PHYSICS 375

Spectroscopy & Atomic Spectra

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Abstract

This experiment was performed to examine how spectroscopy is useful in analyzing the atomic spectrum from mercury, hydrogen, and sodium. It was found that hydrogen has spectral lines with wavelengths 434 ± 25 , 485 ± 28 , 656 ± 38 nm, which led to a hydrogen Rydberg constant of $(1.098 \pm .037) * 10^7$ m^{-1}. Lastly, the wavelengths of the sodium d line doublet were calculated to be 589 ± 24 and 590 ± 24 nm which corresponded to a effective quantum number of $2.545 \pm .037$. Spectroscopy is important to study because it was a stepping-stone towards a quantum theory and is used extensively throughout science. The results of spectroscopy helped verify Einstein's photoelectric effect and ultimately helped lead to a quantum theory. For sodium, spectroscopy reveals a rich structure of the 3p orbital, which hosts states with total angular momentum 1/2 and 3/2. For scientists, it provides an analytical method to determine the chemical make up of materials from distant stars to pharmaceutical drugs.

1   Introduction

1.1   Theory

Diffraction Grating

A diffraction grating is an optical element with spatially periodic lines. At each line the light diffracts and the sum of the secondary waves resulting from Huygen's Principle result in sharp maximums at non-zero orders of the spectrum (the order is p below). The maximums are governed by the following equation
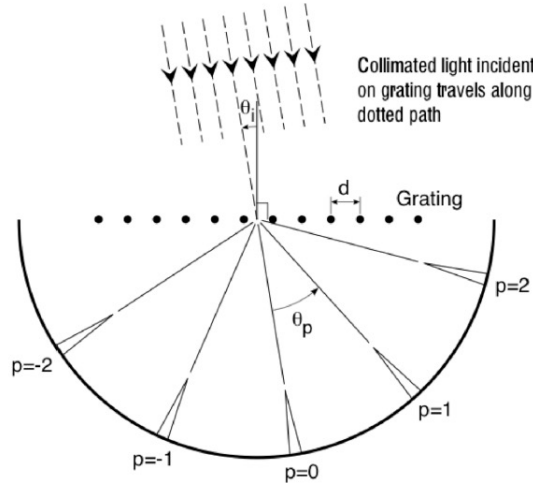

Figure 1: Schematic of light as it propagates through a diffraction grating

$$p\lambda = d(\sin \theta_p + \sin \theta_i), \quad p = \pm1, \pm2, \pm3.... \tag{1}$$

Huygens Principle

Every point of a light beam acts as a source of a forward propagating spherical wave. The sum of these subsequence waves (which interfere) determines the form of the primary wave as it propagates.

Atomic Orbitals

Quantum mechanics confines electrons orbits to spherical solutions to the Schrdinger equation with the appropriate potential and boundary conditions. These solutions characterize the orbitals of electron with four quantum numbers: the principle quantum number n determines the energy level, and takes positive integer values, the azimuthal quantum number l determines the orbital angular momentum, and takes values from 0 to $n - 1$, the magnetic quantum number m determines the angular momentum projected on a direction (typically z), and takes integer values from $-l$ to l, lastly, the spin quantum number s determines the intrinsic angular momentum, and takes non-negative integer (bosons) and half integer (fermions) values.

Fine Structure Splitting

Despite energy levels being degenerate, these electrons can have different total angular momentum given by j

where $j = m+l$. If two electrons in the 2p orbital one with j=1/2 and one with j=3/2 both relax to the 1s orbital—releasing a photon— then the j=3/2 electron will emit a more energetic photon since it carries more angular momentum than the j=1/2 electron yet they fall to the same state. This small, yet observable and measureable effect is called fine structure splitting.

Rydberg Constant

The Rydberg constant represents the wavenumber of the lowest-energy photon that is capable of ionizing hydrogen atom from its ground state. The Rydberg constant has two forms, which are R_M for finitely massive atoms (which all are) and R_∞ for the limit of infinitely massive atoms.

$$\mathcal{R}_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} \tag{2}$$

$$\mathcal{R}_M = \frac{\mu e^4}{8\epsilon_0^2 h^2}, \quad \mu = \frac{mM}{m+M} \quad \text{equivalently} \quad \mathcal{R}_M = \mathcal{R}_\infty \left(1 + \frac{m_e}{M_N}\right)^{-1} \tag{3}$$

Where m_e is the mass of the electron, M is the mass of the atomic nucleus, and M_N is the atomic mass. The Rydberg constant is used in the equation that relates the wavelength of an emitted photon to the energy level transition its parent electron under went. It is also used to relate the energy spectrum of Hydrogen.

$$\frac{1}{\lambda} = \mathcal{R}_M \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{4}$$

$$E_n = -hc\frac{\mathcal{R}_M}{n^2} \tag{5}$$

While the energy spectrum equation only holds hydrogen, since this is the only potential that can be solved in quantum, the equation does approximate other atomic systems. Other atomic systems with one valence electron (like sodium) act like a hydrogen atom because the other (inner) electrons effectively shield the full charge of the nucleus except for the one +1 that the valence electron pairs to cancel. However, this is still an approximation because the valence electron can, and does, spend some time inside the inner shell of electrons. This, so called the *quantum defect*, of an atom slightly modifies equation 5 so that the effective n is no longer necessarily an integer but is shifted by some amount δ_l.

$$E_n = -hc\frac{\mathcal{R}_M}{(n - \delta_l)^2} \tag{6}$$

The effective quantum number is defined to be $n - \delta_l$.

Error Propagation

Traditional error propagation is done in accordance with the following method of error propagation: let f be a function of some random variables x,y,z. Then its uncertainty is derived from:

$$\sigma_f = \sqrt{\left(\frac{\partial f}{\partial x} * \sigma_x\right)^2 + \left(\frac{\partial f}{\partial y} * \sigma_y\right)^2 + \left(\frac{\partial f}{\partial z} * \sigma_z\right)^2} \tag{7}$$

2 Objectives

First Objective

Using accepted wavelength values for mercurys spectral lines calculate the distance between slits in the diffraction grating.

Second Objective

Calculate the Rydberg constant for hydrogen.

Third Objective

Determine wavelengths of the sodium D doublet and compare to the accepted values. Use these to compute the effective quantum number for sodium.

3   Apparatus

The same apparatus was used to accomplish all three objectives. A spectrometer was set up, complete with collimator, object table, telescope and diffraction grating, and aligned such that the incident angle ,θ_i in Figure 1, was zero. Then the different objectives were accomplished by using a mercury, hydrogen and sodium lamp as the incident light source.

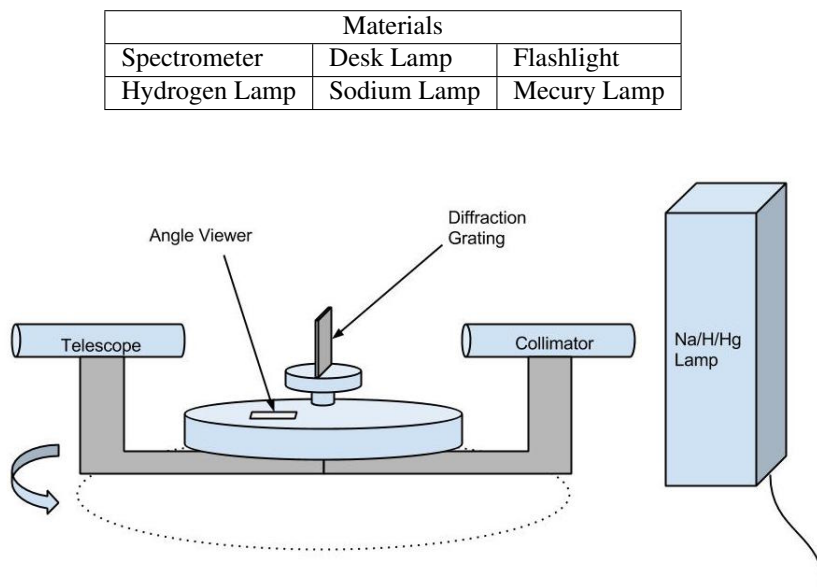| Materials		
Spectrometer	Desk Lamp	Flashlight
Hydrogen Lamp	Sodium Lamp	Mecury Lamp

Figure 2: Schematic of apparatus, lamp provides light which propagates through and is measured by the spectometer

Pictures of the lab setup that was used to perform the experiment can be found on LabArchives under Data & Lab Notes, Lab 6, Day 1 and are called "setup1" and "setup2". More detail of the knobs that are used to tight and adjust various parameters of the spectrometer can be seen in these pictures.

3.1   Experimental Setup

The majority of the experimental setup is aligning the spectrometer so that the incident angle, $\theta_i from Figure 1$, is zero or as close as possible to zero. This ensures that when the angle of the maximum are recorded and analyzed the curve can be linearly fit where $\sin \theta_p$ is the independent variable, λ is the dependent variable, and with a y intercept of zero.

First the diffraction grating must be put into its clamp in the spectrometer. Next, the slit at the end of the collimator must be aligned so that is vertical with the lamp. Next, make the slit smaller, but not so small that it's difficult to see the transmitted light and look through the eye piece of the telescope (do not use Hg lamp for this as it produces UV light that is bad for eyes) and adjust the eye piece in or out to bring the cross hairs into focus. Check that the angular scale is set to zero. If it not set to zero, then the telescope must be unclamped from the optical table and rotated so that the angular scale reads zero.

Then place a piece of glass behind the diffraction grating so it reflects light back towards the telescope. Using a desk lamp, shine light through the cutout of the telescope eye piece. If the illumination is bright enough there when one looks through the eye piece of the telescope they will see two cross hairs. One is the true cross hairs, and the other is the image of the cross hairs reflecting of the mirror. Aligning these two cross hairs ensures that the spectrometer is properly aligned.

4   Procedure

The steps are the same for all lamps used. With the spectrometer aligned to the best of ability and the lamp of interest turned on, rotate the telescope arm towards either the $p = 1$ or $p = -1$ order (see figure 1). Looking through the telescope there will be distinct colored lines separated by varying distances.

Place the crosshairs in the center of each of these spectral lines and record the angle. Note, the spectrometer uses a Vernier scale with arcminutes so the angle should be rounded down to the nearest half degree and then the arcminutes (found on the inner scale) should be added. The angle of the spectral lines should be measured twice for each line. For the mercury spectrum, the $p = \pm 1, \pm 2$ orders should be measured, for the hydrogen spectrum $p = \pm 1$, and for the sodium spectrum $p = \pm 1, \pm 2$.

Each of the lines is a different wavelength of light, but some of the lines will be very close to one another and possibly cannot be resolved at first order. The best way to tell if this is happening is to go to second order, where the separation between lines increases, and see if there are indeed two lines. If there are two lines at second order but they cannot be separated in first order the vertical aperture at the end of the collimator can be squeezed down to help separate the spectral lines.

Important information to be aware of when looking at the spectral lines of all lamps at all orders is background light can be an issue, and there can be reflection and aberrations. First, if there is too much background light (i.e. computer screen) that enters the telescope then the spectral lines will be very difficult to see. This will most likely be an issue since the telescope is swung through various angles and will be looking towards various items immediately around the apparatus. To avoid this a screen was placed opposite the telescope next to the collimator. Another thing to be aware of is there can be reflections and aberrations of the spectral lines that lead to *extra* spectral lines. These lines are not true spectral lines and are rather an abnormality created by the optical system. For example, for the mercury spectrum at first order there were two purple lines found and three green lines found originally. As it turned out these were not true lines of mercury, and this was evident because the lines were shifted slightly up or down with respect to other lines.

5 Experimental Data

5.1 Raw Data

Mercury Spectrum
   The wavelengths of the mercury spectrum were taken from
   http //physics.nist.gov/PhysRefData/Handbook/Tables/mercurytable2.htm and plotted against the angles that were measured. The raw angle measurements are in vectors with base file names hg_angle1 and hg_angle2 on LabArchives. Since there were four orders of the mercury spectrum that were measured ($p = \pm 1, \pm 2$) there were four plots created and fitted.
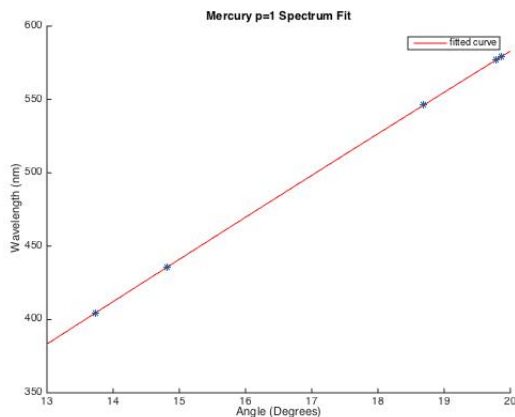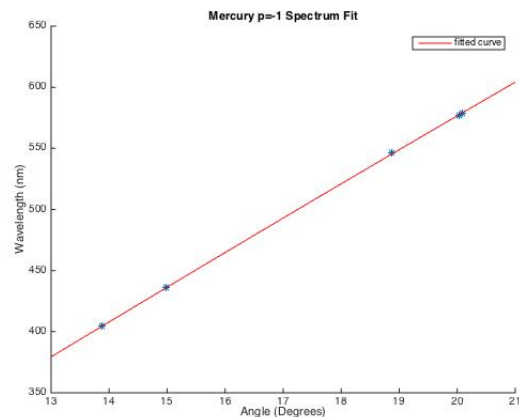

Figure 3: The p=-1 order of the mercury spectrum

Figure 4: The p=-1 order of the mercury spectrum

Hydrogen Spectrum
   From the mercury spectrum d, θ_i are known and then the unknowns in equation 1 are reduced to just the wavelength of the light since θ_p was measured with the order noted. Below are averaged values for the spectral lines that were used for the analysis later. All averaged values have an error of 0.01179 degrees since they were all measured using the same scale and propagated the same way.

p=-1, Angle (degrees)	14.9167	16.6833	22.9083
p=1, Angle (degrees)	14.7500	16.5833	22.6500

Sodium Spectrum

The sodium spectrum has the same data as the hydrogen spectrum did expect with fewer spectral lines and orders $p = \pm 2$. The error in each angle is again 0.01179 degrees for the same reason as previously.

p=-1, Angle (degrees)	20.4667	20.5167
p=1, Angle (degrees)	20.2000	20.2500
p=-2, Angle (degrees)	43.5333	43.5833
p=2, Angle (degrees)	44.5333	44.5833

6   Numerical Analysis

Step-by-step details of the numerical analysis can be found on LabArchives in a Word document call *Travel Log*; however, for conciseness only the major events are included below.

6.1   Mercury Spectrum

As stated previously, there were four orders of the mercury spectrum that were fitted to equation 1. In the case of both of the negative orders, the angles were measured backwards from $360°$ and were converted ($\theta_p \rightarrow 360° - \theta_p$) for comparison. However this does change the sign of the equation and must be corrected by taking $\theta_i \rightarrow -\theta_i$ since $\sin(-x) = -\sin(x)$.

After the $p = \pm 2$ orders were plotted it was recognized that three values between $p = 2$ and $p = -2$ differed by nearly a degree, which indicated that the angles were improperly recorded. Instead of carrying this error forward though the analysis the $p = \pm 2$ orders were not used. Thus after fixing formula θ_i and d from the lower order fits were averaged.

$$\theta_p = .0163 \pm .0250° \tag{8}$$

$$d = 1696 \pm \text{nm} \tag{9}$$

However, the nominal value that the diffraction grating givens is 600 lines per millimeter so the distance between lines (and the uncertainty) must be converted to compare.

$$\frac{1}{d} = (5.8962 \pm .4832) * 10^{-4} \frac{\text{lines}}{\text{nm}} \approx 590 \pm 48 \frac{\text{lines}}{\text{mm}} \tag{10}$$

6.2   Hydrogen Spectrum

Applying equation 1 to the hydrogen measurements the followings values were obtained for the air wavelengths of the hydrogen spectrum by using the Matlab script "H_propagation.m".

p=-1, Wavelength (nm)	436.0915 ± 35.7502	486.4084 ± 39.8731	659.6990 ± 54.0733
p=1, Wavelength (nm)	432.2874 ± 35.3595	484.5372 ± 39.6407	653.6135 ± 53.4956

Converting these wavelengths to the vacuum wavelengths using

$$\lambda_{vac} = n_{air}\lambda_{air} \qquad \text{where} \qquad n_{air} = 1.00029 \tag{11}$$

Which yielded after propagating the error

p=-1, Wavelength (nm)	436.2179 ± 35.8397	486.5494 ± 39.9638	659.8903 ± 54.1681
p=1, Wavelength (nm)	431.4475 ± 35.3595	483.7124 ± 39.6407	652.8378 ± 53.4956

Averaging these and once again propagating the error

$$\lambda = 434 \pm 25, 485 \pm 28, 656 \pm 38 \text{nm} \tag{12}$$

These values correspond, respectively, to the energy level transitions in hydrogen of $n = 5 \rightarrow n = 2$, $n = 4 \rightarrow n = 2$, $n = 3 \rightarrow n = 2$ all of which are part of the Balmer series transitions. With the energy level transitions known equation

2 can be used to compute the Rydberg constant. The Matlab script "H_rydberg_prop.m" was used to both compute the Rydberg constant for hydrogen and propagate the error. The Rydberg constant was calculated as a weighted average of three values using $1/\sigma_{\mathcal{R}}$ as the weights.

$$\mathcal{R}_H = (1.0981 \pm .03677) * 10^7 \text{m}^{-1} \approx (1.098 \pm .037) * 10^7 \text{m}^{-1} \tag{13}$$

This Rydberg constant for hydrogen can then be converted back into the infinitely massive nucleus Rydberg constant using equation 3. Using that $m_e = 9.10938291 * 10^{-31}$kg, $M_N = m_{\text{proton}} = 1.67262178 * 10^{-27}$, and assuming no error in these values, it can be shown that

$$\mathcal{R}_\infty = (1.0986 \pm .03677) * 10^7 \text{m}^{-1} \approx (1.099 \pm .037) * 10^7 \text{m}^{-1} \tag{14}$$

6.3 Sodium Spectrum

Analyzing sodium data follows closely the analysis done on the hydrogen spectrum. First the wavelengths of sodium's spectrum were calculated using the same Matlab program with different measurement values.

p=-1, Wavelength (nm)	592.5449 ± 48.6493	593.9313 ± 48.7630
p=1, Wavelength (nm)	586.1082 ± 48.0428	587.4970 ± 48.1566
p=-2, Wavelength (nm)	583.8412 ± 47.8518	584.3775 ± 47.8957
p=2, Wavelength (nm)	594.9641 ± 48.7634	595.4914 ± 48.8066

Converting these wavelengths to the vacuum wavelengths

p=-1, Wavelength (nm)	592.7168 ± 48.6635	594.1035 ± 48.7771
p=1, Wavelength (nm)	586.2782 ± 48.0567	587.6674 ± 48.1706
p=-2, Wavelength (nm)	584.0105 ± 47.8657	584.5469 ± 47.9096
p=2, Wavelength (nm)	595.1366 ± 48.7775	595.6641 ± 48.8207

Averaging these and once again propagating the error

$$\lambda = 589 \pm 24, 590 \pm 24\text{nm} \tag{15}$$

Using equation 5 with the Rydberg constant previously calculated and these wavelengths the effective quantum number for sodium can be computed.

$$n_{\text{effective}} = \sqrt{\mathcal{R}_{\mathcal{H}}\lambda} = 2.545 \pm .037 \tag{16}$$

7 Error Analysis

7.1 Experiment

Mercury Spectrum

The error in d and θ_i are difficult to compute because there are two components with different origins. First is the error that is introduced because there are uncertainties in the measured quantity θ_p. The other error is directly from the Matlab fitting function. Properly accounting for both of these is very difficult given solely equation 1. Instead a Matlab function openly available on the internet that uses the method of error as described in D. York et. al. *Unified equations for the slope, intercept, and standard errors of the best straight line* was used.

The exact details of the york_fit function can be found on lab archive, but the gist is that the function took a vector for x, a vector y, a vector of error in x, a vector of error in y, and a value or vector for the correlation coefficients. The error in the x variable was propagated for the error in the angle measurements while the error in the given wavelengths was taken to be .0005 as this was half the last digit provided by NIST. The function was able to compute the error in the slope and the y intercept. For the two first order measurements ($p = \pm 1$) the york_fit function gave the following error respectively:

$$\sigma_d = 194.4398, 199.5997\text{nm} \qquad \sigma_{\text{y-int}} = 59.4825, 60.4031 \tag{17}$$

So averaging,

$$\sigma_d = 197\text{nm} \tag{18}$$

However, it did not break the y intercept into the variables responsible. This step was completed after the fit was run (which verified Matlab's fits) as follows, since the y intercept is given by

$$\text{y-int} = d * \sin\theta_i \tag{19}$$

$$\sigma^2_{\text{y-int}} = (d\cos(\theta_i)\sigma_{\theta_i})^2 + (\sin(\theta_i)\sigma_d)^2 \tag{20}$$

All of the variables of this equation were known with the exception of σ_{θ_i}, which is what was of interest, so this value was solved for in both of the first order cases and then since the average of the θ_i is the reported value the error is propagated by applying equation 7 to a simple average with yielded

$$\sigma_{\theta_i} = 0.02499° \tag{21}$$

At first glance it is curious that this error is larger than the value computed for θ_i, but the factors that contribute to the value have error that propagate in large way. It is comforting that the Matlab fits had standard deviation for θ_i that were multiples of the value found. Indeed, if θ_i was extremely close to zero then the error would be a large multiple of the value.

Lastly, the uncertainty for d was propagated to the uncertainty in the lines per length of the diffraction grating by applying equation 7 to

$$\frac{\text{lines}}{mm} = \frac{1}{d} * 10^6 \tag{22}$$

Hydrogen Spectrum

The error was found by applying equation 7 to equation 1 using the Matlab script H_propagation.m. The output of this script gave the uncertainty in the wavelengths for both of the orders that were used for the air wavelengths.

p=-1, Error in Wavelength (nm)	±35.7502	±39.8731	±54.0733
p=1, Error in Wavelength (nm)	±35.3595	±39.6407	±53.4956

The error of the vacuum wavelengths are propagated by multiplying the table above by the index of refraction of air, which is 1.00029 so the errors in the vacuum wavelength spectral lines of hydrogen are given by:

p=-1, Error in Wavelength (nm)	±35.8397	±39.9638	±54.1681
p=1, Error in Wavelength (nm)	±35.3595	±39.6407	±53.4956

Lastly, since the vacuum wavelengths were averaged between $p = \pm 1$ the error was propagated one last time to this average.

$$\sigma_\lambda = \pm 25.1696, \pm 28.1406, \pm 38.0600 \text{nm} \tag{23}$$

The Rydberg constant was calculated using the three calculated values of hydrogen's spectral lines. Thus, each of these three values led to a slightly different value for the Rydberg constant and the error in that value. The error was propagated using the Matlab script "H_rydberg_prop.m" which applied the error propagation equation to equation 4 solved for $\mathcal{R}_\mathcal{M}$. These three errors were then used to generate a weighted average for the Rydberg constant and then finally the error was propagated through the weighted average equation. The final error in $\mathcal{R}_\mathcal{H}$ after the weighted average was found to be

$$\sigma_{\mathcal{R}_\mathcal{H}} = 3.677 * 10^5 \text{m}^{-1} \tag{24}$$

This is also the error of $\mathcal{R}_\infty$ since it was assumed that there was no error in the mass of the electron and proton used.

Sodium Spectrum

The script used for hydrogen was fed the measurements from the sodium lamp and it output the following errors.

p=-1, Error in Wavelength (nm)	±48.6493	±48.7630
p=1, Error in Wavelength (nm)	±48.0428	±48.1566
p=-2, Error in Wavelength (nm)	±47.8518	±47.8957
p=2, Error in Wavelength (nm)	±48.7634	±48.8066

The error of the vacuum wavelengths are propagated by multiplying the table above by the index of refraction of air, which is 1.00029 so the errors in the vacuum wavelength spectral lines of sodium are given by:

p=-1, Wavelength (nm)	±48.6635	±48.7771
p=1, Wavelength (nm)	±48.0567	±48.1706
p=-2, Wavelength (nm)	±47.8657	±47.9096
p=2, Wavelength (nm)	±48.7775	±48.8207

Lastly, since the vacuum wavelengths were averaged between $p = \pm 1, \pm 2$ the error was propagated one last time to this average.

$$\sigma_\lambda = \pm 24, \pm 24 \text{nm} \tag{25}$$

The effective quantum number was calculated using the two calculated values of sodium's spectral lines. Thus, each of these two values led to a slightly different value for the effective quantum number and the error in that value. The error was propagated using the Matlab script "Na_neffective_prop.m" which applied the error propagation equation to equation 16. These two errors were then used to generate a weighted average for the Rydberg constant and then finally the error was propagated through the weighted average equation. The final error in $n_{\text{effective}}$ after the weighted average was found to be

$$\sigma_{n_{\text{effective}}} = .0369 \approx .037 \text{m}^{-1} \tag{26}$$

8 Discussion

Diffraction Grating

The nominal value given for the line per millimeter of the diffraction grating was 600, where as the data taken in the lab indicated this value was 590 ± 48. Indeed, the values are near good agreement especially given the size of the uncertainty; however, the uncertainty is concerning large. The uncertainty is nearly ten percent of the value, which seems odd given that this came entirely from the uncertainty in the measurement of angles.

Hydrogen Spectrum

The experiment found spectral lines with wavelengths of 434 ± 25 , 485 ± 28 , 656 ± 38 nm. NIST reports that the strong spectral lines of hydrogen are at (rounded) wavelengths of 434, 486, 656 nm. Again, the values are almost exact and the experiment is in good agreement with theory given the size of the errors. However, once again the errors are surprisingly large given they are derived from one source.

Rydberg Constant

Analysis found that the Rydberg constant for hydrogen was $(1.098 \pm .037) * 10^7$ m^{-1}, while the infinitely mass nucleus version was found to be $(1.099 \pm .037) * 10^7$ m^{-1}. These values agree well with the values generally accepted which are $1.09678 * 10^7$ m^{-1} for hydrogen and $1.09737 * 10^7$ m^{-1}. The calculated values fall within the uncertainty and accurately reflect the general difference between the two constants. Still, the size of the uncertainty seems excessively large.

Sodium D Doublet

The analysis of the data from the sodium lamp found that the sodium d line doublet was comprised of wavelengths 589 ± 24 and 590 ± 24 nm. The accepted values (after rounding) as reported by NIST are 589 and 590 nm. These are indeed in exact agreement to the third significant figure but there still remains the issue of large uncertainties.

Effective Quantum Number

The effective quantum number that was computed from the measurements was $2.545 \pm .037$ which makes qualitative sense since the valence electron for sodium is in the $n = 3$ energy level and with shift from the quantum defeat it should be slightly less.

9 Conclusion

All of the values that came out of the analysis of the mercury, hydrogen and sodium data are in very good agreement with the generally accepted values. The biggest concern of this experiment is how the errors for all the calculated

values came in around ten percent when the only error this was derived from was an uncertainty of one arcminute in the reading of the angular scale on the spectrometer.

Multiple times the error of calculated values such as the wavelengths of hydrogen and sodium spectral lines were traced back to their source. Each time, the reason the errors end up so large is because of the errors given for the slope and y intercept as given by the york_fit function. The errors that were input to the york_fit were reasonable and based solely on assigning a one arcminute uncertainty to each angular measurement that was recorded. It is further comforting that the error as estimated by taking the standard deviation of the Matlab fits is similar in magnitude to the values given by the york_fit.

After going through the numbers multiple times, the only way the uncertainty in the calculated values could be decreased is to make more accurate angle measurements. Despite one arcminute being nominally small, it makes a large difference when the subject of the study is atomic spectra. The spectrometer set this limit on the precision with which angle could be measured, as did the subjectivity of finding the middle of the spectral line.

To decrease the uncertainty, and be able to verify the theoretical values with better precision a different spectrometer would be the best path to pursue. The table top spectrometer and its angular scale have physical limitation that could be by passed by a spectrometer that could better resolve the angles of the spectral lines and eliminated the subjectivity of finding the center of the line.

References

[1] Fowles, Grant R. *Introduction to Modern Optics*. New York: Holt, Rinehart and Winston, 1968. Print.

[2] "Basic Atomic Spectroscopy Data." *National Institute of Standards and Technology*. N.p., n.d. Web. 2 May 2015.