Observations of Balmer Series of Hydrogen and Calculation of the Rydberg Analog

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Abstract

The emission spectrum of Hydrogen was observed using a properly calibrated spectrometer and diffraction grating. Under the Bohr theory of the atom, the emission spectrum of Hydrogen should align with discrete, quantized wavelengths determined principally by a Rydberg Constant R. The Rydberg constant was determined in two separate ways. First, a Rydberg Constant was determined for each separate band of the emission spectrum, and then each constant was averaged from each band to produce a final Rydberg of $(1.110 \pm 0.053) \times 10^7$. Second, noting that the Bohr theory is in essence a one-parameter model, the Rydberg Constant was fitted to the Bohr theory and the observed wavelengths of the emission spectrum. With this method, the Rydberg constant was determined to be $(1.041 \pm 0.004) \times 10^7$.

Introduction and Relevant Theory

Bohr Model of the Hydrogen Atom

In the Bohr model of the atom, electrons orbit the nucleus at discrete energy levels. When an electron transitions from a higher to a lower energy level, it will emit a photon with an energy equal to the difference in energies of the two states. Since energy levels in an atom are discrete, there are corresponding discrete, predetermined wavelengths of the photons emitted, given by $\lambda = hc/E$. These energy states E_n are given by the following formulation:

$$E_n = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \tag{1}$$

which results from the interactions of the Coulomb and Nuclear forces. As noted above, the energy in an emitted photon E_p is the difference in energies that an excited electron transitions to. We also recall $E = hc/\lambda$ from quantum theory. This results in the following relationship for the energy of an emitted photon:

$$\frac{hc}{\lambda} = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}(\frac{1}{n^2} - \frac{1}{n'^2}) \tag{2}$$

We see that, for a given atom, the terms outside the difference between $\frac{1}{n^2}$ and $\frac{1}{n'^2}$ are constant. We also note that the hc term on the left hand side is constant. The Rydberg Constant R is thus defined as:

$$R = \frac{me^4}{32\pi^2\epsilon_0^2} \tag{3}$$

and therefore equation 2 can be rewritten as[1]

$$\frac{1}{\lambda} = R(\frac{1}{m^2} - \frac{1}{m'^2}) \tag{4}$$

This experiment specifically examined the Balmer series for Hydrogen, which is the emission spectrum of a Hydrogen atom from electrons in the $m' > 2$ excited state to the $m = 2$ state. This results in the Balmer formulation for the Hydrogen atom:

$$\frac{1}{\lambda} = R(\frac{1}{2^2} - \frac{1}{m'^2}) \tag{5}$$

where λ is the wavelength of the spectral lines of the corresponding emission spectra of Hydrogen for $m' = 3, 4, 5, ...$ and so on for integers m'.

Relevant Diffraction Theory

In order to determine an experimental value for the Rydberg Constant R, there are two unknowns: m' and λ. These both are determined by relevant diffraction grating theory. When light is incident upon a diffraction grating, a specific interference pattern is produced given by the following equation[1]:

$$\sin\theta = \frac{n\lambda}{d} \tag{6}$$

where θ is the angular offset on the interference pattern, λ is the wavelength of the incident light, d is the spacing of the diffraction grating, and n is the order of the given node. Thus, given an angle for the offset θ and a diffraction grating, one can calculate a Rydberg constant from the resulting interference pattern by solving for λ in equation 6 and then for R in equation 5.

Experimental Setup and Results

Calibrating the Apparatus

The principal apparatus of the experiment was a spectrometer and an aligned diffraction grating, a Mercury lamp for calibration, and a Hydrogen lamp. Be-

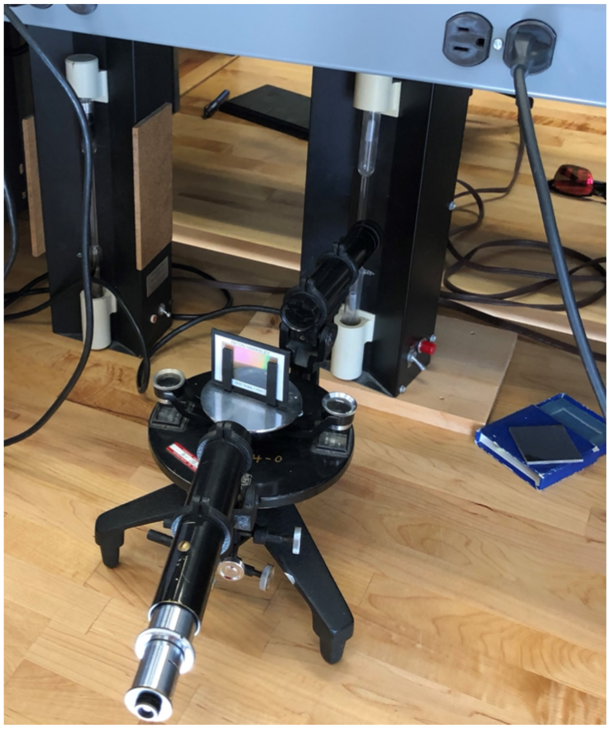

Figure 1: A picture of the apparatus. Photo Credit: Timothy Eng[3]

fore data collection could take place, first the spectrometer had to be calibrated in the following steps[1]:

1. First, one must align the scope for parallax. Aim the scope at a faraway object, and then to an observer adjust the length of the scope until the crosshair and the faraway object move with each other.
2. Second, shine a light into the aperture of the scope and adjust the scope such that the crosshair is horizontally aligned with the light.
3. Then, by inserting a mirror into the scope one can rotate the stage until the crosshair and the light are aligned on one axis.
4. Finally, replace the mirror with the given diffraction grating.

It is worth noting that both these and the following steps require a dimly lit (preferably completely dark) room. After the spectroscope was calibrated, it was aimed at a Mercury lamp in order to calculate the spacing d of the diffraction grating. The wavelengths of the spectral lines of d were known, and thus one only needed an angle θ for each spectral line in order to calculate d using equation 6. In practice, the first two spectral lines of Mercury were visible on either side of the central maximum, i.e. $n = -2, -1, 1, 2$. The diffraction grating was found to be $(1.65 \pm 0.0069) \times 10^6$m, which translates to 607.7 ± 14 lines / mm.

Measurement of Hydrogen

After the above steps were performed, the apparatus is sufficiently calibrated, and one can investigate the Balmer Series of Hydrogen. The spectrometer was placed at the Hydrogen lamp, and a θ_o was recorded at the central maximum. Then, the scope of the spectrometer can be swiveled and additional θ measurements can be taken using the Vernier Scale on the spectrometer. Measurements were taken where the crosshair lined up with the spectral lines.

In practice, spectral lines corresponding to $m' = 3, 4, 5$ (red, cyan, and violet respectively) were observed for orders $n = -3, -2, -1, 1, 2, 3$. Three trials were performed in the experiment, meaning that each set of measurements for every spectral line was performed three times. In practice, the $n = -3$ and $n = 3$ spectral bands for $m' = 3$ were not visible at every trial. With each θ measurement, one can calculate $|\theta_o - \theta|$ to calculate the θ needed for equation 6, which can then be used to find the λ for each m'.

Analyzed Data and Conclusions

The data from the three trials was grouped by color (m') in order to calculate an experimental wavelength for each spectral line. In doing so, the wavelengths for violet, cyan, and red respectively were determined to be 433.3 ± 6.5nm, 483.2 ± 1.4nm, and 638.3 ± 62nm. Note the unusually high uncertainty value for λ for red.

As noted in the abstract, the Rydberg constant R was calculated in two different ways. First, Rydberg Constants were determined for each m using the λ values above, and then were averaged together. The uncertainty in this Rydberg was found using the standard error of the mean. The results for each m' are located in table 1. This yielded a Rydberg constant R_{exp} of $(1.110 \pm 0.053) \times 10^7$. The expected value of R is given by 1.097×10^7[2]. The experimental value R_{exp} differs from the expected value by 1.19%, which is a small deviation of the actual value. Additionally, assuming a Gaussian probability distribution of experimental R values with a mean at R_{exp}, the expected value is only 0.24 standard deviations away from the mean. Quantitatively, this means that on repeated measurement one would receive a less accurate value 81% of the time [4].

Table 1: Rydberg Constant for each color

color	λ(nm)	R	σ_R
red	638.3 ± 62	1.128×10^7	0.110×10^7
cyan	483.2 ± 1.4	1.104×10^7	0.033×10^7
violet	433.3 ± 6.5	1.099×10^7	0.016×10^7

Second, using the three λ values and equation 5, one can plot $\frac{1}{\lambda}$ against m', and fit a Rydberg Constant to that relationship. A plot of $\frac{1}{\lambda}$ vs. $m' = 3, 4, 5$ is shown in figure 2, along with a slope given by the fitted Rydberg constant. Note, again, the large uncertainty in $m = 3$ i.e. the red. Performing a least squares fit of the slope results in an experimental Rydberg constant of $(1.041 \pm 0.0058) \times 10^7$. Analyzing this result in the same way as the other calculated Rydberg constant, we see that the value is 9.6 standard deviations away from the expected value. This results in a minute ($< 0.01\%$) chance that a repeated experiment would yield a less accurate Rydberg in the same analysis, so we can safely say that the fitted Rydberg and the expected Rydberg are distinguishable[4]. Performing a χ^2 fit of this parameter, we get a value of 0.004, which is very low, and is an indicator of the large uncertainty in the measurements.

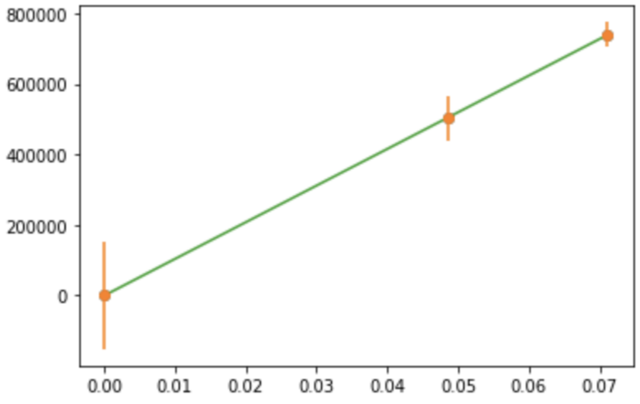

Figure 2: A plot of $\frac{1}{\lambda}$ vs. $(\frac{1}{2^2} - \frac{1}{m'^2})$. Note the large uncertainty in m' = 3 (left-most point).

Returning back to the first method of calculating the Rydberg, we note the low bias of 1.19%. However, it is hard to make any definitive, statistically significant conclusions with the accuracy of 81%, which may have been caused by the large uncertainty in the measured θ values, particularly for the red band. Repeated measurements in order to reduce the uncertainty would be needed in order to draw appropriate conclusions about this experimental Rydberg constant and to prevent overfitting.

Appendix

The fit parameters were calculated using a least squares linear regression, using the numpy python package.

The uncertainty in $\frac{1}{\lambda}$ seen in the points in the plot in figure 2 was calculated via the formulation:

$$\frac{1}{\lambda + \sigma_\lambda} = \frac{1}{\lambda} + \frac{\sigma_\lambda}{\lambda^2} \tag{7}$$

where σ_λ is the uncertainty in a measurement λ.

The probability of achieving the accepted value was performed by assuming a Gaussian distribution of measurements with a mean of the experimental value and and a standard deviation of the uncertainty, and calculating how many standard deviations away from the mean the resulting measurement was according to:

$$\frac{|x - \mu|}{\sigma} \tag{8}$$

where x is the expected value and μ is the experimental value.

References

[1] Introductory notes, Balmer Series, Carl Franck, Cornell Physics 3310 Canvas website, accessed November 23, 2021.

[2] NIST Reference on Constants, Units, and Uncertainty, http://physics.nist.gov/cgi-bin/cuu/Value?ryd, accessed November 23, 2021.

[3] Observing the Balmer Series for Hydrogen to calculate the Rydberg Constant, Timothy Eng, Cornell Physics 3310 Canvas website, accessed November 23, 2021.

[4] Data Reduction and Error Analysis for the Physical Sciences, P.Bevington and D. Robinson, Page 251.