

# Visible Spectrometer

## Experiment VIS

University of Florida — Department of Physics  
PHY4803L — Advanced Physics Laboratory

### Objective

The Balmer spectral lines emitted from a hydrogen discharge lamp are observed with a transmission grating spectrometer and analyzed to obtain the Rydberg constant. Wavelength calibration is achieved by measuring diffraction angles for spectral lines of “known” wavelengths from a helium discharge tube and fitting this data to the grating equation. The wavelengths of the hydrogen lines are then determined and fit to the Rydberg formula. Basic spectroscopic and statistical analysis techniques are covered.

### Theory

#### The Hydrogen Spectrum

The Bohr model assumes the electron moves around the proton in circular orbits with only quantized angular momentum  $L = n\hbar$  allowed, where  $n = 1, 2, \dots$ , is a positive integer and  $\hbar = h/2\pi$  where  $h$  is Planck’s constant. These assumptions lead to discrete energy levels that can be expressed

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \quad (1)$$

where  $e$  is the electron charge,  $\epsilon_0$  is the permittivity of free space, and  $\mu$  is the reduced

mass of the electron-proton  $m_e$ - $m_p$  system,

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad (2)$$

A photon is emitted when the electron makes a transition from a higher energy level to a lower level with the photon carrying away the excess energy  $\Delta E = E_{n_i} - E_{n_f}$ . Because the energy of a photon and its wavelength  $\lambda$  in vacuum are related by  $\lambda = hc/\Delta E$ , Eq. 1 predicts the relation

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (3)$$

where

$$R_H = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} \quad (4)$$

is called the *reduced mass Rydberg*. If the nucleus were infinitely heavy, the reduced mass  $\mu$  becomes  $m_e$ , the mass of the electron. The combination of physical constants

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} \quad (5)$$

is called the *infinite mass Rydberg* or simply the Rydberg. Although  $R_H$  and  $R_\infty$  differ by less than 0.1%, with care, the measurements you make should be just accurate enough to distinguish the difference between them.

Sets of wavelengths (series) are categorized by the quantum number  $n_f$  of the lower level of

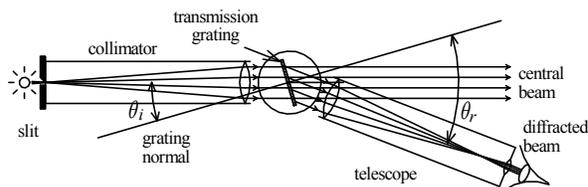


Figure 1: Top view of a transmission grating spectrometer. Note that the incident angle  $\theta_i$  and the diffraction angle  $\theta_r$  are relative to the grating normal.

the transition. The Lyman series is obtained for  $n_f = 1$ ,  $n_i = 2, 3, \dots$  and is in the ultraviolet part of the spectrum; the Balmer series corresponds to  $n_f = 2$ ,  $n_i = 3, 4, \dots$  and is in the visible; the Paschen series, for  $n_f = 3$ , is in the infrared; etc.

The Bohr model is overly simplistic and not in agreement with a more complete quantum mechanical treatment. For example, whereas the Bohr theory predicts the lowest energy or *ground state* (for  $n = 1$ ) has an angular momentum  $\hbar$ , quantum mechanics says it has no angular momentum at all.

Besides the *principal quantum number*  $n$ , quantum mechanics describes states of hydrogen by additional quantum numbers. For example, the orbital angular momentum quantum number  $\ell$  can range from  $\ell = 0$  to  $\ell = n - 1$ . Thus for  $n = 1$ , only  $\ell = 0$  is allowed (the 1s state). For  $n = 2$ , only  $\ell = 0$  (the 2s state) and  $\ell = 1$  (the 2p state) are possible. For higher  $n$ , higher  $\ell$  states are possible.

The Bohr model also does not take into account the intrinsic angular momentum (spin) of the electron or of the nucleus. Where the Bohr model says the internal energy depends only on  $n$ , the real hydrogen atom has more than one energy level for each value of  $n$  that depend on  $\ell$  and other quantum numbers associated with the electron and nuclear spins. These extra energy levels lead to spec-

tral lines that are finely spaced about the Bohr prediction—too finely spaced to see them as separate with our apparatus.

**Exercise 1** (a) Use this Bohr model to derive Eq. 1. Give the  $n = 3$  to  $n = 2$  energy level difference in eV. (b) Learn about the hydrogen fine structure and hyperfine structure and describe their origins. The largest of these effects is the fine structure splitting resulting in two  $n = 2$  energy levels. Look up this splitting and give it in eV and as a fraction of  $n = 3$  to  $n = 2$  transition energy.

## The Diffraction Grating

Wavelength measurements in this experiment are based on the interference of a large number of waves scattered from the grooves of a transmission grating illuminated by incident plane waves of various wavelengths. The geometry is shown in Fig. 1.

**Exercise 2** Draw a figure showing adjacent grating grooves (spaced  $d$  apart) and show that constructive interference occurs for

$$m\lambda = d(\sin \theta_r - \sin \theta_i) \quad (6)$$

where the incident angle  $\theta_i$  and the diffraction angle  $\theta_r$  are measured relative to the grating normal and have the same sign when they lie on opposite sides of the grating normal (as in Fig. 1). The diffraction order  $m$  is a positive integer ( $\theta_r > \theta_i$ ) negative integer ( $\theta_r < \theta_i$ ) or zero ( $\theta_r = \theta_i$ ).

## Dispersion and Resolution

Two important spectrometer properties are dispersion and resolution. Dispersion is a measure of the rate of change of spectral line position with  $\lambda$ . With higher dispersion, the spectral lines are more separated from each other or more spread out. With our spectrometer,

spectral line positions are measured as an angle  $\theta_r$  and dispersion is best represented by the value of  $d\theta_r/d\lambda$ .

**Exercise 3** (a) Obtain an expression for  $d\theta_r/d\lambda$  from the grating equation (Eq. 6) in terms of  $d$ ,  $m$ , and  $\theta_r$ . Show that it increases for larger order number  $m$ , smaller  $d$ , and larger  $\theta_r$ . (b) For a given  $\lambda$ ,  $m$ , and  $d$ , will the dispersion increase, decrease, or remain the same as  $\theta_i$  increases? Hint for part b: As  $\theta_i$  increases,  $\theta_r$  must change as well. Figure out how  $\theta_r$  must change. Then from part (a) you will know how the dispersion will change. The end result is that the answer to part b will depend on the sign of  $m$ , i.e., to which side of the grating normal you are measuring. The dispersion will increase on one side and decrease on the other. You should derive and explain this dependence.

**Exercise 4** If  $\theta_i$  were  $25^\circ$  and the grating had 600 lines/mm, find all angles  $\theta_r$  where a red line at 650 nm and a blue line at 450 nm should appear in first order ( $m = \pm 1$ ) or second order ( $m = \pm 2$ ). Hint: You should get only seven angles not eight. Which one isn't possible? Assume you made measurements at these seven angles—each with an uncertainty in  $\theta_r$  of 4 minutes of arc. (One minute of arc is 1/60 of a degree.) Provide an analytic expression for the propagated uncertainty in  $\lambda$  and determine its value for each measurement.

Resolution describes the ability of the spectrometer to separate two nearby spectral lines. Imagine the wavelength separation between the two spectral lines becoming smaller. The observed lines will begin to overlap each other and at some small separation  $\Delta\lambda$  the ability to discern the lines as separate will be lost. Resolution is a measure of the smallest discernable  $\Delta\lambda$ . When the spectral linewidths are dominated by spectrometer settings, such as

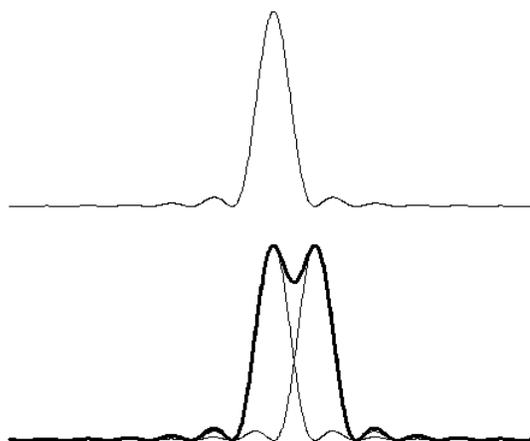


Figure 2: Top: Many-slit diffraction pattern for a single wavelength. Bottom: The thick line is the sum of two diffraction patterns for two different wavelengths separated by the Rayleigh criterion.

slit width and focusing quality, higher dispersion generally implies higher resolution. But the narrowest linewidths are ultimately limited by the number of grating grooves illuminated. As the number of grooves contributing to the diffraction increases, the angular width of the diffraction pattern (and hence the minimum linewidth) decreases. (Large gratings are used when high resolution is needed.)

The Rayleigh criterion gives a generally accepted minimum “just resolvable”  $\Delta\lambda$ . The criterion is that the peak of the diffraction pattern of one line is at the first zero of the diffraction pattern of the other. See Fig. 2. Diffraction theory can be used to show this condition occurs for two lines of wavelengths  $\lambda \pm \Delta\lambda/2$  when

$$\frac{\lambda}{\Delta\lambda} = mN \quad (7)$$

where  $N$  is the number of grooves illuminated, and  $m$  is the order of diffraction in which they are observed.  $\lambda/\Delta\lambda$  is called the resolving power.

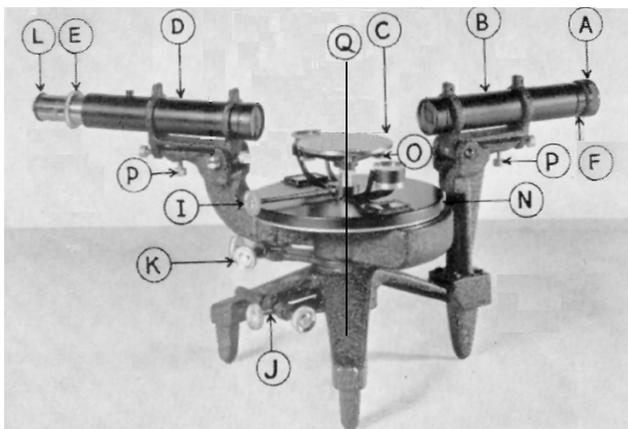


Figure 3: The spectrometer for this experiment. The various components are described in the text.

## Spectrometer

Fig. 3 shows the location of the various spectrometer adjustment mechanisms. Familiarize yourself with them. Components in *italics* below will be referred to throughout the write-up.

Note the two sets of *rotation adjustments* (J and K) near the legs of the spectrometer. The upper one affects rotations of the *telescope* (D), and the lower one affects rotations of the *table base* (N) on which the actual *table* (C) (holding the grating, not shown) is inserted. Also not shown is a mounting post on the table for clamping the grating to the table. Both rotational motions are about the *main spectrometer axis* (Q) which is vertical and through the center of the instrument. Each rotation adjustment has a locking screw and a tangent screw. When the locking screw is loose, the corresponding element (telescope or table base) can be rotated freely by hand. When tightened, the corresponding element can be rotated small amounts with fine control using the tangent screw. There are two precision machined circles (called divided circles) asso-

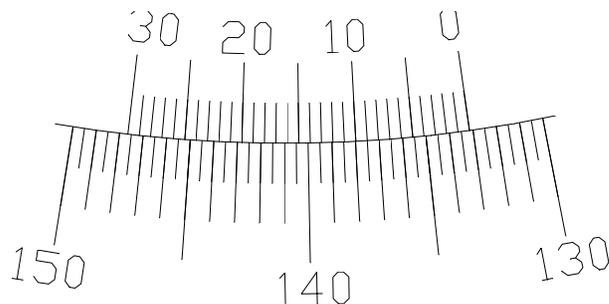


Figure 4: The angular reading is  $133^{\circ} 9'$ . The 0 mark is just after the  $133^{\circ}$  line on the main scale. The  $9'$  mark is directly aligned with a mark on the main scale.

ciated with these elements. The outer circle is rigidly attached to the telescope and has an angular scale from  $0$  to  $360^{\circ}$  in  $0.5^{\circ}$  increments. The adjacent inner circle is rigidly attached to the table base and has two  $0$  to  $30'$  (minutes of arc) vernier scales on opposite sides.

When measuring angles it is important to take readings at both vernier scales. Because of manufacturing tolerances, the two readings will not always be exactly  $180^{\circ}$  apart. By using them both, more accurate angular measurements are obtained. See Fig. 4 for an example of a reading at one vernier scale.

The table is mounted on a post that is inserted into the table base and locked into place with the *table locking screw* (I). Three *table leveling screws* (O) under the table allow the pitch and yaw of the table to be varied.

A *cross hair* inside the telescope is brought into focus by sliding the *eyepiece* (L) in or out. The telescope is focused by rotating the *telescope focusing ring* (E). The *collimator* (B) (on which the *entrance slit* (A) is located) is adjusted for focus by sliding the inner collimator tube in or out. An *index ring* (F) on the collimator tube allows the focusing position to be maintained once found. The ring

has a V-shaped protuberance that fits into one of the V-shaped cutouts spaced  $90^\circ$  apart on the outer collimator tube. Making registration with one of the V's once the proper focusing and slit orientation is obtained, the ring is then tightened into place. This permits the slit orientation to be changed  $90^\circ$  without losing the focus by sliding the tube out slightly, rotating it  $90^\circ$ , and pushing it back into the other V-shaped cutout.

The telescope and collimator also have *leveling screws* (P) that allow their optical axes to tilt up or down. These adjustments are used in a special procedure to orient both optic axes in a common plane perpendicular to the main spectrometer axis. To use them, loosen the upper (locking) screw and rotate the lower (adjustment) screw to tilt the optic axis up or down. When properly adjusted, finger tighten both screws (mostly the locking screw) while maintaining the axis orientation.

A grating mounted on a glass plate with a grating spacing  $d \approx 1/600$  mm will be used for the measurements. The grating should only be handled by the edges of the glass plate. Do not damage the grating by touching it.

### Alignment Procedure

This spectrometer is a semi-precision instrument that can be damaged with improper use. Parts should not be removed for any reason without first checking with an instructor.

1. Carefully take the spectrometer out into the hallway and rest it on a portable table or lab stool. Look through the telescope at the bulletin board at the end of the corridor. This is far enough to be an effectively infinite object distance. With both eyes open and the unaided eye focused on the distant object, simultaneously focus on the cross hair by sliding the eyepiece

in or out and on the distant object using the telescope focus. Both the telescope and cross hair images should now be focused at infinity and there should be no parallax. As you move your eye slightly from side to side, the cross hair should not move relative to the image of the bulletin board. If it does move, the image is not at the cross hair and the telescope focus still needs adjustment. It may help to de-focus the telescope and then readjust the eyepiece to focus only on the cross hair before trying to refocus the telescope. Once both the cross hair and bulletin board are focused and show no parallax, bring the spectrometer back to the lab bench.

2. Loosen the index ring, move it back against the entrance slit assembly and retighten it. You should now be able grab the index ring to move the collimator tube smoothly in and out and rotate it. Line up the telescope to look into the collimator and place a incandescent bulb behind the entrance slit. Looking through the telescope, move the collimator tube in or out until the open slit is in sharp focus. **Do not touch the telescope focusing ring. It must be left where it was from the previous step.** Adjust the entrance slit for a narrow width and orient it horizontally. Check the slit orientation by rotating the telescope slightly and verifying that the cross hair moves parallel to the slit, but don't be concerned if it is slightly high or low relative to the slit image. Carefully—**without moving the collimator tube**—loosen the index ring completely. Then gently move it into one of the V-grooves and retighten it—**again, without moving the collimator tube.** At the end of this step you should have

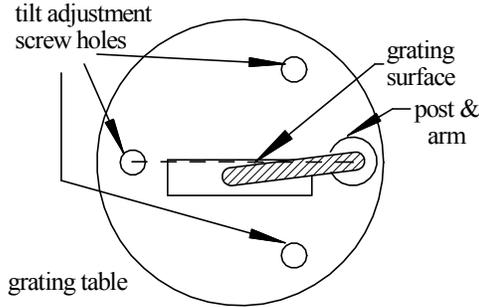


Figure 5: Schematic top-view of the grating placement relative to the three table tilt screws.

a horizontal and sharp image of the entrance slit and a sharp image of the cross hairs.

3. Adjust the telescope leveling screws to get the cross hair centered on the narrow entrance slit. Rotate the telescope along the slit and verify the cross hair stays centered on the slit. Tighten the leveling screws while maintaining the vertical alignment. This ensures the telescope and collimator optical axes are aligned to one another but not necessarily perpendicular to the main rotation axis.
4. Locate the transmission grating plate, which should already be installed in a black mounting bracket. The grating is a decal glued on one side of a glass plate. This side should already be facing the front side of the bracket. (The grating is installed from the back side of the bracket.)

Mount the grating assembly at the center of the table so that the front surface lies along the diameter directly in line with the mounting post and the opposite tilt adjustment screw, thus bisecting the

other two tilt adjustment screws as shown in Fig. 5. Tighten it under the clamp.

Install the grating table into the table base and adjust the table height so the center of the grating is on the optic axis of the telescope/collimator. Tighten the table locking screw. Rotate the telescope until it makes an 80-90° angle with the collimator. Adjust the table base rotation angle as necessary to see (through the telescope) the reflection of the collimator slit (still oriented horizontally and illuminated with the light bulb) off the front surface of the grating. Tighten the table base locking screw. Adjust the telescope rotation angle and either of the two table leveling screws to center the reflected image of the slit on the cross hairs. This step guarantees the grating normal is perpendicular to the main rotation axis. Explain why! (Hint: it requires that the telescope and collimator are aligned with one another before adjusting the table tilt to line up the reflection.)

5. Rotate the telescope half-way to the collimator so that the telescope is then approximately perpendicular to the grating surface. Shine a small flashlight into the side hole near the telescope eyepiece and further adjust the telescope rotation until you can see light reflected from the grating surface. As you get close to perpendicular, a circle filled with reflected light and having about the same diameter as the telescope field of view should appear. Some adjustment of the positioning of the light source going into the side port may be needed to see this reflected field of view, which will probably not be centered vertically. Adjust the telescope leveling screws to center the reflected field of view. If the telescope focusing is cor-

rect, you should be able to see a reflected cross hair in the reflected field of view. If you can not see the reflected cross hair, it means the telescope was not focused at infinity. Adjust the telescope focus by very small amounts to find and focus on the reflected cross hair. Adjusting the telescope focus so that both the direct and reflected cross hairs are in focus (with no parallax between them) focuses the telescope at infinity and is an alternative to focusing it on a distant object. Continue adjusting the telescope leveling screw, rotation angle and focus to align (overlap) the two focused cross hairs with no parallax. Overlapping the cross hair and its reflection is called *autocollimation*, and will also be performed in other steps. In this step, only the vertical alignment is important; it ensures the telescope axis is parallel to the grating normal and thus perpendicular to the main rotation axis. Tighten the telescope leveling screws while maintaining its vertical alignment.

6. Loosen the table locking screw and carefully remove the table and set it aside without upsetting the position of the grating. Align the telescope and collimator to directly view the entrance slit. Adjust the telescope focus, if necessary, to remove parallax. The cross hair and entrance slit must be in focus simultaneously. Adjust the collimator leveling screws so that the telescope cross hair is in vertical alignment with the entrance slit, and then re-tighten them. This step makes the collimator axis parallel to the telescope axis and thus perpendicular to the main rotation axis.
7. Go back to Step 4 and refine your alignment.

The spectrometer should now be in proper alignment. The telescope and collimator focus should be at infinity, Both the cross hair and slit should be in sharp focus with no parallax between them and they should be vertically aligned. The telescope and collimator optical axes should be perpendicular to the spectrometer rotation axis.

8. Put the table/grating back in the table base. Make sure that the front surface of the grating is still centered along the table diameter.
9. Loosen the table base locking screw, adjust the vernier scales so they are roughly  $90^\circ$  to the collimator (and thus easy to view) and re-tighten the table base locking screws.
10. Rotate the table to get an angle of incidence  $\theta_i$  around  $5\text{-}10^\circ$ . The open end of the grating mount should face the collimator. Otherwise, the mount will block the grating at large angles. Adjust the table height so that the grating is centered on the collimator/telescope optic axis and tighten the table locking screw.
11. Again, shine a light into the telescope side hole and adjust the telescope rotation and the table leveling screws to achieve autocollimation. This step ensures the grating normal is perpendicular to the main rotation axis.
12. With the slit still horizontal and illuminated, rotate the telescope to one side and the other and find the “rainbows” on each side. Adjust the grating dispersion plane using the inline table leveling screw (opposite the post in Fig. 5) so that the rainbows on each side remain centered on the cross hairs.

- Repeat from Step 11 until no further adjustments are necessary.

The positioning of the grating on the table, the table itself, and the table base rotation angle determine the grating incidence angle  $\theta_i$  and must be kept fixed throughout the experiment. Thus the grating, the table, and the table base must not be moved again. In particular, it is easy to accidentally turn the table base tangent screw when you mean to turn the telescope tangent screw.

At this point the spectrometer is ready for measurements.

## Measurements

The measurements consists of adjusting the telescope rotation angle to center the cross hair on a colored slit image, a zero-order slit image, or an autocollimation reflection and recording the angular readings from both verniers. Do not make any subtractions or averages before recording. Label column headings  $A$  for one vernier and  $B$  for the other.

A common spectroscopic technique for measuring unknown wavelengths from one source is to first measure known wavelengths from some other sources. These initial measurements are used to calibrate the spectrometer—in this case determine constants such as the grating groove spacing  $d$  and the angle of incidence  $\theta_i$ . While it is perhaps a bit artificial, in this experiment the hydrogen wavelengths will be considered unknown and those from any other sources will be considered known calibration wavelengths. It is recommended that you start with a helium discharge tube as a calibration source, but feel free to use other sources as you see fit. The following measurement and analysis steps outline how this is done.

- Record the telescope angles  $A_n$  and  $B_n$

where the autocollimation reflection occurs and the direct and reflected cross hairs are aligned both vertically and horizontally. The telescope angular readings are then a measure of the grating normal direction.

- Turn the entrance slit vertical and make it reasonably narrow (a few tenths of a millimeter). You will have to make some trade-offs between the slit width and the ability to see weak spectral lines. The narrower the slit, the sharper the lines, but they also get harder to see.
- Place the helium discharge tube just behind and nearly touching the entrance slit. Adjust its position for maximum brightness while viewing the zero order (straight-through, all-wavelengths) slit image. Measure and record the angular reading  $A_i$  and  $B_i$  for the zero order image. This reading is a measure of the incidence angle  $\theta_i$ . Note the “ghost” lines from imperfections in the grating. These ghost lines may also be seen on stronger spectral lines. Ignore them.
- Leave about ten rows clear at the top of the spreadsheet (for intermediary and final results) and make a spreadsheet table with columns for the color of the line and both vernier readings  $A_r$  and  $B_r$  which would then be a measure of the diffraction angle  $\theta_r$ . Record the readings for the brighter lines of the calibration source in all orders attainable on both sides of the zero order image. For helium, Table 1 gives the colors and air wavelengths<sup>1</sup> of only the brightest line

<sup>1</sup>Air wavelengths are measured at roughly standard temperature and pressure and thus they are affected by the index of refraction of air. Comprehension Question 5 discusses the issue of vacuum vs. air wavelengths

for each color. These four wavelengths measured in four orders should be sufficient for a good calibration, but you can use the reference tables in the auxiliary material or data on the NIST web site: [www.nist.gov/pml/data/asd.cfm](http://www.nist.gov/pml/data/asd.cfm) for other calibration sources or for additional wavelengths of other helium lines. Include a column for the order,  $\pm 1$ ,  $\pm 2$ , (and maybe  $\pm 3$  if you see a violet line in third order.) Use positive orders for lines observed on the side of the zero order image where  $\sin \theta_r > \sin \theta_i$  and negative orders for those observed on the other side. There should be about 16 measured lines.

18. Add a column for  $\sigma_r$  — the uncertainty in the measured  $A_r$  or  $B_r$ . It can be given in minutes of arc and can be the same for all lines. It can be adjusted in later analysis steps.
19. Replace the helium discharge tube with a hydrogen tube. Be careful as the tubes can get quite hot. The hydrogen discharge should have a red section in the middle of the tube growing pinkish toward the electrodes. If there are less than a couple of centimeters of red in the middle, it is time to change the tube. Adjust the source/spectrometer heights to get the red section just about touching the entrance slit and the zero order image is as bright as possible.
20. A row or two below the data table for the calibration lines, and with the same columns, make a similar table of color and the  $A_r$  and  $B_r$  readings for the observable lines of the hydrogen spectrum and the order number they are observed at using the same scheme for plus and minus orders as for the calibration lines. You

---

for this experiment.

should be able to see the Balmer lines corresponding to  $n_i = 3, 4, 5$ , and 6 in several orders. In order starting at and away from the zero-order image on either side, they appear as a violet (weak, sometimes extremely weak), blue violet, blue green, and red. Use the video camera to see the weaker lines of hydrogen. Be sure the camera aperture is fully opened and simply position it where you put your eye and focus it. The lines for  $n_i = 6$  and 7 (and perhaps higher) should be measurable in first (and perhaps higher) order. If any of the lines are difficult to measure, feel free to assign them different angular uncertainties  $\sigma_r$ .

**CHECKPOINT: The procedure should be complete through the prior step, and analysis should be complete through Step 5.**

21. Use the sodium lamp and the narrowest possible entrance slit. Observe the sodium doublet lines at 589.0 and 589.6 nm in first order ( $m = 1$ ). They should be easily resolved — appearing as two separate yellow lines. Now place the auxiliary slit over the end of the collimator and orient it vertically. Slowly decrease its width. Since the light leaving the collimator is a parallel beam, as the auxiliary slit is narrowed, less and less grating grooves will be illuminated. Narrow the slit until the doublet is no longer resolved and appears as a single line. Measure the auxiliary slit width at the point where the sodium lines are no longer resolved. Determine how many grating grooves are illuminated. Do the lines then become resolvable when viewed in second order? Discuss the significance of this mini-experiment. Be quantitative.

color	wavelength (nm)
violet	447.15
blue-green	501.57
orange	587.57
red	667.82

Table 1: The stronger visible lines from a helium discharge.

What is the resolving power of the spectrometer in first order assuming diffraction limited performance when the auxiliary slit is removed?

## Data Analysis

### Calibration

The first step is to reduce each pair of angular readings  $A$  and  $B$  to a single value  $H$  by averaging the readings for  $A$  and  $B \pm 180^\circ$ . Choose the sign in  $B \pm 180^\circ$  such that this term is near that of the  $A$  reading. For example, with  $A = 32^\circ 33'$  and  $B = 212^\circ 30'$ , use the  $-$  sign; but for  $A = 325^\circ 15'$  and  $B = 145^\circ 17'$ , use the  $+$  sign. If the set of  $H$  values ends up with values in both the first ( $0^\circ$  to  $90^\circ$ ) and fourth ( $270^\circ$  to  $360^\circ$ ) quadrants, subtract  $360^\circ$  from those in the fourth quadrant. That leaves the angle in the fourth quadrant, but with values from  $0^\circ$  to  $-90^\circ$ . This makes the angles cover a continuous range so plots with  $H$  values on the horizontal axis will come out without an odd-looking gap.

1. Add a column to your data table converting the  $A_r$  and  $B_r$  for each spectral line to an  $H_r$ .
2. The uncertainty  $\sigma_r$  is yours to decide based on your estimate of the precision in measuring the angles, but should correspond to no more than a few minutes

of arc. It can be the same for all spectral lines.

3. In a separate area (above the data table) enter the incidence angle readings  $A_i$  and  $B_i$  and convert to an  $H_i$ . Similarly record the grating normal readings  $A_n$  and  $B_n$  and convert to an  $H_n$ . Give an estimate of their uncertainties  $\sigma_i$  and  $\sigma_n$ .

Recall that the incidence angle  $\theta_i$  and the diffraction angles  $\theta_r$  are relative to the grating normal and are thus given by

$$\theta_i = H_i - H_n \quad (8)$$

and

$$\theta_r = H_r - H_n \quad (9)$$

Equation 6 in terms of  $H$ -readings becomes:

$$m\lambda = d [\sin(H_r - H_n) - \sin(H_i - H_n)] \quad (10)$$

The values  $d$ ,  $H_i$ , and  $H_n$  are constants in the fit and all three can be determined from a linear regression.

**C.Q. 1** (a) Use the trigonometric identity  $\sin(a \pm b) = \sin a \cos b \pm \cos a \sin b$ , but only for the term  $\sin(H_r - H_n)$ , to show that Eq. 10 can be written:

$$m\lambda = D_s \sin H_r + D_c \cos H_r + D_0 \quad (11)$$

where

$$\begin{aligned} D_s &= d \cos H_n \\ D_c &= -d \sin H_n \\ D_0 &= -d \sin(H_i - H_n) \end{aligned} \quad (12)$$

Equation 11 is in the form of a linear regression of  $m\lambda$  (the  $y$ -variable) on the terms  $\sin H_r$ ,  $\cos H_r$  and a constant (the  $x$ -variables). The numerical values for the three coefficients:  $D_s$ ,  $D_c$ , and  $D_0$  obtained from the regression can then be used with Equation

set 12 to determine  $d$ ,  $H_n$  and  $H_i$ . (b) Show that  $d$  and  $H_n$  can be determined from

$$\begin{aligned} d &= \sqrt{D_s^2 + D_c^2} & (13) \\ H_n &= -\tan^{-1}\left(\frac{D_c}{D_s}\right) \\ H_i &= -\sin^{-1}\left(\frac{D_0}{\sqrt{D_s^2 + D_c^2}}\right) - \tan^{-1}\left(\frac{D_c}{D_s}\right) \end{aligned}$$

Keep in mind that Excel's trig functions need arguments in radians and the inverse trig functions return angles in radians. The conversion factor is  $\pi/180$  (radians/degree) and Excel has a PI() function for the value of  $\pi$ . Excel can also translate between degrees and radians with the functions RADIANS(angle in degrees) or DEGREES(angle in radians).

4. Add a column for the Table 1 reference wavelengths  $\lambda$  of each line and another for  $m\lambda$ —the product of the order number and the wavelength. Leave these columns in units of nanometers.
5. In three adjacent columns, but in the same rows with the data, create the Jacobian  $[J_b^{m\lambda}]_{ij} = \partial(m\lambda_i)/\partial b_j$  where the  $b_j$  are the three fitting parameters  $D_s$ ,  $D_c$  and  $D_0$ . That is, make side-by-side columns for  $\sin H_r$  and  $\cos H_r$  (for the  $D_s$  and  $D_c$ , respectively) and a column of ones (for the  $D_0$  term). Note that a subscript or superscript  $b$  in Jacobian and covariance matrices will always represent this set of fitting parameters.
6. Make a column for  $\sigma_{m\lambda}$ , the uncertainty in  $m\lambda$  due to uncertainty in  $H_r$ . From propagation of error, this quantity is given by  $\sigma_{m\lambda} = |\partial(m\lambda)/\partial H_r|\sigma_r$  where  $\sigma_r$  is your uncertainty in  $H_r$  **but it must be converted to radians in this equation**. Determine the formula for the derivative from Eq. 11 to see that the  $\sin H_r$  and

$\cos H_r$  columns in the Jacobian can be reused for this column, but also note that the derivative depends on the fitting parameters, which have not yet been calculated. Thus, reserve a  $3 \times 1$  column vector of cells above the data table for these values and simply start with  $D_s = D_c = D_0 = 1$ . Use these cell addresses when making the column of  $\sigma_{m\lambda}$  values. You will be overriding the parameter values with correct values in Steps 10 and 11 before accepting results as final.

Since the fit depends on the uncertainties  $\sigma_{m\lambda}$  and the uncertainties depend on the derivatives and the derivatives depend on the fit, if we are not careful we will create a circular reference. We can take care of that by telling Excel to allow circular references but restrict how many iterations around the circle are allowed. This would work for the analysis here, but not if the Excel Solver program must be used. Since we might want to use Solver as a check on the analysis, rather than describe the details of using circular references, it is recommended that you use a Copy|Paste Special|Values technique (described shortly) which works in all cases where uncertainties depend on the best fit.

7. You already have the calculated column for  $\sigma_{m\lambda}$ , but it is based on incorrect parameter values:  $D_s = D_c = D_0 = 1$ . So, one column to the right of the calculated column, create a temporary column of ones for the constant copy. Using this column of ones in the linear regression analysis will make it equally weighted. After this equally-weighted fit is complete, you will use the Copy|Paste Special|Values method to achieve a more properly weighted linear regression.
8. Use the weighted linear regression equations and Excel array formulas to first cre-

ate the  $N \times N$  weighting matrix  $[\sigma_{m\lambda}^2]^{-1}$ . There is no reason to display the weighting matrix explicitly on the spreadsheet so name it and create it in the **Name Manager** (located in the **Formula** toolbar). Recall the Excel array formula for the weighting matrix is `=MUNIT(N)/array^2` where  $N$  is the number of calibration wavelengths to be fitted and `array` is the  $N \times 1$  column vector containing the **constant copy** of  $\sigma_{m\lambda}$  values. As described above, it is OK that we start with a column of ones, which will produce a first set of parameters based on an equally-weighted fit.

9. Next to, and in the same rows as the fitting parameters reserved for them in Step 6, leave one column blank (for the parameter uncertainties) and then to the right of the blank column and in the same rows as the fitting parameters make  $[\sigma_b^2]$ , the  $3 \times 3$  covariance matrix for the fitting parameters. Select this  $3 \times 3$  block and use Excel's **MMULT** vector and matrix multiplication function, its **TRANSPOSE** function and its **MINVERSE** function to create  $[\sigma_b^2] = [[J_b^{m\lambda}]^T [\sigma_{m\lambda}^2]^{-1} [J_b^{m\lambda}]]^{-1}$ , where  $[\sigma_{m\lambda}^2]^{-1}$  is the  $N \times N$  weighting matrix and is referenced by the name given to it in the name manager and  $[J_b^{m\lambda}]$  is the  $N \times M$  Jacobian made in Step 5.
10. Now you can get the first set of fitting parameters. In the block reserved for them in Step 6, make the  $3 \times 1$  vector of fitting parameters:  $\mathbf{b} = [\sigma_b^2][J_b^{m\lambda}]^T[\sigma_{m\lambda}^2]^{-1}\mathbf{y}$ , where  $\mathbf{y}$  is the vector of  $m\lambda$  values.
11. The first set of parameters obtained above are based on an equally weighted fit because the weighting matrix was made using an initial column of ones for the  $\sigma_{m\lambda}$  uncertainties. So now do the **Copy|Paste Special|Values** from the (now almost correct) calculated values of  $\sigma_{m\lambda}$  to the constant column from which the weighting matrix is made and the new set of fitting parameters will immediately update to a more properly weighted fit. It won't be totally correct until you do the **Copy|Paste Special|Values** a few more times and the fit stops changing.
12. Fill in the blank row next to the fitting parameters with their uncertainties — the square root of the diagonal elements of the covariance matrix,  $[\sigma_b^2]$ .
13. In the data table, make a new column for the fitted values of  $m\lambda$  (based on Eq. 11). Make plots of  $m\lambda$  vs.  $H_r$ . For the measurements use symbols no line. Error bars should be too small to show on this plot. Overlay a plot for the fit using a smoothed line, no symbols. You may have to sort the rows (sort **all** rows in order of  $H_r$ ) for the fit to show properly on the graph. Or, make a new column of  $H_r$  values (below those in the data table), evaluate the values for  $m\lambda$  they produce and use these columns for the fit.
14. Make a separate column for and plot the residuals:  $\Delta m\lambda = m\lambda - (D_s \sin H_r + D_c \cos H_r + D_0)$  vs.  $H_r$ . Again use symbols, no lines. Error bars of  $\pm \sigma_{m\lambda}$  should be included. Misidentified wavelengths or bad angular measurements should be obvious from the residuals, which should show only random deviations (hopefully, no more than a nanometers or so) centered around zero. Bad points should be rechecked for possible errors in  $H_r$ ,  $m$  or  $\lambda$ . If you cannot reconcile a bad point, remeasure it.
15. Add a cell in the top area of the spreadsheet for the resulting chi square.

You can use the usual formula for  $\chi^2$  or use two MMULT functions to create the equivalent matrix version  $\chi^2 = \Delta \mathbf{m} \boldsymbol{\lambda}^T [\sigma_{m\lambda}^2]^{-1} \Delta \mathbf{m} \boldsymbol{\lambda}$ , where  $\Delta \mathbf{m} \boldsymbol{\lambda}$  is the column of deviations. Even though this is a single cell, you will need to end it with Ctrl|Shift|Enter.

Do you need to take into account the uncertainty in the reference wavelengths? The accuracy of the wavelengths given in Table 1 is less than 0.02 nm.

**C.Q. 2** Use Equation set 13 with the fitting parameters to determine  $d$ ,  $H_i$  and  $H_n$ . (In Jacobians and covariance matrices, this set of parameters will be abbreviated with a subscript or superscript  $d$ .) Use  $[\sigma_b^2]$  and the Jacobian for these equations to determine  $[\sigma_d^2]$ , the covariance matrix for  $d$ ,  $H_i$  and  $H_n$  giving these variables' variances and covariances. Compare the fitted parameter values with the manufacturer's value for  $d$  and your directly measured values for  $H_i$  and  $H_n$ . Hint:  $[\sigma_d^2]$  is obtained from propagation of error as  $[\sigma_d^2] = [J_b^d][\sigma_b^2][J_b^d]^T$  where  $[J_b^d]$  is the  $3 \times 3$  set of derivatives of the  $d$  parameters with respect to the  $b$  parameters according to Equation set 13. Interestingly, in this case it turns out  $[J_b^d]$  is more easily determined (and less prone to mistakes) as the inverse of  $[J_d^b]$ , the set of derivatives of  $b$  parameters with respect to the  $d$  parameters according to Equation set 12. That is,  $[J_b^d] = [J_d^b]^{-1}$ .

## Hydrogen Data

Next, you will use the calibration results to determine the wavelengths of hydrogen lines. You will then analyze the wavelengths to determine the hydrogen Rydberg constant.

16. Make a second table a row or two below the table for the calibration data. It will

have the same columns as for the calibration data, but several modifications and additions will be needed. For starters, the values of  $\lambda$  will not come from reference values. To get them, start by constructing the column for hydrogen  $m\lambda$  values using the calibration formula, Eq. 11, with the three fitting parameters  $D_c$ ,  $D_s$ , and  $D_0$  and the hydrogen  $H_r$  values. But before you do, first make  $[J_b^{m\lambda}]$ —the Jacobian columns for the hydrogen  $H_r$  values as it was made for the calibration measurements. You will need this Jacobian matrix in later steps and you can use it here to create the entire column of  $m\lambda$  values by selecting this column and creating the Excel array formula corresponding to  $m\lambda = [J_b^{m\lambda}]\mathbf{b}$  where  $\mathbf{b}$  is the  $3 \times 1$  array of parameter values.

17. Create the  $\lambda$  column based on the  $m\lambda$  found above and the recorded order  $m$ .

18. Additional columns will be needed for determining a fit of the hydrogen wavelengths to the Rydberg formula (Eq. 3). In particular, make a new column for  $y = 1/\lambda$  and one for the values of  $x = 1/n_f^2 - 1/n_i^2$ . For the latter, first make a column for the initial state quantum numbers  $n_i$  for each measured hydrogen line. Recall that for all Balmer lines,  $n_f = 2$ . You will have to figure out which  $n_i$  goes with each line. Check that a plot of  $y$  vs.  $x$  appears to lie on a straight line through the origin. Check for outliers or other problems. Don't be concerned that you have multiple  $1/\lambda$  values (from different orders) corresponding to each  $x$ . They will all be used for the Rydberg fit and all will properly affect the results.

19. For a properly weighted fit you will need the (diagonal) weighting matrix  $[\sigma_{1/\lambda}^2]^{-1}$

associated with  $\sigma_{1/\lambda}$ , the uncertainties in  $1/\lambda$  due to the uncertainty  $\sigma_r$  in  $H_r$ . The uncertainty in the Rydberg due to calibration uncertainty will be addressed in Step 23.

From propagation of errors, the uncertainty in  $1/\lambda$  is calculated from  $\sigma_{1/\lambda} = |\partial(1/\lambda)/\partial H_r|\sigma_r$ . Since we already have the column for  $|\partial m\lambda/\partial H_r|\sigma_r$  (by copying the formula from the calibration data table), the derivative above can be obtained using the chain rule:  $\partial(1/\lambda)/\partial H_r = (\partial(1/\lambda)/\partial m\lambda)(\partial(m\lambda)/\partial H_r)$ . Show that  $\partial(1/\lambda)/\partial m\lambda = -1/m\lambda^2$  and make a column for these values. They will be used again shortly. Then use that column to make a column for  $\sigma_{1/\lambda} = |(1/m\lambda^2)(\partial(m\lambda)/\partial H_r)|\sigma_r$ , where  $\sigma_r$  **must be in radians**.

20. In the Name Manager, make the  $N \times N$  weighting matrix  $[\sigma_{1/\lambda}^2]^{-1}$  from the Excel array formula `=MUNIT(N)/array^2` where  $N$  is the number of Balmer lines and array is the column of  $\sigma_{1/\lambda}$ -values created in the previous step.

Now you are ready for a one-parameter fit to the Rydberg formula with the  $y$ -values coming from the column of  $1/\lambda$  and the  $x$ -values coming from the single column of  $1/n_f^2 - 1/n_i^2$  values.

21. Make a cell for  $[\sigma_R^{2(r)}]$ : the  $1 \times 1$  covariance matrix (whose only element is the variance of  $R$  due to the uncertainties in  $H_r$ ) as given by  $[\sigma_R^{2(r)}] = [[J_R^{1/\lambda}]^T [\sigma_{1/\lambda}^2]^{-1} [J_R^{1/\lambda}]]^{-1}$ , where  $[J_R^{1/\lambda}]$  is the  $N \times 1$  column vector of  $x$ -values:  $1/n_f^2 - 1/n_i^2$ .
22. For later work, create the  $1 \times N$  row vector for the pseudo inverse  $[J_{1/\lambda}^R]^\dagger = [\sigma_R^{2(r)}][J_R^{1/\lambda}]^T [\sigma_{1/\lambda}^2]^{-1}$  and then create the

fitted Rydberg constant from  $R = [J_{1/\lambda}^R]^\dagger \mathbf{y}$  where  $\mathbf{y}$  is the  $1 \times N$  column vector of  $y$ -values for  $1/\lambda$ .

23. The next step is to find the uncertainty in the Rydberg due to the uncertainty in the calibrations parameters as given by their covariance matrix  $[\sigma_b^2]$ . The equation for this  $1 \times 1$  matrix is  $[\sigma_R^{2(b)}] = [J_{1/\lambda}^R]^\dagger [J_{m\lambda}^{1/\lambda}]^T [J_b^{m\lambda}] [\sigma_b^2] [J_b^{m\lambda}]^T [J_{m\lambda}^{1/\lambda}] [J_{1/\lambda}^R]^\dagger$ .
- The only new quantity in this equation is  $[J_{m\lambda}^{1/\lambda}]$ , the  $N \times N$  diagonal Jacobian matrix obtained in Excel from the array formula `=MUNIT(N)*array`, where array is the  $N \times 1$  column of values for  $-1/m\lambda^2$ . Because  $[J_{m\lambda}^{1/\lambda}]$  is diagonal, it is its own transpose and can be used as such in the equation for  $[\sigma_R^{2(b)}]$  above. Recall,  $[\sigma_b^2]$  is the  $3 \times 3$  parameter covariance matrix determined in the calibration analysis.
24. Make plots of the data and fit for  $1/\lambda$  versus  $x$ . Also make a plot of residuals with error bars. Calculate the  $\chi^2$  for the fit to the Rydberg formula.

## Comprehension Questions

3. For both the calibration fit and the Rydberg fit, discuss the  $\chi^2$  and residuals in relation to your estimates of the uncertainties in the angular measurements. How precise were your  $H_r$  values? Can you conclude your measurements are in agreement with the calibration and Rydberg formulas?
4. Find high-accuracy values for infinite-mass and hydrogen Rydberg for comparison with your value. Does your result test the difference between  $R_H$  and  $R_\infty$ ? Explain.

5. The calibration wavelengths in Table 1 are given in air and the calibration lines were measured in air. We used the calibration and measured the Balmer lines in air so their calculated values are air wavelengths as well. The Rydberg formula, however, is valid for vacuum wavelengths only. The relation between  $\lambda_m$ , an air wavelength, and  $\lambda$ , the corresponding vacuum wavelength is:  $\lambda/\lambda_m = n$  where here  $n$  is the index of refraction of air, which differs from one by less than one part in a thousand. So, is it an issue here? Hint: Check the NIST link at [emtoolbox.nist.gov/Wavelength/Documentation.asp](http://emtoolbox.nist.gov/Wavelength/Documentation.asp) to see that the index of refraction of air is nearly constant over the range of wavelengths measured here and get its value. Would correcting for the index of refraction of air make the Rydberg constant larger or smaller than the value without the correction? How big is the correction to the Rydberg, and is it significant at the precision of your measurements?