, and then in my IB Chemistry HL Class. Much like how the many types of sciences have concepts that are connected to each other, I do a great deal of mathematics in my chemistry such as in units like Stoichiometry. Though it was abundantly clear that both disciplines are deeply intertwined, the topic this exploration is being done on, in classes, had conceptual understanding prioritized above any mathematical calculations associated with it. Thus, I deemed it appropriate to conduct a mathematical exploration into the world of chemistry in order to gain access to an understanding of emission spectra through a new perspective.

### Aim

The aim of this experiment is to mathematically determine the emission spectrum of hydrogen through theoretical calculations, and then prove the validity of these theoretical calculations by processing existing emission data. Thus, the investigation will be split into two parts. In the first part (theoretical), the Rydberg Equation will be derived and the upper bound of the Balmer Series will be extrapolated. The second part of the investigation (experimental) will focus on calculating wavelengths from emission data, thus allowing for the comparison of theoretical and experimental values.

### Background Information

Emission spectra rely on the scientific idea that light can be depicted as both a wave and a particle, and it is widely taught to familiarize students with the concepts of the electromagnetic spectrum, as well as energy levels within an atom. It is a collection of specific wavelengths within the visible light spectrum (380–700nm) (NASA, 2010), that varies based on chemical element. A method of determining the emission spectrum of an element is by passing an electric current through the element in gas form at a low pressure, resulting in the gas (which is contained in a gas discharge tube), glowing a specific color (Libretexts, 2022). The light emitted from the tube from this excitation is then observed through a diffraction grating located on a spectrometer, which shows various discrete wavelengths of light that combine to make up the specific color of that element's gas (Keller, 2020).

In the case of this experiment, I chose the example of hydrogen to explore, as it has only a single electron, thus we are able to make concrete calculations without having to factor in multiple electron movements. In order to understand hydrogen's emission spectrum, it is necessary to familiarize oneself with the two following diagrams:

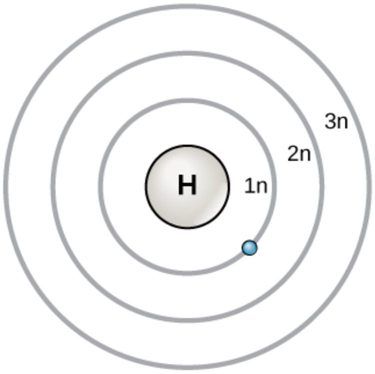
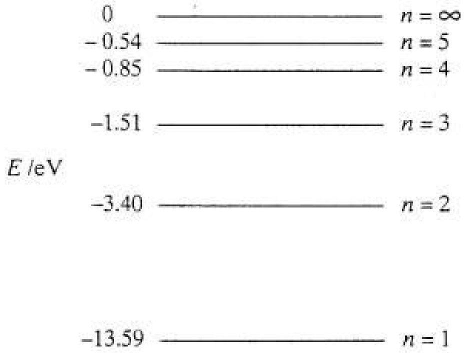
| Figure 1. Hydrogen’s Bohr Model<br>(Boundless, 2022) | Figure 2. Convergence of energy levels<br>(Eliza et al., 1961) |
|---|---|
|  |  |

Figure 1 is what chemists commonly call a “Bohr Model.” It is a commonly constructed model of any element (in the above case, hydrogen) that depicts the nucleus as well as electrons of the atom. Though there are certain limitations to the model, as it does defy principles of uncertainty within chemistry due to its assumption that an electron’s exact position and speed can be determined with full accuracy, for this exploration it will suffice. The circles surrounding the nucleus (labeled 1n, 2n…) are the energy levels of the atom. Though figure 1 only represents 3 energy levels within the hydrogen atom, in actuality the number of energy levels an element has is infinite, much like what is demonstrated in figure 2. The distance between these energy levels (the energy difference between them) decreases as the number of energy levels increase, thus resulting in them eventually converging.

Hydrogen gas, when alight from the mechanism mentioned prior, can be observed to be a very distinct pink color. When the hydrogen atom is in its excited state (when it is energized), its one electron will move up from its ground state to any higher energy level (n=2,3,4…), depending on how much energy has been absorbed. Afterwards, the electron falls down to a lower energy state, which can be the ground state (n=1) or any other lower level (for example, an electron can go from n=6 to n=5), and a photon (particle of light) is emitted (Source: Arlington Central School District). These photons have certain energies based on the original location of the electron on the upper energy level, and where it fell down to afterwards (the distance and energy that corresponds with the distance, refer to fig. 2). Each photon of light released has a specific wavelength and frequency, and can be located on the EM spectrum. Chemists are able to split the emissions of hydrogen into specific series, depending on which energy level the electron falls down to:

| Spectral Series | Location on Spectrum | Transition |
|---|---|---|
| Lyman | Ultraviolet | $n_X \rightarrow n_1$, where $X > 1$ |
| Balmer | Ultraviolet and Visible Light | $n_X \rightarrow n_2$, where $X > 2$ |
| Paschen | Infrared | $n_X \rightarrow n_3$, where $X > 3$ |
| Brackett | Infrared | $n_X \rightarrow n_4$, where $X > 4$ |
| Pfund | Infrared | $n_X \rightarrow n_5$, where $X > 5$ |
| Humphreys | Infrared | $n_X \rightarrow n_6$, where $X > 6$ |

Table 1. Spectral series and their transitions

Note that notation for energy level can be expressed in multiple ways. For example, energy level 5 can be written as: 5n, n=5, and $n_5$. This investigation will use latter notation for its calculations and explanations.

Due to there being infinite energy levels, there are still other series that exist. However, they are unnamed and less relevant. This exploration will specifically only focus on the Balmer series, which contains several wavelengths in the ultraviolet and visible light spectrum. Because this is the only observable series to the human eye, experimentally obtained values that will be presented further in the investigation are only limited to this series within the visible light spectrum, the colors of which are primarily composed of violet, blue-violet, blue-green, and red (Purdue University). Thus, theoretical calculations will also only focus on the Balmer series as well for the sake of further comparison.

## Theoretical Calculations

### Rydberg Equation

The Rydberg Equation is a substitution of the many other equations already present within science. The following will be a narration of how it is derived.

Firstly, it has been established in the background information that the energy emitted by a photon is the same as the energy difference between an electron transitioning from a greater energy level, which will be called $n_i$ (i stands for initial), to a lesser energy level $n_f$ (f stands for final), with both $n_i$ and $n_f$ needing to be positive integers.

$$E_{photon} = \Delta E_{electron}$$
$$E_{photon} = E_{n_i} - E_{n_f}$$

Planck's equation shows the relationship between energy $E$ and frequency $v$ along with Planck's constant, $h$. However, we also know that frequency can be calculated by dividing the speed of light $c$ by wavelength $\lambda$.

Planck's equation: $E_{photon} = hv$

Frequency equation: $v = \frac{c}{\lambda}$

Therefore, we can establish (after substituting the $v$ in Planck's equation) with the value of $v$ in the frequency equation that:

$$E_{photon} = h(\frac{c}{\lambda}) = E_{n_i} - E_{n_f}$$
$$\frac{hc}{\lambda} = E_{n_i} - E_{n_f}$$

Niels Bohr established that any nth energy level is related by dividing the energy of the first energy level $E_1$ by the squared of $n$ ($E_n = \frac{E_1}{n^2}$) (Princeton, 2012). Thus,

$$\frac{hc}{\lambda} = (\frac{E_1}{n_i^2} - \frac{E_1}{n_f^2})$$
$$\frac{hc}{\lambda} = E_1(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$
$$hc \times \frac{1}{\lambda} = E_1(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$
$$\frac{1}{\lambda} = \frac{E_1}{hc}(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$

The energy associated with the first orbit of the hydrogen atom is $-\ 2.18 \times 10^{-18} J\ atom^{-1}$. Both $h$ and $c$ are constants with the values of $6.63 \times 10^{-34} m^2\ kg\ s^{-1}$ and $3.00 \times 10^{8} m\ s^{-1}$ respectively. Therefore, the value of the Rydberg constant for Hydrogen, which is equivalent $\frac{E_1}{hc}$ can be calculated.

$$R = \frac{E_1}{hc}$$
$$R = \frac{-2.18\times10^{-18}}{6.63\times10^{-34} \bullet 3.00\times10^{8}}$$
$$R_{(before\ neg)} \approx -\ 1.097 \times 10^{7}$$

By substituting this value back into the equation that has been derived so far: $\frac{1}{\lambda} = \frac{E_1}{hc}(\frac{1}{n_i^2} - \frac{1}{n_f^2})$, the final equation can be obtained. The $R$ value becomes positive when the positions of $\frac{1}{n_i^2}$ and $\frac{1}{n_f^2}$ are switched because a $-$ is taken out.

$$\frac{1}{\lambda} = -\ 1.097 \times 10^{7}(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$
$$\frac{1}{\lambda} = 1.097 \times 10^{7}(\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

Commonly expressed as: $\frac{1}{\lambda} = R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$

The values for $n_f$ and $n_i$ can be substituted based on which series is being represented as long as $n_i > n_f$. For example, an electron begins ($n_i$) at energy level 6, and then falls down ($n_f$) to level 2, thus going from $n_6$ to $n_2$. This would mean $n_i = 6$ and $n_f = 2$. Using this information, we are able to calculate the wavelength of light that is emitted by the photon from this transition:

$$\frac{1}{\lambda} = R(\frac{1}{2^2} - \frac{1}{6^2})$$

$$\frac{1}{\lambda} = 1.097 \times 10^7(\frac{1}{4} - \frac{1}{36})$$

$$\frac{1}{\lambda} = 1.097 \times 10^7(\frac{2}{9})$$

$$\lambda = \frac{1}{2438666.667}$$

$$\lambda \approx 4.100 \times 10^{-7}$$

The wavelength is found in meters. Wavelengths are commonly expressed in nanometers.

$$4.100 \times 10^{-7}m \times \frac{1\times10^9 nm}{1m} \approx 410nm$$

The following is a table made of the calculations done for the different transitions in the series, the calculation that was just done is highlighted in yellow. Because $n_i$ is able to go up infinitely, 6 wavelengths were calculated using the derived Rydberg equation in order to gather sufficient data to observe the trend of convergence in the figure 3 (all wavelengths are rounded to the nearest whole number).

| Series | $n_i$ | $n_f$ | Wavelength (nm) |
|---|---|---|---|
| Balmer | 3 | 2 | 656 |
| | 4 | 2 | 486 |
| | 5 | 2 | 434 |
| | 6 | 2 | 410 |
| | 7 | 2 | 397 |
| | 8 | 2 | 389 |

Table 2. Calculated wavelengths (theoretical)

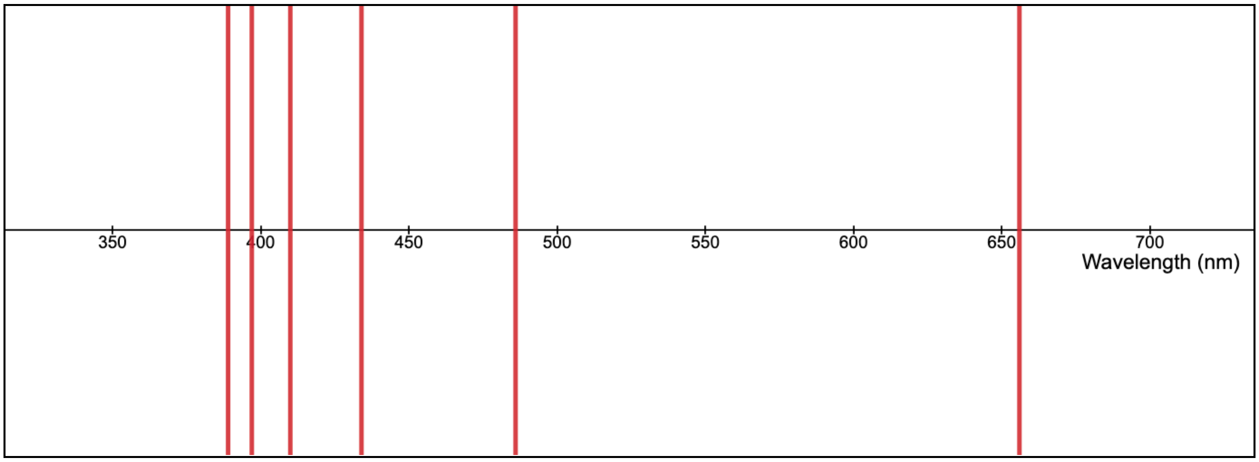


Figure 3. Plotted wavelengths in nm ($x = \lambda$)

As one can observe, the wavelengths in the series tend to converge as there is less of an energy disparity between the higher energy levels. This can be observed as the red lines tend to get closer together towards the left of the spectral graph. However, since $n_i$ is able to be infinitely high considering the limitless number of energy levels of an atom, one must be able to determine the highest value of $n_i$ so that the differences between calculated wavelengths are negligible. This is done by calculating the frequency limit of a series.

First, the frequency must be found from the wavelengths calculated. Additional wavelengths up to $n = 11$ were calculated in table 3 to demonstrate a better pattern of data. All variables have the same significance as prior calculations. A sample calculation here is shown for 656nm, which is the transition $n_3 \rightarrow n_2$.

$$v = \frac{c}{\lambda}$$
$$v = \frac{3.0\times10^8}{656}$$
$$v \approx 457317.0732$$

The energy increase between successive is calculated by subtracting the frequency ($v$) of adjacent energy level transitions. This is used to determine $\Delta v$, which is the difference in frequency between these two energy levels.

$$v\,of\,(n_i \rightarrow n_2) - v\,of\,(n_{i+1} \rightarrow n_2)$$
$$v\,of\,(n_3 \rightarrow n_2) - v\,of\,(n_4 \rightarrow n_2)$$
$$617283.9506 - 457317.0732 = 159966.8774$$
$$\Delta v = 159966.8774 Hz$$

The following table has the calculated values from the transition of $n_3 \rightarrow n_2$ up to $n_{11} \rightarrow n_2$.

| Energy Level Transition $(n_i \rightarrow n_2)$ | Wavelength (nm) | Frequency (Hz) | ΔFrequency (Hz) |
|---|---|---|---|
| 3 → 2 | 656 | 457317.0732 | 159966.8774 |
| 4 → 2 | 486 | 617283.9506 | 73960.289 |
| 5 → 2 | 434 | 691244.2396 | 40463.0775 |
| 6 → 2 | 410 | 731707.3171 | 23960.1892 |
| 7 → 2 | 397 | 755667.5063 | 15540.7199 |
| 8 → 2 | 389 | 771208.2262 | 12081.591 |
| 9 → 2 | 383 | 783289.8172 | 6183.867 |
| 10 → 2 | 380 | 789473.6842 | 4177.1095 |
| 11 → 2 | 378 | 793650.7937 | |

Table 3. Frequency and ΔFrequency for the Balmer series

The value of $\Delta v$ continuously decreases as the value of the upper bound, or $n_i$ increases. Eventually, it will reach zero, meaning that there is no frequency difference between energy levels. Two lines from this data set can be plotted that represent this trend. One line plots the greater frequency against the change in frequency. For example, a coordinate would be (457317.0732, 159966.8774). The other plots the lesser frequency against the change in frequency. For example, a coordinate would be (617283.9506, 159966.8774). Because both lines converge to the same point on the x-axis, it does not matter which one is used. The $x$-intercept, or where the change in frequency is zero, represents the point in which energy levels converge to distances so small the jump between two levels is essentially nonexistent.

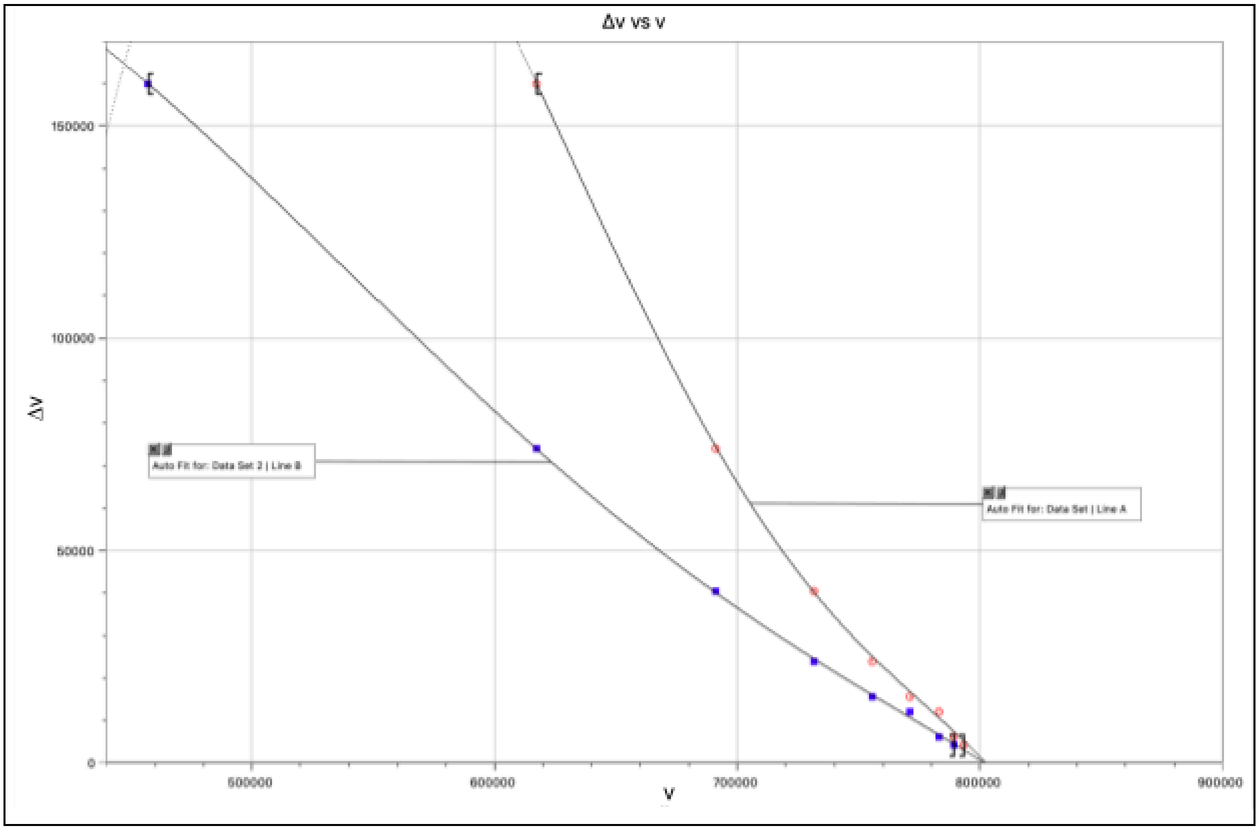


Figure 4. $v\ vs\ \Delta v$

The line for the red dots, which were the greater frequency, will be called $Line\ A$. The line for the blue squares, which were for the lesser frequency, will be called $Line\ B$. Logger Pro gives the equations of the lines are as follows:

A: $y =- 1.498 \times 10^{-22}x^{5} + 4.16 \times 10^{-16}x^{4} - 4.261 \times 10^{-10}x^{3} + 1.89 \times 10^{-14}x^{2} - 30.17x + 1$

B: $y =- 7.801 \times 10^{-24}x^{5} + 1.752 \times 10^{-17}x^{4} - 1.205 \times 10^{-11}x^{3} + 1.169 \times 10^{-6}x^{2} + x + 1$

Additionally, Logger Pro also provides us with the correlation values for each line. A line that showed a perfect correlation (1) was unable to be found, however correlations of 0.9998 for line A, and 0.9999 for line B should still suffice in determining the unknown frequency value. Note that because these lines theoretically converge at the same spot on the x-axis, it makes close to no difference which line is chosen for this calculation:

However, because line B has correlation value closer to 1, (0.9999), the $x$-intercept for it is found:

$$x \approx 795886.5992\ Hz$$

This means that at a frequency approximately $795886.5992Hz$, there is zero difference between the energy levels, meaning that they have fully converged. We can find the $n_i$ value (or the upper bound of the energy levels) of this by first converting the obtained frequency value ($v$) and converting it to wavelength in meters.

$$\lambda = \frac{c}{v}$$

$$\lambda = \frac{3.0\times10^{8}}{795886.5992}$$

$$\lambda \approx 376.93nm \times \frac{1m}{1.0\times10^{9}nm} = 3.79 \times 10^{-7}m$$

Then, through plugging in the calculated wavelength into the Rydberg equation, we can calculate the value of $n_i$.

$$\frac{1}{\lambda} = R(\frac{1}{n_f^{2}} - \frac{1}{n_i^{2}})$$

$$\frac{1}{3.79\times10^{-7}} = 1.097 \times 10^{7}(\frac{1}{2^{2}} - \frac{1}{n_i^{2}})$$

$$2652955.331 = 1.097 \times 10^{7}(\frac{1}{2^{2}} - \frac{1}{n_i^{2}})$$

$$0.241837 = \frac{1}{4} - \frac{1}{n_i^{2}}$$

$$8.16269 \times 10^{-3} = \frac{1}{n_i^{2}}$$

$$\frac{1}{8.16269\times10^{-3}} = n_i^{2}$$

$$\sqrt{122.509} = \sqrt{n_i^{2}}$$

$$n_i \approx 11.068$$

Thus, it can be verified that at a little over $n_i = 11$, energy levels converge at a limit, and all subsequent energy levels (12, 13, etc.) will demonstrate the same wavelength and position on the electromagnetic spectrum. There is however, a slight discrepancy to be noted, because the number was rounded to the nearest whole number, seeing as $n_i$ is required to be a positive integer.

Extrapolating the upper bound of the energy levels or where they all converge may be useful to scientists, because the frequencies and wavelengths are the same beyond a certain calculated value of $n_i$. Thus, there is a recognized limit where going beyond it produces the same result. This avoids any redundancy in calculations, as experimenting just to get the same answer due to this convergence may not have any merit.

## **Experimental Calculations**

The following data was collected from an assignment in my IB Chemistry HL course. Though data on wavelength can be collected through a spectrometer, the most important component of a spectrometer is the diffraction grating, which is a tool that takes advantage of light's ability to diffract, or be separated/spread out into its constituent wavelengths. Equipped with only the latter material, one is still able to calculate the wavelengths of a hydrogen gas by obtaining two vital measurements: the distance between the diffraction grating and the light source, and the distance between the first central and the first maxima. The following measurements are of a small portion of the Balmer series. Only the measurements within this series in the visible light spectrum were able to be obtained, as ultraviolet light is not observable with the human eye.

| Distance between grating and light (m) | Color | Distance between 1st central and 1st maxima (m) | $d_2$ |
|---|---|---|---|
| 0.4030 | Violet | 0.089235 | 0.091 |
| 0.4030 | Blue-Violet | 0.09476 | 0.095 |
| 0.4030 | Blue-Green | 0.10687 | 0.11 |
| 0.4030 | Red | 0.14861 | 0.15 |

Table 4. Obtained experimental values

In order to understand why such values are significant, one must understand the trigonometric applications to this method of data collection.

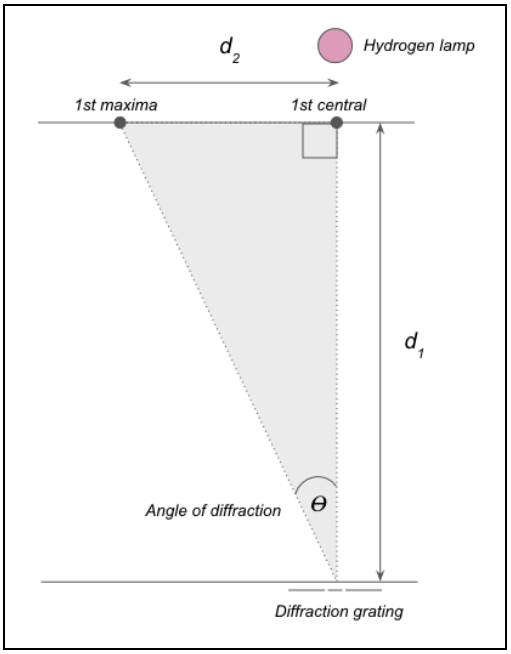
Because the data collection method is able to be modeled as a right triangle (see figure 5), we are able to use the measurements acquired in order to find the angle of diffraction, which is the value needed to calculate wavelength.

In figure 5:

θ = angle of diffraction (in degrees)

Adjacent = distance between grating and light (denoted as $d_1$)

Opposite = distance between 1st central and 1st maxima (denoted as $d_2$)



Thus, the angle of diffraction is able to be calculated with the equation: $tan\theta = (\frac{d_2}{d_1})$

Which becomes: $\theta = tan^{-1}(\frac{d_2}{d_1})$

A sample calculation is done for Violet:

$$d_1 = 0.4030$$
$$d_2 = 0.090$$
$$\theta = tan^{-1}(\frac{d_2}{d_1})$$
$$\theta = tan^{-1}(\frac{0.090}{0.4030})$$
$$\theta \approx 12.589º$$

Figure 5. Experimental trigonometric diagram (by me)

We have established light diffracts. However, its other property is interference. The two slits in which waves of light are observed through result in both constructive and destructive interference. We will be using the equation for constructive interference in this calculation, as it is the type of interference that leads to the appearance of light spots.

Constructive interference: $dsin\theta = m\lambda$
Rearranged to isolate λ, we are able to obtain: $\lambda = \frac{dsin\theta}{m}$

$d$ = distance between slits, measured to be $1.869 \times 10^{-6}m$
θ = angle of diffraction (calculated above, $12.589º$)
$m$ = order of interference, an integer describing the light's interference (in this case, $m = 1$)

$$\lambda = \frac{dsin\theta}{m}$$
$$\lambda = \frac{(1.869\times10^{-6})sin12.589}{1}$$
$$\lambda = (1.869 \times 10^{-6})(0.21796)$$
$$\lambda = 4.07 \times 10^{-7}m \times \frac{1.0\times10^{9}nm}{1m}$$
$$\lambda \approx 407nm$$

The theoretical calculations from earlier from the Rydberg formula can be taken in order to determine the accuracy of the experimental values acquired, as shown in table 5. The percent error was calculated with the following formula:

$$Percent\ Error = |\frac{(Experimental\ Wavelength - Theoretical\ Wavelength)}{Theoretical\ Wavelength}| \times 100$$

For example, here is the calculation made for the percent error Violet:

$$Percent\ Error = |\frac{(407-410)}{410}| \times 100$$
$$Percent\ Error \approx 0.00732 \times 100$$
$$Percent\ Error \approx 0.732$$

This was done for all wavelengths:

| Color | Energy level transition | Theoretical Wavelength (nm) | Experimental Wavelength (nm) | Percent Error (%) |
|---|---|---|---|---|
| Violet | 6 → 2 | 410 | 407 | 0.732 |
| Blue-Violet | 5 → 2 | 434 | 429 | 1.152 |
| Blue-Green | 4 → 2 | 486 | 492 | 1.235 |
| Red | 3 → 2 | 656 | 651 | 0.762 |

Table 5. Comparisons between theoretical and experimental wavelength

As can be seen, the highest percentage of error within these values was 1.235% for the energy level transition between 4 → 2. This is an immensely low value, meaning that the obtained experimental results correspond well with the theoretical wavelengths that were calculated in the first part of the investigation. This demonstrates the accuracy of both the experiment and subsequent calculations, as well as the soundness of the theory that was presented. It is possible that percent error might be very slightly higher or lower than these values, considering rounding to the nearest whole was done when calculating wavelength values.

## Conclusion

Within the simplest concept taught as a foundation for the beginning of every chemistry course lies a depth of mathematical analysis that can be derived both theoretically, and proven experimentally. Within this experiment I was able to theoretically determine the emission spectrum of hydrogen in the Balmer series through deriving the Rydberg equation and extrapolating the limit of $n_i$. I was also able to prove these calculations by using trigonometry to convert my collected data into values that were then compared to the theoretical wavelengths, also using percent error to confirm the accuracy of the investigation. Coming into the exploration, there was a certain doubt that because the chemistry was quite straightforward, the math would be on the easier side. Such thoughts subsided as I was able to fully immerse myself in the research, familiarizing myself with previously lesser-known concepts.

Atomic excitation is the basis for modern inventions like lasers, as well as biological traits like fluorescence (OpenStax). Though hydrogen was explored here, all elements have similar properties, such as the ability to absorb energy to release a photon, as well as a convergence of energy levels. The Rydberg equation can be applied to all hydrogenic atoms, like $He^+$ as long as they are 1-electron systems, with a commonly accepted adaptation of the formula include $Z^2$ (atomic number) multiplied by $R$. However, scientists are still unable to accurately find a formula that encompasses multiple-electron systems, which essentially compose the rest of the periodic table excluding certain ions. Thus, an exploration into what scientists have done so far to find these values theoretically could be done. Additionally, transmittance data has been able to be collected by advanced technology that stems beyond the visible light spectrum. Looking into the equipment and methods behind this acquisition could be an interesting extension to the investigation.

## Sources

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