Determining the Rydberg constant from the Balmer series of hydrogen

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Abstract

We found a value for the Rydberg constant by measuring the wavelengths of the visible hydrogen emission spectral lines and using the Rydberg formula for the Balmer series to fit those wavelengths to a linear plot. We found our value to not agree with the literature value and suspect that is a result of the way we calibrated our equipment.

1 Introduction

The Balmer series is a describes a subset of the spectral line emissions of a hydrogen atom. The wavelengths of the lines in this series are given by the formula

$$\frac{1}{\lambda} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \, [2] \tag{1.1}$$

where $n = 2$, $m = 3, 4, 5, \ldots$, and R is the Rydberg constant, given by

$$R = \frac{m_e e^4}{8\varepsilon^2 h^3 c} = (10973731.568160 \pm 0.000021)\,\mathrm{m}^{-1}[1] \tag{1.2}$$

Note that Equation 1.1 describes much more than just the Balmer series but only the Balmer series is needed for this experiment, and only 4 of the many spectral lines in the series at that. These 4 lines are called H-α (m=3), H-β (m=4), H-γ (m=5), and H-δ (m=6) and they will be used as they are the 4 that (formally) lie within the visible spectrum.

To determine a value for R, the wavelengths of H-α, H-β, H-γ, and H-δ will be measured and a linear fit will be made with $\left(\frac{1}{2^2} - \frac{1}{m^2} \right)$ as the x values and $\frac{1}{\lambda}$ as the y values, thus R will be the gradient.

2 Apparatus

A Heath EU-700 Czerny-Turner monochromator with a photo-multiplier detector and pulse-counting electronics was used to measure the wavelengths of the spectral lines coming from a hydrogen spectral tube. The measurement system has three primary measurement parameters: slit width, dwell time, and step increment. The system counts how many times a photon was incident on the detector for the given wavelength, incrementing through a range of wavelengths measured in Angstroms.

The monochromator reports an incorrect wavelength, off by about 20 Angstroms, so the set-up needed to be calibrated. A HeNe laser of known wavelength (6328 A) was fired at the measurement system as show in Figure 2.1.
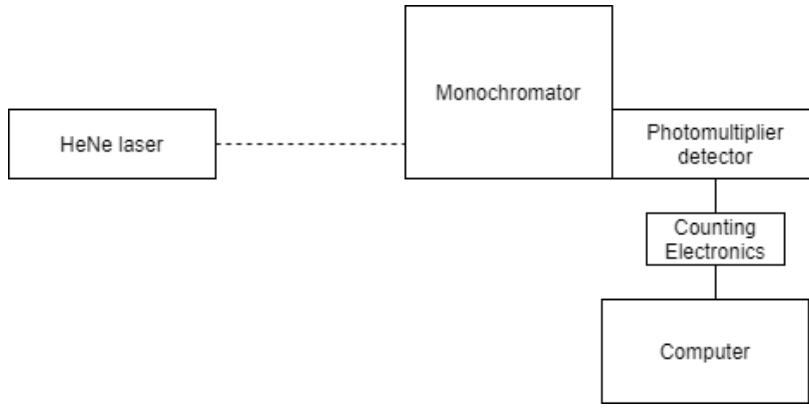
Figure 2.1: Calibration set-up

3 Method

3.1 Calibration

Using the wavelength of the HeNe laser (6328 A) as a known value, measurements were made with a variety of parameters, the details of which can be found in subsection 7.1, around the expected value. Gaussians could be fitted to the data using `scipy.optimize.curve_fit` and a μ and σ extracted for each set. The difference between this μ and the known wavelength is the correction factor that needs to be applied to all measurements taken with this set-up. These corrections were combined in a mean weighted by their uncertainty σ using

$$\bar{\mu}_{wtd} = \frac{\sum\limits_{i=1}^{n} w_i \mu_i}{\sum\limits_{i=1}^{n} w_i} \tag{3.1}$$

$$\sigma_{wtd} = \sqrt{\frac{\frac{\sum\limits_{i=1}^{n} w_i \mu_i^2}{\sum\limits_{i=1}^{n} w_i} - (\bar{\mu}_{wtd})^2}{n-1}} \tag{3.2}$$

where $w_i = \frac{1}{\sigma^2}$ is the weighting [3].

The count data was assumed to be Poissonian and thus the uncertainty on a count of N is simply $\sqrt{N}$. This uncertainty was provided to `curve_fit`. Figure 3.1 shows an example of one calibration run. The final correction was found to be -22.46 ± 0.14.

3.2 Data

Mesurements were made for each of the spectral lines with a variety of parameters, the details of which can be found in subsection 7.2, and their wavelengths found as in subsection 3.1 by fitting a Gaussian. After subtracting the correction factor and combining the uncertainties of the wavelength and correction factor in quadrature, the wavelengths found for each spectral line were combined using Equation 3.1 and Equation 3.2 where again $w_i = \frac{1}{\sigma^2}$. Figure 3.2 shows an example for the fitting done.
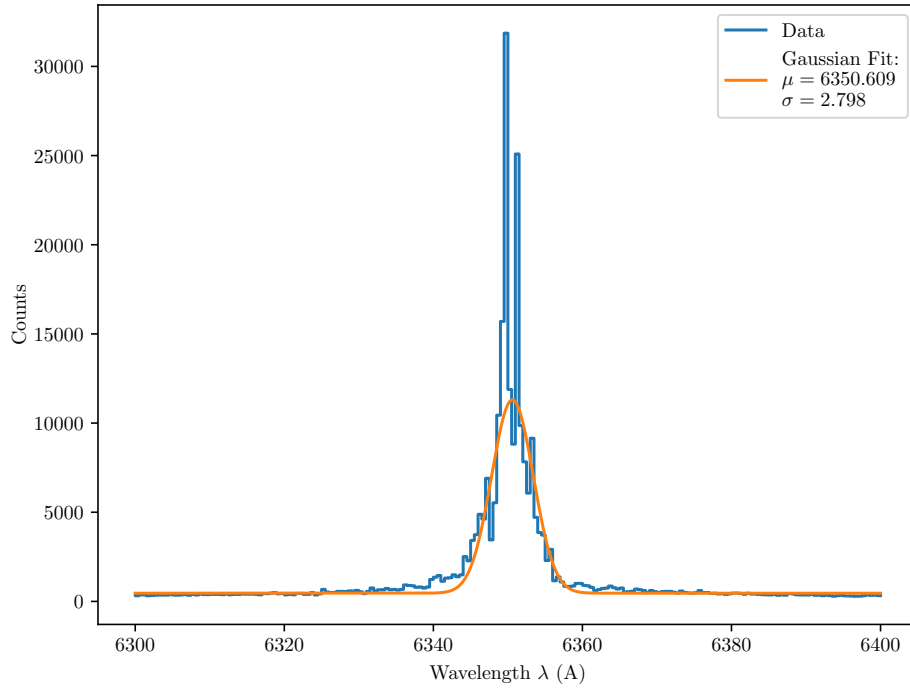
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Figure 3.1: Calibration data with slit width 10 μm, dwell time 200 ms, increment 0.5 A, and on the range 6300-6400 A. The Gaussian was fit using `scipy.optimize.curve_fit` with the initial guess $\mu =$ the position of the maximum of the data and $\sigma = 1$. A vertical shift was included to account for background and an amplitude to account for Gaussians being a PDF.
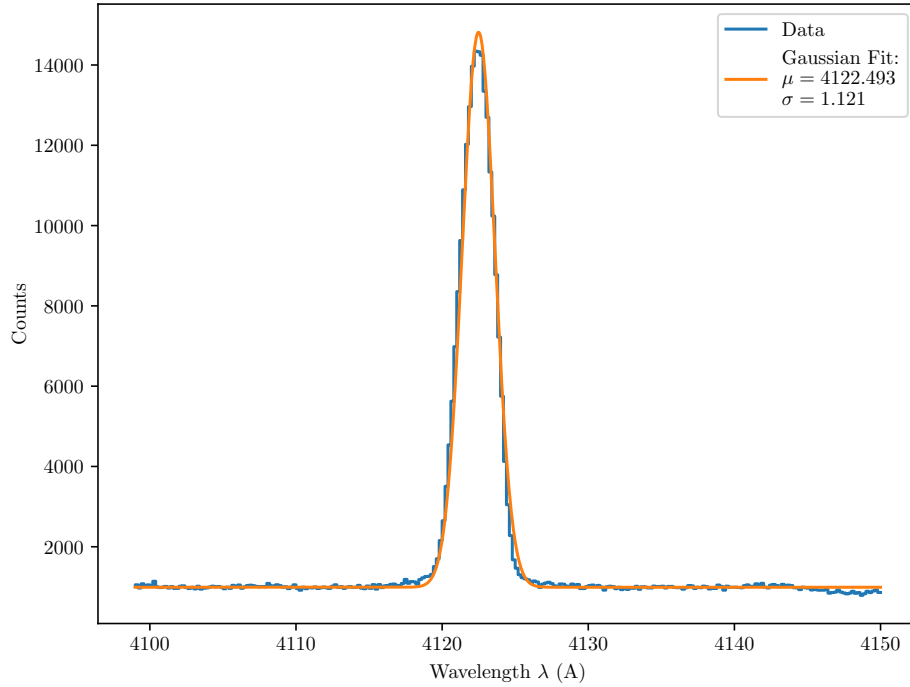

Figure 3.2: Data for spectral line H-δ with slit width 100 μm, dwell time 300 ms, increment 0.2 A, and on the range 4099-4150 A. The expected wavelength is 4101.734 ± 0.006[4] and after correction the measured wavelength is 4100.0 ± 1.1. The initial conditions for this fit were as in Figure 3.1

After wavelengths λ were found for each spectral line, a weighted linear least squares fit was performed as described in [5] with the x values being $\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$ and the y values being $1/\lambda$. Uncertainties on the y values were $\frac{u(\lambda)}{\lambda^2}$. The gradient of this linear fit gives a value for R.

4 Results

	Measured	Literature
H-α	(6563.013 ± 0.041) A	(6562.79 ± 0.03) A
H-β	(4859.94 ± 0.66) A	(4861.35 ± 0.05) A
H-γ	(4338.945 ± 0.043) A	(4340.472 ± 0.006) A
H-δ	(4100.006 ± 0.053) A	(4101.734 ± 0.006) A

Table 4.1: The measured and literature values for the wavelengths of the spectral lines for the Balmer series in hydrogen, measured in Angstrom. Literature values found in [4]. Note the large uncertainty for H-β as there were fewer runs available for that wavelength.
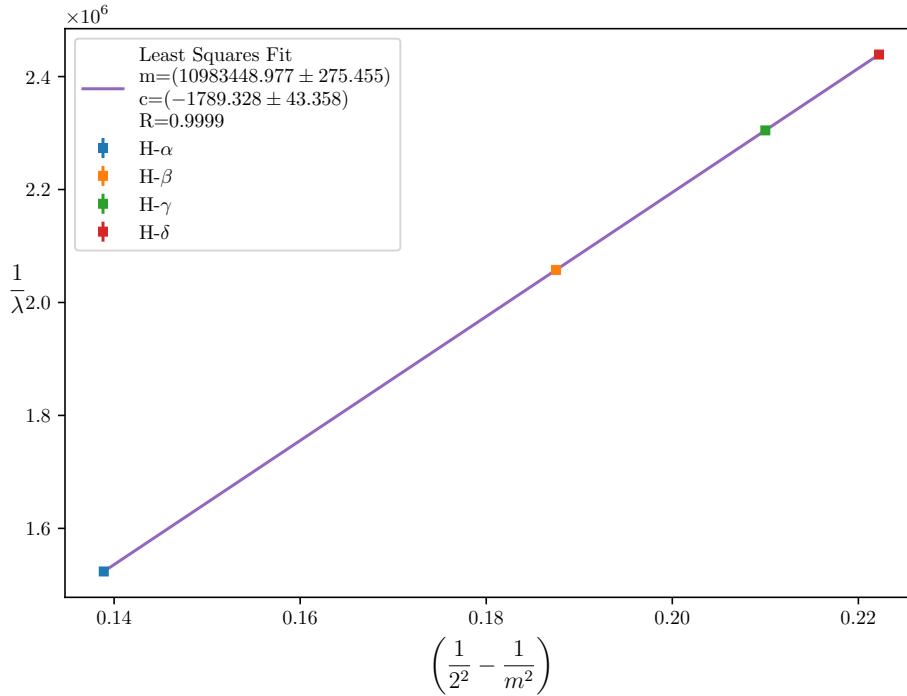

Figure 4.1: Weighted linear least squares fit of the inverse of the measured spectral line wavelengths to Equation 1.1. The uncertainty on the inverse wavelengths is plotted but due to the method described in Equation 1.2 and Equation 3.2, these uncertainties are reduced to the point of being unnoticeable at this scale. The slope m is the Rydberg constant R.

5 Discussion and Recommendations

We find the Rydberg constant to be $(10983450 \pm 280)\,\mathrm{m}^{-1}$, which does not agree within experimental uncertainty with the literature value of $(10973731.568160 \pm 0.000021)\,\mathrm{m}^{-1}$[1]. Note that when discussing hydrogen specifically, the Rydberg constant is modified to account for the small mass of the element: $R_H = R\frac{m_p}{m_e + m_p}[2] = (10967758.3400 \pm 0.0033)\,\mathrm{m}^{-1}$, where m_e is the reduced mass of the electron and m_p is the mass of the proton [1]. We see that our measured value is even further from R_H than from R.

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In the interest of a sanity check, we performed the same linear fitting using the literature values for the wavelengths of the four spectral lines, found in [4], and found a value of $R = (10971003 \pm 93)\,\mathrm{m}^{-1}$, which still does not agree with R_H, but is at least closer to it than our value, implying that our technique is valid to some extent, but our data is where the problem lies.

As can be seen in Table 4.1, the uncertainty on our wavelengths, aside from H-β which did not have the same amount of data, are all approximately the same, and yet the difference between our value and the literature value varies considerably from line to line. This leads us to believe that the main reason for the discrepancy in measured values for R is that the calibration we performed was not sufficient. We suspect that the relationship between measured wavelength and actual wavelength is not linear, or at least was not accurately captured by our one data point. We recommend calibrating using more than one laser, or capturing more than one known wavelength in some other way.

6 Conclusion

We found the value of the Rydberg constant to be $(10983450 \pm 280)\,\mathrm{m}^{-1}$, which does not agree with the literature value of either R or R_H within experimental uncertainty. We suspect that this is a result of the insufficient calibration method and recommend using more than one known wavelength to calibrate. Another source of uncertainty could lie in our lack of good data for the H-β spectral line and we recommend using more than one dataset per wavelength.

References

[1] 2018 CODATA list of the Fundamental Physical Constants, https://physics.nist.gov/cuu/Constants/Table/allascii.txt

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[3] Bevington, P. R., *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, 1969

[4] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2020). NIST Atomic Spectra Database (ver. 5.8), [Online]. Available: https://physics.nist.gov/asd [2021, August 21]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W

[5] Kirkup, L., *Experimental methods for science and engineering students*, (2019)

7 Appendix

7.1 Calibration Data

7.2 Spectral Line Data